FABRICATION AND CHARACTERIZATION OF DYE SENSITIZED POLYMER FILMS FOR HOLOGRAPHIC APPLICATIONS

Thesis submitted to
Cochin University of Science and Technology

By

Beena Mary John

In partial fulfillment of the requirements
for the award of the degree of

DOCTOR OF PHILOSOPHY

Department of Physics
Cochin University of Science and Technology
Cochin-682 022, Kerala, India.

January 2008

Fabrication and characterization of dye sensitized polymer films for holographic applications

Ph.D thesis in the field of Photonics

Author:
Beena Mary John
Department of Physics
Cochin University of Science and Technology
Cochin-682 022, Kerala, India.
E-mail: beenamary@gmail.com

Advisors:

Dr. C. Sudha Kartha
Reader, Dept. of Physics
Cochin University of Science and Technology
Cochin-682 022, Kerala, India.
E-mail: csk@cusat.ac.in

Dr. K. Sreekumar
Reader, Dept. of Applied Chemistry
Cochin University of Science and Technology
Cochin- 682 022, Kerala, India.
E-mail: ksk@cusat.ac.in

Dr. Rani Joseph
Professor, Dept. of Polymer Science & Rubber Technology
Cochin University of Science and Technology
Cochin-682 022, Kerala, India.
E-mail: rani@cusat.ac.in

Cochin University of Science and Technology
Cochin- 682 022, Kerala, India.

January 2008

Certificate

Certified that the work presented in the thesis entitled **"Fabrication and Characterization of Dye Sensitized Polymer Films for Holographic Applications"** is based on the bonafide research work done by Ms. Beena Mary John under our guidance in the Department of Physics, Cochin University of Science and Technology, Cochin-682 022, India and has not been included in any other thesis submitted previously for the award of any degree.

Dr. C. Sudha Kartha (Supervising Guide)
Reader, Dept. of Physics
Cochin University of Science and Technology
Cochin-22, Kerala, India.

Dr. K. Sreekumar (Co-Guide)
Reader, Dept. of Applied Chemistry
Cochin University of Science and Technology
Cochin-22, Kerala, India.

Dr. Rani Joseph (Co-Guide)
Professor , Dept. of Polymer Science & Rubber Technology
Cochin University of Science and Technology
Cochin-22, Kerala, India.

Cochin-22,
14th January 2008

CONTENTS

Preface

Publications
Abbreviations

Chapter 1 **Review on Polymer Based Holographic Recording Media**

1.1 Introduction 3
1.2 Relevance of Holographic Technology 3
1.3 Holography-Major Challenges 6
1.4 Media Requirements 8
1.5 Holographic Recording Materials 10
1.6 Photorefractive Polymers 12
1.7 Photoaddressable Polymers 14
1.8 Polymer Dispersed Liquid Crystals 14
1.9 Photopolymers 16
  1.9.1 Photopolymerizable Media 17
  1.9.2 Binder 18
  1.9.3 Monomer 19
  1.9.4 Photoinitiation System 20
    1.9.4.1 Dye 20
    1.9.4.2 Co-initiator 23
  1.9.5 Photo-Crosslinking Polymers 23
1.10 Review of Art in the Field of Photopolymer Based Recording Media 25
  1.10.1 Liquid Compositions 25
  1.10.2 Dye Sensitized Poly(vinyl alcohol) 26
  1.10.3 Metal Ion Doped PVA 33
  1.10.4 Poly(acrylic acid) 36
  1.10.5 Poly(vinyl chloride) 37
  1.10.6 Poly(methyl methacrylate) 38
  1.10.7 Commercially Available Polymers 39

1.10.8 Other Photopolymers 42
1.10.9 Nano-Photopolymers 44
1.11 Objectives of the Present Work 46
1.12 Conclusion 46
References 47

Chapter 2 **Experimental Details**

2.1 Introduction 65
2.2 Materials Used 65
2.2.1 Host Matrices 65
2.2.2 Dye 66
2.2.3 Monomer 67
2.2.4 Electron Donor 67
2.2.5 Crosslinker 67
2.3 Film Fabrication 67
2.4 Infrared Spectroscopy 68
2.5 Laser Exposure 69
2.6 Optical Absorption Studies 69
2.7 Real Time Transmittance Measurements 70
2.8 Refractive Index Measurements 71
2.9 Recording of Grating 72
2.9.1 Single Beam Method 72
2.9.2 Double Beam Interferometry 73
2.10 Diffraction Efficiency Measurements 74
2.11 Storage and Shelf Life 75
2.12 Multiplexing 76
2.13 Recording of Fourier Transform Hologram 76
2.14 Recording of Holograms 78
2.15 Surface Analysis 78
2.15.1 Atomic Force Microscopy (AFM) 78
2.15.2 Stylus Profilometer 79
2.16 Conclusion 80
References 80

Chapter 3 **Studies on Methylene Blue Sensitized Poly(vinyl chloride) Films Incorporation of Electron Donor and Monomers**

3.1 Introduction 85
3.2 Methodology 87
3.3 Fabrication of Films 88
3.4 Sensitivity of MBPVC Films 89
3.5 Incorporation of Electron Donors 91
3.6 Electron Donating Mechanism of Pyridine 92
3.7 Optimization of Pyridine Concentration 93
  3.7.1 Sensitivity of Pyridine Doped Films 94
  3.7.2 Diffraction Efficiency Measurements 95
  3.7.3 Optical Absorption Studies 96
  3.7.4 Optimization of Exposure 97
3.8 Incorporation of Monomer 97
3.9 Studies on MBPVC/Butyl Acrylate Films 98
  3.9.1 Film Fabrication 98
  3.9.2 Real Time Transmittance 99
  3.9.3 Optical Absorption Studies 100
  3.9.4 Diffraction Efficiency Measurements 100
  3.9.5 Film Behaviour at Higher Incident Power 101
3.10 Studies on MBPVC/Vinyl Acetate Films 102
  3.10.1 Film Fabrication 103
  3.10.2 Sensitivity of MBPVC/VAc 104
  3.10.3 Dye Behaviour 104
  3.10.4 Diffraction Efficiency Measurements 105
3.11 Comparison of MBPVC Films 107
3.12 Conclusion 108
References 108

Chapter 4 **Fabrication and Characterization of Methylene Blue Sensitized Poly(vinyl alcohol) Films**

PART I ***Studies on MBPVA Films with Different Monomers***

4.1.1 Introduction 113
4.1.2 Fabrication of MBPVA Film 114
4.1.3 MBPVA- Acrylic Acid 116
  4.1.3.1 Film Preparation 116
  4.1.3.2 Material Sensitivity 117
  4.1.3.3 Diffraction Efficiency 118
4.1.4 MBPVA-Methacrylic Acid 119
  4.1.4.1 Film Fabrication 119
  4.1.4.2 Studies on MBPVA/MAA Films 119
4.1.5 MBPVA-Butyl Acrylate 121
  4.1.5.1 Film Fabrication 121
  4.1.5.2 Real Time Transmittance Studies 121
  4.1.5.3 Diffraction Efficiency Measurements 122
4.1.6 MBPVA-Acrylonitrile 123
  4.1.6.1 Film Fabrication 124
  4.1.6.2 Real Time Transmittance studies 124
  4.1.6.3 Optical Absorption Studies 125
  4.1.6.4 Diffraction Efficiency Measurements 126
4.1.7 MBPVA/Vinyl Acetate 127
  4.1.7.1 Film Preparation 128
  4.1.7.2 Optimization of PVA/ Vinyl Acetate Ratio 129
  4.1.7.3 Optimization of Methylene Blue Concentration 131
  4.1.7.4 Optimization of pH 133
  4.1.7.5 Optimization of Exposure 133
  4.1.7.6 Optical Absorption Studies 134
  4.1.7.7 Film Properties on Ageing 135
  4.1.7.8 Drawback of the MBPVA/Vinyl Acetate Film 135

4.1.8 Comparison of Different monomers 136
4.1.9 Conclusion 136

PART II ***MBPVA-Vinyl Acetate: A Reusable Recording Medium***

4.2.1 Introduction 138
4.2.2 Film Fabrication 138
4.2.3 Optimization of PVA/ VAc ratio 139
4.2.4 Optimization of Methylene Blue Concentration 141
4.2.5 Optimization of Exposure Energy 142
4.2.6 Effect of Electron Donors 143
4.2.7 Diffraction Efficiency on Storage 144
4.2.8 Dye Behavior 145
4.2.9 Reusability of MBPVA/Vinyl Acetate 147
4.2.10 Film Fabrication- Modified Procedure 149
4.2.11 Resolution of the material 151
4.2.12 Conclusion 151

PART III ***Effect of Additional Monomers on the Storage Life of MBPVA-Vinyl Acetate***

4.3.1 Introduction 152
4.3.2 Film Preparation 153
4.3.3 Effect of Acrylic Acid on MBPVA/Vinyl Acetate 154
    4.3.3.1 Real Time Transmittance 154
    4.3.3.2 Optical Absorption Studies 154
    4.3.3.3 Refractive Index Measurements 155
    4.3.3.4 Diffraction Efficiency Measurements 155
    4.3.3.5 Storage Life of Grating 156
    4.3.3.6 Shelf Life 157
4.3.4 Effect of Methacrylic Acid on MBPVA/Vinyl Acetate 157
    4.3.4.1 Real Time Transmittance 157
    4.3.4.2 Optical Absorption Studies 158
    4.3.4.3 Refractive Index Measurements 159
    4.3.4.4 Diffraction Efficiency Measurements 159

4.3.4.5 Storage Life of Grating 160
4.3.4.6 Surface Analysis 161
4.3.4.7 Shelf Life 162
4.3.5 Conclusion 162
References 162

Chapter 5 **Studies on Dye Sensitized Poly(vinyl alcohol)/ Acrylamide Films**

5.1 Introduction 169
5.2 Film Fabrication 169
5.3 Experimental Details 170
5.4 Optimization of Acrylamide 170
5.5 Optimization of Beam Ratio 172
5.6 Optimization of Dye Concentration 173
5.7 Optimization of Electron Donor 176
5.8 Optimization of Exposure 178
5.9 Thickness Modulation 179
5.10 Efficiency on Storage 180
5.11 Shelf Life of the Film 182
5.12 Resolution of the Film 183
5.13 Surface Profile of the Material 184
5.14 Bragg Detuning 185
5.15 Angular Multiplexing 186
5.16 Recording of FT Hologram 188
5.17 Recording of Hologram 189
5.18 Using Lower Wavelength Lasers 190
5.19 Conclusion 193
References 193

Chapter 6 **Effect of Chromium Doping on the Diffraction Efficiency of Methylene Blue Sensitized PVA/Acrylamide Films**

6.1 Introduction 199
6.2 Effect of Different Crosslinkers on MBPVA/Acrylamide Film 200
  6.2.1 Organic Crosslinker 201
  6.2.2 Metal Ions 202
6.3 Importance of Chromium Doping 203
6.4 Film Fabrication 204
6.5 Effect of Chromium on Samples with Different MB Concentrations 205
6.6 Efficiency on Storage 207
6.7 Self Enhancement of Diffraction Efficiency 208
6.8 Behavior of Dye 211
6.9 Mechanism of Grating Formation 212
6.10 Hologram Recording 212
6.11 Dichromated PVA/AAm Films 213
  6.11.1 Triethanolamine as Electron Donor 213
  6.11.2 DMF as Electron Donor 214
  6.11.3 Diffraction Efficiency Measurements 215
6.12 Conclusion 217
References 217

Chapter 7 **Fabrication of a Self-developing and Stable Copper Doped Photopolymer System**

7.1 Introduction 223
7.2 Why Copper Doping 224
7.3 Experimental Procedure 225
7.4 Material Sensitivity with the Incorporation of Copper Chloride 226
7.5 Effect of Copper Chloride on DE 227
7.6 Diffraction Efficiency on Storage 228
7.7 Stability of Leucoform 229
7.8 Resolution of the Material 230
7.9 Shelf Life of the Material 232

7.10 Dynamic Range of the Material 233
7.11 Recording of FT Hologram 235
7.12 Recording of Hologram 235
7.13 Comparison of Cu Doped and Undoped MBPVA/AAm Films 236
7.14 Conclusion 237
References 237
Chapter 8 **Summary and Conclusion** 239
Major Achievements 245
Future Outlook 246

Preface

Holographic technology is at the dawn of quick evolution in various new areas including holographic data storage, holographic optical elements, artificial intelligence, optical interconnects, optical correlators, commerce, medical practice, holographic weapon sight, night vision goggles and games etc. One of the major obstacles for the success of holographic technology to a large extent is the lack of suitable recording medium.

Compared with other holographic materials such as dichromated gelatin and silver halide emulsions, photopolymers have the great advantage of recording and reading holograms in real time and the spectral sensitivity could be easily shifted to the type of recording laser used by simply changing the sensitizing dye. Also these materials possess characteristics such as good light sensitivity, real time image development, large dynamic range, good optical properties, format flexibility, and low cost. This thesis describes the attempts made to fabricate highly economic photopolymer films for various holographic applications.

In the present work, Poly (vinyl alcohol) (PVA) and poly (vinyl chloride) (PVC) are selected as the host polymer matrices and methylene blue (MB) is used as the photosensitizing dye. The films were fabricated using gravity settling method. No chemical treatment or pre/post exposures were applied to the films. As the outcome of the work, photopolymer films with more than 70% efficiency, a permanent recording material which required no fixing process, a reusable recording material etc. were fabricated. The findings are described in seven chapters preceded by an introductory chapter.

Chapter 1 is a general introduction on holographic recording materials. It describes the requirements of a recording medium for different applications, the advantages of polymer based recording media over other materials etc. It presents an exhaustive review on photopolymer recording materials, which are the materials under study in this work.

Chapter 2 deals with the preparation of polymer films and the different characterization techniques adopted.

Chapter 3 describes the modifications made to the complexed methylene blue sensitized PVC films developed in our laboratory. Attempts have been made to improve the shelf life of the film, and to increase the diffraction efficiency and storage life of the gratings recorded with the incorporation of electron donor and monomers. The diffraction efficiency and storage life of the grating was improved with the incorporation of electron donor. But no improvement in the efficiency was observed for films doped with butyl acrylate and vinyl acetate monomers.

The effect of different monomers on the diffraction efficiency of MB sensitized PVA films are described in Chapter 4. This chapter is divided into three parts. The first part deals with the incorporation of monomers like acrylic acid, methacrylic acid, butyl acrylate, acrylonitrile and vinyl acetate on MB sensitized PVA films. But none except vinyl acetate gave films with good efficiency or sensitivity. The second part is regarding the development of a reusable recording medium based on poly (vinyl alcohol) with vinyl acetate monomer. The optimized film composition showed an efficiency of 6.3%. The efficiency was found to decrease on storage and the grating vanished within 24 hrs. But the material could be reused more than 20 times without considerable decrease in the efficiency. To improve the storage life of the grating recorded in MBPVA/vinyl acetate films, two monomers (acrylic acid and methacrylic acid) were incorporated. The effect of these monomers on the holographic performance of MBPVA/vinyl acetate is explained in the third part of chapter 4. In this case also a sudden fall in the efficiency was observed; but gratings could be stored for long time with a decrease in efficiency. Though the storage life was improved with acrylic acid, the shelf life of the film was limited to 2 months. Methacrylic acid doped MBPVA/vinyl acetate films could be stored for more than one year with an efficiency of 0.07%.

The fabrication of methylene blue sensitized PVA/ acrylamide film is explained in Chapter 5. The film composition was optimized and 70% efficiency was obtained for an exposure of 120mJ/cm^2. Both transmission holograms and fourier transform holograms were recorded on these films. Though 70% efficiency was obtained, its efficiency was found to be decreased on storage. The feasibility of using this film as a panchromatic material is also reported.

For a material to be used in real time applications, it is essential to be free from wet processing. In order to improve the storage life of the recorded grating, certain metal ions and crosslinkers were incorporated to the MBPVA/acrylamide film. The effect of different additives on the storage life is demonstrated in Chapter 6. Of the films with different additives, chromium doped films deserves special attention on account of its better storage life. On chromium doping, the storage life was improved and it depends on the MB concentration also. Interestingly for a particular ratio of methylene blue and ammonium dichromate, a self enhancement in the efficiency was observed. These samples (just after recording) showed highest efficiency of 20% at 500mJ/cm^2 without any pre exposure and chemical fixing. The diffraction efficiency slowly increased to 40% by 3 months. It remains the same for months and then the efficiency gradually decreases and reaches the initial efficiency of 20%. This self-enhancement observed in this case may be mainly due to the dark reaction.

Chapter 7 deals with the fabrication of a stable self developing photopolymer film. This is achieved by doping cupric chloride to the MBPVA/ acrylamide. The efficiency (just after recording) of Cu doped films are less than that of undoped films. The gratings recorded on Cu doped films showed an efficiency of 32% for an exposure of 600mJ/cm^2 and its efficiency remains the same for years. 1400 lines/mm could be recorded on this film.

The summary of the entire work is presented in Chapter 8. The chapter ends with scope of the present work and the future research plans.

Publications

Technology Transfer

The technology for the fabrication of two polymer films is transferred to M/S. Light Logics Holography & Optics. Pvt. Ltd., Trivandrum, India

The technology transferred materials:

1. Polymer film with 70% Efficiency
2. Copper doped polymer film with 32% efficiency

Journal Papers

1. "Enhancement of diffraction efficiency and storage life of poly(vinyl chloride) based optical recording medium with the incorporation of an electron donor", **Beena Mary John,** Ushamani.M, K. Sreekumar, Rani Joseph, C. Sudha Kartha, Appl. Opt., **46**(3) 346-350 (2007).
2. "Copper doped methylene blue sensitized poly(vinyl alcohol)/acrylamide films for stable diffraction efficiency", **Beena Mary John**, Rani Joseph, K. Sreekumar, C. Sudha Kartha, Jpn. J.Appl. Phys., **45**(11), 8686-8690 (2006).
3. "Reusable recording medium based on MBPVA and vinyl acetate", **Beena Mary John**, Ushamani.M, Rani Joseph, K. Sreekumar, C. Sudha Kartha, J. Mod. Opt. **53**(3), 343-355, (2006).
4. "Effect of chromium doping on the diffraction efficiency of methylene blue sensitized PVA/acrylamide films", **Beena Mary John**, Rani Joseph, K. Sreekumar, C. Sudha Kartha, J. Mater. Sci: Mater. Electron., *(Article in press)*

Conference Papers:

International

1. "Effect of chromium doping on the diffraction efficiency of methylene blue sensitized PVA/acrylamide films", **Beena Mary John**, Rani Joseph, K. Sreekumar, C. Sudha Kartha, International Conference on Optical, Optoelectronic and Photonic Materials and Applications (ICOOPMA), London (2007).

2. “Red sensitive photopolymer for permanent holographic storage”, **Beena Mary John**, Rani Joseph, K. Sreekumar, C. Sudha Kartha, International Conference on Optoelectronics, Fiber, Optics & Photonics (Photonics-2006), Hyderabad (2006).
3. “Improvements in the holographic performance of DCPVA films due to the incorporation of a photopolymerizable monomer”, **Beena Mary John**, Saji John K, Rani Joseph, K. Sreekumar, C. Sudha Kartha, International Conference on Optical, Optoelectronic and Photonic Materials and Applications (ICOOPMA), Australia (2006).
4. “Effect of copper chloride on the diffraction efficiency of MBPVA/ acrylamide films”, **Beena Mary John**, K. Sreekumar, Rani Joseph, C. Sudha Kartha, International Conference on Optics and Optoelectronics (ICOL), Dehradun (2005).
5. “Self-enhancement of diffraction efficiency in MBPVA/acrylamide films”, **Beena Mary John**, Rani Joseph, K. Sreekumar, C. Sudha Kartha, International Conference on Optoelectronic Materials and Thin films for Advanced Technology (OMTAT), Kochi (2005).
6. “Three dimensional self-written optical waveguide in a photopolymer”, C.P. Jisha, **Beena Mary John**, V.C. Kishore, V.C. Kuriakose, K. Porsezian, C. Sudha Kartha, International Conference on Optoelectronic Materials and Thin films for Advanced Technology (OMTAT), Kochi (2005).
7. “Preparation and characterization of a new photopolymerizable holographic material based on polyvinyl alcohol and vinyl acetate”, Ushamani.M, Nisha V.S, **Beena Mary John**, K.Sreekumar C.Sudha Kartha, Rani Joseph, MACRO, Trivandrum (2004).
8. “Effect of electron donors on diffraction efficiency of MBPVA/PAA Blend", **Beena Mary John**, Ushamani.M, Nisha V.S, Rani Joseph, K.Sreekumar, C. Sudha Kartha, International Conference on Advances in Polymer Technology, Cochin (2004).
9. “Characterization of eosin dye doped PVA medium for holographic recording using Ar^+ laser beam”, Nisha V.S, Ushamani.M, **Beena Mary John**, C. Sudha Kartha, K.

Sreekumar, Rani Joseph International Conference on Advances in Polymer Technology, Cochin (2004).

National Conference

1. "Influence of butyl acrylate on the diffraction efficiency of PVC based holographic recording medium", **Beena Mary John**, Ushamani.M, Rani Joseph, K. Sreekumar, C. Sudha Kartha, National Conference on Current Trends in Material Science (CTMS), Chengannur (2007).
2. "A photopolymerizable holographic recording media with spectral sensitivity in the entire visible region", **Beena Mary John**, Pramitha V, Nimmi K.P, K. Sreekumar, Rani Joseph and C. Sudha Kartha, 31st OSI Symposium on Contemporary Optics and Applications, Baroda (2007).
3. "A new self-developing and stable copper doped photopolymer system for holographic applications", **Beena Mary John**, Rani Joseph, C. Sudha Kartha, 19th Kerala Science Congress, Kannur (2007).
4. "Methacrylic acid monomer for enhancing the storage life of gratings recorded on methylene blue sensitized PVA-vinyl acetate films", **Beena Mary John**, Ushamani.M, Sreekumar K, Rani Joseph, C. Sudha Kartha, 17th AGM MRSI, Lucknow (2006).
5. "Role of vinyl acetate monomer in the diffraction efficiency of poly (vinyl alcohol) film", **Beena Mary John**, Ushamani.M, Rani Joseph, K. Sreekumar C. Sudha Kartha, 16th AGM MRSI, Pune (2005).
6. "MBPVA/ acrylamide system for holographic recording using red, green and blue lasers", **Beena Mary John**, Nisha V.S, Ushamani.M, Rani Joseph, K. Sreekumar C. Sudha Kartha, 15th AGM MRSI, Varanasi (2004).
7. "Diffraction efficiency measurement on eosin doped poly(vinyl alcohol) using 488nm line of Ar^+ laser", Nisha V.S, Ushamani.M, **Beena Mary John**, K. Sreekumar, C. Sudha Kartha, Rani Joseph, 15th AGM MRSI, Varanasi (2004).

ABBREVIATIONS

AA	Acrylic Acid
AAm	Acrylamide
ADC	Ammonium Dichromate
AFM	Atomic Force Microscopy
AN	Acrylonitrile
BA	Butyl Acrylate
CGH	Computer Generated Holograms
CIEO	Centre for Industrial and Engineering Optics
CMBPVC	Complexed Methylene Blue Sensitized Poly (vinyl chloride)
CROP	Cationic Ring Opening Polymerization
DCG	Dichromated Gelatin
DCP	Dichromated Pullulan
DCPAA	Dichromated Poly(acrylic acid)
DCPVA	Dichromated Poly(vinyl alcohol)
DE	Diffraction Efficiency
DHEBA	N,N’-Dihydroxyethylenbisacrylamide
DMAA	Dimethyl Acrylamide
DMF	Dimethyl Formamide
ED	Electron Donor
ErB	Erythrosin B
ESR	Electron Spin Resonance
Fe: PVA	Ferric Chloride Doped Poly(vinyl alcohol)
FT	Fourier Transform
GA	Gluteraldehyde
GB	Giga Byte
HBP	Hyperbranched Polymers
HEMA	2-Hydroxyethylmethacrylate
HMA	N-Hydroxymethyl acrylamide
HOE	Holographic Optical Element
H-PDLC	Holographic Polymer-Dispersed Liquid Crystal

HUD	Head-Up Displays
LC	Liquid Crystals
LVDT	Linear Variable Differential Transformer
MAA	Methacrylic acid
MB	Methylene Blue
MBA	N,N'-Methylenbisacrylamide
MBDCG	MB Sensitized Dichromated Gelatin
MBDCPVA	MB Sensitized Dichromated Poly(vinyl alcohol)
MBG	Methylene Blue Sensitized Gelatin
MBPVA	Methylene Blue Sensitized Poly(vinyl alcohol)
MBPVA/AAm	Methylene Blue Sensitized Poly(vinyl alcohol)/ Acrylamide
MBPVC	Methylene Blue Sensitized Poly (vinyl chloride)
PAA	Poly(acrylic acid)
PAP	Photoaddressable Polymer
PDLC	Polymer-Dispersed Liquid Crystal
PMMA	Poly(methyl methacrylate)
PR	Photorefractive
PVA	Poly(vinyl alcohol)
PVA/AAm	Poly(vinyl alcohol)/Acrylamide
PVC	Poly(vinyl alcohol)
PVK	Poly(vinyl carbazole)
RB	Rose Bengal
RI	Refractive Index
SAN	Styrene-Acrylonitrile Copolymer
SE	Self Enhancement
SNR	Signal to Noise Ratio
TB	Tera Byte
TEA	Triethanolamine
Tg	Glass Transition Temperature
VAc	Vinyl Acetate
WORM	Write-Once-Read-Many

Chapter 1

Review on Polymer Based Holographic Recording Media

A general introduction on holographic recording materials is given in this chapter. The requirements of recording medium and the advantages of polymer based recording media over other materials etc. are presented. This chapter includes an exhaustive review on photopolymer recording materials, which are the materials under study.

1.1 Introduction

The awe-inspiring example of laser technology, holography is now spreading from research laboratory to industry, and finds wider employment in data storage and other engineering applications. In this chapter, the potency and major challenges of holographic technology and the particulars of the Achilles' heel, the recording media are elucidated. A brief review on the available literature on polymer based recording media is given in the context of its contribution towards the realization of theoretical predictions of holography.

1.2 Relevance of Holographic Technology

Holography is a very useful tool in many areas, such as in commerce, scientific research, medicine, and industry. Holographic technology is on the dawn of quick evolution in various new areas including artificial intelligence, optical interconnects, optical correlators, holographic optical elements, medical practice, holographic weapon sight, night vision goggles, games etc. So, holograms are not just 3-D images!

Storage requirements all over the world are exploding, making data storage one of the biggest challenges in the expanding multimedia market. For more than thirty years, optical storage via volume holography has been the `Holy Grail' of photonics. The next generation of data storage system is expected to use optical holography to store information throughout the three dimensional volume of a material. Volume holography will offer capacities approximately 1 TB (terabyte) (~10000 holograms) in a storage crystal with a size of a sugar cube having data transfer rate of 1GB/s at access times less than 100 µs/bit [1-2]. In addition to high storage density, holographic data storage promises fast access times, parallel search through databases, high data security, and high data transfer rates due to inherent parallelism of its page-wise storage and retrieval. Combining high storage densities, fast transfer rates, with reliable, low cost media, makes holography poised to become a compelling choice for next-generation storage and content distribution needs. In addition, the flexibility of the technology allows the development of a wide variety of holographic storage products that ranges from handheld devices for consumers to storage products for the enterprises. By this growing technology we could realize 2GB of data on a postage stamp or 20 GB on a credit card sized disks or 200 GB on a disk. Optical data storage systems have significant merits over the existing digital system in the level of security achieved. Optical encryption techniques can be applied on a holographic data storage system much conveniently by encrypting data in the optical domain. The parallel processing and encryption / decryption of two- dimensional pages have made secure holographic databases superior to the existing digital technologies [3-4].

Holographic optical elements (HOEs) are diffractive structures that are constructed holographically by the interference of two beams of light. Typically one beam resembles the ‘play back’ beam which illuminates the HOE in the final system. The second beam corresponds to the ‘image’ beam which is supposed to exit the HOE upon its playback [5]. HOEs can be approximated as holograms of point sources or collimated beams of light, such that light from one source is imaged onto the other. Optical elements such as lenses, beam splitters, diffraction gratings and filters can be produced by holographic imaging. These HOEs have the advantage of being low cost (due to their simple design, small size and light weight) and are easily reproducible by embossing polymer materials [6]. HOEs can duplicate most of the functions provided by glass optics if optical system operates over narrow spectral bandwidth or requires chromatic dispersion. Some of the unique functions of HOEs are multiple function optics, independent of substrate shape, large optical apertures, lightweight and narrow spectral response. HOEs have realized certain optics that could not be produced with previous optical technologies [7]. Areas such as optical sensors, optical interconnect, optical information processing, fiber optics, optical scanners, optical disc pick up heads and solar concentrators have benefited from the use of HOEs [8-14]. As stated earlier, the advantages of HOEs are multifold. Firstly, since the HOEs are thin and planar, the optical systems can be made more compact. Secondly, several elements performing complicated functions can be integrated into one HOE. The frontline recording materials for the fabrication of HOEs have been the conventional silver halide emulsions, materials such as dichromated gelatin (DCG), photoresists, and photopolymers etc. have been employed in the fabrication of the HOEs. The most commercially available silver halide materials have faded away from the market [6]. Recently, Mihaylova *et al.* introduced the use of a photopolymer (2mm thick) holographic grating in electronic speckle pattern shearing Interferometry [15].

Security holograms offer a unique solution to product and document counterfeit providing unambiguous visual authentication that requires no external device or reader for verification. The use of small holograms in credit cards, which are made to prevent falsification, has made holograms a well known concept. Holograms show up more and more often on tickets and original covers. Important areas of application are bar-code readers in shops, warehouses, libraries and so on, which is based on holographic components like optical gratings.

In the aircraft industry head-up displays (HUD) are an important example of holographic technology. HUD helps the pilots so they do not need to look down onto the instrument panels, because the instruments are projected onto the windscreen with the help of holographic technology, and thus make flying easier [16].

The unique advantage of holographic interferometry arises from the fact that holography permits storing a wavefront for reconstruction at a later time. Wavefronts which were originally separated in time or space, or even wavefronts of different wavelengths, can be compared by holographic interferometry. As a result, changes in shape of quite rough surfaces can be studied by interferometric precision. One of the most important applications of holographic interferometry is non-destructive testing. It visually reveals structural faults without damaging the specimen. Holographic interferometry has also proved its utility in aerodynamics, heat transfer, and plasma diagnostics etc. [17].

Holography finds its application in medicine also. Doctors use three-dimensional holographic CAT scans to make measurements without invasive surgery. This technique is also used in medical education. Holographic interferometric techniques have been widely applied with success for the study of different parts of human body including cornea, tooth mobility, tympanic membrane, basilar membrane, joint, chest, and bones. Endoscopic holography is a powerful tool for non contact high resolution imaging and nondestructive measurements inside the natural cavities of human internal organs. The internal hologram recording endoscope produces full three-dimensionality of the reconstructed image with parallax and a large focal depth. This technique can be used for cellular structure analysis and may even substitute biopsy in tumor diagnosis.

Today there are hundreds of potential real world applications for holography and it has far surpassed being limited only to the realm of art, although it is hard to deny that indeed art is an excellent application. Holography has been used to make archival recordings of valuable and/or fragile museum artifacts. Holography has been used by artists to create pulsed holographic portraits as well as other works of art [18].

1.3 Holography-Major Challenges

Although holography was conceived in 1948, it was not considered a potential storage technology until the development of the laser in the 1960s. While data storage using volume holography has been proposed long ago it has failed to become a commercial technology because of lack of compact laser systems, methods, detectors, input devices and recording medium [19].

- ***Laser:*** Though a variety of lasers have been used for holography over the years, a data storage system that is commercially available requires a compact, efficient and ultimately low cost source. The main requirements are coherence and wavelength compatibility with the material. Conventional semiconductor lasers, though compact and efficient, generally lack the coherence length required for holography. Similarly gas lasers like Ar^+ can be used in the laboratory to characterize materials, but the need for external cooling, the large size, and the immense power requirements preclude their use in real systems. Now the problems have almost overcome and the two lasers that are particularly relevant are the diode pumped frequency doubled Nd:YAG, and the InGaP DFB lasers [20].

- ***Methods:*** Traditional multiplexing strategies proposed previously resulted in complex systems which are difficult to implement. More importantly, geometric constraints severely limited the maximum density in thin media. The introduction of shift multiplexing, which was conceived at Caltech lead to a paradigm shift in holographic storage system design concepts [21]. The idea of accessing holograms by simple translation of the media in a manner similar to conventional disk drives greatly simplified device architecture concepts.
- ***Detectors:*** Speed and cost are crucial for the output device. Since the last few years several components essential to the development of any viable holographic storage system have been developed. The three key devices are low cost, highly coherent laser sources, a high speed, high throughput input device, and finally a high speed, low cost output device. Although high-speed CCD detectors have been developed; the prospect for low cost, high performance devices is questionable. CMOS Active Pixel Sensors are a better solution. These devices, made in a conventional silicon process, have high probability for high yield and low cost manufacturing. In addition, these devices may allow integration of complex processing functions on the detector. CMOS is an inherently fast, (ns switching response), low power technology allowing great device versatility.

- ***Data Input Devices*** (Spatial Light Modulators, SLM): SLM is used to display the data to be stored in a two dimensional page format. Suitable devices developed for the display industry have recently come into existence.
- ***Materials/Media:*** There has been no viable material for this technology. Media for holographic storage has long been one of the primary focus points for researchers [22]. Though a number of materials have been developed, none meet all the requirements and hence it remains as one of the major constraints for the success of holographic technology [20].

1.4 Media Requirements

Any material used to record a hologram must respond to exposure to light with a change in its optical properties. In the absorption or amplitude modulating materials the absorption constant changes as a result of exposure, while in phase modulating materials thickness or refractive index (RI) changes due to the exposure. In the phase modulating materials, there is no absorption of light and the entire incident light is available for image formation, while the incident light is significantly absorbed in an amplitude modulating material. Thus a phase material can produce a higher efficiency than an amplitude material. Also in phase modulating media, the amount of phase modulation can be made as large as desired. A practical recording media can be considered as a combination of these two. The complex amplitude transmittance T of a recording material can be written as

$$T=\exp(-\alpha d)\exp[-i(2\pi nd/\lambda) \quad \ldots\ldots\ldots\ldots\ldots(1.1)$$

where α is the absorption coefficient of the material, d is the thickness and n is the refractive index [17]. The material should be of high optical quality. The media performance is assessed in terms of parameters like diffraction efficiency (DE), sensitivity, resolution, signal to noise ratio (SNR), temporal stability etc. [23]. For real time applications like digital data storage, the material should be free from wet chemical processing and it should be self developing. For the commercial availability of material it should be economic with ease of fabrication steps.

Diffraction Efficiency: The diffraction efficiency η of a hologram is defined as the ratio of the power diffracted into the desired image to that illuminating the hologram. DE is proportional to the square of the gradient of the amplitude transmittance T versus exposure E curve as well as to the squares of input modulation and modulation transfer function. The maximum DE is obtained where the slope of the T versus E curve is steepest. This is usually at a slightly higher exposure than that corresponds to the steepest part of the T versus E curve [17]. For an ideal recording material, plots of $\sqrt{\eta}$ versus E with input modulation as a parameter and plots of $\sqrt{\eta}$ versus input modulation with E as a parameter should be straight lines.

Sensitivity: The sensitivity can be defined in terms of the square root of efficiency in writing plane wave, unity modulation depth gratings with a given fluence It, where I is the total intensity in W/cm^2 and t is the exposure time [20]. Hence the sensitivity $S_{\eta 1/2}$ is

$$S\eta^{1/2} = \eta^{1/2}/Itl\ (cm/J) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.2)$$

where, l is the effective interaction length.

Dynamic Range: It refers to the total response of the medium when divided up among many holograms multiplexed in a common volume of the material. If media response is quantified as the square root of the efficiency, dynamic range can be defined for M multiplexed holograms as

$$\mathbf{M\# = \sum_{i=1}^{M} \eta_i^{1/2}} \ldots\ldots\ldots\ldots\ldots\ldots (1.3)$$

where, η_i is the diffraction efficiency of each hologram. *M#* or ‘M’ number’ describes the scaling of DE with number of holograms [20].

Though a number of materials were developed, most of the currently available recording media have been optimized for display rather than data storage applications. The requirement for a media for digital holographic data storage arises from the page-wise recording and recovery of digital data and the three-dimensional nature of holography. Media must (i) be optically flat and of low scatter so that pages of data (arrays of bits) can be imaged through the material, recorded and recovered with low probabilities of error; (ii)have adequate dynamic range to support the overlap of large numbers of holograms, each with sufficiently high diffraction efficiencies to ensure high data read rates; (iii)be thick enough to support the independent storage of large numbers of holograms to yield high densities; (iv) exhibit high photosensitivity to yield high data write rates; and (v) undergo limited changes in their dimensions and bulk refractive index (RI) upon recording to ensure the fidelity of data recovery [20].

The requirements of media for digital holographic data storage are shown in Table1.1.

Table 1.1. The requirements of media for digital holographic data storage

Material	Requirements
Refractive index contrast	$\Delta n > 5x10^{-3}$
Thickness of media	> 500 µm
Dynamic range (M#)	≥10
Optical scatter	$<\sim 10^{-5}$ of reference beam power
Optical flatness	$<\sim \lambda/2$
Photosensitivity (Vis-NIR)	100-1000mJ/cm^2
Dimensional stability	within <0.5%
Processing for readout	Solvent/ heat free
Readout	Nonvolatile
Archival life of stored data	>5-10 years environmental stability and thermal stability

1.5 Holographic Recording Materials

Several holographic recording media are under investigation for last four decades. Silver halide photographic emulsions are still the most widely used recording material for holography, mainly because of its relatively high sensitivity, high resolving power and the commercial availability [24]. Though greater than 70% efficiency could be achieved in Agfa Gevaert 8E75 HD and Kodak 649F plates, it requires wet chemical development and hence cannot be used in data storage devices and other real time applications [25-26]. DCG is one of the best holographic recording materials because of its well known properties: high DE, large capacity for RI modulation, high resolution (as much as 5000 lines/mm), high signal-to noise ratio, and good environmental stability (with a cover plate or a thin protective coating) [27-28]. A major shortcoming of DCG, limited spectral sensitivity, has overcome by dye doping (xanthene and methylene blue) [29-30]. But just like silver halide emulsions, gelatin also require wet developing process and the energy requirement is very high. An alternating material, silver halide sensitized gelatin, combines the relatively high sensitivity of photographic materials and low scattering and high light stability of DCG [17]. It involves exposing a silver halide photographic emulsion and then processing it so as to obtain a volume phase hologram consisting solely of hardened gelatin.

Photoresists, light sensitive (UV-500 nm) organic films which yield a relief image after exposure and development, are employed in holography mainly for the production of master plates for embossed holograms and for manufacturing holographic gratings. It requires wet chemical processing and its sensitivity in the blue region is very low. Another class of materials of interest is photochromics. Though the material is reversible, organic photochromics are prone to fatigue and a limited life. Inorganic photochromics are grain free and have high resolution and it requires no processing and can be erased and reused almost indefinitely. However, despite these advantages, their use has been limited so far by their low DE and low sensitivity. Photothermoplastics which are reversible and uses thermal fixing process have reasonably high sensitivity and efficiency. But the equipment required for charging and heating the layer is very expensive and the resolution of the material is limited to 1000 line/mm.

Because of irreversibility and large dynamic range, photorefractive (PR) crystals such as $LiNbO_3$, $LiTaO_3$, $BaTiO_3$, $KNbO_3$, $Bi_{12}TiO_{20}$, are widely employed in holographic data storage [31-32]. However, the difficult crystal growth and sample preparation required for inorganic PR crystals has limited the widespread use of these applications [33].Due to its cost and the impermanence of holograms written therein, it is unlikely to be included in a commercial product. In addition, holograms recorded in this medium are erased on read out, making crystals like $LiNbO_3$ unsuitable for archival storage applications [34-35].

For a long time organic materials have found importance in holography. Biological materials like bacteriorhodopsin (photochromic retinal protein), have been used for many applications in optical image processing, such as optical memories and real time holography [36-39]. Now-a-days varieties of polymer compositions are emerging as holographic recording material. They include photopolymers, photorefractive polymers, photoaddressable polymers, polymers dispersed liquid crystal etc. The following section describes the use of different types of polymers used in holography.

1.6 Photorefractive Polymers

Rapid advances in the field of PR polymers and composites have led to the development of high performance materials with RI modulations approaching 0.01 and DEs close to 100%. The PR effect refers to spatial modulation of the index of refraction under nonuniform illumination via space-charge-field formation and electro-optic nonlinearity. The effect arises when charge carriers, photogenerated by a spatially modulated light intensity, separated by drift and/or diffusion processes and become trapped to produce a nonuniform space-charge distribution. The resulting internal space-charge electric field then modulates the RI to create a phase grating, or hologram, which can diffract a light beam. Because such a hologram can typically be erased by uniform optical illumination, PR holograms are dynamic, that is, they may be erased and rewritten, one of many properties that distinguish PR materials from other mechanisms for hologram formation [20-40].To produce the PR effect, the material should consist of a photoinduced charge generator, a transporting medium, trapping sites, and molecules that provide optical nonlinearity. In contrast to inorganic crystals, the spectral sensitivity of PR polymer can be changed by using different dopent sensitizers [20, 41].

The first proven polymeric PR material was made in 1990 and was composed of an optically nonlinear epoxy polymer bisphenol-A-diglycidylether 4-nitro-1,2-phenylenediamine, which was made photoconductive by doping with 30 wt. % of the hole transport agent diethylamino benzaldehyde diphenylhydrazone [42-43]. The first milestone in this field occurred with the report by the IBM group, having a net gain and DE of 1% in 125µm thick samples of the composite FDEANST: PVK: TNF [44]. Shortly after that Arizona group reported on a composite based on photoconductor PVK:TNF: doped with the chromophore DMNPAA with 6% efficiency [45]. By improving the sample fabrication conditions, enabling higher fields to be applied, these composites exhibited nearly 100% DE, net gain coefficients of 200cm^{-1} and fully reversible index modulation amplitudes of 0.007 with a response time of 100-500 ms [46]. The most commonly used polymer binder is poly(vinyl carbazole)(PVK). High-performance material of this class was developed by using inert polymers like poly (methyl methacrylate) (PMMA) and bisphenyl-A-polycarbonate [47-48]. PR polymers are alternatives to their inorganic or semiconductor counterparts owing to their low cost, ease and flexibility of fabrication, large size, and superior performance [49]. Limitations of these organic materials for direct practical applications are the requirement of high bias voltages (3–10 kV for a typical 100 µm thick sample) and their slow response time [50].

1.7 Photoaddressable Polymers

In principle all materials that react to light with a change of specific properties can be described as photoaddressable polymers (PAPs). These PAPs are basically azobenzene containing liquid crystalline copolymers. Polyacrylates, polymethacrylates, polisiloxanes, polycarbonates, polyurethanes, polyimides and aliphatic polyesters have been investigated as the main chain [51-57].

Azobenzene chromophores exist in two isomeric states: the long rod like trans form and the bent cis configuration. The isomerization can be induced by light in both directions, from trans to cis and from cis to trans, whereas the cis isomer can also undergo a thermal back relaxation to the thermodynamically more stable trans isomer. Illumination leads to a series of trans-cis-trans isomerization cycles, resulting in a photo-stationary equilibrium that depends on the wavelength of the actinic light and the temperature of the sample [58-59]. Photoinduced reversible surface-relief-gratings have been well documented as a unique and fascinating property of azobenzene-containing polymers. This is a well known candidate for both polarization holography and photolithography [60]. Upon exposure to an interference pattern, large surface modulations can be produced on azo polymer films [61-62]. The photofabricated surface structures are stable below the glass transition temperatures (Tgs) of the polymers and can be removed by optical erasure or by heating the samples to a temperature above their Tgs [63-64]. Complex surface relief structures can be prepared by methods such as sequentially superimposed inscriptions with beams having different wavelengths or polarization directions [65-66]. To induce photo-optical changes, different dichroic dyes such as spiropyranes, spirooxazines, stilbenes and fulgides are also used [67-72].

1.8 Polymer Dispersed Liquid Crystals

Liquid crystals (LCs) are an interesting medium for exploring electro-optical effects due to their large dielectric anisotropy and optical birefringence.

There has been a fascinating marriage of two polymer-related technologies over the past few years: photopolymer holography and polymer-dispersed liquid crystals (PDLCs) [73-74]. The result is a new type of material known as holographic PDLC (H-PDLC). Intriguing features of this material include its high index modulation, true volume hologram character, unique anisotropic nature, and electro-optical behavior [75]. Generally, an H-PDLC sample is made by sandwiching the pre-polymer syrup between two glass slides coated with a transparent conductor. The DE of the recorded hologram can be controlled by applying an electric field across an H-PDLC cell. Pre-polymer syrups are typically a combination of a fast-curing multifunctional monomer, a photoinitiator dye, a coinitiator, a reactive diluent, and a liquid crystal. The choice of a suitable photoinitiator dye for free radical polymerization is challenging as few dyes are available for use in the visible region (450–650 nm). Rose Bengal acetate ester has been found to be useful for writing gratings using Ar^+ laser lines (476, 488, 514 nm) or a Verdi laser line (532 nm) [76]. Other photoinitiators used for making H-PDLC gratings with the Ar^+ laser lines are dibromoflourescein and 7-diethyl aminocoumarin [77-78]. There are a number of problems associated with these long wavelength dyes in terms of thermal and photochemical stability and bleaching speed. For high DE, especially in reflection gratings, a high concentration of small nematic droplets in the LC layer is needed [78].

Two classes of monomers have been used for H-PDLC formulation, one based on free-radical addition polymerization reaction and the other, a combination of free-radical and step-growth mechanism. Free radical addition polymerization of multifunctional monomers leads to formation of polymer of high molecular weight in a few seconds. Multifunctional acrylate monomers with functionality greater than 4 are effective in this regard. The monomers that have been used are dipentaerythritol hydroxy pentaacrylate, urethane acrylate oligomer, and bisphenol-A-diacrylate. Urethane resins with functionality ranging from 2 to 6 were also used [79-80]. Another class of monomers used in H-PDLC gratings is the commercially available Norland resins [81]. These contain polyfunctional thiols and allenes and undergo a combination of free-radical and step-growth polymerization. The most widely used resin in PDLC research is NOA 65 (Norland Optical Adhesive) [82]. Though efficiencies of the order of 70% were obtained, its resolution is limited. The choice of LC plays a very important role in the electro-optical performance and DE of the H-PDLC. Almost all H-PDLC publications report the use of nematic LC with positive dielectric anisotropy, $\Delta\varepsilon$ [83-84]. High RI (Δn) and $\Delta\varepsilon$ are both important parameters in the choice of LC as they result in higher diffraction efficiency (DE) and lower switching fields. It is also important that the RI of the cured polymer matches that of the ordinary index of the liquid crystal. There is one report of an H-PDLC reflective display device using a smectic LC [85]. The efficiency obtained for H-PDLC containing rose Bengal (RB) as photoinitiator and n-Phenylglycine as coinitiator showed only 12% DE, whereas 18% DE was reported for an azo-dye doped polyimide (20nm thick) polarization sensitive layers, when recorded with a 458 nm Ar^+ laser [86-87].

1.9 Photopolymers

The term photopolymerization means the initiation by light of a chain polymerization process. In the more general sense, photopolymerization implies the increase of molecular weight caused by light [88]. Photopolymers are photoactive materials capable of recording spatial variations in light intensity through irreversible changes in their RI. When exposed to interfering light beams, as in hologram formation, the systems undergo photopolymerization reactions that encode the fine spatial interference pattern of the incident light. Both the phase and the amplitude information needed for hologram recreation are stored [89]. Photopolymers have been exploited in a variety of applications requiring versatile holographic storage media, such as HUDs, data storage, HOEs, and waveguides [90-97]. Although other holographic storage materials have been used to develop these technologies, it is widely believed that the high sensitivity, low cost, and versatility of photopolymeric media would enable more widespread commercial applications of holography [97-99].

Photopolymerization is a chemical process by which small molecules or monomers are combined to make very large molecules or polymers. Photopolymer can be activated through a photosensitizer to exhibit refractive index changes due to polymerization or cross-linking. Photopolymers can be classified into two, photopolymerizable materials and photo-crosslinkable materials.

1.9.1 Photopolymerizable Media

Photopolymerizable systems for recording holograms typically comprise one or more monomers, a photoinitiation system, and an inactive component often referred to as binder. The photoinitiation system comprises a photosensitizing dye and a coinitiator (charge transfer agent- usually it is an amine). Other components are sometimes added to control a variety of properties such as pre-exposure shelf life and viscosity of the recording medium. The resulting formulation is typically a viscous fluid, or a solid with a low glass transition temperature, that is prepared for exposing either by coating on a solid or flexible substrate, or by containing it between two transparent solid substrates [20].

The basic recording mechanism involves several stages: photoinitiation, propagation and termination [100-101]. The photopolymerization begins by absorption of light by the photoinitiator, which results in the formation of primary free amine radicals. A redox reaction takes place between the excited dye molecule and the amine, generating the semireduced dye radical, which is not involved in the initiation of polymerization reaction [102-103]. A second electron transfer between the amine and the radical and a protonation process give rise to leucoform (colourless form) of the dye. In the second step of the initiation, the amine cation radical loses a proton to become the α-amino radical. In the second stage (propagation), the α-amino radical is subsequently adds to the carbon-carbon double bonds of the monomer unit to form a growing radical of one repeat unit in length, and thus initiates the polymerization reaction. Monomer depletion in the exposed regions causes a concentration gradient, which then induces monomer diffusion from the unexposed regions. When the photopolymer is exposed to an interference pattern, the monomers in the constructive interference region get polymerized. Because of the polymerization in the exposed regions, diffusion of monomer occurs from the destructive to constructive interference region. This causes RI modulation and results in grating formation. Here the absorbance modulation that occurs during exposure also contributes to the grating formation. Two separate paths exist for termination. The first is the normal bimolecular combination, in which two growing macro radicals come together and terminate. The second path for termination is disproportionate, in which a labile atom (usually hydrogen) is transferred from one polymer radical to another [104-106].

1.9.2. Binder

Monomers and the photoinitiation system are usually mixed with a third component, binder, to form a photoinitiator system. The binder is sometimes a polymer that is included to modify the viscosity of the formulation, to aid sample preparation and to enhance holographic exposure [20]. Though the binder is not directly involved in the photochemical reaction, the selection of binder is an important factor. The binder should be insensitive to humidity and environmental changes. The host matrix is a crucial component affecting physical properties of the recording medium such as its rigidity, environmental stability, dimensional changes upon holographic exposure etc. Polymeric materials such as PMMA, Polydiacetylene, PVK, poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), polythiophene, Poly(vinyl chloride) (PVC) etc. have been investigated for holographic applications [100, 107-109]. Binders can also be small molecules or oligomers [35]. System with polymeric binders include Du pont’s HRS recording material, while polaroid’s ULSH photopolymer employs either a small molecule or polymeric binder [110-111]. A recording medium of millimeter thickness or more and exhibiting high photoinduced RI change is required to achieve high storage density by recording multiple volume holograms, separated from each other by the Bragg effect, in the same spatial location [112-113]. For holographic data storage, the major limitations imposed by organic polymeric binders are the limited thickness of the medium, usually less than 200 µm, and temperature and light induced dimensional changes that can distort the holograms and degrade the fidelity with which the stored images can be retrieved. An approach to prepare thicker photopolymers is to use resins consisting of two independent photopolymerizable systems. Matrix forming oligomers are first precured to a gel state and then the hologram is recorded by photoinduced polymerization of monomers dissolved in the resin [35, 114]. However, this approach does not simultaneously achieve high dimensional stability and maximum photoinduced RI change. To increase the rigidity of the material, higher levels of procuring are required, which decreases diffusional mobility of the monomer in the resin and degrades holographic properties of the photopolymer [115-116]. The shrinkage observed during UV curing in a holographic solgel material was attenuated (from 1.3% to 0.4% of the material's initial thickness) with the inclusion of tetra methyl orthosilicate [117]. In addition, some monomeric species are inevitably consumed (polymerized) during the procuring step, which in turn reduces dynamic range of the holographic recording and, ultimately, limits the data storage capacity of the material [35]. As an alternative to this, a photopolymerizable glass can be used as the binder [118].

1.9.3. Monomer

Monomers are incorporated to the polymerizable recording media to establish high DE due to RI modulation. Vinyl monomers such as acrylate and methacrylate esters are used in most photopolymer systems [100, 104, 119-121].

Vinyl polymerization can be initiated by ionic species as well as free radicals, but almost all examples of photopolymerization are of a free-radical in nature [122].

A wide variety of vinyl monomers are available, and can be included in recording systems to control important holographic properties [35]. Monomers that contain more than one vinyl group are often added to produce a molecular architecture comprising a crosslinked network of polymer chains that improves dimensional stability and image fidelity. Other properties that can be influenced by the monomer choice are recording sensitivity, dynamic range, shrinkage and environmental stability of the exposed hologram [20].

Monomers capable of polymerizing by cationic ring opening polymerization (CROP) mechanism have recently been applied to volume holographic recording [111]. In CROP polymerization, chain growth is initiated when a strong acid protonates the epoxy oxygen. A second monomer reacts with this activated monomer through a ring-opening mechanism, typically forming a tertiary oxonium ion and the beginning of a growing chain. Polymerization continues as additional monomers add through the indicated ring-opening reaction sequence to form a chain with (n+1) repeating units [123]. The holographic disk developed by Aprilis, Inc. was based on a CROP polymer [124].

1.9.4. Photoinitiation System

Holographic photopolymer systems typically use at least two different molecules to form a photoinitiation system that is sensitive to the recording wavelength. A photoinitiator generally comprise of a photosensitizing dye and a charge transfer agent.

1.9.4.1. Dye

A dye is a coloured substance that can be applied in solution or dispersion to substrate; thus giving it a coloured appearance. The absorption of light by coloured substance is due to electronic transitions between different orbital within the molecule and the wavelengths absorbed are determined by energy differences between the orbitals. Every dye or pigment therefore exhibits a pattern of absorption plotted as ordinate against wavelength as abscissa and this graph is the characteristics of the colouring matters. The hue of a dye depends on the wavelength it absorbs. Any change which affects the π system will affect the hue. A structural change which causes the absorption band to longer wavelengths is called bathochromic shift. The reverse shift, towards shorter wavelength is known as a hypsochromic effect.

The dye molecule contains two groups; the chromophore and the auxochrome. The chromophore is a group of atoms which control the colour of the dye [125]. The auxochrome is a salt forming group, which helps to improve the colour of the dye. The chromophore is usually electron withdrawing, and auxochromes are normally electron donating. The two groups are connected by a conjugated system. All organic dyes decolorize on reduction, and the colour is associated with unsaturation. The colour of the organic dye is associated with the presence of certain groups of atoms, which are called chromophores. Examples of these include the nitro, nitroso, azo, ethylene and carbonyl groups and it will be seen that all are unsaturated. Compounds containing such groups are known as chromogens and they do not behave as dyes unless they are also substituted by basic or weakly acidic groups such as $–NH_2$, $-NH(CH_3)$, $-N(CH_3)_2$ or $–OH$ [126]. The presence of such groups will increase the colour-fielding power of a chromophore and for this reason they become known as auxochromes.

Polymer formation initiated by dye is accomplished by the photopolymeric reaction produced by the absorption of light by photoinitiator in the regions of constructive interference with conversion to its triplet state [102-103]. When the photopolymer material is exposed to laser beam, in addition to the RI change, absorbance modulation also takes place. With the proper choice of photosensitizer, holograms can be recorded throughout the spectral range from ~400nm to ~650 nm. A variety of dyes have been used as sensitizer which include methylene blue (MB), yellowish eosin , rose bengal (RB), chrysodine, fluorescien, erythrosin B (ErB), methyl orange, mordant yellow, malachite green, brilliant green, riboflavin, rhodamine 6G etc. [127-148]. To form a true molecular dispersion, the dye and other matrix additives must be compatible.

Among the different dye doped systems, MB doped polymers are of special interest owing to its sensitivity to the commonly available He-Ne laser. MB is a basic dye belonging to thiazine group. The dye is commonly known as tetramethyl thionine and to an organic chemist it is 3,7-bis-(dimethylamino)-phenantholinium chloride and to some histologists it is swiss blue. It is a dark green coloured powder having a molecular weight of 319.86 and the absorption peak, if pure resides at 668nm and 609 nm [149]. The absorption peak shifts according to the pH of the solution. The absorption peak at pH values of 0.65, 2.10, 3.4, 6, 8.2 is at 880, 665nm, 880 nm, 880 nm and 840 nm respectively [150-153].At neutral pH the absorption peak is at 665 nm [154]. The absorption peak was at the orange red region of the spectrum for a pH value of 2.0 [155]. An orange colour basic dye is observed in highly basic solution of pH > 13. The photochemical reduction of MB results in the formation of leuco MB through the photoreduction of intermediate state [156-158]. The mechanism of photoredution of MB is given below [102, 149, 159-160].

D +hυ $\longrightarrow$ Ds
Ds $\longrightarrow$ D+$h\upsilon_f$ (Fluorescence)
Ds $\longrightarrow$ D+Q (heat) (Internal conversion)
Ds $\longrightarrow$ DT (Transition to triplet state)
DT $\longrightarrow$ D+$h\upsilon_f$ (Phosphorescence)
DT+AH_2 $\longrightarrow$ DH+AH
2DH $\longrightarrow$ DH2+D (semiquinone formation)
2AH $\longrightarrow$ Product (disappearance of free radical)
D-Ground state of the dye, Ds-Singlet state of the dye
D_T-Triplet state of the dye, AH_2-Reducing agent

Yingjin *et al.* observed the photoinduced hydride transfer reaction between MB and leuco crystal violet under steady illumination of visible light and of photosensitization by benzophenone and α-nitronaphthalene with UV light [161]. The kinetics and thermodynamics of electron transfer reaction of dye with metal ions are also reported [162-163]. The free energy for the self exchange reaction of metal ions as well as the quantum yield for the radical was evaluated. Somer *et al.* observed the photoreduction of MB and thionine in water by red light [164]. Reaction energy consideration requires two photon to reduce each MB molecule. They also studied the influence of light intensity and MB concentration on the rate constant, and proposed two photon mechanisms involving a long-lived dimmer intermediate molecule.

1.9.4.2. Co-initiator

As the direct initiation of polymerization by light is difficult and has a poor yield, the initiation is usually achieved by radical or cationic polymerization and it requires the use of a photoinitiator (dye and charge transfer agent). The cation radical of the charge transfer agent (electron donor) produced during laser exposure initiates the polymerization reaction. Electron donors (EDs) like diphenyliodonium chloride, p-toluenesulphinate, acetylacetone, triethanolamine (TEA) etc. are used as charge transfer agent [100, 106, 165-166]. It has been found that the radical yield can be increased by introducing some additives into the photoinitiating system (N-methyl diethanolamine, diphenyliodonium salt etc.) and thus the efficiency of the photoinitiation process can be enhanced [3,167]. The idea behind the use of these additives is the fact that radicals that are generated by photoexcitation and inhibit the polymerization process interact with introduced additives to form new radicals active in polymerization [168].

1.9.5. Photo-Crosslinking Polymers

Photocrosslinkable systems constitute a major class of materials for many applications like production of HOE, fiber optic couplers, laser scanners and optical interconnects [169-172]. There are two kinds of photocrosslinkable systems: those made of gelatin and those of polymers. These subsystems are also called biopolymers and synthetic polymers respectively. DCG has some limitations such as low environmental stability and rigorous procedures of wet processing [173]. The photocrosslinking materials consist of a polymer matrix and a photo initiator. When the polymer film is exposed to laser beam, the photoinitiator undergoes photochemical reactions and crosslinks with the polymer matrix. Due to this photocrosslinking, RI modulation occurs and results in the formation of grating. Dichromated recording media such as dichromated PVA (DCPVA), dichromated PAA (DCPAA), ferric chloride doped PVA (Fe: PVA) etc are coming under this category [174-177]. Because of their unique properties such as transparency, homogeneity and photochemical stabilities, they constitute important media for non-linear optical devices. In metal ion doped polymers the first step is the absorption of light by the metallic center. The primary mechanism in most cases is an electron transfer in the excited state [174]. The accepted scheme is that light irradiation reduces the sensitizer Cr^{+6} to Cr^{+3} first, and then Cr^{+3} cross links polymeric molecules, which enhances the RI, reduces the solubility of the exposed regions and creates the hologram [178].

It was discovered that pullulan (polysaccharide polymer of linear structure) sensitized with ammonium dichromate (dichromated pullulan or DCP) possess good holographic properties [179-180]. The material has useful characteristics such as good environmental stability, simple fabrication, high DE (50% after processing), and high resolution (6000 lines/mm). The chemical treatment of Pullulan with a mixture of water and isopropyl alcohol is simple. The existence of strong surface-relief modulation on DCP is also reported [181]. Later the profile changes of DCP surface relief gratings under high humidity conditions and the influence of storage life on the DE and surface profile of DCP gratings were also investigated [182].

Other dichromated materials, such as cellulose triacetate, pectin, gum arabic, and starch are also good materials for recording holograms [183-184]. With its special properties, such as strong relief modulation, stratified sensitivity, strong real-time effect, etc., dichromated cellulose triacetate has obtained some preliminary applications in HOEs [183, 185-186]. Just after hologram recording, dichromated cellulose triacetate plates were baked at 70–90 °C for 40–50 min and processed in a 3% (wt./volume) sodium hydroxide solution for not more than 3 min at room temperature. After that it was soaked in a 10% ethylidene lactic acid solution for 10 min, and finally rinsed the hologram with flowing water for approximately 30 min and dried it in flowing air. Just after hologram formation, the photocrosslinking polymers exhibit very low efficiency and the efficiency was improved after thermal or chemical processing [183, 187].

1.10 Review of Art in the Field of Photopolymer Based Recording Media

Volume phase holograms in photopolymers have found many potential applications in optical data storage, optical data processing and the production of HOEs. Compared with other holographic materials, photopolymers have the great advantage of recording and reading holograms in real time and the spectral sensitivity could be easily shifted to the type of recording laser used by simply changing the sensitizing dye. Also these materials possess characteristics such as good light sensitivity, real time image development, large dynamic range, good optical properties, format flexibility, and low cost [101,188].

1.10.1. Liquid Compositions

The first photopolymer recording systems for holography, as proposed in the late sixties and early seventies, were based on metal acrylate solution contained in recording cells [189-190]. The photopolymer system developed by Close *et al.* was based on acrylates solution sensitized with MB. DE of ~ 45% was obtained for an exposure energy of 30 mJ/cm^2 at 643 nm [189]. The recorded holograms were stabilized by post exposure using xenon flash lamp (3mJ/cm^2) and thermal fixing [190-192]. Improvements in the performance of acrylamide (AAm) photopolymers were achieved by crosslinking with ethylene bisacrylamide and by photoreduction with TEA, acetyl acetone and hydroquninone [166]. With the incorporation of TEA, 65% DE was obtained at 50mJ/cm^2, whereas the efficiency obtained for acetyl acetone incorporated solution was only 20%. A photo polymer consists of liquid acrylic monomer, a cellulosic binder, a photo initiating system and a plasticizer was reported [193-196]. A liquid photopolymer containing a 1:1 mixture of 4,5-diiodosuccinyl fluorescein and MB, which upon visible-light irradiation shows a clear enhancement in the sensitivity and the polymerization rate is also reported [165]. A similar behaviour has been observed in the polymerization of AAm with a 3:7 mixture of Eosin and MB in water [197]. Fimia *et al.* described an aqueous photopolymer containing AAm, zinc acrylate and N,N'-methylenbisacrylamide (MBA) as monomers, 4,5-diiodosuccinylfuorescein (2ISF) and MB as initiators and sodium p-toluenesulphinate as coinitiator [165]. This formulation exhibited a clear enhancement of high-energy sensitivity upon irradiation with 514 or 633 nm lasers, with respect to the same mixture but with only one of the two dyes, reaching maximum DE of 15-20% with 15-60 mJ/cm^2. This enhancement is explained by the more efficient photogeneration of initiator radicals by the ground-state formation of an ion-pair complex between cationic (MB) and anionic (2ISF) chromophores. The addition of a binder such as PVA enabled the solution to be cast and dried onto the glass substrate [198].

1.10.2. Dye Sensitized Pol(vinyl alcohol)

PVA has many optical uses, which result from its lack of colour, its clarity and its high transmission in the near infrared and ultraviolet. PVA films can be oriented to give high degree of birefringence and high tensile strength in the stretch direction. Additional properties which account for its versatility are its hydrophilic character, easy dyeability, ability to be Crosslinked.

PVA came into use as hologram recording material from late 70's onwards [198-199]. Its many hydroxyl groups cause it to have high affinity to water, with strong hydrogen bonding between the intra and intermolecular hydroxyl groups, greatly impeding its solubility in water. Aqueous solution of PVA is considered as a molten gel. Aqueous solution of PVA of high degree of hydrolysis increase the viscosity with time, and may finally gel. The viscosity of solution increases with concentration and decreases with temperature [200]. The high viscosity of PVA solution enables its use as a binder in the photopolymer system and thick films could be fabricated with PVA. PVA film is hard and brittle at low humidities, but soft and tough at high humidities

One of the most widely used holographic recording photopolymers currently available is based on AAm. They exhibit high dynamic range and photosensitivity, real-time image development, good optical properties, format flexibility, and can be easily processed [104, 201-202]. O'Neill *et al.* have studied the mechanism of hologram formation in acrylamide-photopolymer [105]. Gallego *et al.* carried out the three dimensional analysis of holographic memories on PVA/AAm films [203]. PVA/AAm systems have been reported with different sensitizing dyes and other matrix additives.

A Polymer system composed of AAm sensitized by MB and TEA in PVA matrix is a widely studied one [204]. The energetic sensitivity of this kind of material is greatly increased when a bifunctional monomer is added. Crosslinking agent such as MBA has incorporated to speed up the polymerization reaction [205]. Carretero *et al.* observed a decrease in the transmittance curves as a function of the age of the polymer film consists of AAm and MBA. The decrease in transmittance of the material was due to the appearance of noise gratings caused by scattering centers which are formed. The formation of these centers is due to the precipitation of monomers over the surface of the film. This phenomenon was attributed to the formation of random solid micro particles of MBA, which is the less soluble monomer, favored by temporal evaporation of the water resident in the film [23]. Blaya *et al.* described the mechanism of grating formation in MBPVA/AAm films and obtained 80% efficiency in their polymer system fabricated using CAMAG scientific thin layer chromatography plate coater. Though high efficiency and sensitivity (40mJ/cm^2) were achieved, the resolution is limited to 1000 lines/mm [106]. The polymer film consist of 5% PVA (molecular wt. 25,000), AAm (0.34M), MBA (.053M), TEA(.2M) and MB (2.1x10^{-4}M),) showed 80% DE at a spatial frequency of 1000 lines/mm [206]. In that case, RI changes are produced when a molecular space lattice of AAm chains is formed, and MBA builds cross-links to form a copolymer which is transparent. The drawback of this composition is that the concentration of both monomers cannot be increased indefinitely owing to their solubility in the PVA matrix. The maximum AA to MBA molar ratio used is 6 to 1; the increase in the concentration of bisacrylamide produces precipitation of this monomer over the surface of the film and a decrease in the SNR. Blaya *et al.* presented the holographic characterization of the MBPVA/AAm incorporated with a Crosslinker, N,N'-dihydroxyethylenbisacrylamide (DHEBA) [207]. The photopolymerizable film used in their experiment was prepared using a TLC coater and the drying period was 20hrs. The gratings recorded using 633 nm He-Ne laser by keeping the beam ratio as 1:1 and spatial frequency as 1100 lines/mm showed 70% DE at a recording fluence of 5 mJ/cm^2. When the crosslinking agent is added, the energetic exposure necessary to reach the maximum DE decreased. In this case the copolymerization process produces higher temporal changes in the modulation index. This fact may be due to the higher rate of copolymerization and at the same time the formation of layers instead of linear polymeric chains. Though the rate of polymerization increases with AAm, it is not possible to increase the concentration of AAm and DHEBA indefinitely because the compatibility and solubility of these monomers in the polymer film is limited. Neumann *et al.*

described a simple technique suitable for the direct laser writing of surface relieves (~3µm height) in dry photopolymerizable film comprised of AAm, MB, TEA and PVA dissolved in ethanol and water [208].

Fimia *et al.* developed a holographic photopolymer systems consist of AAm, Zinc acrylate and MBA as monomers, a photoinitiator system consist of MB and RB in 4:1 ratio and p-toluensulfunic acid and they obtained ~35% efficiency using He-Ne laser [209]. Later Belendez *et al.* analyzed the noise gratings formed on MB:RB –acrylamide system [128]. Among the different sources of noise in holography, self induced gratings (also called noise gratings) are due to scattering from inhomogeneities in the recording material and have an important spurious effect on volume holography. Mallavia *et al.* reported that an ion pair isolated from RB and MB acted as the photoinitiator in the photopolymer formulation [129]. This photopolymer system showed wide spectral response and obtained 30% DE at 514nm and 60% DE at 633 nm.

PVA/AAm films were also fabricated with yellowish eosin as sensitizing dye [106, 210]. Garcia *et al.* studied the influence of beam ratio and intensity on the optical quality of transmission holograms of diffuse object stored in eosin doped PVA/AAm systems [211]. They used a SNR of 0.94 with a DE of 13% for a beam ratio of 20 and intensity of 1.2mW/cm^2. The variation in transmittance produced when a photopolymer is irradiated with a pulsed laser was analyzed and DE (~60%) and sensitivity close to those achieved with continuous lasers have been obtained [212]. The second order fourier component of the RI formed in phase diffraction gratings recorded in eosin doped PVA/acrylamide was studied by Neipp *et al.* [213]. Gallego *et al.* determined the temporal evolution of DE of a hologram stored in an eosin doped PVA/AAm /dimethyl acrylamide (DMAA) photopolymer system by measuring the angular response of the hologram immediately after exposure and in subsequent hours [214]. The efficiency was found to be decreased on storage and the, fast temporal evolution of the diffraction grating stored was due to residual DMAA. With the addition of DMAA, the crystallization with high AAm concentrations has prevented and thicker layers were obtained. Gallego *et al.* proposed several methods to eliminate the residual monomer in eosin/PVA/AAm films in order to stabilize the holographic gratings [215]. The residual dye and residual monomer are the main problems in achieving high DEs stable under white light. In order to polymerize the residual monomer, the gratings were illuminated with coherent green light and incoherent white light and heated the grating at 80^0C for different times. The conservation of gratings dried in critical conditions of humidity and temperature were also studied. After stabilization the diffraction efficiencies achieved were higher than 90%. SeO_2 crystals were incorporated to a polymer system containing PVA, AAm and eosin to improve the stability after exposure. The initial sensitivity of SeO_2 incorporated crystals was lower than that of undoped film [216]. Thirty holograms were multiplexed on a photopolymer system consist of AAm, MBA and eosin, using the exposure schedule [217-218]. A mean DE of 9.5% was obtained for the modulated recording lights and larger dynamic range M#=9.2 were obtained as a result of decreasing the attenuation of light in depth of the material. The optical modulation properties of Eosin PVA/AAm for a very wide range of thicknesses (ranging from 75 to 800 µm) were studied by a technique based on a Young's based double beam interferometer [219].

The formation of photoinduced surface relief modulation in an ErB doped acrylamide-based photopolymer system is also reported [146]. The surface relief formation in a photopolymer containing AAm is reported by Boiko *et al.* [220]. Jallapuram *et al.* studied the effect of binder molecular wt. on the DE and found that it had no substantial improvement of DE at higher spatial frequencies [221]. The spatial resolution of the polymer system was found to be increased with MBA concentration. Gong *et al.* developed a PVA based holographic recording material composed of ErB as dye, TEA as electron donor, AAm and N-hydroxymethyl acrylamide (HMA) as monomers [222]. The recording was obtained by the copolymerization of AAm and HMA and an efficiency of nearly 50% were achieved with energetic exposure of 80mJ/cm^2 using 514nm Ar$^+$ laser. HMA is a monofunctional monomer and its reactivity is quite different from the multifunctional acrylamide derivatives. HMA has a hydroxyl groups that favour the solubility in polar and protic solvents such as water and of course PVA of aqueous solutions. HMA can improve the optical quality and flatness of the film and can reduce the noise [222]. Sheriff *et al.* investigated the angular multiplexing in an Er B doped PVA/AAm formulated in the Centre for Industrial and Engineering Optics (CIEO) with a view of further optimization for holographic data storage [2]. Series of 18–30 gratings were angularly multiplexed in a volume of photopolymer layer (≈160 µm thick) at a spatial frequency of 1500 lines/ mm. Since the photopolymer is a saturable material, an exposure scheduling method was used to exploit the entire dynamic range of the material and allow holographic gratings of equal strength to be recorded. The M# of the material was calculated as 3.6 for CIEO photopolymer layers. An investigation of the photoinduced surface relief modulation in thin and thick layers of an AAm based photopolymer system developed at the CIEO was reported [146-148, 223]. Post-exposure of the gratings recorded on the photopolymer system (consisted of AAm, MBA, TEA, PVA and Er B) to uniform UV light lead to more than 30% increase in the surface relief amplitude. The surface relief amplitude modulation was found to decrease with increase of TEA content [224].

PVA/AAm films sensitive to 500-630 nm was fabricated with methyl violet as photoinitiator [225]. The recording characteristics of the holographic film were examined and the compositions were optimized. Only 8% efficiency was obtained and the recorded gratings gradually disappeared on storage.

In addition to the experimental findings, numerous theoretical works which accurately describe material behavior were also reported with mathematical models. The ability of a diffraction grating recording in photopolymer materials was proved at the late 1960s of the last century and it was also shown that the grating growth is caused by the diffusion process [226]. The mode proposed by Zhao *et al.* described the evolution of grating formation in photopolymer using a four harmonic expansion of the standard 1-Dimensional diffusion equation [227]. Colvin *et al.* presented a quantitative model to describe the formation of volume holograms in a polymeric medium containing photopolymerizable acrylate monomers that undergo spatially modulated gelation as a result of exposure to a visible ‘‘write’’ beam [116]. Sheridan *et al.* developed the nonlocal polymerization driven diffusion model, which extended the Zhao model to include a nonlocal spatial response to account for high spatial frequency cut-off [228]. A square root relationship shown to exist between the polymerization rate and the illuminating intensity was also reported [123, 229-230]. Kinetics of the polymerization process have been examined for the cases when the chain termination mechanism is either bimolecular (two chains terminating mutually) or primary (chain terminated with a free radical) [231-232]. Renotte *et al.* applied the nonlocal diffusion model to successfully model higher harmonic grating components recorded in both polymer and PDLC based materials [233]. Sutherland *et al.* examined the effects of shrinking and swelling and outlined an extension to the nonlocal diffusion model [234]. 3-D effects have also been examined and shown to play an important role when recording gratings in thick polymer layers greater than 200µm [130, 203]. Kelly *et al.* carried out the temporal analysis of grating formation in Er B doped PVA/AAm films using nonlocal diffusion model [235]. The characteristics of the gratings stored on eosin doped PVA/AAm based thick photopolymers were analyzed by considering the attenuation of light in depth and using an algorithm based on the rigorous coupled wave theory [236]. A new method to record many holograms multiplexed with similar DE values taking into account the different effective optical thickness of each hologram has been proposed for PVA/AAm films [237].

The main drawback of an AAm based photopolymer as far as the environment is concerned is the AAm, a substance which has been known to be carcinogenic for many years [238]. So a photopolymer system which is less toxic than AAm system has been developed. The new photopolymer formulation consist of 5'-riboflavin monophosphate as Dye, sodium acrylate as monomer, DHEBA as crosslinker [239]. The new system showed 50% efficiency at 300mJ/cm^2.

Experimental results on dye sensitized PVA films with monomers like lithium acrylate and mixture of methacrylates are reported [120-121]. PVA films were also fabricated without the incorporation of monomer. Methyl orange doped PVA possess all the good characteristic of a known polarization sensitive material [240]. Recording media fabricated by doping PVA with azo dyes and Rhodamine 6G are used for real time holography and non-linear optics [107]. The evaluation of third order nonlinearities of azo dye/PVA systems and the characteristics of Chrysodine/PVA as a nonlinear wave-guide is reported. Also degenerate four-wave mixing experiments using a novel geometry have been carried out in rhodamine 6G/PVA films. Azo dyes like chrysodine and mordant yellow 3R on PVA were found to be erasable with DE of about 27% [242]. A linear polyol incorporated eosin PVA system with 15% DE was reported by Ponce *et al.* [243].

1.10.3. Metal Ion Doped PVA

Metal ions such as Ferric (Fe^{+3}) and Dichromate (Cr^{+6}) have been used in conjunction with PVA for recording holograms in real time.

The photochemistry of Cr^{+6} has been investigated over decades and it has been generally accepted that the photo reduction of Cr^{+6} leads to Cr^{+3} in the presence of organic-reducing substances like secondary alcohols [244]. From the earlier works done on DCPVA, Duncalf and Dunn suggested that the insolubilization of DCPVA after exposure was caused by complex formation between Cr^{+3} with PVA [245]. Ziping et al. recorded holograms of 30% efficiency on DCPVA and developed a technique to fix the holograms by heat treatment [246]. Lelievre *et al.* recorded holograms with polarized light and obtained 30% DE [174]. Changkakoti *et al.* employed two simple techniques of development using ethyl alcohol and have achieved 60% DE for fixed holograms [247]. Maniavannan *et al.* studied the influence of different chemical parameters (e.g., pH and electron donors) on DCPVA and 70% efficiency was obtained using 488 nm Ar^+ laser (the efficiency was monitored real time using 687 nm Krypton laser) [248]. The EDs influence significantly the DE of recorded holograms. From all different nitrogen containing compounds, dimethyl formamide (DMF) showed the best performance while using with dichromated systems. The primary photo processes in DCPVA photographic materials using ESR (Electron Spin Resonance) spectroscopy were explained. Spin trapping experiments with N-tert-butyl-α-phenyl nytrone gave evidence for the formation of radical adduct from the polymer matrix. The effect of different electron donors diazobicyclo(2,2,2) octane, (1,1,3,3-tetramethylguanidine, 2{[2-(dimethylamino)ethyl] methylamino} ethanol and TEA on the photo sensitivity and real-time DE of volume holographic transmission gratings has been reported [249]. Later the formation of reflection hologram in DCPVA was reported and the holograms self developed during recording and required no thermal or chemical development [250]. The sensitizer of dichromated light-sensitive systems, Cr^{+6}, is considered to be reduced to Cr^{+3} through the intermediate ionic stages, Cr^{+5} and Cr^{+4}. Cr^{+4} is very labile and transfers to Cr^{+5} quickly [251]. This Cr^{+5} react with PVA and produces crosslinked PVA and Cr^{+3}. This crosslinking induce RI modulation in the exposed regions and cause the formation of holograms. Though there were some disagreements between the reported photochemical mechanisms of DCPVA, the works done by Pizzocaro *et al.* confirmed that Cr^{+5} is directly responsible for the hologram formation in DCPVA. A self enhancement of DE was reported in DCPVA [252-253].

The major shortcoming of dichromated material is that its spectral sensitivity is limited to wavelengths shorter than 500 nm. To overcome this, DCPVA films were fabricated with suitable dyes. Holographic performance of the undeveloped and developed DCPVA films with three different xanthene dyes namely fluorescene, eosin, and RB are evaluated through DE profiles [254]. In addition a systematic ESR spectroscopic investigation also performed on these systems to study the mechanism of holographic recording and observed the influence of xanthene dyes in the photo processes. With the incorporation of xanthene dyes the sensitivity and DE of the material was improved. Couture *et al.* studied the effect of different dyes such as RB, eosin, and malachite green on the DE and sensitivity of DCPVA films [140]. Though no significant improvement in the DE was observed, the sensitivity was improved from 15J/cm^2 to ~2J/cm^2. The spectral sensitivity in the green region was also improved. The effect of TEA on the holographic parameters was also reported [141].

Photoreduction of ferric salts by UV light has been known for more than a century. Oster *et al.* found that ferric salts can be photoreduced by visible light through dye sensitization [255]. The ferric salt photoreduces to the ferrous form (Fe^{+2}) as a result of photoreduction of the dye in the presence of an ED. Sugawara *et al.* devised a photosensitive liquid system with a mixture of AAm, MBA coupled with Ferric ion and tert-butyl hydroperoxide. This recording system is sensitive from 200-500 nm and exhibits high diffraction efficiency and the holograms were fixed by an overall UV exposure [256]. Manivannan *et al.* presented Fe^{+3} doped PVA systems for hologram recording [248]. Although volume holograms recorded in Fe: PVA films exhibited a high peak DE of ~ 80% (after fixing), the energy sensitivity of this recording medium was low. To improve the energy sensitivity, t- butyl hydro peroxide has been introduced to the film [257]. It was reported that the UV exposure induces modification of both the RI and the absorption co-efficient of Fe: PVA thin films [258]. In Fe:PVA system, Fe^{+3} is reduced to Fe^{+2} with the removal of one chlorine radical [259]. The Fe^{+3} doped in polymer matrix undergo excitation upon irradiation and removes the needed one electron from the polymer matrix which undergoes photocrosslinking in the form of holographic gratings [260].

The electronic mechanism involved in the optical behavior of the mixed Fe-Sn-doped polymers under UV exposure was reported [261]. Optical absorption, m-line spectroscopy as well as Mossbauer measurements were performed on different UV exposed (Fe+Sn) doped polymer films. The related electron transfer process is different in (Fe+Sn): PVA and Fe: PVA. In Fe: PVA, electron transfer takes place from the polymer matrix to the metal ion ($Fe^{3+} \rightarrow Fe^{2+}$) whereas in (Fe+Sn): PVA the electron transfer is from metal ion to the polymer matrix ($Sn^{2+} \rightarrow Sn^{4+}$) is occurred.

1.10.4. Poly(acrylic acid)

Another synthetic polymer which is very attractive in holography is PAA doped with metal ions and organic dyes [177,262]. Photosensitive materials comprising of acrylic acid and catalyst are used to record holograms in the presence of laser beam [263]. Volume transmission holograms have been recorded in DCPAA polymer films [264]. Using an angular multiplexing technique, twenty holograms with equal DEs have been stored in one specific area. As an application in optical computing, multiple holograms were recorded in DCPAA polymer films. Conventional volume transmission holograms of a 3D scene have been recorded on DCPAA-DMF films under 488nm light [265]. The recorded holograms can be efficiently reconstructed either with red light or with a low energy beam in the blue region without any post thermal or chemical processing. DCPAA films have been used to fabricate planar waveguides [266]. Computer generated holograms (CGH) with a sinusoidal amplitude profile have been copied onto DCPAA-DMF films by contact copying technique [267]. Contact copying was done by placing CGH over the recording film and exposing it with white light. The efficiencies achieved for thick and thin films are 16% and 1.2% respectively. Photoinduced holographic surface relief gratings have been fabricated using 442nm laser and they are obtained without any chemical treatment or wet processing [268-270]. The depth of the modulation was approximately 520 nm and the pitch of the grating was ~6.2µm. DCPAA films with DMF have been used to fabricate surface relief gratings as multiple beam splitters and they can be used in a variety of applications that necessitate moderate beam uniformity [271]. The ratio of the maximum to the minimum DE and the total useful energy fraction are approximately 6 and 8 respectively. In addition to this, PAA films are used for the production of IR holograms [272]. Ushamani *et al.* fabricated MB sensitized polymer film by blending both PVA and PAA in 7:3 ratio [109]. The storage life of gratings recorded on MBPVA/PAA blend was better than that of MBPVA films [108, 138]. The effect of different EDs on the sensitivity and efficiency of MBPVA/PAA blend also was studied [273]. Later, the development of dichromated blend of PVA/PAA is also reported [274].

1.10.5. Poly(vinyl chloride)

Ushamani *et al.* reported the feasibility of using PVC matrix as an optical recording medium by making it as copper acetate complexed methylene blue sensitized polyvinyl chloride (CMBPVC) films [275]. Later a systematic analysis on the effect of pH on the bleaching property and DE of CMBPVC were presented [276]. Direct imaging done on pure and CMBPVC films revealed the optical quality of the film. Unlike in other matrices, the change of state occurring to the dye molecules (MB) on laser irradiation is permanent in PVC and it exists in the leuco form itself [108]. Since the material was not comprised of any monomer or ED as in the conventional photopolymerizable recording medium, the only contribution to the recording mechanism was the absorbance modulation. The gratings recorded on the CMBPVC films showed an efficiency of 4.46% at 1500 mJ/cm^2 for the intensity ratios of the first order diffracted beam to that of the transmitted beam [136, 276]. Though change in absorbance on storage (after laser exposure) is not observed in this material, the recorded grating vanished within few hours [277].

1.10.6. Poly(methyl methacrylate)

Photopolymer comprising PMMA (poly(methyl methacrylate)) as the base is primarily sensitive to some region of the visible spectrum with sensitizers such as p-benzoquinone. DEs of ~70% were obtained with exposures of 1-8 J/cm^2. Mixtures of photopolymers containing PMMA have obtained RI change of 10^{-2} by photo induced polymerization [278-280]. Holographic characterizations like thickness, effect of ageing, effect of dye concentration are done on azo dye doped PMMA films [281]. These films under actinic (488nm) showed a local change in refractive index with high DE. The real time kinetics of photo-reversability of azo dye in PMMA matrix is also reported [282]. MB sensitized PMMA is an efficient medium for three-dimensional holographic grating [283]. Both phase and amplitude holograms can be written in the MBPMMA with He-Ne laser. Diffraction efficiency of nearly 60% was found for thick holograms after 10 hrs exposure. Methyl red sensitized PMMA films have been used in transient polarization holography [284].

To alleviate the shrinkage effect in thick materials, some techniques for fabricating photopolymer materials have been proposed and demonstrated [285-288]. Among these recording materials, PMMA is one of the most popular polymer bases for the binder, due to its good dimensional stability and good optical quality. Recent research has shown that PMMA doped with phenanthrenequinone (PQ) could be very attractive for volume holographic recording because it is easy to form in bulk with negligible photochemically induced dimensional change and good optical quality [217, 289-290].

1.10.7. Commercially Available Polymers

In order to respond to today's growing demand, a number of photopolymers have been commercialized. It includes photopolymers developed by DuPont, Polaroid, Aprilis etc.

Among commercially available photopolymer materials DuPont's dry photopolymers seem to have gained the highest popularity [291]. The DuPont polymers are coated on Mylar polyester film of 50µm thickness. A removable cover sheet of 25µm Mylar or 60µm PVC film is used to protect the slightly tacky photopolymer. The photopolymer thickness typically range from 10-50µm. Potential applications for optical storage and interconnection systems have been reported on Dupont's polymer [91, 292-295]. The commercial photopolymers designed for holographic recording by Dupont have been studied extensively and provide excellent material photosensitivity and RI contrast [17, 110, 296-298]. However, their application to data storage is severely limited due to their need for solvent processing, limited thickness, and high polymerization-induced shrinkage (4-10%) [92]. Lougnot *et al.* have developed a solvent-free system with small multifunctional acrylate monomers [299-300]. As only thin media (<50 µm) can be prepared, these films are unsuitable for high-density data storage. Aubrecht *et al.* studied the recording of holographic volume diffraction gratings in Du Pont's photopolymer HRS-150 both theoretically and experimentally [301]. DuPont have released polymer films for reflection and transmission holograms. The blue-green sensitive photopolymers of DuPont HRF-800X001-15 (in the experimental phase) and OmniDex 706 (commercial) typically have sensitivity ranges of a few mJ/cm^2 under visible light irradiation [302-303]. The recording media of the HRF series (HRF-150, HRF-800) contain aromatic or aliphatic acrylate monomers in cellulose acetate butyrate [110]. In such media, holograms were recorded with nearly 100% DE at an exposures of 3mJ/cm^2. It was shown that, in a 100-µm layer, information could be recorded with a density of 10 bµm^{-2} (6.5 Gbin^{-2}). Optical disks with a thick photosensitive recording layer ensure an information capacity of 40 GB and the reading speed of 50 megabyte/s, with the angular selectivity being Δθ = 0.09° [304-305]. Moreau *et al.* investigated the recording dynamics of Omnidex photopolymer film from DuPont and different experiments are detailed that lead to the determination of material kinetic parameters [306]. The recording behavior of the DuPont photopolymer was fully characterized by using peristrophic multiplexing. From its recording behavior, an exposure schedule to multiplex equal strength holograms in the same volume has been derived. This method of determining the exposure schedule was put to the test by multiplexing 1,000 holograms in a piece of photopolymer that is only 100 microns thick [307]. Dupont's HRF-150 photopolymer film was investigated for use in 3-D holographic memories [292]. Measurements of sensitivity, hologram persistence, the lateral speed of the photoinitiated reaction, and the variation of DE with modulation depth, spatial frequency /tilt angle, and intensity are reported. HRF-150 has excellent sensitivity and good resolution for transmission holograms recorded with blue-green light [308-309]. After recording, the hologram is fixed by exposing the film to uniform UV light for 45 seconds or by thermal treatment [291, 310].

The commonly used Polaroid (USA) photopolymer film is DMP-128 [311]. It is a flexible film and is useful for making high density reflectors. Because of the unique open structure it can be filled with liquid crystals to make disappearing HOEs and narrow band filters. Dye-sensitized photopolymerization reactions of vinyl monomers incorporated into a polymer matrix have been demonstrated by Polaroid for holographic recording [312-313]. The holographic performance of DMP-128 is highly exploited and it provides permanent fixed holograms [120]. The recording medium is based on poly-N-vinyl pyrrolidone polymer matrix containing a mixture of lithium acrylate, acrylic acid, bisacrylamide, and MB and its spectral sensitivity ranges from 442 to 647 nm

[110, 120, 314]. This medium provides recording holograms with DE of 80–95% at exposures of 5 mJ cm^{-2} [315]. The thickness of the polymer film was less than 45 µm. Moreover, not only scalar but also polarization holograms could be recorded on these films. Later Polaroid materials have been prepared in thicknesses of 150-200 µm [316]. The draw back of Polaroid films is that it require wet processing to fix the hologram.

The recording medium HMD-120 offered by Aprilis (Maynard, MA,USA) was created on the basis of organo silicon monomers participating in cationic photopolymerization and acrylate monomers polymerized by the radical mechanism [317]. This medium differs from the media considered above in that the photosensitive layer experiences a low shrinkage during hologram writing. Aprilis's proprietary high-performance, Write Once Read Many (WORM), holographic storage media was released in November 2002. It is the first commercially viable holographic storage media for the removable storage market. The media technology provides storage device manufacturers with a medium that can support a storage capacity of 200 GB and a data transfer rate of 100 megabyte/s in CD/DVD form factor (120 mm in diameter). Aprilis's media can store data in pages of a million bits at a time in contrast to today's standard single word transfer rates, giving it a distinct and sustainable advantage in recording and retrieval times over magnetic and optical technologies [124,318].

'InPhase' also released 'two-chemistry' polymer based holographic disc. But it is not yet clear is whether the cost of such systems will be attractive to customers [124]. The search for a large scale, commercial, volume holographic material has lead to the development of photopolymers by Canon. The canon system is based on PVK. This material requires solvent process to enhance the image efficiency [319].

PolyGrama has marketed liquid photopolymer systems and the solid type photopolymer is under development [320]. These liquid pourable resins are specially designed for plate sandwich. After some quantity is added near the plate center, clamping the plates (maintaining pressure) will spread the viscous (~200-500 cps) material in thin 5-10μm emulsion stable for laser light exposure. SM-635TR (Red sensitive with 85% DE and sensitivity of 3-5mJ/cm²), SM-515TR, (green sensitive), SM-488TR (blue sensitive) are the commercialized polymers from Polygramma. The shelf life is limited to 6 months when kept at 20^0C. Subsequent to the holographic recording, the material has to be permanently fixed by a white light post-exposure with a 20W fluorescent (~15 min.) or 75W halogen lamp at 15cm (~3min.) (Curing time may vary for different size and thickness). The major drawback of this material is it is available only in liquid form.

1.10.8. Other Photopolymers

In recent years, many types of photopolymerizable systems have been developed as materials for recording holograms. Wang *et al.* developed a blue sensitive photopolymer system that consists of camphor quinine as photosensitizer [137]. Boyd *et al.* formulated a polymer compositions containing N-vinyl carbazole and N-vinyl-2-pyrrolidinone as disks of approximately 1 cm in diameter and 20–1400μm thick and 20 holograms were multiplexed at an angular separation of 2^0 [89]. Holographic film comprised of VAc and maleic anhydride, ethylene vinyl acetate copolymers, copolymers of VAc with tetrafluoroethylene, polyvinyl acetate etc have been reported [322-324]. 70% efficiency was obtained on polymeric composition with 2-benzoxyethyl acrylate and N-vinyl cabazole as monomers and poly(vinyl acetate) as polymeric binder. But the material showed a shrinkage [325]. Acrylate oligomer-based photopolymer system consists of several monomers (isobornyl acrylate, hexanediol, diacrylate, phenoxyethyl acrylate, N-vinylcarbazole, N-vinylpyrrolidinone, vinyl benzoate and tert-butyl hydroperoxide) developed by Schilling *et al.* exhibited very low shrinkage [35]. Besides this holographic materials based on styrene - acrylonitrile copolymer (SAN) is well reported [326-328].

$M_\#$ values up to 13 have been achieved in an epoxy resin containing 1,2,7,8-diepoxyoctane and epoxypropoxypropyl-terminated dimethylsiloxane [329]. Multiple digital data pages (480 kbits per page) were holographically recorded on acrylate-based photopolymer material used [330]. The photopolymer material consists of a mixture of a difunctional acrylate oligomer, monomers and a photoinitiator. The mixture is compressed to the desired thickness between two optically flat pieces of glass and is optically partially polymerized [116]. Epoxy resin containing methyl methacrylate monomer and carbazole exhibits none-shrinkage and an efficiency of 55% [332].

A photopolymer composition consist of AAm and MBA in a ratio of 36.7:1 and bacteriorhodopsin have showed 1.5% efficiency [333]. The gel solution was prepared by mixing the AAm -Purple membrane solution with the polymerization catalyst ammonium and initiator N,N,N’,N’-tetramethyl ethylene diamine and was poured into two rectangular glasses. After polymerization, the glasses were removed and the Purple membrane film was covered with two gel drying (48hrs) cellulose films and held firmly in a drying cell.

Simon *et al.* investigated an organic star block copolymer and mesoporous silica MCM-41 material for electron holography [334]. Permanent holographic storage with nearly 100% DE (at $0.2J/cm^2$) and RI modulation up to $4.5x10^{-3}$ has been demonstrated in a photopolymerizable organically modified silica glass containing radical generating titanocene photoinitiator [118]. Holographic gratings in a photopolymerizable sol-gel glass based on AAm as monomer and eosin as photoinitiator showed a DE of 55% at an exposure of $8mJ/cm^2$ [335]. A photopolymerizable silica glass (effective thickness of 1.1 mm) based on AAm and MBA as monomers, TEA as coinitiator and yellowish eosin as photoinitiator showed a DE of 80 % with an energetic exposure of 10 mJ/cm^2 [188].

Polymerization of a mixture of HEMA (2-hydroxyethylmethacrylate) and ethylene glycol di-methacrylate was reported and a diffraction efficiency of 30%

at 514nm and 60% at 623 nm were found. Xanthene dye was used for sensitization [336].

A self-processing photopolymer material suitable for hologram recording in the near infrared region (at 780 nm) has been studied [337-338]. It has been shown that the amount of pre-polymerizing exposure plays a crucial role in the build-up of the holographic grating. By a proper choice of the pre-exposure, the inhibition period can be reduced and DE of the order of 70% can be achieved.

Holographic photopolymers that enable holograms to be recorded only in a targeted layer of the multilayer disk have not yet been developed. Yagi *et al.* of NTT Photonics Laboratories proposed a thin-film multilayer waveguide holographic memory card (read-only memory), and it has much tolerance for variation in the read-light wavelength and for expansion and contraction of the hologram materials [339]. Hirabayashi *et al.* developed a two-color-absorption photopolymer in which holograms could be recorded by simultaneous irradiation with a 660 nm interference light and a 410 nm gate light. The polymer contain bis(silyl)pentathiophene as a two-color-photosensitive dye and 2,2-dimethoxy-2-phenylacetophenone as a radical photopolymerization initiator. The sensitivity and DE of 25 µm thick layers are ranging from 1.2x 10^{-9} to 3.7x 10^{-9} cm^2/mJ and 1% to 4% respectively. A three-photopolymer-layer waveguide structure was formed with this photopolymer , where each photopolymer layer and high RI adhesive layer serves as a core layer and is sandwiched between two low RI glass substrates that serve as clad layers. Gate light propagated through the adhesive layers, reference and object beams intersected the photopolymer layers, and different diffraction patterns could be written in each layer [340].

1.10.9. Nano-Photopolymers

Inorganic materials possess a wide variety of RIs that give us the opportunity of obtaining much higher index modulation as compared with conventional photopolymers. The inclusion of nanoparticles also contributes to rapid build up of fixed holograms and noticeable suppression of polymerization shrinkage, giving high recording sensitivity and dimensional stability. It was also confirmed that the distribution of dispersed nanoparticles followed the light intensity interference pattern in photopolymers, indicating holographic control of nanoparticle-distribution morphology that opens new device and sensor applications in photonics [341]. To prepare such a material system with good optical quality (i.e., a low light-scattering photopolymer giving a high contrast hologram), it is required that the doped nanoparticles be uniformly dispersed without substantive aggregation and unwanted chemical reaction with a host monomer. To relax this somewhat severe requirement, nano structured polymers that possess highly branched main chains such as dendrimers and hyperbranched polymers (HBPs) was employed as another candidate for size and refractive-index controllable nanoparticles [342-343]. Among them HBPs are preferable. They would behave themselves like well-shaped nanoparticles (i.e., hard nano-spheres). It is also possible to control the optical properties of a HBP molecule (such as an index of refraction and the photosensitivity) and to add other photonic functionalities (such as optical nonlinearity) by means of chemical treatment of functional end groups. Tomita *et al.* have proposed an organic-inorganic nanocomposite photopolymer system in which inorganic (silica or titania) nanoparticles having a large RI difference from a polymerized monomer are dispersed in a methacrylate monomer [344-347]. The holographic recording in HBP-dispersed methacrylate photopolymers in which HBPs act as organic nanoparticles showed very high efficiency (>90%) [348-349]. Photoinduced phase transitions of nanoparticles are of particular interest for applications, for instance optical data storage. Arnaud *et al.* studied the thermal commutation of nano particles with diameters varying from 100 nm to 600 nm [350]. Sakhanao *et al.* developed a holographic photopolymerizable nanocomposites by the addition of TiO2 or ZrO_2 NP (size~6-8 nm) in CH_2Cl_2 to the monomeric mixture containing

1.5 wt% of UV photoinitiator (Irgacure 1700) followed by evaporation of the solvent [351]. Photoinduced second order nonlinear optical effects were observed in ZnSe nanocrystalline incorporated PVA matrix [352]. With the incorporaarion of silica nanopariticles, a refractive index modulation of 0.005 has achieved in PMMA [353]. The silica nanopartice dispersed PMMA is a potential candidate for both photonic and electroluminescence devices. The nanoparticle dispersed polymers can solve the limitations of todays recording materials.

1.11. Objectives of the Present Work

In order to respond to the industry's growing demand for applications like holographic data storage, HOEs, holographic displays, optical waveguides etc. much emphasis has been put on methods to develop new photopolymerizable materials with high efficiency and high sensitivity. Designing of cost effective light sensitive systems that polymerize at an ever faster rate and can hold data with environmental stability have become a growing challenge. With this intention, the research work was conducted on the development of dye sensitized polymer films. The objectives of the present work was the improvements in the holographic performance of MBPVC films, development of new polymer materials for holography, Fabrication of MBPVA/AAm films with improved efficiency and development of permanent recording material without any fixing techniques etc. For the present study MB was used as the sensitizing dye and PVA and PVC were selected as base matrices. The thesis work includes the fabrication of various photopolymer systems and its characterization. The following chapter details the results obtained on various photopolymer films fabricated.

1.12. Conclusion

The importance of holographic technology in the information era is presented. Description of available recording media with special emphasis to photopolymers is given. A detailed review on the polymer based recording is also presented.

References

1. K. Singh, Proc. 31st OSI symp. on contemporary optics and applications, Vadodara, India 176 (2007)
2. H. Sherif, I.Naydenova, S.Martin, C.M. Ginn , V.Toal, J.Opt.A,Pure Appl.Opt.,7, 255 (2005)
3. V. A. Barachevskii, High Energy Chemistry, 40, 131(2006)
4. Y. Takashima, L. Hesselink, Opt.Lett., 31,1513 (2006)
5. T.W.Stone, B.J. Thompson, SPIE milestone series, Vol.MS34, SPIE optical engineering press (Washington) (1991)
6. Guest editorial, Opt. Laser. Eng., 44, 871 (2006)
7. http://www.Hololight.net
8. A.B.V. Lugt, IEEE ,10,139 (1964)
9. S. Bara , C.G. Reino,J. Mod.Opt., 36, 21 (1989)
10. R. Kannan, S.V. Pappu, Opt.Laser.Technol., 204,10 (1988)
11. C.Shekhar, R.S. Sirohi, J.Opt. (Paris),16, 225 (1985)
12. H.J.Rabal, W.D.Farlan, M.Garavaglia, Opt.Commn., 65, 343 (1988)
13. N.George, T.Stone, Opt. Commn., 67, 185 (1988)
14. J.Schwidr, Opt. Eng., 35, 826 (1996)
15. E. Mihaylova, I.Naydenova, B. Duignan, S. Martin, V. Toal, Opt. Laser. Eng., 44, 965 (2006)
16. Optical engineering Science Series 24-practical volume holography- RRA Syms- oxford science publications
17. P.Hariharan, Optical holography principle, techniques and applications, Cambridge university press (1987)
18. L. Winslow, Current Applications for Holographic Images
19. W. L . Wilson, K. Curtis, M . Tackitt, , A . Hill, A. Hale, M. Schilling, C . Boyd, S . Campbell, L .Dhar, A. Harris, Opt. Quant. Elect., 32, 393(2000)
20. H. Coufal, D. Psaltis, G. T . Sincerbox, Holographic data storage (Springer) (2000)
21. D.Psaltis, M. Levine, A. Pu, K. Curtis,G. Barbastathis, Opt. Lett., 20 (1995)
22. R. B. Johnson , R. G. Driggers, Marcel Dekker, Encyclopedia of Optical Engineering,Ed., New York (2002)

23. L. Carretero, S. Blaya, R. Mallavia, R. F. Madrigal, A. Fimia, J. Mod. Opt., 45, 2345 (1998)
24. V.Weiss, A.A.Friesem, J.Opt.Soc.Am.A.,11 , 2004 (1994)
25. S.Kumar, K.Singh, J.Opt.(India) 19,108 (1990)
26. I.Banyasz, Opt.Commn., 267, 356 (2006)
27. B. J. Chang , C. D. Leonard, Appl. Opt., 18, 2407 (1979)
28. C. G. Stojanoff, O. Brasseur, S. Tropartz, H. Schuette, Proc. SPIE, R. A. Lessard, Ed 2042, 301 (1993)
29. D. Pantelic, B. Muric, Appl. Opt., 40, 2871 (2001)
30. T. Keinonen, S. Parkkonen, T. Jaeaeskelaeinen, J. Mod. Opt.,45, 2561 (1998)
31. L. Dhar, A. Hale, H. E. Katz, M. L. Schilling, M. G. Schnoes, F. C. Schilling, Opt. Lett., 24,487 (1999)
32. R.K.banyal, B.R.prasad, Opt.Commn., 274, 300 (2007)
33. W. E. Moerner, A. G.Jepsen, C. L. Thompson, Annu. Rev. Mater. Sci., 27,585 (1997)
34. F.H.Mok, M.C.Tackitt, H.M.Stoll, Opt. Lett., 16, 605 (1991)
35. M.L.Schilling, V.L.Colvin, L.Dhar, A.L.Harris, F.C. Schilling, H.E.Katz, T.Wysocki, A.Hale, L.L.Blyer, C.Boyd, Chem. Mater., 11,247(1999)
36. N. Hampp, A. Popp, C. Bruchle, D. Oesterhelt, J. Phys. Chem., 96, 4679 (1992)
37. J. D. Downie , D. T. Smithey, Appl.Opt., 35, 5780 (1996)
38. N. Hampp, A. Miller, C. Bruchle, D. Oesterhelt, GBF Monogr. 13, 377 (1989)
39. F. Wang, L. Liu, Q. Li, Opt. Lett., 21, 1697 (1996)
40. O. Ostroverkhova, W. E. Moerner, Chem. Rev., 104, 3267 (2004)
41. K.Y.Law, Chem.Rev., 93, 449 (1993)
42. S.Ducharme, J.C.Scott, R.J.Twieg, W.E. Moerner, OSA Ann. Meet. Boston, MA (1990)
43. S.Ducharme, J.C.Scott, R.J.Twieg, W.E. Moerner , Phys. Rev. Lett., 66,1846 (1991)
44. M.C.J.M Donckers , S.M. Silence, C.A. Walsh, F.Hache, D.M. Burland , W.E. Moerner, Opt.Lett,18, 1044 (1993)
45. B, Kippelen, Sandalphon, N.Peyghambarian, S.R.Lyon, A.B.Padias, H.K. Hall J.Elecron.Lett., 29, 1873(1993)

46. K.Meerholz, B.L.Volodin, B. Kippelen, N.Peyghambarian, Nature, 371, 497 (1994)
47. S.M.Silence, J.C.Scott, J.J. Stankus, W.E. Moerner, C.R.Moylan, J.Phys. Chem., 99,4096 (1995)
48. R. Burzynski , Y.Zhang , S.Ghosal ,M.K. Casstevens , J. Appl. Phys.,78,6903 (1995)
49. B. Kippelen , N. Peyghambarian, Polymers for Photonic Applications II, K. Lee, Ed. (Springer-Verlag), Vol. 161, Chap. 2(2003)
50. M. Eralp, J. Thomas, G. Li, S. Tay, A. Schülzgen, R. A. Norwood, N. Peyghambarian, Opt. Lett., 31, 1408 (2006)
51. S.J.Zilker, T.H.Bieringer, D.Haarer, R.S.Stein, J.W.Van Egmond, Adv.Mater., 10,855 (1998)
52. M.Eich, J.Wendorff, Makromol. Chem. Rapid Commn., 8,467(1987)
53. R.Ortler, C.Braeuchle, A.Millera, G.Riepl, Makromol.Chem. Rapid Commn., 10,189 (1989)
54. M.Eich, J.Wendorff, B.Reck, H.Ringsdorf, Makromol. Chem. Rapid Commun., 8, 59 (1987)
55. O.Watanabe, M.Tsuchimori, A.Okada, H.Ito, Appl. Phy.Lett., 71,750 (1997)
56. R.H.Berg, S.Hvilsted, P.S.Ramanujam, Nature, 383,505(1996)
57. Z.Sekkat, J.Wood, W.Knoll, W.Volksen, R.D.Miller, A.Knoesen, J.Opt.Soc.Am.B, 14, 829 (1997)
58. G.Zimmermann, L.Chow, U. Paik, J.Am.Chem.Soc., 80, 359 (1979)
59. A. Natansohn, P. Rochon, Chem. Rev., 102, 4139̃ (2002)
60. B. Liu, M. Wang, Y. He, X. Wang, J. Appl. Phys., 42, 5726 (2003)
61. P.Rochon, E.Batalla, A.Natansohn, Appl. Phys. Lett., 66, 136 (1995)
62. D.Y.Kim, S.K.Tripathy, L.Li, J. Kumar, Appl. Phys. Lett., 66, 1166 (1995)
63. C.Barrett, A.Natansohn, P. Rochon, J. Phys. Chem., 100, 8836 (1996)
64. M.S.Ho, C.Barrett, J.Paterson, M.Esteghamatian, A.Natansohn, P. Rochon, Macromolecules, 29, 4613(1996)
65. S.K.Tripathy, D.Y.Kim, L.Li, J.Kumar, Chem. Tech., 28, 34 (1998)
66. N.K.Viswanathan, D.Y.Kim, S.Bian, J.Williams, W.Liu, L.Li, L.Samuelson, J. Kumar, S.K.Tripathy, J. Mater. Chem., 9, 1941 (1999)

67. C.B.McArdle, Ed.,Applied photochromic polymer systems, (London)Blackie (1992)
68. V.P. Shibaev, Ed., Polymers as electrooptical and photooptical active media, (Berlin) Springer (1996)
69. I.Cabera, V.Krongauz, H.Ringsdorf, Angew. Chem.Int.Ed.Engl.,26,1178 (1987)
70. S.Yitzchaik, I.Cabrera, F.Buchholtz, V.Krongauz, Macromolecules, 23,707(1990)
71. L.Natarajan, V.Tondiglia, T.Bunning, R.Crane, W.Adams, Adv. Mater. Opt.Electron.,1,293 (1992)
72. S. Fu , Y. Liu, Z. Lu , L. Dong , W. Hu , M. Xie, Opt.Commn., 242, 115 (2004)
73. R.L.Sutherland, L.V.Natarajan, V.P.Tondiglia, T.J.Bunning, Chem. Mater., 5,1533 (1993)
74. K.Tanaka, K.Kato , S.Tsuru , S.Sakai., J. Soc. Inf. Display 2,37(1994)
75. T. J. Bunning, L. V. Natarajan, V. P. Tondiglia, R. L. Sutherland, Annu. Rev. Mater. Sci., 30,83(2000)
76. Stalder M, Ehbets P, Opt. Lett., 19,1(1994)
77. K.Tanaka , K.Kato , M.Date, Jpn. J. Appl. Phys., 38, L277 (1999)
78. T.Karasawa , Y.Taketomi , Jpn. J.Appl. Phys., 36,6388 (1997)
79. C.C.Bowley, A.K.Fontecchio, G.P.Crawford, Proc. SID99 Dig., 958 (1999)
80. C.C.Bowley, A.K.Fontecchio, J.J.Lin, H.Yuan ,G.P. Crawford, MRS Proc., 559, 97 (1999)
81. Norland Products Inc., 695 Joyce Kilmer Avenue, New Brunswick, NJ 08902
82. P.Drzaic , Liquid Crystal Dispersions.Singapore: World Scientific, pp.429 (1995)
83. K. Komorowska, G. Pawlik ,A. C. Mitus, A. Miniewicz, J.Appl. Phy., 90, 1836 (2001)
84. A. L. Alexe-Ionescu, R. Barberi, M. Iovane, A. T. Ionescu, Phy. Rev. E, 65, 011703 (2001)
85. M.Date, Y.Takeuchi , K.Kato,. J. Phys. D:Appl. Phys., 31,2225 (1998)
86. C. C. Bowley , G. P. Crawford , Appl.Phy.Lett.,76, 2235 (2000)
87. C. Provenzano, P. Pagliusi , G. Cipparrone, Opt.Exp.,15, 5872 (2007)
88. G. Oster , N.L. Yang,Chem. Rev., 68,125 (1968)

89. J. E. Boyd, T. J. Trentler, R. K. Wahi, Y. I. Vega-Cantu, .V. L. Colvin, .,Appl. Opt., 39, 2353(2000)
90. W. Chao ,S. Chi, J. Opt., 29, 95 (1998)
91. A. Pu , D. Psaltis, Appl. Opt., 35,2389 (1996)
92. U.S. Rhee, H. J. Caulfield, J. Shamir, C. S. Vikram, M. M. Mirsalehi, Opt. Eng., 32, 1839 (1993)
93. W. Gambogi, K. Steijn, S. Mackara, T. Duzick, B. Hamzavy, J. Kelly, Proc. SPIE 2152, 282 (1994)
94. I. Semenova ,N. Reinhand, Proc. SPIE,3294, 207 (1998)
95. C. Zhao, J. Liu, Z. Fu, and R. T. Chen, Appl. Phys. Lett., 71,1464 (1997)
96. J. E. Ludman, J. R. Riccobono, N. O. Reinhand, I. V. Semenova, Y. L. Korzinin, S. M. Shahriar, H. J. Caulfield, J. M. Fournier, P. Hemmer, Opt. Eng., 36, 1700 (1997)
97. T. J. Trout, J. J. Schmieg, W.J. Gambogi, A. M. Weber, Adv. Mater.,10, 1219 (1998)
98. J. T. Gallo , C. M. Verber, Appl. Opt., 33, 6797 (1994)
99. L. Dhar, M. G. Schnoes, T. L. Wysocki, H. Bair, M. Schilling, C. Boyd, Appl. Phys. Lett., 73, 1337 (1998)
100. V. Weiss, E. Millul, Appl. Surf. Sci., 106, 293 (1996)
101. S. Blaya, L.Carretero, R. Mallavia, A. Fimia, R. F. Madrigal, Appl. Opt., 38, 955 (1999)
102. R.H Kayser, R.H Young, Photochem.Photobiol.,24,395 (1976)
103. S.G Cohen, A.Parola, G.H Parson, Chem Rev., 73, 141-1(1973)
104. S Blaya, L.Carretero, R.F Madrigal , A.Fimia, Jpn. J. Appl. Phys., 41,3730 (2002)
105. J.R. Lawrence, F.T. O'Neill , J.T. Sheridan ,Optik,112,449 (2001)
106. S.Blaya, L.Carretero, R.Mallavia, A.Fimia, R.F.Madrigal, M.Ulibarrena, D.Levy, Appl.Opt., 37,7604 (1998)
107. R.A.Lessard, C.Malouin, R.Changkakoti , G.Manivannan, Opt. Eng., 32, 1665 (1993)
108. M.Ushamani, K.Sreekumar, C.S. Kartha , R. Joseph, J. Mod. Opt., 51, 743(2004)
109. M.Ushamani, K.Sreekumar, C.S. Kartha , R. Joseph, Appl.Opt. 43, 3697 (2004)
110. W.K.Smothers, B.M.Monroe, A.M.Weber, D.E.Keys, Proc.SPIE,1212,20 (1990)

111. D.A.Waldman, R.T.Ingwall, P.K.Dal, M.G.Horner, E.S.Kolb, H.Y.S. Li, R.A.Minns, H.G.Schld, Proc. SPIE, 2689,127(1996)
112. J. F. Heanue, M. C. Bashaw, L. Hesselink, Science, 265, 749 (1994)
113. H. Coufal, Nature (London) 393, 628 (1998)
114. W. L. Wilson, K. Curtis, M. Tackitt, A. Hill, A. Hale, M. Schilling, C. Boyd, S. Campbell, L. Dhar, A. Harris, Opt. Quantum Electron., 32, 393 (2000)
115. J. G. Ferry, Viscoelastic Properties of Polymers (Wiley, New York) (1980)
116. V. L. Colvin, R. G. Larson, A. L. Harris, M. L. Schilling, J. Appl. Phys., 81, 5913 (1997)
117. G. Ramos, A A. Herrero, T. Belenguer, F. D. Monte, D. Levy, Appl. Opt., 43, 4018
118. P.Cheben, M. L. Calvo, Appl.Phy.Lett., 78, 1490 (2001)
119. A. M. Weber, W. K. Smothers, T. J. Trout, D. J. Mickish, Proc. SPIE, 1212, 30 (1990)
120. R.T.Ingwall, M.Troll, Opt. Eng., 28, 586 (1989)
121. W.J. Tomlinson, E.A Chandross, H.P. Weber, G.D. Aumiller, Appl.Opt., 15, 534 (1976)
122. A.W.Adamson, A.H.Sporer, J. Inorg. Nucl. Chem., 8, 209 (1958)
123. G.Odian, Principles of polymerization, John Wiley and sons, New York, Second Ed. (1981)
124. K.Kincade, Laser Focus World, Oct. 68 (2003)
125. M.Satake, Y.Mido, Chemistry of Colour, Discovery publishing house, New Delhi (1995)
126. R.Floye, J.E. Schneider , P.D. Dittmer, Antiviral Res. 61,141(2004)
127. G. Pradeep, S. Cyriac, S. Ramkumar ,C S. Kartha, Jpn. J. Appl. Phy., 38, 137(1999)
128. A. Belendez, A.Fimia , L.Carretero , F.Mateos, Appl.Phys. Lett., 67, 3856 (1995)
129. R. Mallavia, A. Fimia, C. Garcia J.Mod.Opt., 48,941 (2001), R. Sastre, J.Mod.Opt.,48, 941(2001)
130. S. Gallego, M. Ortuno, C. Neipp, A. Marquez, A. Belendez, I. Pascual, J. V. Kelly, J. T. Sheridan, “Opt. Exp., 13, 1939 (2005)
131. M. Ortuno et al Appl. Opt., 42, 7008 (2003)
132. I.Naydenova et al , Appl. Opt., 43, 2900(2004)

133. M.J.Huang et al , Chin. Opt. Lett., 1, 41(2003)
134. F.X. Zhai, A.R.Wang, Q. Yin, J.H. Liu, M.J.Huang, Chin. Phys. Lett., 22, 2843 (2005)
135. A.L.K. Skei, V.I.Zakhrov, N.A.Perfilor, B.T.Placheaov, A.P.Fedorova, Opt. Spektrosk., 50,403(1981)
136. M. Huang, S.Wang, A.Wang, Q.Gong, F.Gan, Chin. Opt. Lett., 3,268 (2005)
137. M. M. Wang ,S. C. Esener, Appl.Opt., 39, 1826 (2000)
138. M. Ushamani, K.Sreekumar, C.S. Kartha, R. Joseph, Proc. SPIE, 5290, 352 (2004)
139. Ushamani.M, C.S. Kartha, R. Joseph, Proc.Kerala state Science congress, 2001, Jan 29-31
140. J.J.A.Couture, R.A.Lessard, R. Changkakoti, G Manivannan , Proc. SPIE., 2043, 37(1993)
141. J.J.A. Couture, Proc. SPIE., 1559, 429(1991)
142. Y.Liu, H.Wang, M.Tian, J.Lin, Opt.Lett., 20,1495 (1995)
143. R.A.Lessard, C.Molouin, R.Changakokti, G.Manivannan, Opt Eng., 32, 1665 (1993)
144. C. Solano, Appl. Opt, 28, 3524 (1989)
145. C. Solano, G. M.Ponce, C. Castaneda, Appl. Opt., 45, 5207
146. I. Naydenova , E. Mihaylova , S.Martin , V. Toal, Opt.Exp. 13, 4878 (2005)
147. S. Martin , C.A.Feely , V.Toal, Appl. Opt., 36, 5757 (1997)
148. R. Jallapuram , I. Naydenova , S.Martin , R.Howard , V. Toal , S. Frohmann , S. Orlic , H.J. Eichler , Opt. Mater., 28, 1329 (2006)
149. R. Azmat, Kinetics of methylene blue with organic reductants, , PhD thesis, Univ. of Karachy (2004)
150. V.Rehak, J.Poskocil, Collect.Czech.Chem.Commn., 44, 20159 (1979)
151. T.Ohno, T.L. Osif, N.N.Lichtin, Photochem.Photobio., 30,541(1979)
152. P.V. Kamat, N.N.Lichtin, Am.Sect.Int.Sol.Energy.Soc.,4, 175(1981)
153. R.Bonneau, J.J. Dubien and J.Faure, J.Photochem.photobio.,17,313(1973)
154. S.Matsumoto, Bull. Chem. Soc. Japan, 37, 4919 (1964)
155. C.A.Parker, C.G.Hatchard, Proc.Chem.Soc., 66,147(1962)
156. H.Obata, K.Kagasaka, M.Koizumi, Bull. Chem. Soc. Japan, 32,125 (1958)

157. L.A.Kelly, M.A.J.Rodgers, J.Phy.Chem.,99,131(1995)
158. I.Okura, K.T.Nguyen, J.Mol.Catal.,5,131(1979)
159. M.Imamura, M.Koizumi, Bull. Chem. Soc. Japan, 28,117(1955)
160. L.Linqdqvist, Arkiv. For Kemi, 16,79 (1960)
161. L.Yingjin, Y.Shunzo, S.Yoshimi, Photochem. Photobiol., 143,153 (2001)
162. A.K.Chibisov, G.V. Zacharova, J.Inf. Rec. Mater., 15,395(1987)
163. V.V. Rylkova , E.A.Cheshvi, Opt. Specktro., 63,1030 (1987)
164. G.Somer, A.Temizer, Photochem. Photobiol.,40,575 (1984)
165. A. Fimia, F. Mateos, R. Mallavia, S. Blaya, A. Beleândez, R. Sastre, F. A.Guerri, J.Mod. Opt., 46, 1091(1999)
166. S.Sugawara, K.Murase, T.Kitayama, Appl.Opt., 14,378 (1975)
167. J.P. Fouassier, F.M. Savary, Opt. Eng., 35,304 (1996)
168. J.P. Fouassier, F.M. Savary, Opt. Mem. Neur.Network, 4,18 (1995)
169. L.Solymar, D.J.Cooke, Volume Holography and volume gratings, Academic press, New York (1981)
170. G.Kaempf, H.Loewer, M.W.Whitman, Polym. Eng. Sci., 27,1421(1987)
171. H.I.Bjelkhagen, “selected papers on holographic recording materials”, SPIE milestone series MS130, SPIE Optical engineering press, Bellingham (1995)
172. B.J.Chang, Opt. Eng.,19,642 (1980)
173. T. G. Georgekutty , H. K. Liu, Appl. Opt., 26, 372 (1987)
174. S.Lelievre, J.A.Couture, Appl.Opt., 29, 4384 (1990)
175. G. Manivannan, R. Changkakoti, R. A. Lessard, J. Phys. Chem., 97, 7228 (1993)
176. A. Graube, Opt. Commn., 8, 251 (1973)
177. T Galcera, X.Jouan, M.Bolte, J.Photochem. Photobio. A, 45, 249 (1988)
178. J. Kosar, Light-Sensitive Systems: Chemistry and Applicationof Nonsilver Halide Photographic Processes (Wiley, New York, 1965)
179. T. Sano, Y. Uemura, A. Furuta, U.S. Patent 3,960,685 (1976)
180. S. Savic , D. Pantelic, D. Jakovijevic, Appl. Opt., 41,4484 (2002)
181. D. Pantelic, S. Savic, D. Jakovljevic, “Opt. Lett., 23, 807 (1998)
182. S. Savic , D. Pantelic, Appl. Opt., 46,287(2007)
183. K. Wang, L. Guo, L. Zhou, J. Zhu, Appl. Opt., 35, 6369 (1996)

184. K. Yokono , K. Nishide, U.S. Patent 4,254,193 (1981)
185. L. Guo, Y. Guo, X. Cheng, P. Hsu, “Chin. J. Lasers, 1,361 (1992)
186. K. Wang, Appl. Opt., 34, 6666 (1995)
187. T. Keinonen, R. Grzymala, Appl.Opt.,38, 7214 (1999)
188. L.Carretero, A. Murciano, S.Blaya, M.Ulibarrena, A.Fimia, Opt. Exp., 12, 1780 (2004)
189. D.H. Close etal. Appl. Phys. Lett., 14, 159 (1969)
190. J.A. Jenny, J. Opt. Soc. Am. 60,1155 (1970)
191. J.A. Jenny, Appl.Opt.,11,1371(1972)
192. J.A.Jenny, J.Opt.Soc.Am., 61,1116 (1971)
193. R.H.Wopschall, J.Opt.Soc.Am.,61,649A (1971)
194. W.S.Colburn,K.A.Haines,Appl.Opt.,10,1636(1971)
195. B.L.Booth, Proc. Soc. Photo-Opt.Instrum.Eng.,123,38(1977)
196. R.H.Wopschall, T.R.Pampalone, Appl.Opt., 11,2096 (1972)
197. C. S. H. Chen, J. Polym. Sci. A, 3, 1127(1965)
198. M.J.Jendy, J.J.Robilliard, Opt. Commn., 13, 25(1975)
199. V.R.Gowarikar, N.V.Viswanathan, J.Sreedhar, Polym. Sci. New age (P) Ltd Publishers (1996)
200. Polyvinl alcohol Properties and applications Ed.by C.A.Finch, pub. By John Wiley & sons, (1972)
201. M.J.Huang , H.W. Yao, Z.Y.Cheng , Acta Phys. Sin., 51 ,2536 (2002)
202. S. R. Guntaka, V. Toal , S. Martin, Blackwell Publishing Ltd ,J Strain, 40, 79 (2004)
203. S. Gallego, M. Ortuno, C. Neipp, A. Marquez ,A. Belendez, I. Pascual, J. V. Kelly , J. T. Sheridan, Opt.Exp.,13, 3543(2005)
204. S. Calixto, Appl. Opt., 26, 3904 (1987)
205. S. Martin, P. Leclere, Y. Renotte, V. Toal, Y. F. Lion, Opt. Eng., 33,3942 (1994)
206. S. Blaya, L. Carretero, A. Fimia, R. Mallavia, R. F. Madrigal, R. Sastre, F. A. Guerrij, J. Mod. Opt., 45,2573(1998)
207. S. Blaya , R. Mallavia, L. Carretero, A. Fimia , R. F. Madrigal, Appl.Phys.Lett.,73,1628 (1998)

208. J.Neumann, K. S. Wieking, D.Kip, Appl. Opt., 38, 5418 (1999)
209. A. Fimia, R. Fuentes, F. Mateos ,R. Sastre, J . Pineda, F. A.Guerri, J.Mod.Opt., 41,1867(1994)
210. C. Garcia, A. Fimia, I. Pascual, Appl. Phys. B, 72, 311 (2001)
211. C.Garcia, I.Pascual, A.Fimia, Appl. Opt.,38,5548(1999)
212. C.Garcia, I.Pascual, A.Costela, I.G.Moreno, C.Gommez, A.Fimia, R.Sastre,Appl. Opt.,41,2613(2002)
213. C. Neipp , A. Belendez,S. Gallego, M. Ortuno , I. Pascual, J. T. Sheridan, Opt.Exp.,11,1835 (2003)
214. S. Gallego, M. Ortuno, C. Neipp, C. Garcia, A. Belendez , I. Pascual, Opt.Exp.,11,181(2003)
215. S. Gallego, C.Neipp, M. Ortuno, A. Belendez , I. Pascual, J.Mod.Opt., 51,491(2004)
216. D.Kim, Y.Kim, S.Nam, J.Lim, J.Ind.Eng.Chem.,12,762 (2006)
217. A. Pu, K. Curtis, D. Psaltis, Opt. Eng., 35, 2824 (1996)
218. F.R.Ling, B. H.Tong, S. Jiang, B. Wang, Y.L. Zhang, J. Opt. Soc. Am. A, 24,1945 (2007)
219. S. Gallego, A. Marquez, D. Mendez, C. Neipp, M. Ortuno, M. Alvarez, E. Fernandez, A. Belendez, Appl.Opt.,46, 7506 (2007)
220. Y. Boiko, V. Slovjev, S. Calixto , D. Lougnot, Appl. Opt., 33, 787 (1994)
221. R.Jallapuram, I.Naydenova, V.Toal, S.Martin, R.Howard, Proc. of Intl. Conf. on Laser applications and Optical Metrology (ICLAOM), Eds. C.Shakher, D.S.Mehta, Anamaya Publishers, New Delhi, 275(2004)
222. Q.X. Gong, S.L.Wang , M.J. Huang, F.X. Gan, Chin.Phys.,14,1009 (2005)
223. I.Naydenova , K.Pavani , E.Mihaylova , K.Loudmer , S. Martin , V.Toal Proc. SPIE, 5827 ,163 (2005)
224. K. Pavani, I. Naydenova, S. Martin, V. Toal, J. Opt. A: Pure Appl. Opt., 9,43 (2007)
225. K.Tsuchida, M.Ohkawa, S.Sekine, Opt.Eng., 46,015801(2007)
226. U.Rhee, H.J.Caulfield, C.S.Vikram, J.Shamir, Appl. Opt.,34, 846 (1995)
227. G. Zhao, P. Mouroulis, J. Mod.Opt., 41, 1929 (1994)

228. J. T. Sheridan, J. R. Lawrence, J. Opt. Soc. Am. A, 17, 1108 (2000)
229. J. H. Kwon, H. C. Chang, K. C. Woo, J. Opt. Soc. Am. B, 16, 1651 (1999)
230. J. R. Lawrence, F. T. O'Neill, J. T. Sheridan, J. Opt. Soc. Am. B, 19, 621 (2002)
231. J. V. Kelly, F. T. O'Neill, J. T. Sheridan, C. Neipp, S. Gallego, M. Ortuno, J. Opt. Soc. Am. B, 22, 407 (2005)
232. S. Blaya, L. Carretero, R. F. Madrigal, M. Ulibarrena, P. Acebal, A. Fimia, Appl. Phys. B, 77, 639 (2003)
233. S. Massenot, J. L. Kaiser, R. Chevallier, Y. Renotte, Appl. Opt.,43, 5489 (2004)
234. R. L. Sutherland, V. P. Tondiglia, L. V. Natarajan, T. J. Bunning, J. Appl. Phys., 96, 951 (2004)
235. J. V. Kelly, M. R. Gleeson, C. E. Close, F.T.O' Neill, J. T. Sheridan, Opt. Exp., 13,6990 (2005)
236. S. Gallego, M. Ortuno, C. Neipp, A. Marquez , A. F.Belendezelena, I. Pascual, Opt.Exp.,14,5121(2006)
237. S.Gallego, M. F. Ortuno, C. Neipp, E. Fernandez, Opt.Exp., 15, 9308 (2007)
238. F. Mendel, J. Agric. Food. Chem., 51,4504 (2003)
239. M. Ortuno1, E. Fernandez, S. Gallego, A. Belendez, I. Pascual, Opt.Exp., 15, 12425 (2007)
240. T.Todorov, L.Nikolova,N.Tomova, Appl. Opt.,23,4309(1984)
241. R.A.Lessard, C.Molouin, R.Changakokti, G.Manivannan, Opt Eng., 32, 1665 (1993)
242. J.J.A.Couture, Appl. Opt.,30,2858 (1991)
243. G.M. Ponce, C. Solano, Opt.Exp.,14,3776 (2006)
244. F.W.Westheimer, Chem.Rev.,45,419 (1949)
245. B. Duncalf ,A.S. Dunn, J.Appl.Polym.Sci., 8, 1763 (1964)
246. F.Ziping, Z.Jugin, H.Dahsiung, Guangxue Xuebao,4,1101(1984)
247. R. Changkakoti, R.A.Lessard, J. J. A. Couture, OSA annual meeting, Nov.(1990)
248. G Manivannan, R. Changkakoti, R.A Lessard, Opt. Eng., 32,671 (1993)
249. M. Barikani, E. Simova, M. Kavehrad, Appl.Opt., 34, 2172 (1995)
250. R. Changkakoti, G.Manivannan, S.Ganguly, R.A.Lessard, Opt. Memory and neural networks, 4,35(1995)

251. C. Pizzocaro, C. Lafond, M. Bolte, J. Photochem. Photobio. A: Chem., 151, 221 (2002)
252. R .Grazymala, T. Keinonen, Appl. Opt.,37, 6623 (1998)
253. T.Keinonen, R. Grazymala, Appl.Opt., 38, 7214 (1999)
254. G.Manivannan, G. Mailhot, M. Bolte ,R. A. Lessard, Pure Appl. Opt., 3, 845 (1994)
255. G.K.Oster, G.Oster, J.Am.Chem.Soc., 81,5543(1959)
256. K.Sugegawa, S.Sugawara, K.Murase, Electon Commn. Jap. 58-c,132(1975)
257. R. Changkakoti, G Manivannan, A.Singh, R.A Lessard, Opt. Eng., 32, 2240 (1993)
258. V. Kuncsery, G. Filotiy, R. Podgorsekz, M. Biebricherz ,H .Frankez, J.Phys. D: Appl. Phys., 31, 2315 (1998)
259. B.A.Budkevich, A.M.Polikanin, V.A.Pilipovich, N.Ya, Petrochenko, Optical spectroscopy,50,621(1989)
260. G.Manivannan, R.A.Lessard, Polymers in optics: Physics, Chemistry and applications, R.A.Lessard, W.F.X. Frank , Eds., Cr63,307(1996)
261. M.C.Valsangiacom, M.Bulinski, I.Iova, G.Schinteie, C.Kuncser, G.Flioti, D.Bejan, Romn. Report. Phy., 55,283(2003)
262. C. Pizzocaro, R.A. Lessard, M Bolte, Can. J. Chem., 76, 1746 (1998)
263. D.J. Margerum, A. Jocobsm, 3,694,218 (Cl.96,35-1,GO3C) (1972)
264. R.A.Lessard, G.Manivannan, R.Changkakoti, Opt. Mem. Neural Networks, 4,203(1995)
265. G.Lemelin, A.Jourdain, G.Manivannan, R.A.Lessard, Pue. Appl.Opt.,5,95(1996)
266. F.Trepanier, G.Manivannan, R.Changkakoti, R.A.Lessard, Can. J. Phys., 71, 423 (1993)
267. G.Manivannan, G.Lemelin, R.Changkakoti, , R.A.Lessard, Appl. Opt., 33, 3478 (1994)
268. R.Beaulieu ,R A. Lessard, M Bolte, Program of the SPIE, Quebec, 13-16 July, (1998)
269. R. Beaulieu , R A. Lessard, M Bolte,D.Kip, L.Glabasnia, Program of the Soc. Imag. Sci. & Tech. / SPIE, San Jose, 24-30, Jan. (1998)
270. R. Beaulieu , R A. Lessard, D.Kip, M Bolte, DAMP/DOP 1997, Ottawa, 30Oct-1nov.(1997)

271. R. Beaulieu , R A. Lessard, M Bolte, T.Galstyan, Int. Conf. on Appplication of photonic Technology, Ottawa, July 27-30(1998)
272. R. M. Beaulieu , R A. Lessard, Proc. SPIE 4087,1298 (2000)
273. B. M. John, M.Ushamani, V.S.Nisha, R. Joseph, K.Sreekumar, C. S. Kartha, Proc. of APT- 04 ,Cochin , (2004)
274. R.A.Lessard, M. Bolte, Y. Israeli, A. Rivaton, Proc. of Intl. Conf. on Optics and optoelectronics -ICOL 2005, Dehradun, India (2005)
275. M. M.Ushamani, K.Sreekumar, C.S. Kartha, R.Joseph, Appl.Opt.,41, 1984 (2002)
276. M.Ushamani, N. G. L. Deenja, K.Sreekumar, C.S. Kartha , R. Joseph, Bull. Mater. Sci., 26,343 (2003)
277. M.Ushamani, “Studies on photosensitive polymers for optical recording” PhD Thesis, Cochin Univ. of Sci. and Tech., (2002)
278. H.Franke, H.G.Festl, E.Kratezig, Colloid Polym.Sci., 262,213(1984)
279. M.Kpietz, M.D.Lechner, D.G.Steinmeir, Macromol. Chem. Rapid Commn., 4,113(1983)
280. H.Franke, Appl.Opt.,23,2729(1984)
281. V.P.Pham, G.Manivannan, R.A.Lessard, Thin solid films, 270,295 (1995)
282. V.P.Pham, G.Manivannan, R.A.Lessard, P.O.Riccardo, Int. Conf. Lasers, 734 (1994)
283. Stanislaw, Barkiewicz, A.Miniewic, Appl.Opt.,34,5175(1995)
284. T.Todorov, N.Tomova, L.Nicolova, Opt. Commn., 47,123(1983)
285. S. H. Lin, K. Y. Hsu, W. Z. Chen, W. T. Whang, Opt. Lett., 25, 451 (2000)
286. K. Y. Hsu, S. H. Lin, W. Z. Chen, W. T. Whang, Proc. SPIE, 3801, 66 (1999)
287. J. Mumbru, I. Solomatine, D. Psaltis, S. H. Lin, K. Y. Hsu, W. Z. Chen, W. T. Whang,Opt. Commn., 194, 103 (2001)
288. S. H. Lin, W. Z. Chen, W. T. Whang, K. Y. Hsu, Proc. SPIE, 3801, 100 (1999)
289. K. Y. Hsu, S.H. Lin, Y.N. Hsiao, W. T.Whang, Opt. Eng., 421390 (2003)
290. Y.N. Hsiao , W.T. Whang, S. H. Lin, Opt. Eng., 43, 1993 (2004)
291. W.J.Gambogi, A.M.Weber, T.J.Trout, Proc. SPIE, 2043, 2 (1993)
292. K.Curtis, D.Psaltis, Appl. Opt., 33, 5396 (1994)
293. H.J.Zhou, V.Morozov, J.Neff, Appl. Opt., 34, 7457(1995)

294. J.Liu, C.H.Zhao, R. Lee, R.T.Chan, Opt. Lett., 22, 1024(1997)
295. R.L.Q. Li, Z.H.Fu, R.T.Chen, J. Lightwave Technol., 15, 2253(1997)
296. K.Curtis,D. Psaltis, Appl. Opt., 31, 7425(1992)
297. B.M.Monroe, W.K.Smothers, D.E.Keys, R.R.Krebs, D.J.Mickish, A.F.Harrington, S.R.Schicker, M.K.Armstrong, D.M.T. Chan, C. I. Weathers, J.Imaging Sci., 35, 19 (1991)
298. B. M. Monroe, J. Imaging Sci., 35, 25(1991)
299. D. J. Lougnot,C.N. Turck, Pure Appl. Opt., 1, 251(1992)
300. D. J. Lougnot, N.Noiret, C.N.Turck, Pure Appl. Opt., 383(1993)
301. I. Aubrecht, M. Miler, I. Koudela, J.Mod.Opt.,45,.1465(1998)
302. S. Stevenson, Proc. SPIE, 3011, 231(1997)
303. S.H.Stevenson, M.L.Armstrong,P.J. O’Connor, D.F.Tipton, Proc. SPIE, 2333, 60 (1995)
304. W.K.Smothers, B.M.Monroe, A.M.Weber, Proc. SPIE, 1212, 20(1990)
305. S. Diez, R.Elsner, R.Madonald, Scientific Technology Polymer Advances Materials, Prasad, P.N., Ed., New York: Plenum(1998)
306. V. Moreau, Y. Renotte, Y. Lion, Appl. Opt., 41, 3427(2002)
307. Pu, Allen, Holographic 3-D disks and optical correlators using photopolymer materials, PhD Thesis, California Inst. of Techn. (1997)
308. W.K.Smothers, T.J.Trout, A.M.Weber, D.J.Mickish, 2nd Int. Conf. on holographic systems, Bath, UK(1989)
309. W.J.Gambogi, W.A.Gerstadt, S.R.Mackara, A.M.Weber, Proc. SPIE, 1555,256(1991)
310. K.Curtis, 3-D photopolymer disk for correlation and data storage, and cross talk in volume holographic memories, PhD Thesis, California Inst. of Techn. (1994)
311. B.D. Guenther,W. Hay, Holographic Properties of DMP-128 Photopolymers., PhD Thesis, Duke Univ., Durham Nc(1986)
312. R.T.Ingwall, H.L.Fielding, Proc. SPIE, 523, 306 (1985)
313. R.T.Ingwall, M.Troll, W.T.Vetterling, Proc. SPIE, 747, 67(1987)
314. Troll, M. , Formosa, J., Proc. SPIE, 1051, 90 (1989)
315. J.J.Butler, M.A.Rodriques, M.S.Malcuit, Opt.Commn., 155, 23(1998)

316. D.A.Waldman, H.Y.S.Li, Proc. SPIE, 3010, 354(1997)
317. D.A.Waldam, C.J.Butler, D.H.Raguin, Proc.SPIE, 5216,10 (2003)
318. http://www.aprilisinc.com
319. T.Kuwayama, N.Taniguchi, Y.Kuwae, N.Kushibiki, Appl.Opt.,28,2455(1989)
320. http://www.polygrama.com
321. J. E. Boyd, T. J. Trentler, R. K. Wahi, Y. I. V.Cantu, V. L. Colvin , Appl. Opt., 39, 2353 (2000)
322. S.T.Lopez, A.O.Perez, L.C.Leyva, I.F.Tapia, M.O.Gutierrez, Proc. SPIE, 5290, 332(2004)
323. D. R. Schoenfeld, V. Krneta, M. C. Cole, P. A. Whiteside, US Patent 71737449(2007)
324. D. J. Mickish, S. R. MacKara , T. J. Trout, US Patent 5633100 (1997)
325. S.J. Luo, G.D.Liu, Q.S.He , M.X.Wu, G.H.Jin, M.Q.Shi, T.Wang, F.P. Wu , Chin. Phys.,13 , 1428(2004)
326. David R. Boswell, US patent. 5753349 (1998)
327. O. Junichi, O. Shigeru, US patent , 5236809, (1993)
328. S. Yao, X. Qin, X. Yu, Q. Zhang , G. Xu, Z. Wang, Y. Dong, X. Jing, Y. Sun, B. Huang, Trans. Nonferrous Me. Soc. China, 15, s88 (2006)
329. T. J. Trentler, J. E. Boyd, .V. L. Colvin, Chem. Mater., 12, 14319 (2000)
330. L. Dhar, K. Curtis, M. Tackitt, M. Schilling, S. Campbell, W. Wilson, A.Hill, C. Boyd, N. Levinos, .. A.Harris, Opt. Lett., 23. 1710 (1998)
331. V. Colvin, R. Larson, A. L. Harris, M. Schilling, J. Appl. Phys., 81, 5913 (1997)
332. G.D. Liu, Q.S.He, S.J.Luo , M.X.Wu, G.F.Jin, M.Q. Shi, F.P.Wu, Chin.Phys.Lett., 20,1733 (2003)
333. A. Fimia, P. Acebal, A. Murciano, S. Blaya, L. Carretero, M. Ulibarrena, R. Aleman M. Gomariz, I. Meseguer, Opt.Exp.,11,358 (2003)
334. P.Simon, R. Huhle, M. Lehmann, H. Lichte, D.Monter, T. Bieber, W. Reschetilowski, R. Adhikari, G. H. Michler . Chem. Mater., 14, 1505 (2002)
335. S. Blaya, A. Murciano, P. Acebal, L. Carretero, M. Ulibarrena, A. Fimia, Appl. Phy.Lett., 84, 4765(2004)
336. A.Fimia, Appl. Opt.,32,3706(1993)

337. I.Banyasz, Opt.Commn., 181,215(2000)
338. W.K.Smoothers, B.M.Monroe, A.M.Weber, D.E. Keys, Proc. SPIE, 1212,20 (1990)
339. S. Yagi, T. Imai, A. Tate, M. Hikita, S. Tomaru, S. Imamura, T. Tamamura, Y. Kurokawa, M. Yamamoto, Intl. Symp. on Optical Memory, Kauai Island, Hawaii, (1999)
340. K. Hirabayashi, H. Kanbara,. Yuhei Mori, T. Kurihara, M. Shimizu, T. Hiyama, Appl. Opt., 46,8403(2007)
341. Y. Tomita, N. Suzuki, K. Chikama, Opt. Lett., 30, 839 (2005)
342. D. A. Tomalia, A. N. Naylor, W. A. Goddard, III Angew. Chem., 102, 119 (1990)
343. K. Ishizu, K. Tsubaki, A. Mori, S. Uchiuda, Prog. Polym. Sci., 28, 27 (2003)
344. N. Suzuki, Y. Tomita, T. Kojima, Appl. Phys. Lett., 81, 4121 (2002)
345. Y. Tomita , H. Nishibiraki, Appl. Phys. Lett., 83, 410 (2003)
346. N. Suzuki , Y. Tomita, Jpn. J. Appl. Phys., Part 2,42, L927 (2003)
347. N. Suzuki and Y. Tomita, Appl. Opt. 43, 2125 (2004)
348. Y.Tomita , K.Furushima, K. Ochi , K. Ishizu, A. Tanaka, M. Ozawa, M. Hidaka, K. Chikama, Appl. Phys. Lett., 88,071103(2006)
349. Y. Tomita. SPIE News room 10.1117/2.1200612.0475(2006)
350. C. Arnaud, F. Guattari, G. Pauliat, G. Roosen, T. Forestier, C. Desplanches, N. Daro, J.F. Letard, J. Degert, E. Freysz, EOS annual meeting-2006 (Paris)
351. O. V. Sakhno, L. M. Goldenberg, J. Stumpe , T N Smirnova, Nanotechnology 18, 105704 (2007)
352. H.Jorkaala, H.Stennenen, J.Opt.A.Pure Appl. Opt.,4,366(2002)
353. H.Takahashi, J.Yamauchi, Y.Tomita, Jpn.J.Appl.Phys., 44,L1008(2005)

Chapter 2

Experimental Details

For the present study, poly (vinyl alcohol) and poly (vinyl chloride) were selected as base matrices and methylene blue was used as the photoinitiator. Films were fabricated with the inclusion of different monomers, electron donors and crosslinkers in the system and characterized to have maximum diffraction efficiency, storage life and sensitivity. The materials used and the experimental procedures adopted in the present investigation are given in this chapter.

2.1.Introduction

In recent years, there has been a lot of interest in the study on polymer based holographic recording materials because of their high efficiency, low cost, and ease of preparation. As each composition of the photopolymer influences its characters greatly, it is important to optimize the compositions [1]. The current chapter details the various experimental techniques adopted for characterizing the polymer films developed in our laboratory. Brief descriptions of the different materials used for the fabrication of films are also presented.

2.2.Materials Used

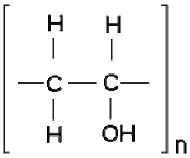
Photopolymer systems for recording holograms typically comprise one or more monomers, a photoinitiator system and an inactive component often referred to as a binder. Other components are sometimes added to control a variety of properties such as pre-exposure shelf life, stability and viscosity of the recording medium [2]. The following section describes the various constituents used for the fabrication of photopolymer films.

2.2.1. Host Matrices

Both poly (vinyl chloride) (PVC) and poly (vinyl alcohol) (PVA) were selected as the host matrices or binder.

PVC, the leading plastic material, is a member of the large family of polymers broadly referred to as vinyls, all have the vinyl group ($CH_2=CH-$) in common. It is produced by the polymerization of a colourless gas, vinyl chloride ($CH_2=CHCl$) possessing a faintly sweet odour. The polymerization of vinyl chloride can result in the formation of molecules with a number of isomeric forms $-(CH_2-CHCl)-_n$. PVC used was of suspension grade with K value 70 and molecular wt. 2,60,000 supplied by Reliance Industries Ltd, Mumbai, India. Cyclohexanone (supplied by Qualigens, Mumbai) was used as the solvent of PVC.

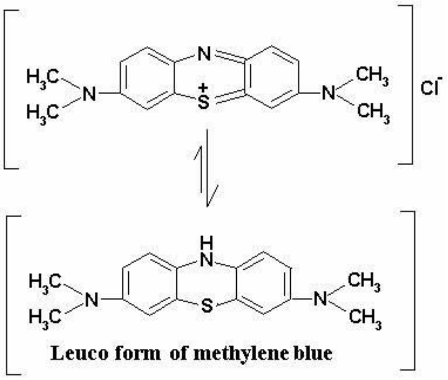
PVA is prepared by the hydrolysis of poly (vinyl acetate) and the structure of PVA is shown below.



When the PVA is dissolved in water, the vinyl alcohol units link up to form chains of about 2,000 units and it results in a highly viscous solution. PVA (cold) with molecular wt. 1, 25,000 used in the study was supplied by MERCK, Mumbai and CDH, Mumbai. PVA supplied by both MERCK and CDH showed the same holographic performance.

2.2.2. Dye

The photoinitiator system comprises of a photosensitizer dye and a charge transfer agent. In the present study, methylene blue (MB) was used as the photosensitizing dye. MB dye of microscopy grade was supplied by Qualigens. Chemically MB is 3, 7-bis (dimethyl amino) phenantholinium chloride. MB is a basic dye of thiazine group and is also known as swiss blue and tetramethyl thionine [3]. The absorption maxima of MB, if pure, reside at 668 nm and 609 nm. According to the mechanism, the photoexcited dye (in the (n, π*) triplet state) is reduced by transfer of electron or hydrogen. The semireduced dye radical is either reoxidized to the ground state by oxygen or is not regenerated, but is transformed to the leuco dye, i.e. photobleached. The structure of MB and its leuco form are shown below.



2.2.3. Monomer

Different monomers were incorporated to the polymer matrices to establish the grating formation induced by refractive index modulation. MBPVC films were fabricated with vinyl acetate (Lancaster) and butyl acrylate monomer. The monomers used with PVA were acrylamide (SRL, Mumbai), acrylic acid (CDH), methacrylic acid (CDH), vinyl acetate (Lancaster), butyl acrylate (MERCK) and acrylonitrile (S D Fine, Mumbai).

2.2.4. Electron Donor

To initiate the polymerization reaction, different electron donors or charge transfer agents were incorporated as co-initiator. The electron donors used with PVC are pyridine (Qualigens), dimethyl formamide (SD Fine), triethylamine (MERCK) and dimethylamino benzaldehyde (CDH). Triethanolamine (S D Fine), triethylamine, dimethyl formamide (S D Fine) and hexamine (CDH) were used with PVA as co-initiator.

2.2.5. Crosslinker

To improve the storage life, organic and inorganic crosslinkers were incorporated. The organic crosslinker selected was glutaraldehyde ($C_5H_8O_2$) supplied by Loba Chemie, Mumbai. Metallic salts such as cupric chloride ($CuCl_2.2H_2O$) supplied by MERCK, ammonium dichromate $(NH_4)_2Cr_2O_7)$ supplied by S D Fine, cadmium acetate ($Cd(CH_3COO)_2.2H_2O$) supplied by Sarabhai Chemicals, Baroda , stannous chloride ($SnCl_2$) supplied by MERCK, zinc acetate ($Zn(OOCCH_3)_2.\ 2H_2O$) supplied by S D fine, lead nitrate ($Pb(NO_3)_2$) supplied by MERCK and Ferric chloride ($FeCl_3$) supplied by Qualigens,were incorporated.

2.3.Film Fabrication

Microscopic glass slides were used as the substrate. The glass slides were soaked in freshly prepared chromic acid for 12hr, washed and cleaned with soap solution. It was washed in running water followed by distilled water and dried in an oven.

The various techniques for coating polymer solution include dip coating, spin coating, doctor blading, gel casting, gravity settling, spraying etc. [4-6]. Among these, in the present work gravity settling method was adopted. The method was easy to setup and the procedure was simple. The coating was done by pouring known volume of viscous solution on cleaned glass slides kept on a leveled surface. The solution equally spreads over the slides. The glass slides were covered to protect from dust. The films were fabricated at room temperature under normal laboratory conditions. Depending on the film constituents, the drying period varied from 24 to 48 hr. No pre exposure, UV curing or baking was applied to the films. Though the edge effect due to surface tension could not be avoided, fairly uniform films were obtained after drying. When micro-slides having dimensions 75mm x 25mm x 1.4mm were used, films were of uniform thickness in the central portion (i.e. area of 69 x19 mm^2), except at the edges (3 mm from edges) . The films fabricated on large slides (82mm x 60mm x 1.4mm) were of uniform thickness in the central portion (i.e. area of 69 x47 mm^2), except at the edges (6.5 mm from edges). The thickness of the film could be controlled by varying the viscosity of the solution (by changing the wt. % of binder) and the volume of polymer solution poured on glass slides.

2.4. Infrared Spectroscopy

Atoms or atomic groups in molecules are in continuous motion with respect to one another and they vibrate about some mean position. Infrared (IR) spectrum of a compound is the superposition of absorption bands of specific functional groups. Each functional group is indicated by the presence of absorption bands in the spectrum. The subtle interactions with the surrounding atoms or molecules impose the stamp of individuality of the spectrum of each compound. The systematic interpretation of the IR spectrum is of great help in determining whether a reaction has occurred to give the predicted product [7]. IR analysis was carried out to find out the structural changes that occur in the material on laser exposure. As most of the monomers used in the present study are volatile, the presence of the monomers after drying of the films was confirmed from IR analysis. The Fourier transform Infrared (FTIR) spectrum of the polymer films were recorded using a Thermo Nicolet, Avatar 370 FTIR spectrometer. The resolution of the instrument was 0.9cm^{-1}.

2.5. Laser Exposure

The holographic characterization of polymer films was done by exposing the films to lasers of suitable wavelengths. In the present study only continuous wave lasers were used. As the highest spectral sensitivity of MB is in the red region of spectra, He-Ne laser having emission at 632.8 nm were used for most of the characterizations. The different lasers used were 15mW linearly polarized He-Ne laser (Melles Griot), unpolarized He-Ne lasers (10 mw and 5mW, Melles Griot), and 1mW He-Ne laser (Spectra Physics). The other lasers used for characterization include frequency doubled Nd: YAG laser (532 nm, 20mW – Coherent), 43 series Ar$^+$ laser (488 nm, 140 mW -Melles Griot) and switchable He-Cd laser (441.6 nm (80mW) and 325 nm (20mW) –Kimmon). The laser beam was expanded using a spatial frequency filter arrangement [8-9]. The power density was measured using a power meter (Ophir model PD-2000). The exposure was calculated as *power density x time*. The exposure time was controlled by an electronic shutter (Thorlabs). All the holographic experiments were performed on a vibration isolation table. For this an indigenously fabricated table and table supplied by TMC with compressor were used [10].

2.6. Optical Absorption Studies

When the polymer film is exposed to suitable wavelengths, the dye molecules in the exposed region are converted to the leucoform and as a result an absorbance modulation occurs in the exposed area. The absorption spectra of both unexposed films and exposed films were recorded using JASCO V-570, Hitachi-330 and Hitachi -3410 UV-Visible-NIR spectrophotometer. The absorption spectra were taken with the undoped polymer films as reference plate. The absorbance modulation was determined as the difference between absorbance before exposure and that after exposure [8, 11].Though dye is converted to the leucoform on laser exposure, on storage the dye has different behavior in each polymer matrices. The dye molecules could exist in the leucoform itself, it returns to the original state or it is transferred to other states. UV-Visible spectral analysis was done to study the dye behavior on laser exposure in MBPVA and MBPVC films with different matrix additives. To study the stability of this leuco form or the dye behaviour on storage, absorption spectra of the exposed regions on storage was recorded. The change in absorbance on storage is determined as the absorbance just after exposure and the absorbance on storage [12].

2.7. Real Time Transmittance Measurements

Real time transmittance measurements were carried out to find out the material sensitivity by exposing the samples to suitable laser for a known time. The transmittance at regular intervals was monitored using a power meter [13-14]. The experimental setup for real time transmittance measurements is shown in Fig.2.1. The relative transmittance T/T_0 was determined; where T is the real time transmittance of the sample on laser exposure and T_0 is the transmittance of the samples without dye. As the material sensitivity increases the transmittance increases at low exposures. This is because even at low exposure, the dye molecules were getting excited and initiate the photochemical reaction and then it is converted to the leucoform. From the relative transmittance, rate of bleaching could be found out by taking the slope of the relative transmittance Vs time curve at different times.

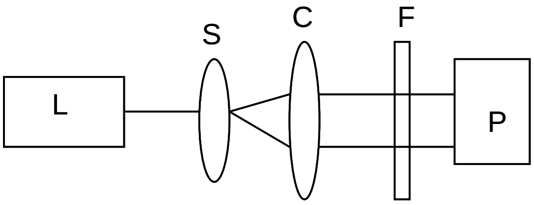


Fig.2.1 Experimental setup for real time transmittance measurements. L-Laser, S-Spatial Frequency Filter, C-Collimating lens, F-Film, P-Power meter

2.8.Refractive Index Measurements

On laser exposure, monomers in the exposed region get polymerized and monomer from the unexposed region diffuses to the exposed regions. This induces a change in refractive index (RI) between the exposed and unexposed regions. Photocrosslinking also induces RI modulation. The RI modulation arising in the film due to photopolymerization reactions and photocrosslinking was measured using Atago DR M2 Abbe' refractometer. RI of the unexposed films and that of the exposed films were measured and refractive index modulation was calculated as the difference of these two values [15].

In Abbe' refractometer, the sample is sandwiched into a thin layer between an illuminating prism and a refracting prism (Fig.2.2). The refracting prism is made of glass with high RI. Monobromonaphthalene in which RI (1.63) is higher than that of the polymer film, was used as the contact liquid. The refractometer is designed to be used with samples having RI smaller than that of the refracting prism. A halogen lamp is used as the light source and interference filters are used to have appropriate wavelengths (546 nm, 589 nm, and 680nm). In the present study the samples were illuminated by inserting a 680nm filter. The light source is projected through the illuminating prism, the bottom surface of which is ground, so each point on this surface can be thought of as generating light rays traveling in all directions. Inspection of Fig. 2.2 shows that light traveling from point A to point B will have the largest angle of incidence (θ_i) and hence the largest possible angle of refraction (θ_r) for that sample. All other rays of light entering the refracting prism will have smaller θ_r and hence lie to the left of point C. Thus, a detector placed on the back side of the refracting prism would show a light region to the left and a dark region to the right. Samples with different RI will produce different angles of refraction (the angle of incidence and the refractive index of the prism are fixed) and this will be reflected in a change in the position of the borderline between the light and dark regions. Before each measurement, the position of the borderline was determined by calibrating the scale using glass plate with known RI (1.516) and distilled water. The measurement accuracy of the instrument is ±0.0002.

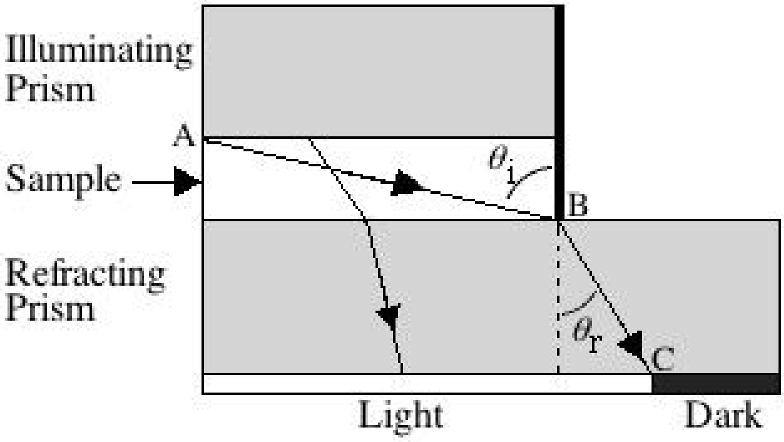


Fig.2. 2 Cross section of part of the optical path of an Abbe refractometer

2.9. Recording of Grating

To optimize the concentration of matrix additives and exposure requirements, gratings were recorded on the films using suitable lasers. For this two different experimental setups were adopted.

2.9.1. Single Beam Method

Long period gratings were recorded on the films using single mirror technique as shown in Fig. 2.3 [11, 13]. In this method, the expanded beam was allowed to fall on a thick back silvered mirror kept at an angle. The beams reflected from different surfaces of the mirror interfere and these interference fringes are allowed to fall on the polymer film. In this case, the interfering beams were not of equal intensities and the inter beam angle is less than 2^0. So the fringe visibility and spatial frequency are very low. This technique was employed where the material resolution was below 150 lines/mm. The spatial frequency can be varied by adjusting the distance between the mirror and film and by varying the thickness of the mirror. The advantage of this technique is that it is more easy to setup and it has more vibration stability than the double beam interferometry. This technique was adopted to record gratings on materials with low resolution. The major drawback of this technique is that the beam ratio cannot be controlled and the spatial frequency is limited to 150 lines/mm.

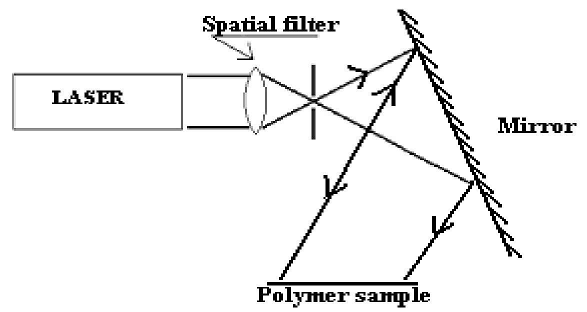


Fig. 2.3 Experimental setup to record long period gratings (single beam technique)

2.9.2. Double Beam Interferometry

To record gratings having high spatial frequencies, double beam interferometry was used. The experimental setup is shown in Fig. 2.3. The laser beam (L) was split in to two using a beam splitter (B) with R/T ratio 50/50 and these beams were directed to the film using front silvered mirrors (M). These beams were expanded using spatial frequency filter (E) and collimated (C). The collimated laser beams are allowed to interfere inside the film (F). The exposure time was controlled by an electronic shutter (S) placed in front of the laser. Gratings were recorded by varying the inter beam angles so as to record gratings with different spatial frequencies. The spatial frequency (number of lines recorded on the material) was determined using Bragg's equation.

$2d\sin\theta = n\lambda$ ……….(2.1)

Number of lines, $N = 1/d$ …………(2.2)

Where, θ is the angle between a collimated beam to that of the normal to the film (half the inter-beam angle) and λ is the wavelength of laser used for grating recording. To record gratings with different fringe visibility, the intensity of each beam is adjusted by placing appropriate neutral density filters.

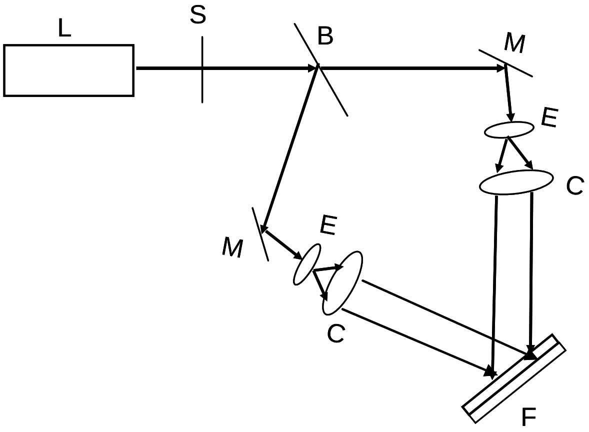


Fig. 2.3 Experimental setup to record gratings – double beam interferometry; where L-Laser, S-Shutter, B-Beam splitter, M-Mirror, E-Beam expander with spatial filter, C-Collimating lens, F-Polymer film coated on glass

2.10. Diffraction Efficiency Measurements

The experimental setup to measure the diffraction efficiency (DE) is shown in Fig.3.4. Unexpanded laser (L) beam was allowed to fall on the grating recorded film (F) placed at Bragg's angle. The diffracted beam was observed on the screen at Bragg angle and its intensity was measured using Ophir 2000 power meter (P). The intensity of the laser beam was reduced to 1µW using neutral density filters (N). The intensity of incident beam (I_i), diffracted beam (I_d) and directly transmitted beam (I_T) was measured. The diffraction efficiency was calculated as the ratio of the intensity of first order diffracted beam to that of the incident beam.

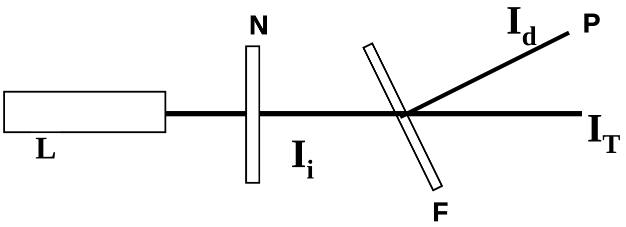


Fig. 2.4 Experimental setup for diffraction efficiency measurements.
where L-laser, N-ND filter, F- grating recorded film, P-power meter

The angular response of the recorded gratings was determined by varying the angle of reconstructed beam and by monitoring the diffracted beam intensity. As it was easier to control, the film was rotated instead of the laser beam.

When gratings were recorded with single beam method, diffracted patterns were visible on either side of the directly transmitted beam. As it was not possible to find out the interfering angle from the recording geometry, the spatial frequency was determined from the angle of diffraction. The diffracted pattern is focused to a screen placed behind the film. The value of $Sin\theta$ is determined as '$\text{Sin}\theta = A/B$' and substituted in equation 2.1. Where, A is the separation between the first order diffraction pattern and that of the transmitted beam and B is the distance between the film and screen. As θ is small, $sin\theta \sim \theta$.

2.11. Storage and Shelf Life

In dye doped films, the diffraction efficiency can be reduced or remained unaltered on storage. Storage life gives the idea that how long the material can hold (store) the recorded grating. The storage life of the grating was determined by measuring the DE of gratings after each day of grating formation.

Shelf life is defined as the film properties on ageing of the samples. To study the shelf life of the film, gratings were recorded on the film on each day after film preparation and efficiency was determined. It includes optical absorption studies, RI measurements etc on each day after preparation of the film. It gives the idea that how long the material can be utilized.

2.12. Multiplexing

Volume holography allows multiple pages of data to be stored in the same volume. The great attraction is the possibility of large storage capacity, with the individual high-density data pages addressed by changing the angle, wavelength, or phase code of the reference beams resulting in rapid parallel storage and retrieval of digital data. There are a number of multiplexing techniques like angular multiplexing, peristrophic multiplexing, phase coded multiplexing, shift multiplexing, spatial multiplexing etc. using which we can achieve high storage densities can be achieved [2]. Pairs of methods are combined with some restrictions to achieve higher capacity e.g. angle and peristrophic multiplexing, angle and wavelength multiplexing. In the present work a number of gratings were recorded on the same volume by angular multiplexing, i.e. by varying the inter beam angle.

2.13. Recording of Fourier Transform Hologram

The Fourier transform (FT) hologram is a useful configuration for holographic storage. In this arrangement the most useful components of the frequency spectrum can be formed into a relatively compact object beam. This increases the information density and allows more effective use of the recording material. By using this technique, two dimensional holograms can be recorded on the material with diminutive consumption of sample area and the noise in the image could be reduced by incorporating suitable filters in the fourier plane. Another benefit is that FT holograms are less sensitive to misalignment and to imperfections in the recording material and optical system. However, when the object field has regular or periodic components, the spectrum will contain a series of high intensity peaks [16].

In the present study FT was constructed using lenses. The field distribution at the back focal plane of the lens is the FT of the field distribution at the front focal plane of the lens [8]. FT holograms were recorded on the films using the experimental setup shown in Fig.2.5; where S-Laser, B-beam splitter, E-beam expander with spatial filter, C-Collimating lens, M-Mirror, O-object (transparency), L_1 and L_2-Lens, C_f-Focusing lens , F-Polymer film, D-CCD [17]. The light from the He-Ne laser was split into two using a beam splitter. The transmitted beam was expanded using a spatial frequency filter and collimated. Usually in storage devices the object beam is allowed to pass through a spatial light modulator (SLM), but in the present study, a transparency containing letters was used as the object. The object was placed at the front focal plane of the lens (Object plane) 'L_1'and its FT was displayed at the back focal plane of the same lens (FT plane). The film was kept at the back focal plane of the lens 'L_1'. The reflected light which was taken as reference wave (pointed beam) was allowed to fall on the photosensitive plate and allowed to interfere with the FT. Since the FT of the transparency is characteristic of the transparency, a recording of the FT will also contain all the information about the object. Thus the hologram recorded contains information about the object and is termed a FT hologram. Another lens 'L_2'was placed so that the film was at the front focal plane of 'L_2'. After blocking the object beam, the image was observed on the screen positioned at back focal plane of 'L_2' (Image plane). A CCD camera was (Pixelfly PCO 225 XS 7346) replaced the position of screen and the holograms were stored in the computer.

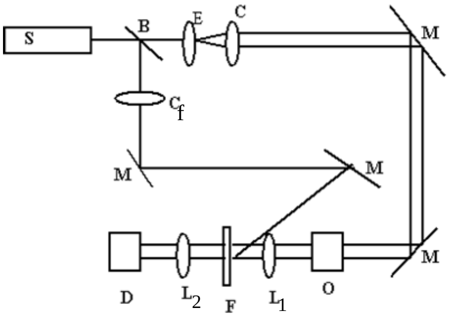


Fig.2.5 The experimental technique used for recording FT hologram. where S-Laser, B-beam splitter, E-beam expander with spatial filter, C-Collimating lens, M-Mirror, O-object (transparency), L_1 and L_2-Lens, C_f-Focusing lens , F-Polymer film, D-CCD

2.14. Recording of Holograms

Transmission holograms were recorded on the polymer film using single beam technique as shown in Fig. 2.6. Laser beam (S) was expanded using a spatial frequency filter arrangement (E). Object (O) is placed in the path of the expanded laser beam and polymer film (F) is placed near the object at an angle. The laser beams scattered by the object act as the object wave and directly transmitted beam act as the reference wave. The position of the film was adjusted to collect maximum object wave. The reference wave and object wave interfere at the film and thus the hologram is created. The hologram was reconstructed by illuminating with an expanded laser beam.

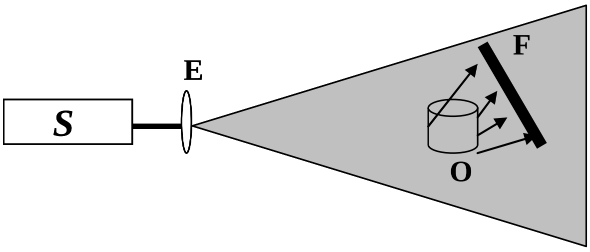


Fig.2. 6 The experimental technique used for recording transmission hologram. where S-Laser, E-beam expander with spatial filter, O-object, F-Polymer film

2.15. Surface Analysis

The surface analysis of the gratings was done using Atomic force microscopy (AFM) and stylus Profilometer.

2.15.1. Atomic Force Microscopy (AFM)

AFM is a form of scanning probe microscopy where a small probe is scanned across the sample to obtain information about the sample’s surface. The information, gathered from the probe’s interaction with the surface, could be as simple as the physical topography. Datas are collected as the probe is scanned in a raster pattern across the sample to form a map of the measured property relative to X-Y position. Thus the AFM image shows the variation in the measured property (height or magnetic domains) over the area imaged. The AFM probe has a very sharp tip, often less than 100Å diameter, at the end of a small cantilever beam. The inter-atomic forces between the probe tip and the sample surface cause the cantilever to deflect as the sample's surface topography changes. A laser beam reflected from the back of the cantilever, measures the deflection of the cantilever. This information is fed back to a computer, which generates a map of topography and/or other properties of interest. An AFM-model Nanoscope-E (Digital Instruments), employed in contact mode was used for the present study.

2.15.2. Stylus Profilometer

Dektak 6M stylus Profilometer was used for thickness measurements and surface analysis. The stylus profiler is an advanced thin and thick film step height measurement tool capable of measuring step even below 100Å. Dektak 6M profiler contains the mechanical and optical components for sample placement, sample viewing and scanning/measurement. A diamond tipped stylus (radius - 12.5µm) permits accurate measurements in a wide range of applications and the surface profile was obtained as hills and valleys. A camera (field of view - 1.1 to 4.6 or 70x to 280x) is attached to the scan head, viewing the sample at 45^0 viewing angle. This instrument is used to profile the surface topography and waviness as well as measuring surface roughness in a sub nanometer range. The stylus is mechanically coupled to the core of an LVDT (linear variable differential transformer). As the stage moves the sample, the stylus rides over the sample surface. Surface variations cause the stylus to be translated vertically. Electrical signals corresponding to the stylus movement are produced as the core position of the LVDT changes. The LVDT scales an ac reference signal proportional to the position change, which in turn is conditioned and converted to a digital format through a high precision integrating analog to digital converter. The digitalized signals from a single scan are stored in computer memory for display. The schematic representation of Dektak 6M is shown in Fig. 2.7. A variable intensity white light LED was used for illuminating the sample. The Scan length of the instrument ranges from 50µm to 30mm. Scan duration (time taken to complete a given scan) in conjunction with scan length, determines the horizontal resolution of a scan. The scan duration could be set from 3 to 200s for a maximum of 60,000 data points (points along the scan path at which data are taken) per scan. The scan resolution indicates the distance between data points and it is automatically adjusted. The vertical resolution was 40Å. The stylus force can be varied from 1 to 15 mg force and for the present study 5mg was selected as the stylus force [18].

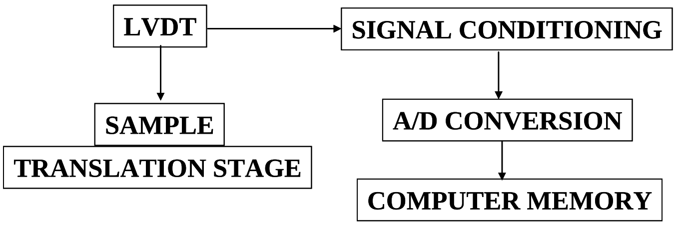


Figure 2.7 Block Diagram of Stylus Profiler

2.16. Conclusion

The film fabrication process and the details of the experimental techniques are described. The fabrication and characterization of various photopolymer systems are described in the coming chapters.

References

1. S.Gallego, M.Ortuno, C.Neipp, A.Marquez, A.Belendez, E. Fernandez, I. Pascual, Opt. Exp., 14, 5121 (2000)
2. H.J. Coufal, D.Psaltis, G.T.Sincerbox , Holographic data storage, (Springer) (2000)
3. K.Venketaraman, Chemistry of synthetic dyes, Academic Press, Newyork, 4, 498 (1971)
4. R.G.Brandes, E.E.Francois, T.A. Shankoff, Appl. Opt., 8,2346 (1969)
5. D.G.Mcauley, G.E.Simpson, W.J.Murbach, Appl. Opt., 12, 232 (1973)
6. M.Ushamani, K. Sreekumar, C.S. Kartha, R. Joseph, Appl.Opt.41, 1984 (2002)
7. J. R. Dyer, Application of absorption spectroscopy of organic compounds, Prentice Hall of India, New Delhi (1991)
8. Optical Electronics, A.Ghatak, K.Thyagarajan, Camebridge university Press, (1989)

9. Ushamani M, Studies on photosensitive polymers for optical recording, PhD Thesis, Cochin Univ. of Sci. and Tech., India, (2002)
10. P.T.Ajithkumar, Holographic methods in the studies of thin film stress, vibration analysis and pattern recognition, PhD thesis, Cochin Univ. of Sci. and Tech., India (1991)
11. M.Ushamani, N. G. L. Deenja, K.Sreekumar, C.S. Kartha, R.Joseph, Bull. Mater. Sci., 26, 343 (2003)
12. M.Ushamani, K.Sreekumar, C.S. Kartha, R. Joseph, J. Mod. Opt., 51, 743 (2004)
13. M. Ushamani, K.Sreekumar, C.S. Kartha, R. Joseph, Appl. Opt., 43(2004)
14. M. Ushamani, K. Sreekumar, C. S. Kartha, R. Joseph, Appl.Opt.,41, 1984 (2002)
15. B. M. John, M.Ushamani, R. Joseph, K.Sreekumar, C.S.Kartha, J. Mod. Opt., 53, 343 (2006)
16. K.Tyagarajan, A.K. Ghatak, Lasers theory and applications, Macmillian India Ltd (1984)
17. B.M.John, R.Joseph , K.Sreekumar, C.S.Kartha Proc. of 8th Intl. Conf. on Opto-electronics, Fiber optics and photonics (Photonics -06), Allied Publications, 2,609 (2006)
18. Dektak 6M Manuel, Veeco metrology group, Arizona (2004)

Chapter 3

Studies on Methylene Blue Sensitized Poly(vinyl chloride) Films: Incorporation of Electron Donor and Monomers

Methylene blue sensitized Polyvinyl chloride (MBPVC), recording medium introduced by our research group, is a pioneer in the kind of holographic materials. The present study aims at the fabrication of MBPVC films with the incorporation of an electron donor and monomers to establish photopolymerization. The diffraction efficiency, sensitivity and storage life of MBPVC film is improved by the addition of the electron donor, pyridine. The addition of pyridine enhanced the diffraction efficiency by two times and storage life of the gratings to 2-3 days. The effect of two monomers is also studied.

3.1 Introduction

The development of suitable recording media is one of the challenges in the area of holography. The main advantage of using photopolymers for holography is its self-developing property and the complete dry processing of the system. There is a surging interest in the use of light sensitive polymers for optical storage because the widespread magneto-optical technology is reaching physical limitations arising from the super paramagnetic effect. Many research groups are trying to develop new photopolymers for holography for the last three decades. Polymeric materials such as poly(methyl methacrylate) (PMMA), Poly(diacetylene) (PDA), poly(vinyl carbazole) (PVK), poly(vinyl alcohol), (PVA), poly(acrylic acid) (PAA), polythiophene, etc have been widely investigated for holographic applications [1-8]. Besides these, our research group has introduced dye sensitized Poly (vinyl chloride) (PVC) film, one of the promising material in the realm of optical recording media [9-10].

PVC is produced by the polymerization of vinyl chloride. Though commercially the initiation of polymerization is carried out by the generation of free radicals produced by peroxides, azo compounds and persulfates, initiation by sunlight is also reported [11-12]. The chemical initiators may be activated by heat to produce free radicals. UV light and radio active sources are also employed in the polymerization of vinyl chloride [13]. Four basic processes utilized for polymerization of PVC, are emulsion polymerization, suspension polymerization, bulk or mass polymerization and Solution polymerization [14-15].

PVC degrades on continuous exposure to sunlight. The first sign is discoloration to yellow and then to tan. Other changes like embrittlement and loss of tensile strength also occur. Degradation is a function of intensity of radiation, wavelength, angle of exposure, direction of exposure and time. Only the UV region below 355nm is sufficiently strong to cause dissociation. UV stabilizers such as benzophenone, benzotriazoles and substituted acrylonitriles are used to overcome the problem of degradation [14].

Stabilized PVC is interesting on account of its properties like dimensional and environmental stability, ease of fabrication, non-toxicity, stability against UV radiations, transparency in the visible spectral region etc. For different applications, films of different thicknesses have to be fabricated. Shrinkage during the drying process is one of the major problems encountered by the polymer films. But shrinkage is comparatively less in PVC and hence it could be fabricated in any desired thickness. The drying period of PVC is also less compared to other matrices like PVA and gelatin. PVA and gelatin based films are influenced by humidity and it will adversely affect the efficiency and storage life [16]. But PVC is not influenced by humidity and hence the film could be stored in normal laboratory conditions without taking much precautions. In addition to these, PVC has good resistance to a wide range of chemicals like inorganic solutions, detergents, aliphatic hydrocarbons including oils and waxes.

The feasibility of using PVC matrix as an optical recording medium has been reported by converting it into copper acetate complexed methylene blue (MB) sensitized polyvinyl chloride (CMBPVC) films [9]. Polymer solution was prepared by dissolving suspension grade PVC in cyclohexanone to get 13.5% PVC solution. PVC solution was doped with the sensitizer solution prepared by dissolving methylene blue (MB) and copper acetate (2:1 ratio) in glacial acetic acid. The films were fabricated using gravity settling method. The influence of pH on the film sensitivity was studied and direct imaging was done on these films [17]. On exposing to the laser beam, the dye molecules in the exposed region were excited and converted to the leucoform. Unlike in other matrices, the change of state occurring to the dye molecules (MB) on laser irradiation is permanent in PVC and it exists in the leuco form itself [18]. Since the material was not comprised of any monomer or electron donor (ED) as in the conventional photopolymerizable recording medium, the only contribution to the recording mechanism was the absorbance modulation. The gratings recorded on the CMBPVC films showed an efficiency of 4.46% at 1500 mJ/cm^2 for the intensity ratios of the first order diffracted beam to that of the transmitted beam [10, 17]. The efficiency for the intensity ratios of diffracted beam to that of the incident beam was only 0.26%. Though change in absorbance on storage (after laser exposure) is not observed in this material, the grating recorded vanishes within few hours [19]. Also in CMBPVC films, the complexing agent, copper acetate was found to precipitate on storage.

In the present study attempts have been made to improve the shelf life of the film, and to increase the diffraction efficiency (DE) and storage life of the gratings recorded in the CMBPVC system. To achieve this, EDs or monomers have to be incorporated to the polymer system. For this, the preparation technique has been modified. This chapter describes the effect of an ED and few monomers on DE and storage life of the grating.

3.2 Methodology

The complexing agent, copper acetate, used in the previous studies, was found to be precipitated on storage [9]. To improve the shelf life of the material, films were prepared without adding the complexing agent. Films were fabricated using gravity settling method and characterized using a 15 mW, CW, He-Ne laser (632.8 nm). The relative transmittance of films with and without copper acetate was determined as explained in section 2.7. This was done by exposing the films to a He-Ne laser; the incident power density on the film was 5mW/cm^2. The relative transmittance of both CMBPVC and MBPVC films is shown in Fig. 3.1. Even without copper acetate, the film showed almost the same behavior in the transmittance curve. In this case also, the change of state occurring to the dye molecule on laser exposure was stable on storage. Due to the lack of monomers, there is no refractive index (RI) modulation occurring in this material as expected in the case of photopolymers. So the recorded gratings are of amplitude gratings. So trials were made to incorporate EDs and monomers to the MBPVC system to establish RI modulation and thereby improving the efficiency and storage life of the grating. Due to the low solubility of monomers and electron donors, the efforts made to incorporate a monomer or ED in MBPVC solution prepared as described in the reported works went in vein. Though films were fabricated using emulsion grade PVC, the films were totally insensitive to laser. So the preparation technique was modified and by the modified procedure, monomers and ED could easily be incorporated to the MBPVC solution [20]. This gave an enhancement of DE and the gratings recorded on such films could be stored for 2-3 days.

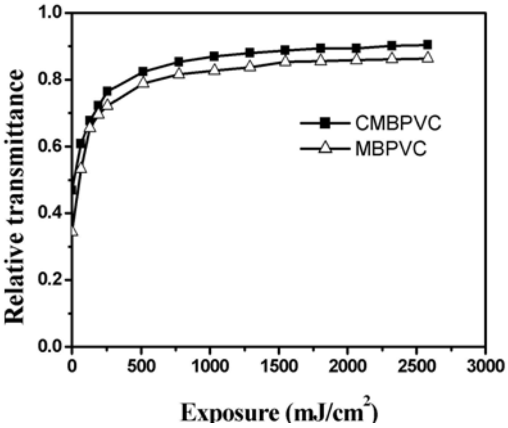


Fig.3.1 Relative transmittance of CMBPVC and MBPVC films

3.3 Fabrication of Films

Instead of sensitizing the PVC solution by adding MB as in the earlier case, MB solution was prepared by dissolving MB in cyclohexanone to have a dye concentration of 1.59 x10^{-2} mol/l and to this, suspension grade PVC powder having k value 70 was dissolved to obtain 15% MBPVC solution. This MBPVC solution was casted on micro slides using gravity settling method and the drying period was 18 hrs. As MB is only partially soluble in cyclohexanone, its concentration cannot be determined accurately. But an optimum soluble concentration was taken for all the studies.

The films were characterized by real time transmittance measurements, DE measurements, optical absorption studies and RI measurements. As the resolution of material is limited, attempts made to record gratings using double beam interferometry was not successful. Therefore, gratings were recorded as explained in section 2.9.1.

3.4 Sensitivity of MBPVC films

The material sensitivity was determined by monitoring the real time transmittance and it is defined as the increase in transmittance on laser exposure. As the material sensitivity increases, the transmittance increases at low exposures. This is because, even at low exposure, the dye molecules get excited and initiate the photochemical reaction and it is converted to the leucoform. The relative transmittance was determined by taking the transmittance ratio of dye-sensitized sample to that of the undoped sample. Fig. 3.2 shows the relative transmittance Vs exposure for MBPVC films prepared by the conventional method and that by the new procedure for an incident intensity of 5mW/cm^2. In Fig. 3.2, MBPVC$_1$ represents the transmittance of films prepared by the earlier method and MBPVC$_2$ represents that prepared by the new method. Here the relative transmittance of films prepared using the earlier method is higher than that prepared by the new method. So the material sensitivity of MBPVC$_2$ is low compared to that of MBPVC$_1$. But the change of state occurring to MB molecule is stable in MBPVC$_2$ as in MBPVC$_1$. Gratings recorded on MBPVC$_2$ films for an exposure of 2000 mJ/cm^2 showed a DE of 0.2% and the storage life of the grating was extended to 24 hrs. Electron donors or monomers could be incorporated to the MBPVC$_2$ without affecting the quality of film. Table 3.1 gives the comparison of MBPVC$_1$ and MBPVC$_2$ films. The resolution of both MBPVC$_1$ and MBPVC$_2$ films are limited to 120 lines/mm.

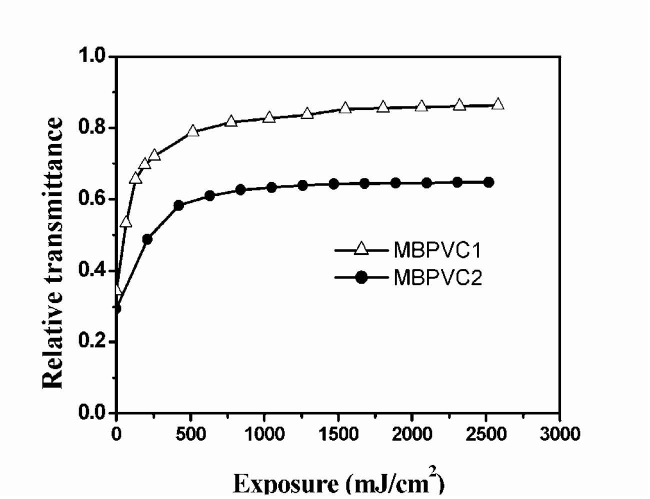


Fig. 3.2 Relative transmittance of MBPVC films prepared by two different procedures.

Table 3.1. Comparison of MBPVC prepared using old and new procedures; MBPVC$_1$ and MBPVC$_2$

Properties	**MBPVC$_1$**	**MBPVC$_2$**
Material sensitivity	High	Low
Diffraction Efficiency at 2000mJ/cm^2	0.24%	0.2%
Storage life	4 hrs	24 hrs
Possibility of incorporation of electron donor and monomer	No	Yes

Though both MBPVC$_1$ and MBPVC$_2$ consists of same species; they differ in the sequence of addition of components and its properties. The incompatibility of monomer or ED in MBPVC$_1$ may be due to the formation of any intermediate product formed during the addition of the components. To check this FTIR spectrum of MBPVC$_1$ and MBPVC$_2$ solution were recorded and depicted in Fig. 3.3. Both spectra showed same behaviour and no additional peaks were observed as expected. Only slight variation in intensity was observed.

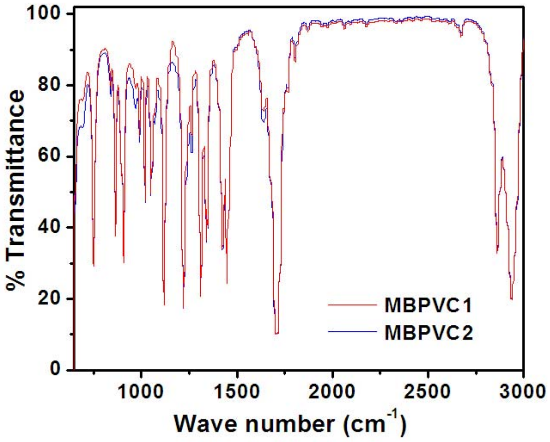


Fig. 3.3 FTIR spectra of both MBPVC$_1$ and MBPVC$_2$ solution

3.5 Incorporation of Electron Donors

The direct initiation of polymerization by light is difficult and has a poor yield. So the initiation is usually achieved by radical or cationic polymerization and it requires the use of a photoinitiator (dye and charge transfer agent). The cation radical of the ED produced during laser exposure initiates the polymerization reaction. Usually in PVA based recording systems like PVA/acrylamide and PVA/vinyl acetate, triethanolamine (TEA) was used as charge transfer agent [4, 21]. The sensitivity of eosin PVA/acrylamide was improved with the incorporation of diphenyliodonium chloride [22]. The role of dimethyl formamide (DMF) as electron donor in different polymer matrices is also reported [23-25].

Even though TEA is the most widely used ED in photopolymer systems, it is not compatible with PVC. When TEA is incorporated to MBPVC solution b coloured), an opaque film (violet coloured) was obtained. Diethanolamine incorporation resulted in gray coloured opaque film. Trials have been done with many EDs and the compatibility was the major issue. Film transparency and film stability are equally important for holographic films. Though several electron donors were tried to be incorporated in the MBPVC solution, only DMF, pyridine, triethylamine and dimethylamino benzaldehyde (DBA) were found to be compatible with MBPVC and resulted in transparent films. The relative transmittance of these films on exposing to a laser beam (632.8 nm) of intensity 7mW/cm^2 is shown in Fig. 3.4. In all cases the dye molecules in the exposed regions remained in the leucoform. But the shelf life was poor and the film faded on storage in all cases except pyridine doped films. In most cases the unexposed regions faded on storage or the colour of the films was gradually changed from blue to violet. Due to the film stability, pyridine was selected as the electron donor for further study.

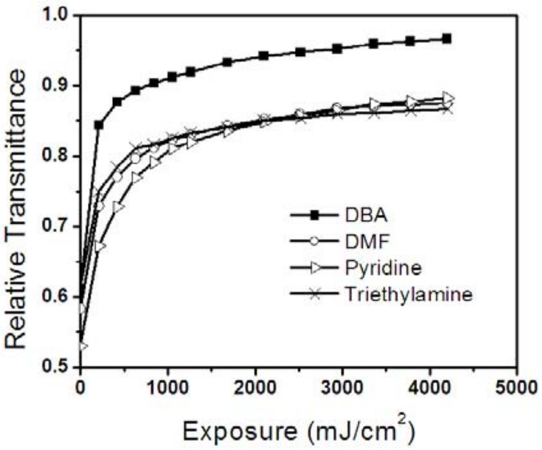


Fig.3.4 The relative transmittance of MBPVC$_2$ films with different electron donors

3.6 Electron Donating Mechanism of Pyridine

Pyridine is the nitrogen containing aromatic analogue of benzene and the structure is shown in Fig 3.5.The Nitrogen in pyridine is linked to two carbon atoms and has a lone pair, and is therefore sp^2 hybridized. This leaves one electron in an unhybridized *p* orbital, which contributes to the π system. The lone pair on the nitrogen is in sp^2 hybridized form, which means it is directed away from the ring but in the same plane. The lone pair of electrons is not involved in the aromatic system, and stick out away from the molecule. The lone pair makes pyridine capable of acting as a base and an ED.

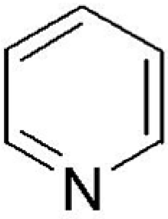


Fig.3.5 structure of Pyridine

When the MBPVC films were exposed to red wavelength, MB molecules absorb light and get excited, and transferred to triplet state by an intersystem crossing [26]. Electron transfer takes place between this excited MB and pyridine and MB gets reduced forming the cation radical of pyridine. This reduced MB again reacts with the cation radical and undergoes a protonation process and then it is converted to leucoform. The pyridine radicals formed can be added to the C=C of monomer molecules and initiates the polymerization reaction.

3.7 Optimization of Pyridine Concentration

MBPVC solution was sensitized with pyridine and films were prepared by varying the pyridine concentration from 0.59 to 3.54 M. Above this concentration, precipitate was formed and the film lost its properties. The sample without pyridine was named as P_0 and the films with pyridine were named as P_X (where *x* varies from 0.5 to 3). These films were used for the optimization of pyridine concentration. The FTIR spectra of pyridine doped samples were recorded and Fig. 3.6 shows the spectra of both undoped and pyridine doped samples (P_1). The peaks at 750cm^{-1} (aromatic substitution), 1580cm^{-1} (aromatic group) indicates the presence of pyridine.

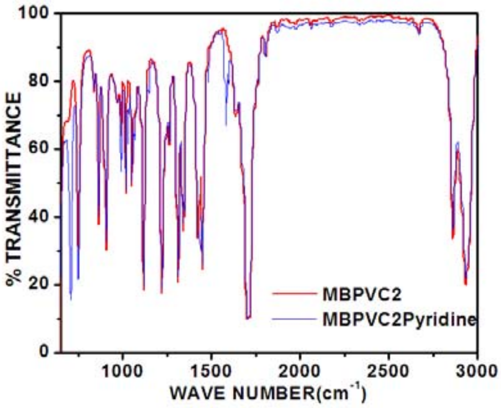


Fig. 3.6 FTIR spectra of both undoped and pyridine doped samples (P_1)

3.7.1 Sensitivity of Pyridine Doped Films

The relative transmittance of pyridine doped films was determined by exposing the films to an incident intensity of 7mW/cm^2. The relative transmittance of films with different pyridine concentration is shown in Fig. 3.7. The relative transmittance is highest for P_1 samples i.e. for films with pyridine concentration 1.126 M. The rate of bleaching of the P_1 film is shown in Fig. 3.8. Within 2 minutes the transmittance became constant and no further bleaching took place. Thus, within that time all the dye molecules got transferred to the leuco form.

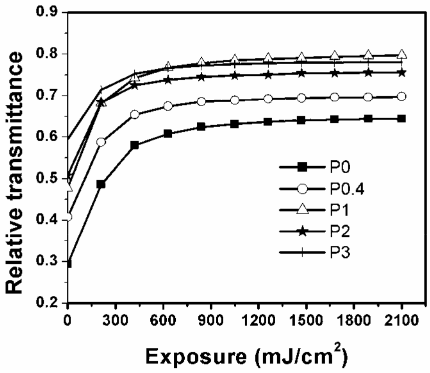


Fig. 3.7. Relative transmittance of samples with different pyridine concentrations

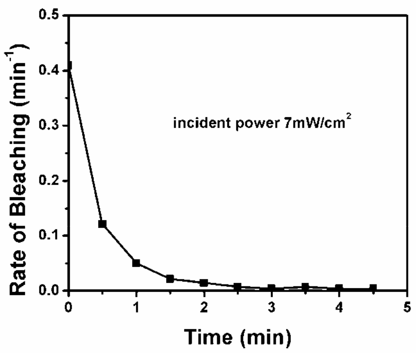


Fig. 3.8 Rate of bleaching of sample with pyridine concentration 1.126 M (sample P_1)

3.7.2 Diffraction Efficiency Measurements

To optimize the pyridine concentration, gratings were recorded on the samples at a fluence of 2000mJ/cm^2 and DE was determined. The power at the interfering position was 5mW/cm^2 and the reconstructed power was 150µW. The efficiency increased with pyridine concentration, reached a maximum and then decreased. The highest efficiency of 0.46% was obtained for films with pyridine concentration of 1.13 M (sample P_1). The variation of DE with pyridine concentration is shown in Fig.3.9. For high concentrations of pyridine, noise in the diffracted pattern was very high. Maximum spatial frequency of the grating recorded in MBPVC/Pyridine film was 120 lines/mm.

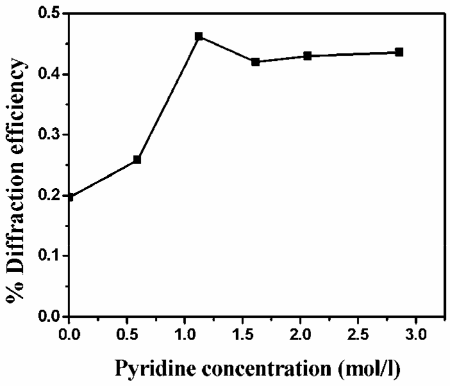


Figure 3.9 Variation of diffraction efficiency with pyridine concentration

The RI of pyridine doped films was determined before and after exposing to the laser beam and the change in RI was calculated. The change in RI with pyridine concentration is plotted in Fig. 3.10. Highest RI modulation was obtained for P_1 sample which showed highest efficiency.

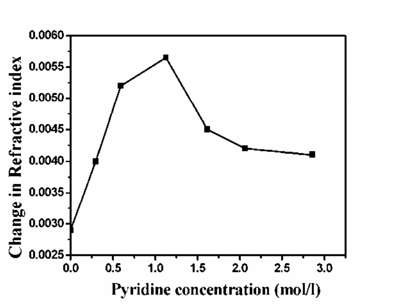


Figure 3.10. Change in refractive index with pyridine concentrations

3.7.3 Optical Absorption Studies

The change in absorbance on laser exposure (2100 mJ/cm^2) was determined using Hitachi -3410 UV-Vis-NIR spectrophotometer and plotted in Fig. 3.11. Highest absorbance modulation occurs for P_1 sample. The film that showed highest RI and absorbance modulations gave maximum DE. Like CMBPVC, here also the change of state (leuco form) occurring to the dye molecule is permanent. Fig. 3.12 shows the absorption spectra of sample P_1 on storage. The dye molecules exist in the same leuco form even after 1 year. No degradation was observed on storage of the films.

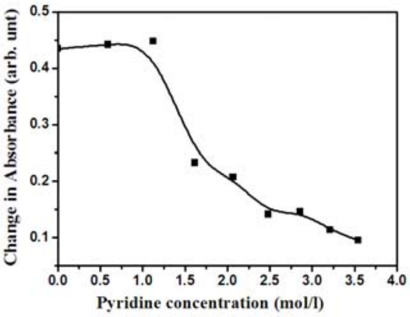


Fig. 3.11 Variation of absorbance modulation with pyridine concentrations

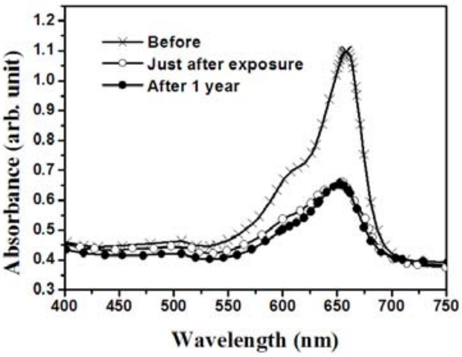


Fig. 3.12 Change in absorbance with pyridine concentrations

3.7.4 Optimization of Exposure

To optimize the energy required for the grating formation, gratings were recorded on sample P_1 at different exposures. Maximum DE (0.46%) was obtained for exposure energy of 1500 mJ/cm^2 and it remained constant from 1500 to 3000 mJ/cm^2. DE of P_1 films at different exposures is plotted in Fig. 3.13. Gratings recorded on these films were not stable and the DE decreased on storage. But with the addition of pyridine, the storage life was slightly improved to 2-3 days.

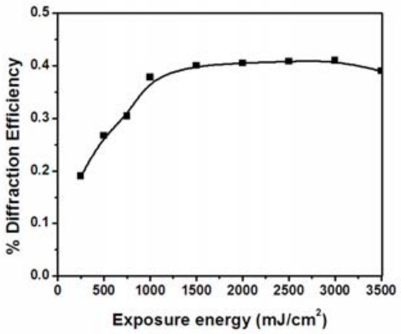


Fig. 3.13 Diffraction efficiency of P_1 films at different exposures

3.8 Incorporation of Monomer

As per the theory of photopolymers, with the addition of monomers, laser induced photopolymerization will be higher. There will de increased modulations of RI and this can improve the efficiency. To facilitate RI modulation in the PVC matrix, two monomers of different family (one is acrylic and the other is vinyl) were incorporated. The monomers selected were butyl acrylate and vinyl acetate [27]. The following sections describe the effect of these two monomers on DE and storage lives of the gratings recorded on MBPVC films.

3.9 Studies on MBPVC/Butyl Acrylate Films

Butyl acrylate (BA) is a colour less liquid monomer having pungent odour and RI of 1.416. It comes under the category of acrylic monomer. The term “acrylic monomers” is a convenient designation for all acrylate and methacrylate monomeric esters, as well as for the corresponding acrylic and methacrylic acids. Acrylate ester can be produced by the acetylene process by using appropriate alcohol. Carbon monoxide is introduced to produce BA through combination with additional acetylene and butanol. The kinetics of homopolymerization of BA initiated with various types of initiators has been studied and reported by several researchers [28-30]. Anuradha *et al.* investigated the kinetics and mechanism of photopolymerization of BA intimated by 1-(Bromoacetyl) pyrene and 1-Acetylpyrene triphenyl arsonium bromide in detail [31]. Manga *et al.* reported the use of photoinitiators to achieve controlled free-radical polymerization of *n*-butyl acrylate in Pyrex tubes [32]. Free radical photopolymerization of n-BA in the form of static thin film was investigated by Boodhoo *et al.* The photopolymerization was carried out by utilizing 366 nm UV radiation and the photoinitiator used was 2, 2-dimethoxy-2-phenylacetophenone. [33] In the present study the initiators used are MB and pyridine.

3.9.1 Film Fabrication

Films were fabricated by adding BA to the MBPVC solution sensitized with pyridine. Pyridine concentration was kept as 1.13 M as optimized above and BA concentration was varied from 0.125 to 2.19 mol/l [20, 27]. Beyond this concentration, there was a great reduction in the viscosity. The films were dried after 18 hrs and these films were used for detailed study. The FTIR spectrum of P_1 and BA doped P_1 are shown in Fig. 3.14.

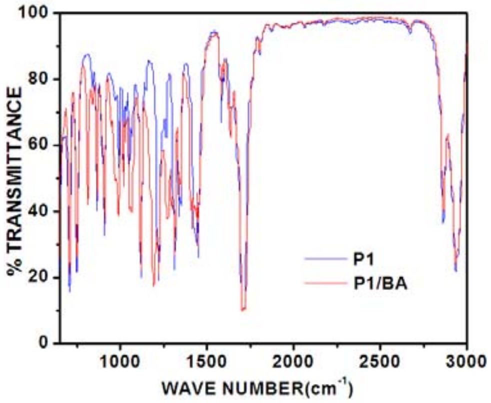


Fig. 3.14 FTIR spectrum of P_1 and butyl acrylate doped P_1 samples

3.9.2 Real Time Transmittance

The relative transmittance of BA doped films was determined by exposing it to an incident intensity of 7mW/cm^2. The relative transmittance of films with different BA concentration is shown in Fig. 3.15. It is clear that with the introduction of BA, the relative transmittance and hence the sensitivity decreases. As the monomer concentration increases, the films become more insensitive to laser exposure.

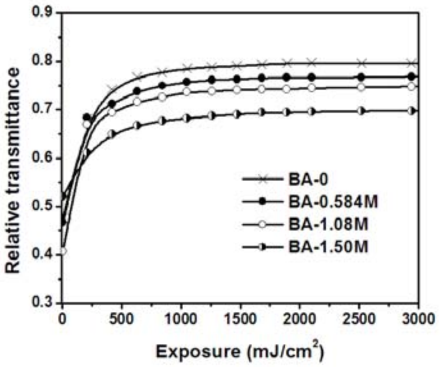


Fig. 3.15 Relative transmittance of films with different butyl acrylate concentration

3.9.3 Optical Absorption Studies

The optical absorption spectra were recorded (Using JASCO V-570 model) by exposing the MBPVC/BA films to 7mW/cm^2 for 10 minutes. Like CMBPVC and MBPVC/Pyridine films, here also the leuco form is stable on storage. Fig. 3.16 is a plot of absorption spectra on storage for a typical MBPVC/BA film.

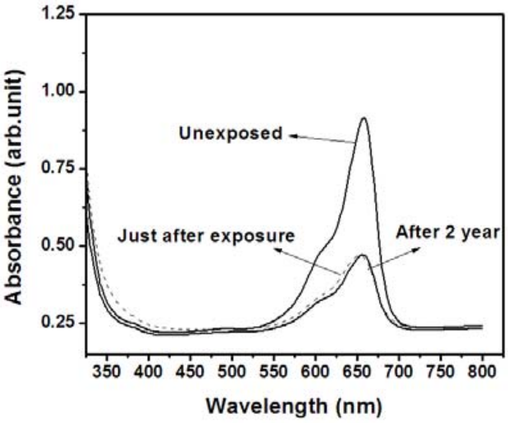


Fig. 3.16 Absorption spectra of MBPVC/BA films on storage

3.9.4 Diffraction Efficiency Measurements

Though the films get fully bleached even for an exposure of 1000 mJ/cm^2, gratings could not be recorded on the film at this exposure. To study the effect of BA on DE of MBPVC films, gratings were recorded on these films at an exposure of 2000mJ/cm^2 (incident intensity was 5mW/cm^2). To reconstruct the grating, it was illuminated with 120μW laser beam. Though the DE remained almost constant (0.17-0.18%) for BA concentrations ranging from 0.246 to 1.5M, highest DE of 0.182% was obtained for films with 1.08 M. Above this concentration, the DE decreased. But here the efficiency was less than that of MBPVC/pyridine films without monomer (0.46%) and the efficiency was not improved even at high exposures. The variation of DE with BA concentration is plotted in Fig. 3.17. The RI modulation of MBPVC/BA films on laser exposure was determined and is depicted in Fig. 3.18. RI modulation occurred in MBPVC/BA films were less compared to that obtained in films without BA (Fig. 3.11), which implies that BA remains in the film unreacted and the given exposure was insufficient to initiate the photopolymerization reaction.

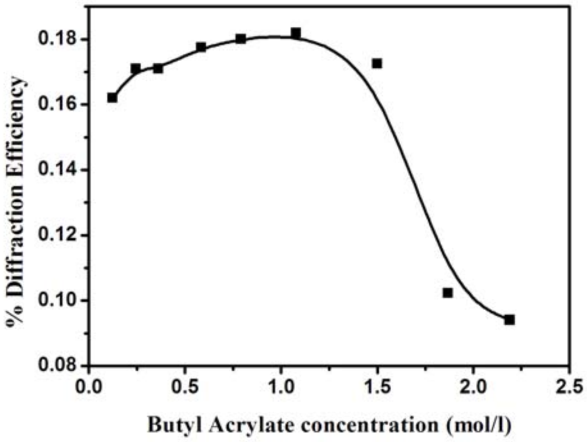


Fig. 3.17 The variation of diffraction efficiency with BA concentration.

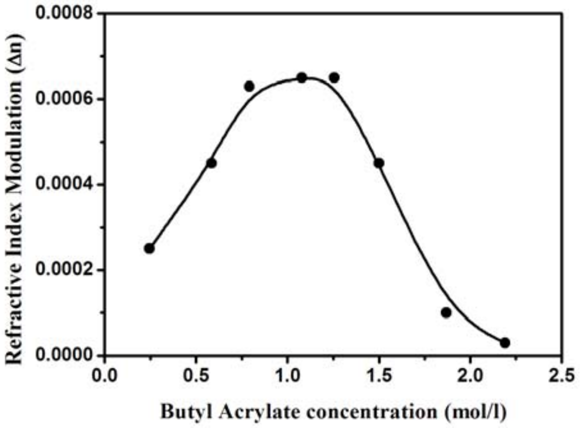


Fig. 3.18.The refractive index modulation of MBPVC/BA films on laser exposure

3.9.5 Film Behaviour at Higher Incident Power

In the above experiment, gratings were recorded at an incident power density of 5mW/cm^2 (exposure energy 2000 mJ/cm^2). But when gratings were recorded with high incident power, 7mW/cm^2, (keeping the exposure energy as 2000 mJ/cm^2), 0.38% efficiency was obtained. The low efficiency while using a laser beam of 5mW/cm^2 may be due to the high threshold power required for the MBPVC/BA system. In other words, reciprocity law is not obeyed by the MBPVC films with BA and high input power is required for better diffraction efficiency.

The relative transmittance of MBPVA/BA sample (BA =1.078 mol/l) which showed highest DE and RI modulation was determined for different incident intensities (3mW/cm^2, 5mW/cm^2 and 7mW/cm^2) and plotted in Fig. 3.20. The relative transmittance while using an incident intensity of 7mW/cm^2 was much higher than that while using 3mW/cm^2 and 5mW/cm^2 even at same exposures (*exposure energy = power density x time of exposure*). Since the transmittance increases at high incident powers, the efficiency may also be improved at higher incident powers. Hence it is expected that better efficiency will be obtained with high power lasers.

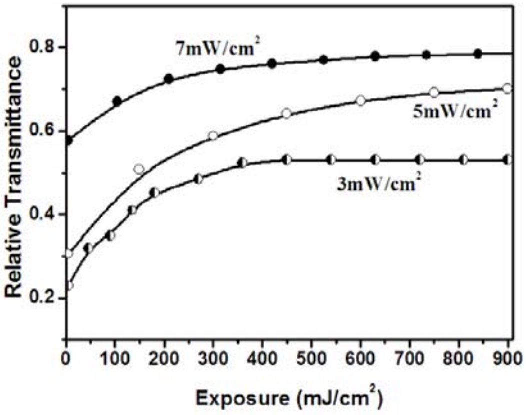


Fig. 3.20 The relative transmittance of MBPVA/BA film for different input powers

3.10 Studies on MBPVC/Vinyl Acetate Films

Vinyl acetate (VAc) is a colourless liquid at room temperature (B.P=72.7^{0}C) having RI of 1.3952. There are reports on photopolymerizable holographic medium with polyvinyl acetate as binder [34].

Though generally VAc polymerizes by solution polymerization, light induced polymerization is also reported [35]. Melville *et al.* reported the light induced polymerization of VAc by a rotating sector method [36-37]. The most efficient source for photopolymerization is UV light (254 nm). VAc polymerizes in the presence of light to a colourless, transparent mass. The quantum efficiency, the number of radicals formed by one quantum of light, is 0.3 for VAc [38]. To increase the efficiency of initiation, sensitizers are often added. The sensitizers usually absorb light over a wider wavelength range and thereby increase the efficiency. Azo compounds have been found to act as very good sensitizers [39-40]. Other sensitizers are carbonyl compounds such as benzoin and benzil, peroxides such as benzoyl peroxide and di-t-butyl peroxide, uranyl salts, ω-bromo acetophenone, acriflavine-ascorbic acid and ferrous salt-oxalic acid-persulfate [41-47].

3.10.1 Film Fabrication

Films were fabricated by adding different amounts of VAc monomer to the MBPVC solution doped with pyridine. The VAc concentration was varied from 0.417 to 3.1mol/l. The drying period was 18 hrs. The FTIR spectrum of P_1 and VAc doped P_1 samples are shown in Fig. 3.21.

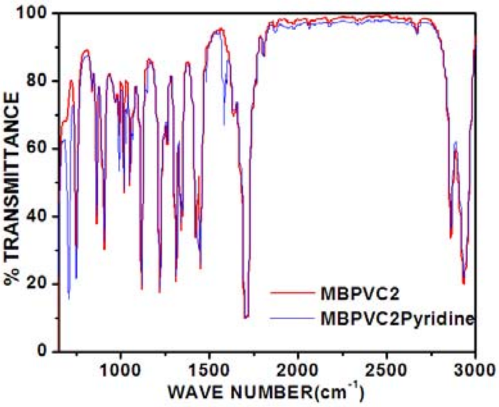


Fig. 3.21 FTIR spectrum of P_1 and Vinyl acetate doped P_1 samples.

3.10.2 Sensitivity of MBPVC/VAc

Real time transmittance measurements were carried out as discussed in section 2.7. by exposing to a power density of 7mW/cm^2. Fig.3.22 is a plot of relative transmittance of MBPVC/VAc films at different exposure. As the VAc concentration increased, the relative transmittance also increased. Highest relative transmittance was obtained for samples with 2.54mol/l VAc. Above this concentration, the relative transmittance decreased.

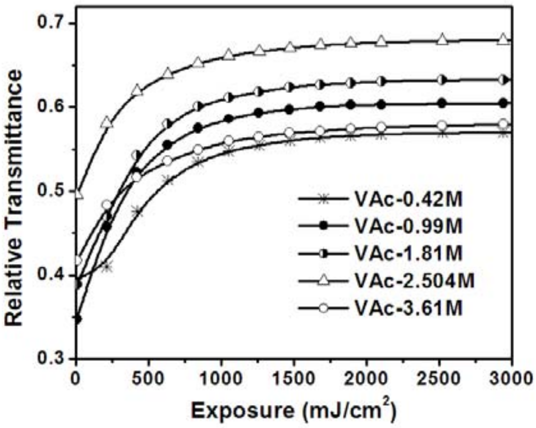


Fig.3.22 Relative transmittance of MBPVC/VAc films at different exposure

3.10.3 Dye Behaviour

The absorption spectra of MBPVC/VAc films were recorded (using Hitachi -3410 model) by exposing the films to a power density of 7mW/cm^2 for 10 min. Fig.3.23 is the absorption spectra of the unexposed film and exposed film on storage. Though a slight change in the absorption spectrum was observed, the dye molecule exists in leucoform itself. Stability of leucoform is a peculiar property of MBPVC films, irrespective of the matrix additives. But in the case of CMBPVC films, successive exposures were given to the laser irradiated spot to maintain the leuco state [9]. But in the cases of MBPVC, MBPVC/BA and MBPVC/VAc, the leucoform is stable even with a single exposure and no refreshment is required.

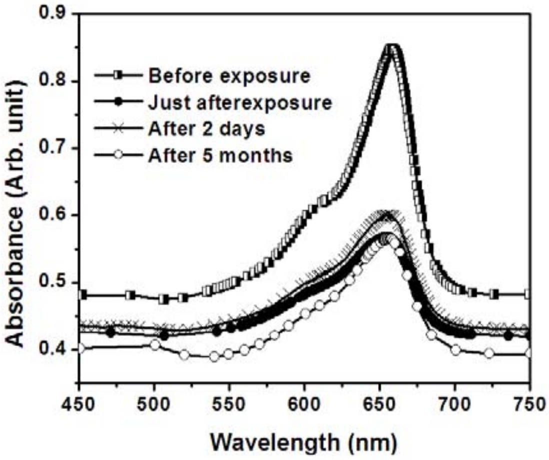


Fig.3.23 Absorption spectra of MBPVC/VAc films on storage

3.10.4 Diffraction Efficiency Measurements

To optimize the VAc concentration, gratings were recorded for an exposure of 2000 mJ/cm^2 and a spatial frequency of 120 lines/mm. The power at the interfering position was 5mW/cm^2 and the reconstructed power was 150µW. Highest efficiency (0.33%) was obtained for films with 2.1M VAc. Like BA doped films, VAc also failed to improve the efficiency. Both monomers resulted in a reduction of efficiency. The D.E vs. concentration graph is shown in Fig. 3.24. Refractive index modulation on laser exposure was also determined and plotted in Fig. 3.25. The refractive index modulation of MBPVC/VAc is less than that of films without VAc. To find out the energy requirement of MBPVC/VAc films with 2.1mol/l VAc, gratings were recorded by varying the exposure and efficiency was measured. The variation of efficiency with exposure energy is plotted in Fig. 3.26. The efficiency remains the same from 1500 mJ/cm^2 to 2500 mJ/cm^2. Though the leucoform is stable, the DE decreased on storage. The decrease in efficiency on storage is depicted in Fig.3.27. The gratings vanished after 3 days and could not be read even with high reconstructing powers.

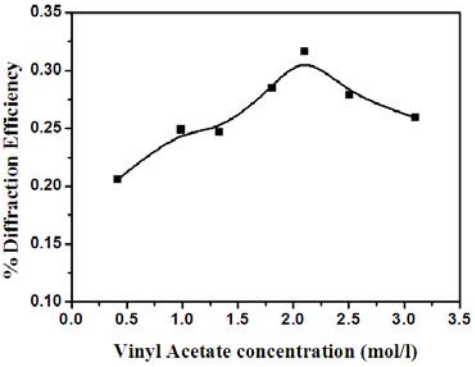


Fig.3.24 The variation of efficiency with vinyl acetate concentration

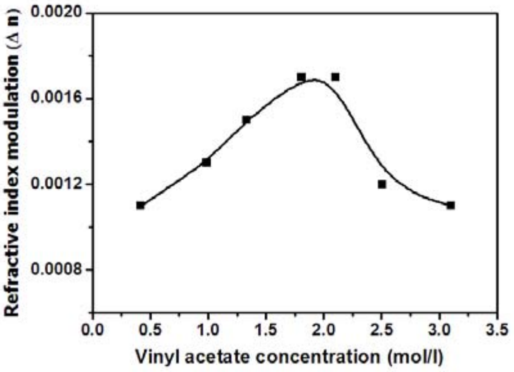


Fig.3.25.Refractive index modulation on laser exposure

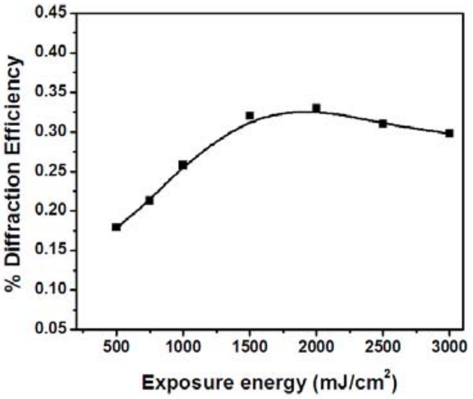


Fig.3.26. The variation of efficiency with exposure

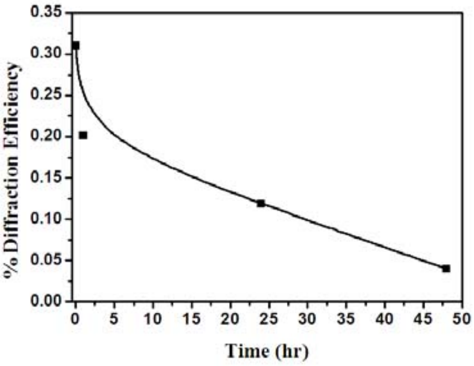


Fig.3.27. Diffraction efficiency on storage

3.11 Comparison of MBPVC Films

The storage life and DE of CMBPVC films were improved with the incorporation of pyridine. Pyridine acts as the ED and accelerates the photoreduction of MB. But as expected, the monomers have not improved the DE. Comparison of DE, storage life of the gratings, exposure and RI modulation of different MBPVC based systems are shown in Table.3.2. The resolution of the material is limited to 120 lines/mm irrespective of the matrix additives.

Table3.2. Comparison of holographic properties of different MBPVC based systems

Properties	$CMBPVC_1$	MBPVC2	MBPVC/Pyr	MBPVC/BA	MBPVC/VAc
DE (%)	0.26	0.2	0.46	0.18 at 5mW/cm^2 0.36 at 7mW/cm^2	0.33
Exposure (mJ/cm^2)	1500	2000	1500	2000	1500
RI modulation	0.0001	0.0001	0.0057	0.0006	0.0017
Storage life of grating	4 hr	1 day	3 days	3 days	3 days

3.12 Conclusion

The preparation technique of the CMBPVC system developed in the lab was modified and pyridine was incorporated to the PVC matrix as charge transfer agent. The DE and storage life of the gratings recorded on MBPVC was improved with the incorporation of pyridine. Maximum DE obtained for an exposure of 1500 mJ/cm^2 was 0.465 and the grating could be stored for 2-3 days. MBPVC films were fabricated by incorporating BA and VAc monomers. This is the first report of the MBPVC matrix with monomers. Though the efficiency was not improved with the incorporation of monomer for the given recording power, higher efficiency can be achieved with higher recording powers.

References

1. R.A.Duarte-Quiroga, S.Calixto, D.L.Loughnot, Appl.Opt., 42, 1417 (2003)
2. S.Blaya, M.Murciano, P.Acebal, L. Carretero, M.Ulibarrena, A.Fimia, Appl. Phys. Lett., 84, 4765 (2004)
3. M.M.Wang, S. C.Esener, Appl.Opt., 39,1826 (2000)
4. S.Blaya, L.Carretero, R.Mallavia, A.Fimia, R.F.Madrigal, M.Ulibarrena, D.Levy, 37, 7604 (1998)
5. R.T. Ingwall, M. Troll, Opt. Eng., 28, 586 (1989)
6. J.M.Moran, I.P.Kaminow, Appl. Opt., 12, 1964 (1973)
7. R.A.Lessard, C.Malouin, R.Changkakoti, G.Manivannan, Opt. Eng., 32, 665 (1993)
8. M.Ushamani, K.Sreekumar, C.S. Kartha, R. Joseph, Appl. Opt., 43, 3697 (2004)
9. M.Ushamani, K. Sreekumar, C. S. Kartha, R. Joseph, Appl.Opt.,41, 1984 (2002)
10. M. Ushamani, K. Sreekumar, C. S. Kartha, R. Joseph , Proc. SPIE, 5290, 352 (2004)
11. I. Ostromislensky, Chem. Zeitung 36, 199 (1912)
12. R. Klatte, German Patent 278, 249,130 (1917)
13. W. Mund, M.Van, Meerssche , J. Momigny, Bull. Soc. Chim. Belges, 62, 645 (1953)
14. H. A. Sarvetnick, "Polyvinyl chloride, plastic applications series" , Robert E. Krieger publishing company, New York (1972)
15. G. E. Ham, Ed., "vinyl polymerization", Vol.1, Part1, Marcel Ekker Inc, New York (1967)

16. K. Wang, L. Guo, J. Zhu, W. Zhang, B. Cheng, Appl. Opt., 37, 326 (1998)
17. M.Ushamani, N. G. L. Deenja, K.Sreekumar, C.S. Kartha, R. Joseph, Bull. Mater. Sci., 26, 343 (2003)
18. M. Ushamani, K.Sreekumar, C.S. Kartha, R. Joseph, J. Mod. Opt., 51, 743 (2004)
19. M. Ushamani, "Studies on photosensitive polymers for optical recording" PhD Thesis, Cochin Univ. of Sci. and Tech., India (2002)
20. B. M. John, M.Ushamani, K.Sreekumar, R. Joseph, C.S. Kartha, Appl. Opt., 46, 346 (2007)
21. B. M. John, M.Ushamani, R. Joseph, K.Sreekumar, C.S. Kartha, J. Mod. Opt., 53, 343 (2006)
22. V. Weiss, E. Millul, Appl. Surf. Sci., 106, 293 (1996)
23. R.Changkakoti, S.S.C Babu, S.V.Pappu, Appl. Opt., 27, 324 (1988)
24. C. Pizzocaro, R. A. Lessard, M. Bolte, Can. J. Chem. /Rev. Can. Chim., 76, 1746 (1998)
25. G.Manivannan, R.Changkakoti, R. A. Lessard, Opt. Eng., 32, 671 (1993)
26. S.Blaya, L. Carretero, R. Mallavia, A.Fimia, R. F. Madrigal, Appl. Opt., 38, 955 (1999)
27. B. M. John, Ushamani M, R.Joseph, K.Sreekumar, C.S. Kartha, Proc. National Conf. on current trends in material science-CTMS-07, India, 224 (2007)
28. M.A.Dube, K.Rilling, A.Pendilis, J. Appl. Polym. Sci., 43, 2137 (1991)
29. R.Jovanovic, M.A.Dube, J. Appl. Polym. Sci., 94, 871 (2004)
30. N. R. Cameron , A. J. Reid, Macromolecule, 35, 9890 (2002)
31. A. Mishra, S. Daswal, J. Macromol. Sci., Part A: Pure and Appl. Chem., 43, 955 (2006)
32. J. D Manga, A Polton, M Tardi, P Sigwalt, Polym. Int.,45, 14 (1998)
33. K.V.K. Boodhoo , W.A.E. Dunk , M.S. Jassim , R.J.Jachuck , J. . Appl. Polym. Sci., 91, 2079 (2004)
34. A.M.Weber, United States Patent 5013632 (1991)
35. G. E. Ham,Ed., Vinyl polymerization, Marcel Ekker Inc(New York), Vol.1, Part1, Chapter 4, (1967)
36. N.Grassie, H.W. Melville, Proc. Roy. Soc. (London), A207, 285 (1951)

37. H.W. Melville, Proc. Roy. Soc. (London), A237, 149 (1956)
38. T.Motoyama, K. Tembo, 14, 70 (1950)
39. G.M.Burnett, M.H.George, H.W. Melville, J.Polym. Sci., 16, 31 (1955)
40. W.I.Bengough , H.W. Melville , Proc. Roy. Soc.(London), A225, 330 (1954)
41. S.Okamura, T.Motoyama, Kobunshi Kagaku, 15, 487 (1958)
42. V.G.Shlyk, CA, 52, 8616 (1958)
43. H.Kwart, H.S.Broadbent, P.D.Bartlett, J.Am.Chem.Soc. , 72, 1060 (1950)
44. S.Okamura, T.Motoyama, Mem.Fac.Eng. Kyoto.Univ., 21, 312 (1959)
45. T.Osawa, S.Sukegawa, M.Masaki, Kobunshi Kagaku,17, 367, (1960)
46. G.Takayama, Kobunshi Kagaku,17, 644, (1960)
47. S.Okamura, Kobunshi Kagaku, 7, 289, (1950)

Chapter 4

Fabrication and Characterization of Methylene Blue Sensitized Poly(vinyl alcohol) Films

This chapter deals with the effect of different monomers on the diffraction efficiency and storage life of methylene blue sensitized poly (vinyl alcohol) (MBPVA) films. The chapter is divided into three parts. The first part deals with the incorporation of different monomers to the MBPVA film. The Second Part is regarding the development of a reusable recording medium based on PVA with vinyl acetate monomer. The Effect of additional monomers on the holographic performance of MBPVA/vinyl acetate is explained in the third part of this chapter.

PART I

Studies on MBPVA Films with Different Monomers

4.1.1 Introduction

In recent years, many types of Photopolymerizable systems have been developed for applications such as holographic data storage, optical memories, holographic displays, holographic optical elements, optical computing and holographic interferometry [1-4]. Formation of volume gratings in polymer provides an attractive recording mechanism for holographic storage, allowing for relatively large permanent refractive index (RI) modulation ($\Delta n \sim 10^{-2}$) in an inexpensive media with high recording sensitivity [5-6]. One of the most known polymeric matrices for holographic recording is poly(vinyl alcohol) PVA, which is a water-soluble polymer that undergoes crosslinking when illuminated with UV radiation. In order to use a visible wavelength for holographic purposes, a photoinitiator of the crosslinking mechanism is inserted. As a consequence, PVA has been doped with different photoreactive centers in looking for a good information storage system, among them the chromium salts and the organic dyes [7-13]. Majority of the reported works on photocrosslinking as well as photopolymerizing recording media are based on PVA [7, 14-21]. Dye sensitized PVA films are extensively used in holography because of its excellent optical properties, high efficiency, high sensitivity, high water solubility and ease of fabrication [22]. PVA is available with different molecular weights and hydrolysis degrees, which determine its optical properties [23]. Experimental results on dye sensitized PVA films with various monomers like acrylamide, lithium acrylate and mixture of methacrylates are reported [24-27].

This chapter deals with the incorporation of different monomers like acrylic acid (AA), methacrylic acid (MAA), butyl acrylate (BA), acrylonitrile (AN) and vinyl acetate (VAc) in the PVA matrix. PVA with molecular wt.

1,25,000 was used for the preparation of films. Methylene blue (MB) was used as the photosensitizing dye and the films were characterized using He-Ne laser having emission at 632.8 nm.

4.1.2 Fabrication of MBPVA Film

10% PVA solution was prepared by dissolving 10 gm of PVA in 100 ml distilled water. PVA solution was sensitized with MB to have a dye concentration of 6.19×10^{-4} M. As triethanolamine (TEA) is the commonly used coinitiator in dye sensitized PVA, here also the same has been chosen [28-30]. Films were fabricated with and without TEA and its concentration was varied from 0.01.to 1M. Films were fabricated on micro slides using gravity settling method and the drying period was 36 hrs. A 10mW, CW, He-Ne laser (unpolarized beam) was used for characterization. Real time transmittance studies were carried out by exposing the films to a power density of $5mW/cm^2$.

The relative transmittance and hence the sensitivity was higher for films containing higher concentration of TEA. This is because TEA facilitates the photoreduction of MB and hence speeds up the photochemical reaction [4, 31-32]. But higher concentration of TEA adversely affected the film properties and hence 3.35×10^{-2} M was chosen as the optimum concentration. This concentration was maintained throughout the study. Fig. 4.1.1 is the plot of relative transmittance of MBPVA films with and without TEA. In the case of films with TEA, an exposure of 300 mJ/cm^2 was sufficient to bring all the dye molecules to leucoform. But in the case of films without TEA, saturation energy was higher than $1800mJ/cm^2$ [33]. Gratings were recorded on these films using the experimental setup described in section 2.9.1 by varying the exposure energy. The optimum exposure energy for MBPVA/TEA was $500mJ/cm^2$ (2% efficiency) whereas for MBPVA films it was $700mJ/cm^2$ to have the same efficiency. In both cases the diffraction efficiency (DE) was found to be decreased on storage. Fig. 4.1.2 and Fig.4.1.3 is the absorption spectra of MBPVA (using Hitachi- 330) and MBPVA/TEA ((using

JASCO-V-570) films on storage. In both undoped films and TEA doped films, the change of state occurring to dye molecule is not stable and on storage the absorbance modulation decreases. As the film does not contain monomer, the grating formation is due to the absorbance modulation and the decreases in efficiency on storage may be due to the unstable leucostate.

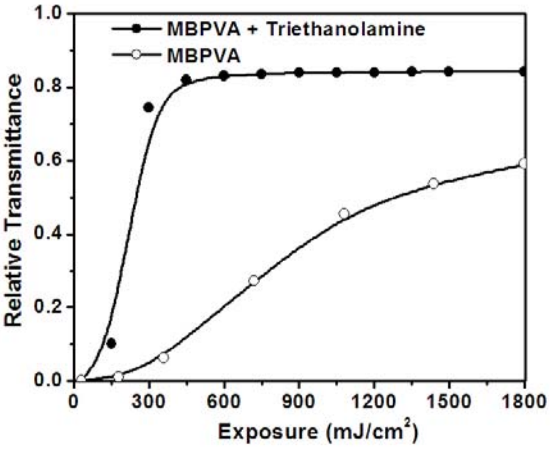


Fig. 4.1.1 Relative transmittance of MBPVA films with and without TEA

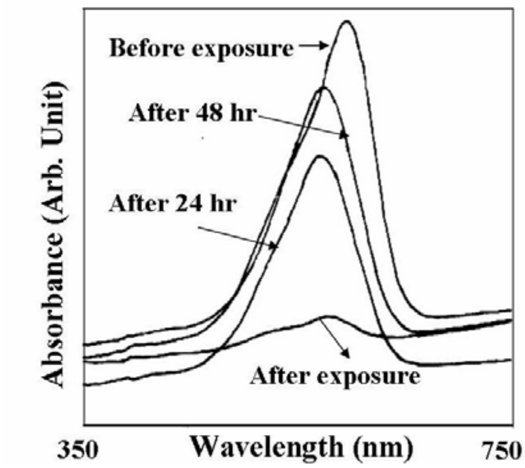


Fig. 4.1.2 The absorption spectra of MBPVA film on storage.

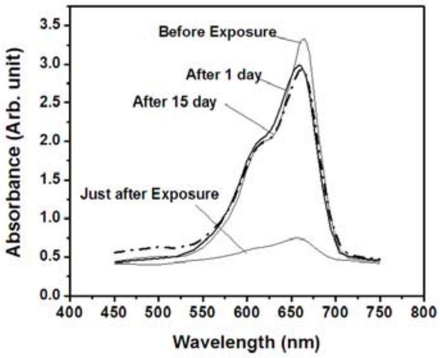


Fig.4.1.3 The absorption spectra of MBPVA/TEA film on storage

4.1.3 MBPVA- Acrylic Acid

Acrylic acid (AA) or 2-propenoic acid ($C_3H_4O_2$) is the simplest unsaturated carboxylic acid with both one double bond and one carboxyl group linked to its C3. Krul *et al.* reported the development of a thermally stable holographic film contains a copolymer of methyl methacrylate with AA and 9, 10-phenanthrenequinone [34]. Various acrylates (esters and salts of acrylic acid) like lithium acrylate, bornyl acrylate, butyl acrylate, hexanediol diacrylate etc. are being used in holography [26, 35-37]. Beside these, poly (acrylic acid) (PAA) plays an important role in the fabrication of photo-crosslinking polymers [38-41]. Fabrication of MB sensitized films by blending both PVA and PAA is reported by our research group [33, 42-44]. Later, the development of dichromated blend of PVA/PAA is also reported [45]. In addition to these, PAA films are also used for the production of Infrared holograms [46]. Here the effect of AA monomer on the DE of PVA matrix is evaluated.

4.1.3.1 Film Preparation

MBPVA solution was prepared to have 6.19×10^{-4} M MB and 3.35×10^{-2} M TEA. To this solution, AA was added and its concentration was varied from 0.019 to 0.8M. Films were fabricated using this solution and the drying period was 48 hrs. Films with AA concentration equal to 0.4M or above could not be dried even after 4 days. It was observed that as the AA concentration increased, the film became sticky and hence not suitable for further studies. So the films with 0.019 to 0.28M acrylic acid were used for further studies. The same behaviour was reported in the case of MBPVA/PAA blend, where the sticky nature was due to the difficulty of removing water from PAA [33].

4.1.3.2 Material Sensitivity

Film sensitivity was determined by monitoring the real time transmittance for an incident power density of 5mW/cm^2. Fig. 4.1.4 is the plot of relative transmittance with exposure of MBPVA/AA films. The threshold energy (minimum energy requirement for dye excitation) for AA doped films is above 400mJ/cm^2, whereas it was only 100mJ/cm^2 for MBPVA films. It is observed that the sensitivity decreases with AA concentration. The AA monomer may hinder the dye excitation and hence the photochemical reaction. [22, 42]. There was another possibility for evaporation of AA monomer during the drying process. When the films were prepared without the co-initiator, TEA, the films were totally insensitive to laser. The absorption spectra of MBPVA/AA films were recorded and are shown in Fig. 4.1.5. Here the recovery of dye molecule from leucoform is slower than that of MBPVA film.

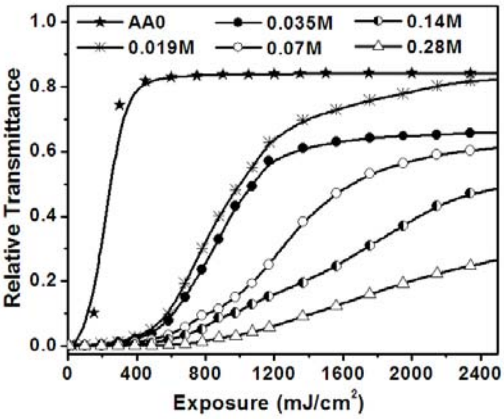


Fig. 4.1.4 Relative transmittance with exposure for MBPVA/acrylic acid films

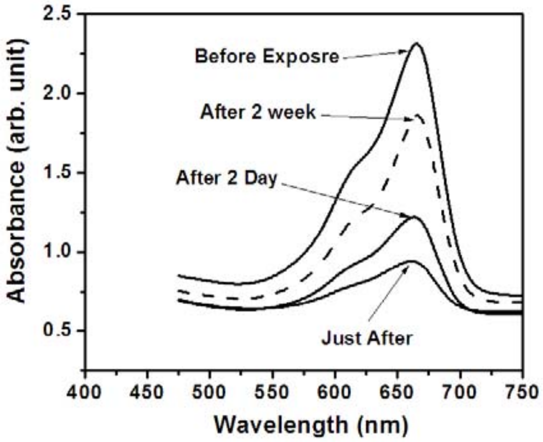


Fig. 4.1.5 The absorption spectra of MBPVA/AA film on storage

4.1.3.3 Diffraction Efficiency

Gratings were recorded on films at 1000 mJ/cm^2 as explained in section 2.9.1. The efficiencies of AA doped samples were less than that of undoped film. The variation of DE with AA is shown in Fig. 4.1.6. Though the storage lives of gratings were better than that of undoped films, the gratings vanished after 3 weeks. On storage, AA oozed the film surface and film properties started to loose after 2 week of preparation of the films.

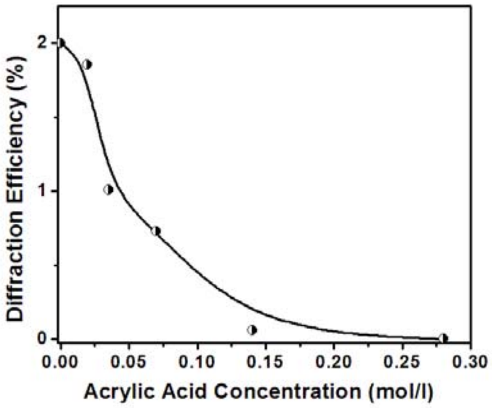


Fig. 4.1.6 DE of MBPVA films with different acrylic acid concentration

As no improvement in efficiency and sensitivity were achieved by AA doping, no further studies were done on these films.

4.1.4 MBPVA-Methacrylic Acid

Methacrylic acid (MAA) or 2-methyl-2-propenoic acid is used industrially in the preparation of its esters, known collectively as methacrylates, such as methyl methacrylate. Though MAA monomer is not directly involved in holography, polymer of its ester, Poly(methyl methacrylate) (PMMA) and poly(methacrylate) are extensively used in holography [47-50]. Recently a Korean research team reported the enhancement of phase stability of PMMA/acrylamide films with the incorporation of MAA [51-52]. The following section describes the effect of inclusion of MAA monomer in MBPVA film.

4.1.4.1 Film Fabrication

MBPVA solution was prepared with $6.19\text{x}10^{-4}$ M MB and $3.35\text{x}10^{-2}$ M TEA. MAA concentration was varied from 0 to 0.147M. Films were casted using gravity settling method and the drying period was 48 hrs. Films with higher MAA content showed sticky nature just like AA doped films.

4.1.4.2 Studies on MBPVA/MAA Films

Real-time transmittance of the film was determined by exposing the films to a power density of 5mW/cm^2. Fig. 4.1.7 is the plot of relative transmittance with exposure for MBPVA/MAA films. Like AA doped films, here also the threshold energy was above 400mJ/cm^2. The material sensitivity decreased with the concentration of MAA. The absorption spectra on storage are plotted in Fig. 4.1.8. Gratings were recorded on these films for an exposure of 1000mJ/cm^2. The efficiency of MAA doped films was less than that of undoped films. The variation of DE with MAA is plotted in Fig. 4.1.9. The storage life of the grating was 2 weeks with decrease in efficiency. The shelf life of the film was 6 months. As the efficiency was not improved by MAA doping, another monomer was tried.

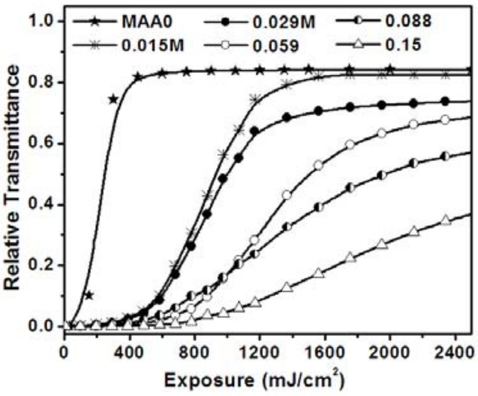


Fig. 4.1.7 Relative transmittance Vs exposure for different MBPVA/MAA films

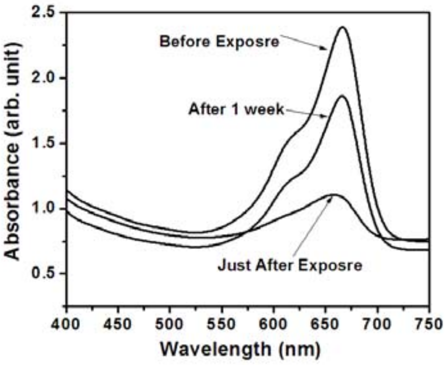


Fig. 4.1.8 The absorption spectra of MBPVA/MAA film on storage

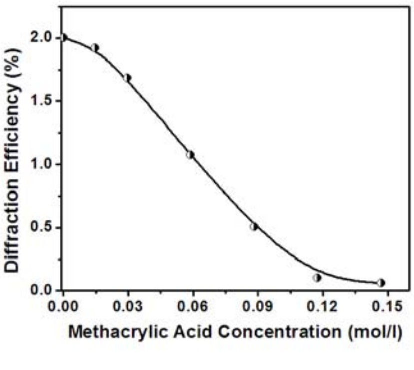


Fig. 4.1.9 The variation of diffraction efficiency with MAA

4.1.5 MBPVA-Butyl Acrylate

As the above mentioned two carboxylic acid monomers do not improve the efficiency of MBPVA, an acrylic ester, butyl acrylate (BA) was incorporated to the MBPVA film. Alkyl acrylates are clear, volatile liquid; slightly soluble in water and complete soluble in alcohols, ethers and almost organic solvents. And hence the preparation of MBPVA/BA was not an easy task.

4.1.5.1 Film Fabrication

To 10% PVA solution, different volumes of BA were added by keeping the total volume of solution as 10 ml. The PVA/BA ratio was varied from 10:0 to 6:4. On pouring BA to PVA solution, an oily layer was formed on the surface. To get a homogeneous solution, methanol was added to the system and on continuous stirring a homogeneous solution was obtained. As the amount of BA increased, the amount of methanol required also increased. The volume of PVA, BA and methanol taken for different samples were shown in the Table 4.1.1. MBPVA/BA solutions were prepared by sensitizing 10 ml of the above solutions with MB (6.19×10^{-4} M) and TEA (3.35×10^{-2} M). The drying period was less than 24 hrs.

Table 4.1.1 The volume of PVA, BA and methanol taken for different samples

PVA (ml)	BA (ml)	Methanol (ml)	Volume of BA in10 ml solution (ml)
10	0	0	0
9.5	0.5	2.5	0.4
9	1	3.5	0.741
8.5	1.5	4.5	1.034
8	2	5.5	1.29
7	3	6.5	1.818
6	4	10	2

4.1.5.2 Real Time Transmittance Studies

Real-time transmittance was determined by exposing the MBPVA/BA films to a power density of 5mW/cm^2. The relative transmittance of each sample is shown in Fig. 4.1.10. Though the sensitivity was lower than that of undoped films, it was more sensitive than MBPVA/AA and MBPVA/MAA films. The threshold energy for MBPVA/BA film with 0.28M monomer was 100mJ/cm^2. From the absorption spectra (using JASCO-V-570) shown in Fig. 4.1.11, it is evident that the conversion of dye from leucoform is very fast in the case of MBPVA/BA film.

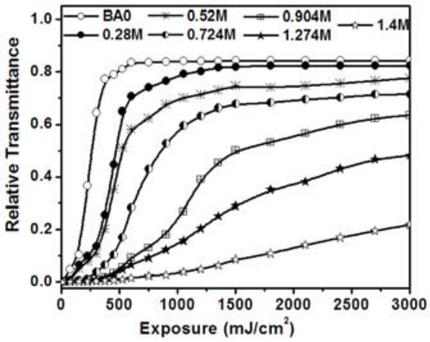


Fig. 4.1.10 The relative transmittance of MBPVA/BA films

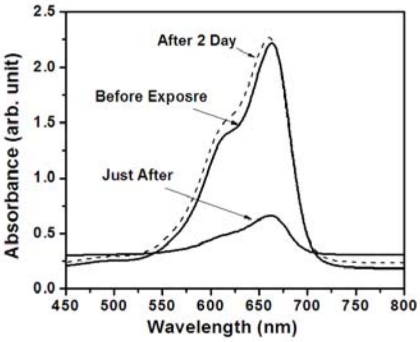


Fig. 4.1.11 The absorption spectra of MBPVA/BA film on storage.

4.1.5.3 *Diffraction Efficiency Measurements*

Gratings were recorded on these films for exposures of 500, 1000 and 2000 mJ/cm^2 using single beam method, which is explained in section 2.9.1. The variation of DE with BA concentration is depicted in Fig. 4.1.12. Here also the efficiency was not improved with monomer incorporation. The storage life of the grating was less than 6 hrs. The very short life of the grating may be due to the instability of leuco form of the dye. Though the storage life of the grating was poor, the shelf life of the film was more than 6 months. Due to the very short storage life of the grating, further studies were not done on this material.

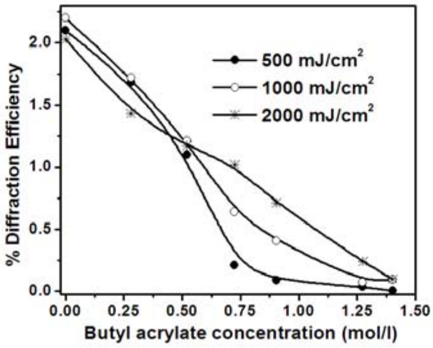


Fig. 4.1.12 The variation of diffraction efficiency with BA concentration

4.1.6 MBPVA-Acrylonitrile

Acrylonitrile (AN), a pungent-smelling colorless liquid, consists of a vinyl group linked to a nitrile. Several researchers have made the kinetic study of polymerization of AN. The photopolymerization of AN sensitized by 8-acryloyloxyquinoline and Poly acryloyloxyquinoline as well as combining with carbon tetra bromide was reported [53]. The sensitizers also entered into the Poly (acrylonitrile) chains and the molecular weights of the resulting Poly (acrylonitrile) were lower. According to Bamford, thermal and light induced polymerizations of AN showed an initial increase in rate with time and the photochemical after-effect depends on the duration of irradiation. The photopolymer prepared near room temperatures could be used as the initiator for the polymerization of AN and other vinyl monomers at higher temperatures [54]. The photopolymerization of AN sensitized by C_{60}, naphthalene, N-(p-phenoxy-phenyl) methacrylamide etc. have been reported [55-57]. The photopolymerization of AN in the presence of dyes such as FD&C Blue #1, FD & C Red #40, Crystal Violet, Basic Fuschin, etc. have been reported [58]. Besides this holographic materials based on styrene - AN copolymer (SAN) is well reported [59-62].

4.1.6.1 Film Fabrication

To 10% PVA solution, different volumes of AN were added by keeping the total volume of solution as 10 ml. The PVA/AN ratio was varied from 10:0 to 6:4. On pouring AN to PVA solution, an oily layer was formed. To get a homogeneous solution, methanol was added and continuous stirring was given for 30 min. The volume of PVA, AN and methanol taken for different samples were shown in the Table 4.1.2. MBPVA/AN solutions were prepared by sensitizing 10 ml of the above solutions with MB ($6.19x10^{-4}$ M) and TEA ($3.35x10^{-2}$ M). The solution was casted and transparent films were obtained after 24 hrs.

Table 4.1.2 The volume of PVA, AN and methanol taken for different samples

PVA (ml)	AN (ml)	Methanol (ml)	Volume of AN in10 ml solution (ml)
10	0	0	0
9	1	3	0.769
8	2	3	1.54
7	3	4	2.143
6	4	6.6	2.409

4.1.6.2 Real Time Transmittance studies

Real-time transmittance measurements were carried out by exposing the films to a power density of 5mW/cm^2. Fig. 4.1.13 is the plot of relative transmittance with exposure for MBPVA/AN films. The films were highly sensitive and the threshold energy was only 75mJ/cm^2. Among the different films, the one having 2.5 M Acrylonitrile showed highest sensitivity.

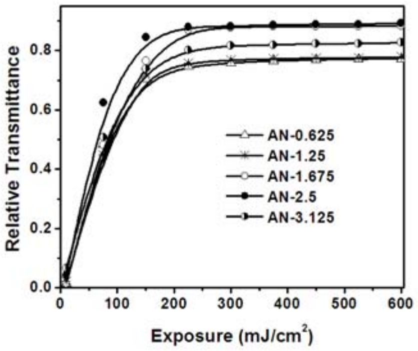


Fig. 4.1.13 Relative transmittance with exposure for MBPVA/AN films

4.1.6.3 Optical Absorption Studies

The absorption spectra of the unexposed and laser exposed (3000mJ/cm^2) films were recorded using JASCO V-570 spectrophotometer. The change in absorbance on laser exposure was determined and plotted in Fig. 4.1.14. Highest absorbance modulation occured for films with 1.25M AN. In the case of AN doped films also the leucodye is not stable. The Absorption spectra of MBPVA/AN on storage is shown in Fig. 4.1.15.

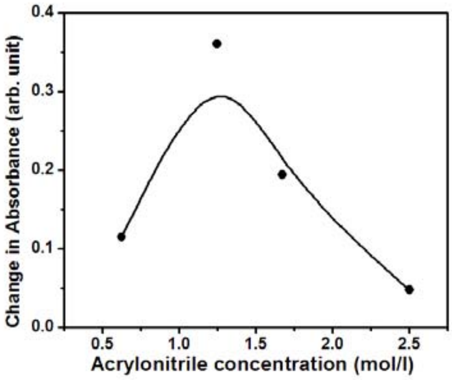


Fig. 4.1.14 The change in absorbance on laser exposure

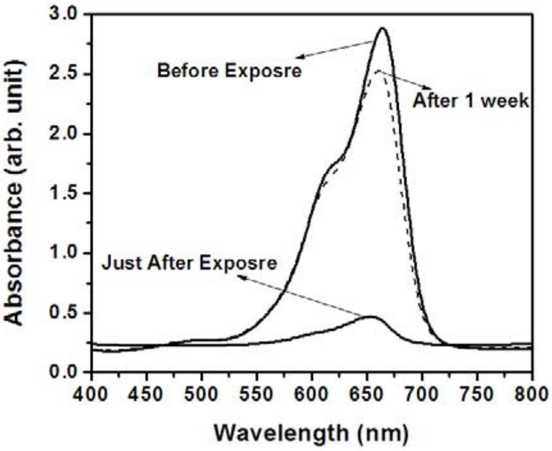


Fig. 4.1.15 The Absorption spectra of MBPVA/AN on storage.

4.1.6.4 Diffraction Efficiency Measurements

To optimize the monomer concentration, gratings were recorded for an exposure of 200mJ/cm^2 using the experimental setup described in section 2.9.1. The variation of DE with AN is plotted in Fig. 4.1.16. Highest efficiency of 2.72% was obtained for AN concentration of 2.5M. In the case of AN doped films also the efficiency was found to decrease on storage. The diffraction efficiency was measured after 3 days of recording and is plotted in Fig. 4.1.17. The gratings could be retrieved for 10 days after recording. The better storage life of the grating may be due to the slow recovery of dye molecule from leucoform (Fig. 4.1.15). The maximum spatial frequency obtained using the above described recording geometry was only 120 lines/mm. To increase the spatial frequency of gratings, gratings were recorded on the films using double beam interferometry as explained in section 2.9.2. The maximum resolution that can be attained on this material was 300 lines/mm. Fig. 4.1.18 is the plot of diffraction efficiency with exposure for films with different AN concentration. The spatial frequency was maintained as 300 lines/mm. Highest efficiency of 1.7% was obtained for films with 0.25M Acrylonitrile, for an exposure of 40mJ/cm^2. But the storage life decreased with increase in spatial frequency.

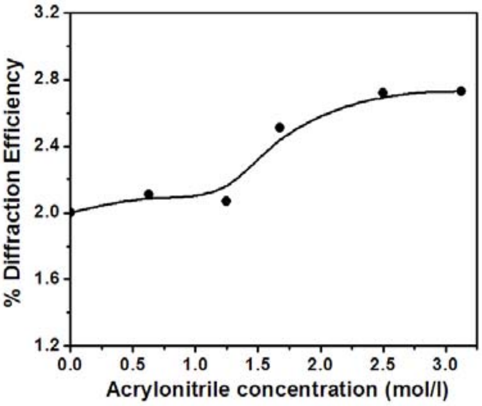


Fig. 4.1.16 The variation of DE with AN for a spatial frequency of 120 lines/mm

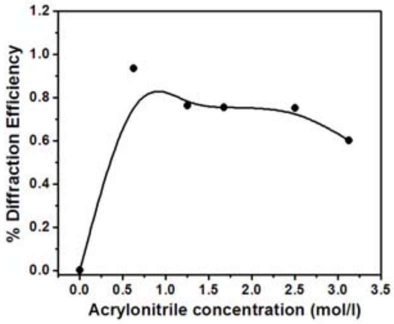


Fig. 4.1.17 The diffraction efficiency on storage (3 days after grating formation)

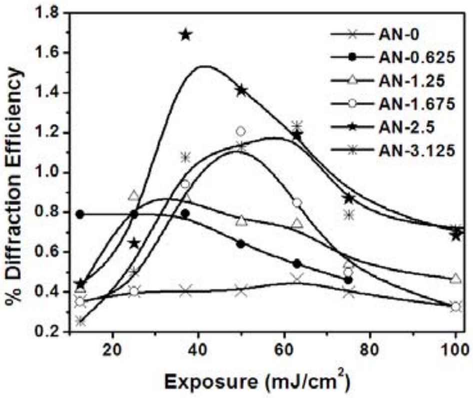


Fig. 4.1.18 DE with exposure for different AN concentration. (spatial frequency=300 lines/mm)

With the incorporation of AN, the sensitivity and efficiency of MBPVA was improved. But as the progress was not much commendable, another monomer was incorporated to MBPVA.

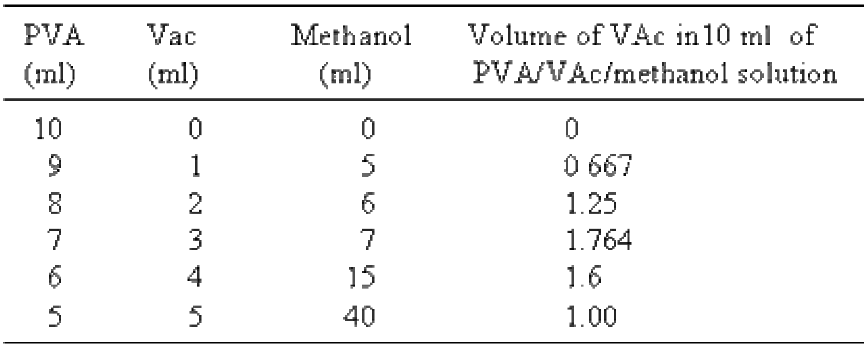
4.1.7 MBPVA/Vinyl Acetate

As different acrylic monomers were not induced much enhancement in the DE of MBPVA, a vinyl monomer, vinyl acetate (VAc) was introduced to the MBPVA film. As described in the previous chapter, the photopolymerization of VAc is well-known. Holographic film comprised of VAc and maleic anhydride, ethylene vinyl acetate copolymers, copolymers of VAc with tetrafluoroethylene, polyvinyl acetate etc have been developed [63-65]. But in all those cases, VAc was acted as the binder. Here VAc is incorporated to the PVA matrix as a Photopolymerizable monomer.

4.1.7.1 Film Preparation

The PVA/ VAc ratio was varied by keeping the total volume of the solution fixed at 10 ml. On pouring VAc to 10% PVA solution, an oily layer is formed on the surface. To get a homogeneous solution, methanol was added to the system and then a white precipitate was formed. Continuous stirring was given to have a homogeneous solution. While adding sufficient amount of methanol, the oily layer and the precipitate become fully dissolved. Solutions were prepared by varying the (PVA): (VAc) v/v ratio from 10:0 to 4/6. As the amount of VAc increases, the amount of methanol required was very high and the viscosity of solution decrease. From 5/5 ratio onwards, the white precipitate remained even after the solution become non-viscous. The amount of PVA, VAc and methanol taken for different samples were shown in the Table 4.1.3. The solution with PVA/VAc ratio of 7:3 contains the highest concentration of VAc. MBPVA/VAc solutions were prepared by sensitizing 10 ml of the PVA/VAc solutions with MB ($6.19x10^{-4}$ M) and TEA ($3.353x10^{-2}$ M). Films were fabricated on micro slides using gravity settling method and the drying period was 24 hr. In all cases except PVA/VAc (5:5) ratio, good quality films were obtained.

Table 4.1.3.The amount of PVA, VAc and methanol taken for different samples



PVA (ml)	Vac (ml)	Methanol (ml)	Volume of VAc in10 ml of PVA/VAc/methanol solution
10	0	0	0
9	1	5	0 667
8	2	6	1.25
7	3	7	1.764
6	4	15	1.6
5	5	40	1.00

4.1.7.2 Optimization of PVA/ Vinyl Acetate Ratio

Real time transmission studies were carried out to get an idea about how fast the bleaching process and hence the amplitude modulation is taking place in these films. The samples were exposed to a power density of 6mW/cm^2 for 10 minutes and the relative transmittance was determined. The relative transmittance of films with different PVA/VAc ratio is shown in Fig. 4.1.19. The highest values of relative transmittance obtained when the PVA/VAc ratio is 7:3. From the relative transmittance, rate of bleaching was determined and is plotted in Fig. 4.1.20. In all cases the rate of bleaching decrease with exposure and it reached nearly zero at 500mJ/cm^2. Therefore it was better to record gratings at exposures less than 450mJ/cm^2.

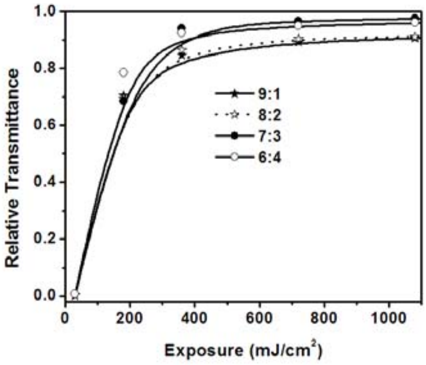


Fig. 4.1.19. The relative transmittance of films with different PVA/VAc ratio

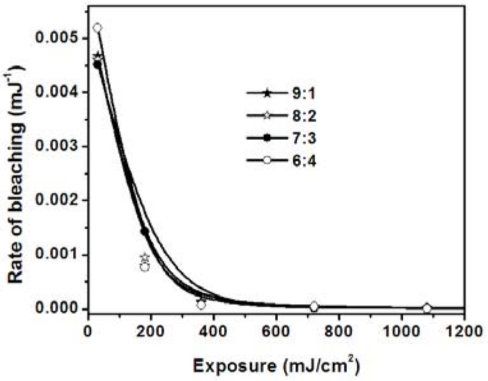


Fig. 4.1.20 The rate of bleaching with time

In order to optimize the PVA/VAc ratio, gratings were recorded on the so prepared films for an exposure of 420 mJ/cm^2 by using the experimental technique described in section 2.9.1. The incident power (during recording) was 5.3 mW/cm^2 and the spatial frequency was 120 lines/mm. The reconstructed power was 1.3µW. Fig. 4.1.21 shows the variation of DE with VAc concentration. As VAc increases, the rate of polymerization and the rate of monomer diffusion increased and hence the DE increases. Highest value of DE (3.02%) obtained for a PVA/VAc (v/v) ratio of 7:3 (VAc concentration is 1.496 M).

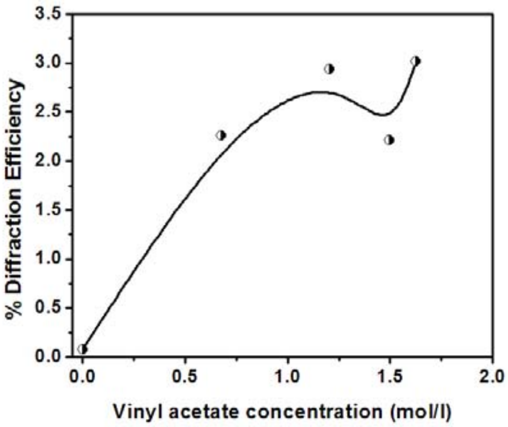


Fig. 4.1.21 The variation of DE with VAc concentration.

To find the RI modulation on laser exposure, the films were exposed to 500 mJ/cm^2 and the RI modulation was determined as explained in session 2.8. Fig. 4.1.22 shows the variation of change in RI on laser exposure with VAc content. From the graph it is evident that as the VAc concentration increased, the change in RI also increased. The DE depends on the constituents of each component in the recording media. As each component, contributes to the RI gradient, DE may increase or decrease [28, 66].

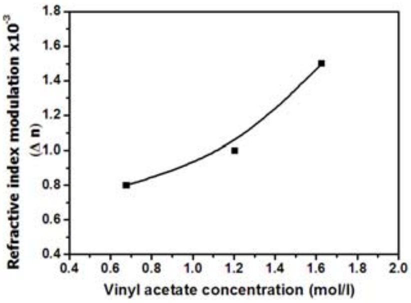


Fig. 4.1.22 The variation of change in refractive index on laser exposure

4.1.7.3 Optimization of Methylene Blue Concentration

To find out the optimum dye concentration on MBPVA/ VAc system, films were fabricated with PVA/VAc (v/v) ratio as 7:3 and the MB concentration was varied from 1.74x10^{-5} M to 2.4x10^{-3} M. Gratings were recorded as discussed in section 2.9.1 and DE was determined for each sample.

Real time transmittance was found out by exposing the films to a power density of 6mW/cm^2 for 10 minutes. The relative transmittance and rate of bleaching of films with MB concentration is shown in Fig. 4.1.23 and Fig. 4.1.24 respectively. The highest values of relative transmittance obtained for MB concentration of 4.2x10^{-4} M. Rate of bleaching of films with low dye concentration decreased with exposure. Above 4.2x10^{-4} M dye, the rate of bleaching slowly increased with time and reached a maximum and then decreased. This may be due to high threshold requirement at higher dye concentrations.

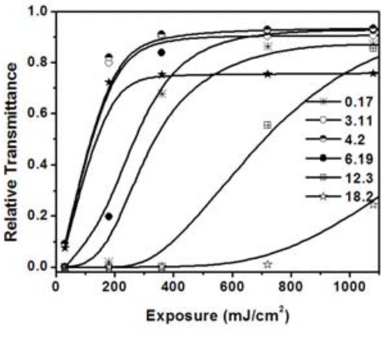


Fig. 4.1.23 The relative transmittance with different MB concentration

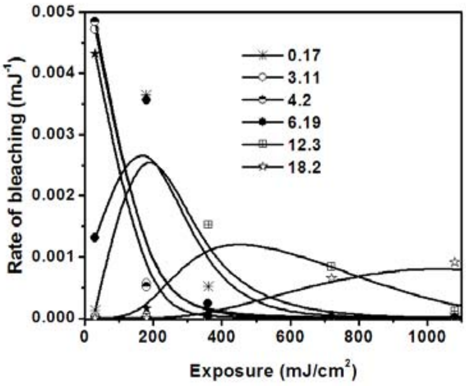


Fig. 4.1.24 Rate of bleaching of films with MB concentration

To optimize the dye concentration, gratings were recorded for an exposure of 420 mJ/cm^2 by using the experimental technique described in section 2.9.1. The variation of DE with dye concentration is shown in Fig. 4.1.25. Maximum DE of 5.5% could be obtained for a dye concentration of 4.2x10^{-4}M. As the dye concentration increases the DE decreased. With the given exposure, gratings were not formed on films with 2.404x10^{-3} M methylene blue. At high concentration, the given exposure is insufficient to bleach the sample and due to this the efficiency decreased. There is another possibility to form dimers, trimers or more complex structures with increase in dye concentration [67].

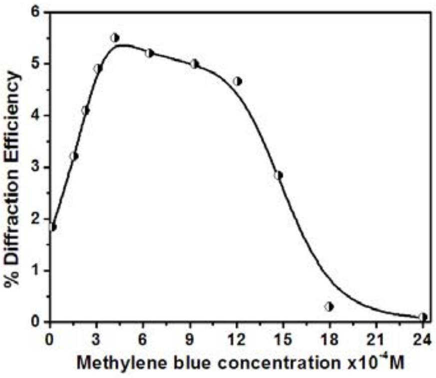


Fig. 4.1.25 The variation of diffraction efficiency with dye concentration

4.1.7.4 Optimization of pH

It has been reported that the pH variation of the coating solution plays an important role on the DE of a holographic material [68-72].To find out the optimum pH of MBPVA/VAc solution, films were prepared with neutral, basic and acidic pH. Samples were made acidic by the addition of HCl and basic by the addition of ammonium hydroxide. The DE of basic sample was less than that of neutral sample. Grating could not be recorded on samples with pH less than 7 or it was completely insensitive to laser. So the pH of the original system was taken as the optimum pH. These conditions were maintained in the entire study. The variation of DE with pH is shown in Fig. 4.1.26.

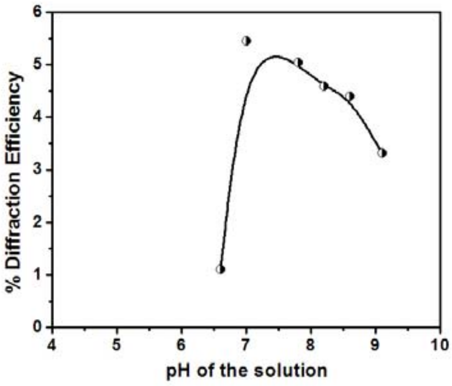


Fig. 4.1.26 The variation of diffraction efficiency with pH

4.1.7.5 Optimization of Exposure

To optimize the exposure of MBPVA/VAc, gratings were recorded by varying the exposure keeping the spatial frequency as 120 lines/mm. Fig. 4.1.27 shows the variation of DE with exposure. As the exposure increased, the efficiency also increased. This is because as the incident energy increase, more dye molecules are getting excited and hence the number of radicals which initiates the polymerization reaction increases. As a result the polymerization rate and monomer diffusion rate increased and the efficiency increased. The highest value of DE (5.5%) obtained for an exposure of 420mJ/cm^2. The gratings recorded on the film could be read for one week with decrease in DE.

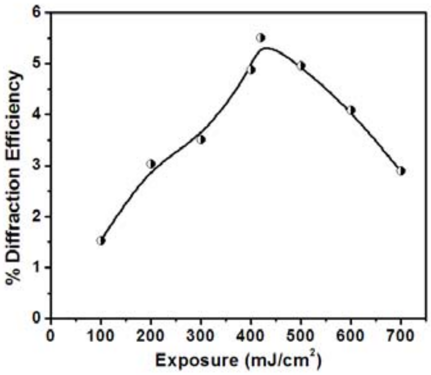


Fig. 4.1.27 The variation of diffraction efficiency with exposure

4.1.7.6 Optical Absorption Studies

To study the behaviour of dye, the absorption spectra of the film with optimum concentration were recorded on storage and are depicted in Fig. 4.1.28. Here the recovery of dye is very fast and a small shift in the absorption spectra was observed on storage. The decrease in efficiency on storage might be due to the instability of leucoform.

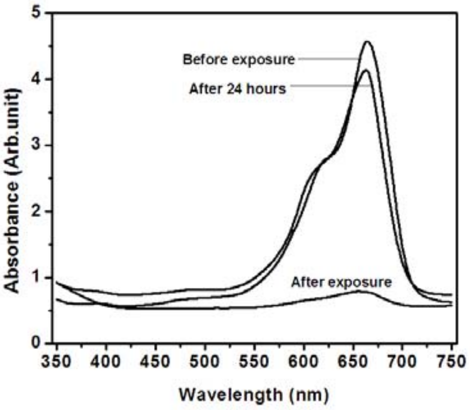


Fig. 4.1.28 The Absorption spectra of MBPVA/VAc on storage

4.1.7.7 Film Properties on Ageing

To find out the shelf life of the film (DE on ageing of the films), gratings were recorded on the same set of films after a number of days of preparation. The exposure energy was maintained as 420 mJ/cm^2. The efficiency was found to decrease on ageing and is plotted in Fig. 4.1.29. This is because on aging the monomer content decrease due to the polymerization of vinyl acetate. As a result the monomer diffusion rate, polymerization rate and the change in RI decreases.

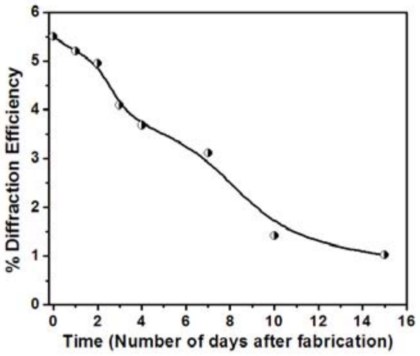


Fig. 4.1.29 The efficiency on ageing of the film

4.1.7.8 Drawback of the MBPVA/Vinyl Acetate Film

The films were dried at room temperature. The humidity highly depends on the drying period. During hot days, (temperature~32°) the drying period was 24hr, but it extended to 72hrs during rainy season (temperature~28°C). Though 5.5% efficiency was obtained for MBPVA/VAc films prepared in hot days, the efficiency obtained during rainy season was less than 1%. It is doubted that VAc is escaping from the film during the drying period. It is expected that in hot days, due to high temperature, the polymerization of VAc may get started and the VAc in the unexposed film is in an oligomer state. As a result, VAc added to the solution is remained in the film. In rainy season, it takes lot of time for drying. Therefore as time goes, VAc monomer escapes and finally the films are with very low concentration of VAc. To avoid this, films were dried in vacuum oven. But the films so obtained were not of good quality and as a result the gratings recorded were of very high noise. In order to have consistent results, the preparation technique was modified and is described in the second part of this chapter.

4.1.8 Comparison of Different monomers

Among the different monomers studied, VAc was found to be the better one because of its efficiency and sensitivity. Table 4.1.4 is the comparison of MBPVA films with different monomers.

Table 4.1.4 Comparison of MBPVA films with different monomers

Film	DE (%)	Exposure (mJ/cm^2)	Resolution lines/mm	Storage life of grating
MBPVA	2	700	<200	1 week
MBPVA/TEA	2	500	<200	1 week
MBPVA/AA	1.82	1000	<200	3 week
MBPVA/MAA	1.9	1000	<200	3 week
MAPVA/BA	1.7	500	<200	6 hrs
	2.72	200	120	10 Days
MBPVA/AN	1.7	40	300	1 Day
MBPVA/VAc	5.5	420	120	1 week

4.1.9 Conclusion

MBPVA films were fabricated by incorporating different monomers like AA, MAA, BA, AN and VAc. From the optical absorption studies it was observed that the leucoform of dye is not stable in all these cases. But the behaviour of dye varied with the type of monomer. The leucoform is more stable in the case of AA and MAA doped films. But the sensitivity and shelf life of these films were very poor. The recovery of dye from leucoform was very fast in the case of BA doped films. On storage the absorption spectra of all the films were shifted to the blue region. This may be due to the conversion of MB molecules to the thionine state. Gratings were recorded on these films and in all cases the efficiency decreased on storage. Only the AN doped films and VAc doped films showed improvement in the efficiency with monomer incorporation. Though the MBPVA/VAc films showed an efficiency of 5.5%, the shelf life of the film was poor. The second part of this chapter describes the modification made to the MBPVA/VAc film and the feasibility of using it as a reusable recording material.

PART II

MBPVA-Vinyl Acetate: A Reusable Recording Medium

4.2.1. Introduction

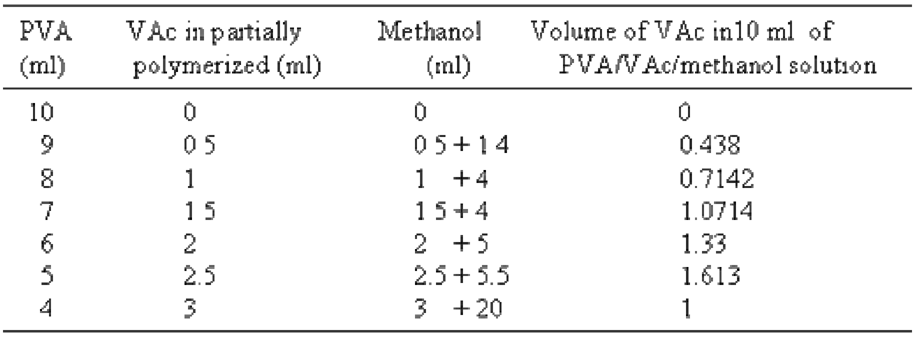
As the MBPVA/VAc films described in Part I of Chapter 4, did not give consistent results, the film fabrication steps were modified. The photopolymer formulation used in this study comprises of VAc in partially polymerized form, to undergo photopolymerization, embedded in a matrix of PVA sensitized with MB and initiated with TEA. Here the DE of grating recorded in the photopolymer media with allowance for diffusion of VAc monomer is analyzed. From the studies it was observed that this material is a reusable recording media unlike other photopolymer materials [73]. Though a variety of photopolymer recording media have been developed with long shelf life and high diffraction efficiency (DE), they are 'write-once-read-many-times' (WORM) materials [26-27, 33]. For holographic data storage, there is an ever-increasing demand for inexpensive rewritable storage media with high capacity and high data transfer rate. The aim of the current work is to explore the possibility of taking advantage of the reusable property of this material.

4.2.2. Film Fabrication

In the modified method, VAc was partially polymerized by solution polymerization using benzoyl peroxide initiator. Partially polymerized VAc was prepared by refluxing VAc (20 ml), methanol (20 ml) and benzoyl peroxide (0.1g) at 70ºC in a two-necked flask fitted with an additional funnel, reflux condenser, thermometer and a stirrer. Just after the initiation, the temperature was lowered to 50ºC and continuous stirring was given for 30 minutes. This partially polymerized VAc/methanol solution thus obtained was mixed with 10% PVA solution. As discussed in section 4.1.7.1, an oily layer was formed and it was dissolved by adding methanol. The mixture was then sensitized with MB and TEA. The solution was casted on micro glass slides heated to 40°. When the solution was casted on unheated glass slide, precipitation was found throughout the film. The layer was left to drying for about 24 hr.

Solutions were prepared by varying the (PVA): (VAc/ methanol) v/v ratio from 10:0 to 4:6. The amount of PVA, VAc, partially polymerized VAc and methanol taken for different samples were shown in the Table 4.2.1. MBPVA/VAc system was prepared by sensitizing the above solution with MB (4.2x10^{-4} M) and TEA (3.35x10^{-2}M). Transparent films with good optical clarity and lack of scattering centers were obtained.

Table 4.2.1 The amount of PVA, VAc and methanol taken for different samples



PVA (ml)	VAc in partially polymerized (ml)	Methanol (ml)	Volume of VAc in10 ml of PVA/VAc/methanol solution
10	0	0	0
9	0 5	0 5 + 1 4	0.438
8	1	1 + 4	0.7142
7	1 5	1 5 + 4	1.0714
6	2	2 + 5	1.33
5	2.5	2.5 + 5.5	1.613
4	3	3 + 20	1

4.2.3. Optimization of PVA/ VAc ratio

Exposing the sample to a power density of 5mW/cm^2 for 5 minute, real time transmission studies were carried out and the relative transmittance Vs exposure (Fig. 4.2.1) was plotted. From the graph it is clear that the relative transmittance remained the same above 500mJ/cm^2. So gratings were recorded on these samples at a fluence of 500mJ/cm^2. To optimize the PVA/VAc ratio, grating recording and refractive index measurements were carried out at 500mJ/cm^2.

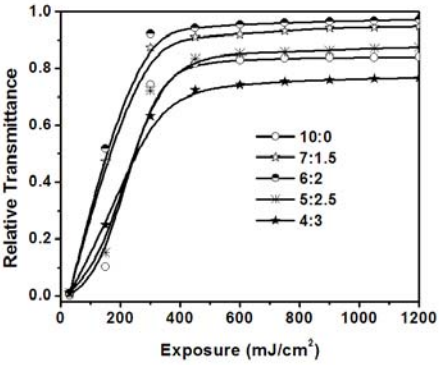


Fig. 4.2.1 Relative transmittance of MBPVA/VAc films

Gratings were recorded using single beam method at an exposure of 500mJ/cm^2. Fig.4.2.2 shows the variation of DE with VAc. As the VAc concentration increases, DE increases. Maximum DE was obtained for a PVA: VAc ratio of 5:2.5 (VAc concentration of 1.51mol/l) and the value was 3.6%. Because of the poor miscibility of PVA and VAc; the VAc concentration could not go above this value. In the previous study (Section 4.1.7), though the efficiency fluctuates with atmospheric temperature and humidity, 5.5% efficiency was obtained (where VAc concentration was 1.496mol/l). Nevertheless the films prepared using partially polymerized VAc showed steady efficiency irrespective of the ambient change. So further optimization was needed to achieve better efficiency.

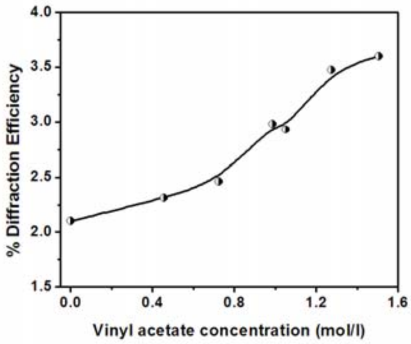


Fig. 4.2.2 Variation of Diffraction efficiency with VAc concentration

Fig. 4.2.3 is the plot of the variation of RI modulation (on laser exposure) with VAc concentration. The change in RI increases with VAc concentration. DE depends on the concentration of each component in the recording media. The RI change on laser exposure is highest in the case of 5:2.5 samples (i.e. films with highest VAc) and it was 0.0017. This implies that the photopolymerization is more prominent in the case of 5:2.5 or 2:1 samples.

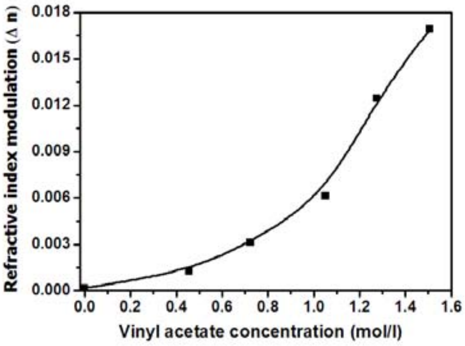


Fig. 4.2.3 Refractive index modulation on laser exposure

4.2.4.Optimization of Methylene Blue Concentration

Polymer formation initiated by a dye is accomplished by the photopolymerization reaction produced by the absorption of light by the photoinitiator in the regions of constructive interference with conversion to its triplet state [31-32]. When the photopolymer material is exposed to laser beam, in addition to the RI change, a change in absorbance also takes place. So in this case the grating formation is due to the combined effect of both absorbance and RI modulation. As the dye molecule initiates the photopolymerization reaction, the dye concentration has a major role in the DE of the medium.

To find out the optimum dye concentration on MBPVA/ VAc system with PVA/VAc ratio 5:2.5, MB concentration in the sample was varied from 3.5x 10^{-4} to 12.4 x 10^{-4} mol/l. To optimize the MB concentration, gratings were recorded on these samples for an exposure of 500mJ/cm^2 and DE measurements were carried out. As the dye concentration was increased the DE also increased and reached a maximum and then decreased (Fig. 4.2.4). The optimum dye concentration was found to be 9.3x10^{-4}M and the DE obtained was 6.2%.

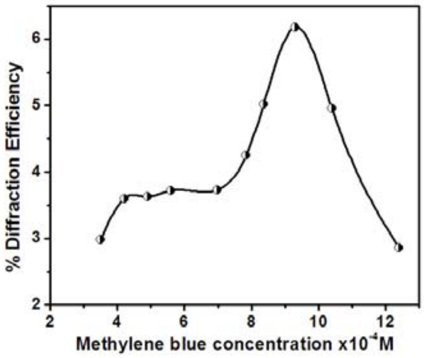


Fig. 4.2.4 Diffraction efficiency with MB concentration

4.2.5.Optimization of Exposure Energy

To optimize the exposure energy of the sample, gratings were recorded on the sample at different fluence. Fig. 4.2.5 shows the variation of DE with exposure energy. As the exposure energy increases, the efficiency increased. This is because as the incident energy increase, more dye molecules are getting excited and hence the number of radicals, which initiated the polymerization also increased. As a result the polymerization rate and monomer diffusion rate increased and the efficiency also increased. From 500mJ/cm^2 onwards the efficiency remained almost the same and the highest value of DE obtained was 6.28% for an exposure of 750mJ/cm^2. The DE decreased above 750mJ/cm^2. The photograph of the diffracted pattern obtained is shown in Fig.4.2.6. Holograms were recorded on MBPVA/VAc film and because of the low efficiency; the holograms were not photographed.

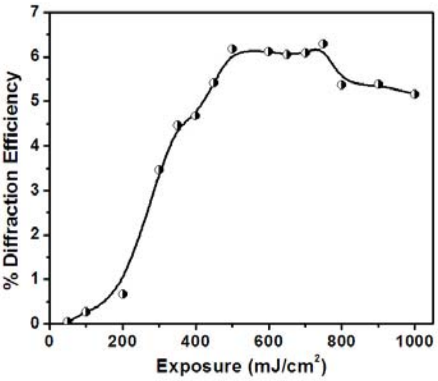


Fig. 4.2.5 The variation of DE with exposure energy

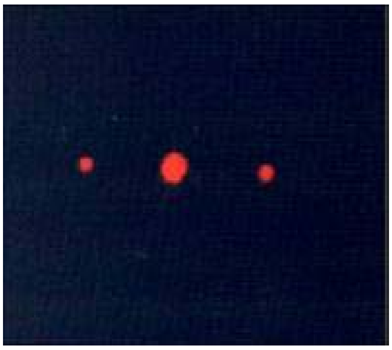


Fig. 4.2.6 The photograph of the diffracted pattern obtained

4.2.6. Effect of Electron Donors

To study the effect of electron donors (ED) on MBPVA/VAc film, three different electron donors such as TEA, triethylamine and dimethyl formamide (DMF) were chosen. Films were prepared by keeping the ED concentration as 0.034 M. Films were also fabricated without any ED. On drying DMF doped films were not of good quality. Gratings were recorded on the other three films by varying the exposure. Triethylamine doped films were of low sensitivity and hence it is not suitable as charge transfer agent. The films without any ED showed an efficiency of 5.6% at 800mJ/cm^2. The concentration of TEA was varied and gratings were recorded on those films. The DE obtained for different concentrations of TEA and triethylamine is depicted in Fig.4.2.7. On increasing the TEA concentration, even at low exposure the efficiency increased. On further increasing the TEA concentration, the films were found to loose its quality. The MBPVA/VAc films with 0.045M TEA showed highest efficiency of 6.3% at 500 mJ/cm^2.

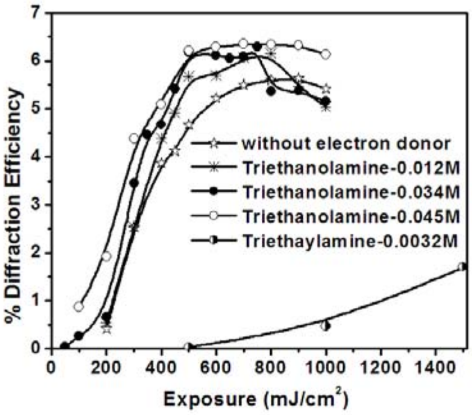


Fig. 4.2.7 The diffraction efficiency obtained for different electron donors

4.2.7. Diffraction Efficiency on Storage

A sharp decrease in the efficiency was observed in this sample within 30 minutes and thereafter the efficiency decreased very slowly. After 4 hrs the diffracted pattern gets blurred and no diffraction pattern was observed after 24 hrs. The decrease in DE with time is plotted in Fig.4.2.8. This decrease in efficiency is due to the migration of monomer in the unexposed region to that of the exposed region and the deexcitation of dye molecule from leucoform to the original form [73, 75]. The recovery of the dye molecule was monitored by measuring the transmittance of the completely bleached sample, keeping the input power below the threshold power. The transmittance at different time is plotted in Fig.4.2.9. From the graph, it is observed that there is a drastic decrease in the transmittance value in the first 30 minutes. The sharp decrease in the DE observed within thirty minutes is therefore suspected to be due to the deexcitation of dye molecules.

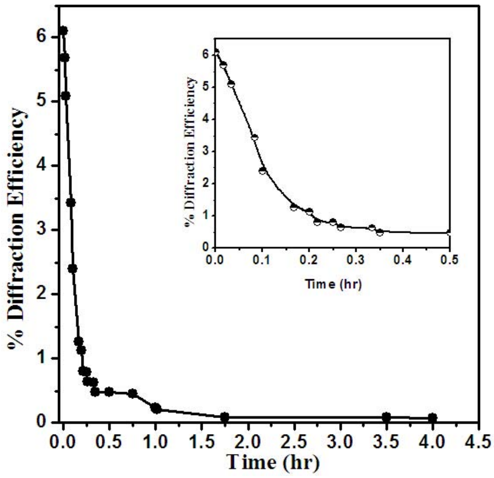


Fig. 4.2.8 The decrease in diffraction efficiency with time

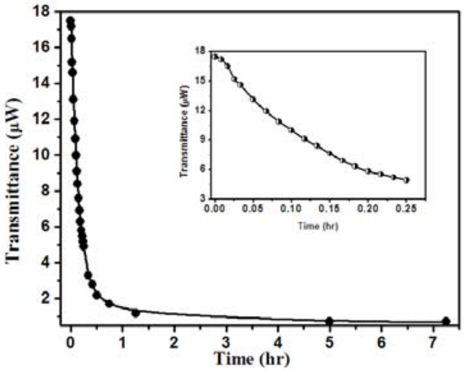


Fig. 4.2.9 Recovery of the dye: The transmittance at different time

To check the shelf life of the film, gratings were recorded on the film on each day after preparation. The same efficiency could be obtained even when the recording was done after 2 years of preparation. Though gratings were recorded on the optimized films using double beam interferometry, the resulted efficiency was very low. Though the material had long shelf life the resolution is limited to 120 lines/mm.

4.2.8. Dye Behavior

From the reported works, it is clear that MB has different behavior in different polymer matrices. In the case of MBPVC the change of state occurring for MB was found to be permanent, and no recovery of dye back to the original state was observed on storage [76]. But in most of the studies with MB in different polymer matrices, it is observed that the exposed area recover its original color after some time and chemical or thermal treatment is necessary for fixing the data. In the case of MBPVA/acrylamide a change in state of MB was observed on laser irradiation, which is shown by a shift in absorption spectrum after exposure [28, 33]. In MB sensitized gelatin (MBG) also a shift in the absorption spectra observed and the dye molecules are converted to the thionine state [77]. The wavelength shift in the absorption spectrum of MBPVA is also due to the formation of thionine state on deexcitation (Fig. 4.1.2 and 4.1.3). In the case of MBPVA/VAc, from the UV- VIS absorption spectrum of the sample before and after 24 hrs (Fig. 4.2.10), it is clear that this leuco form returns to its original state within 24 hrs. No shift in absorption band was observed which indicates that the leuco MB is deexcited to the original state and not to the thionine state as in the case of conventional systems like MBPVA/acrylamide, MBPVA/PAA blend and MBG. Since the material showed the same absorption spectra after deexcitation it is felt that this material could be reused.

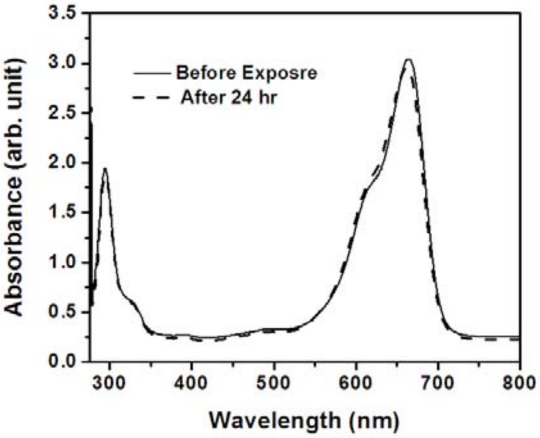


Fig. 4.2.10 The absorption spectra of MBPVA/VAc before and after irradiation

4.2.9. Reusability of MBPVA/Vinyl Acetate

To check the reusability of the MBPVA/VAc system gratings were again recorded on the same area of the same film after 24 hrs (i.e. after the absorption spectra showed complete recovery) and the DE was measured. The same film was reused a number of times by recording grating on the same spot. For this, gratings were recorded on the samples with optimum dye concentration (9.3x 10^{-4} mol/l) at fluence of 500mJ/cm^2. Different samples were reused after an interval of 24 hr, 36 hr and 48 hr and the DE was determined in each time. These samples were labeled as R24, R36 and R48. The DE of these samples on reusage is plotted in Fig. 4.2.11. In all the three cases, the DE decreased on reusing and remained almost constant after using it a number of times.

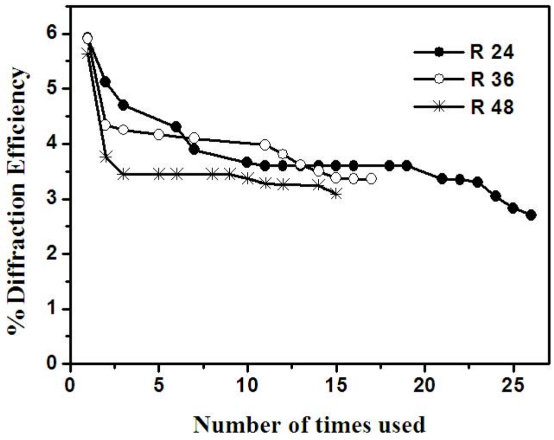


Fig. 4.2.11 Diffraction efficiency on reusing of the sample (optimum composition)

R24 samples were reused 24 times by recording grating on the same spot. The initial DE was 5.92%. It was observed that on reusing the film the efficiency decreased. After reusing it around 10 times, the efficiency remained almost constant and the value was 3.6%. After 24 times of usage the efficiency again decreased. On reuse, the recovery of the dye from leucoform is very slow. After 24 times of usage the dye is not coming back to the original state. Though the recovery of the dye is not complete, the grating recorded on this material after reusing it 24 times is not permanent. From the experiments it is observed that, the DE of the samples R36 and R48 also showed the same trend on reuse. But the DE is less than that of R24 sample. So it is better to reuse the material after 24 hrs. The reusability of MBPVA/VAc can be explained as follows. When the material is exposed to an interference pattern, monomer in the region of constructive interference gets polymerized. According to the diffusion model, there will be free monomer remaining in the material after the gratings are formed, even for long exposure times [78]. So the unreacted monomer diffuses from the unexposed to the exposed region. From our studies it was observed that the material could be reused more than 20 times with considerable readability. To check whether the reusability is the property of VAc monomer, the same experiments were performed on MBPVA/VAc films with low dye concentration and MBPVA film. It was found that the MBPVA/VAc films could be resued irrespective of the dye concentration.

In MBPVA/VAc the dye molecules are deexciting to the original state. So it contributes the same change in absorbance on reuse. So both the unreacted monomer diffusion and the deexcited dye molecules contribute to the reusability of MBPVA/VAc system. But on using it several times, the used region is smearing out of monomers. And as a result no diffusion takes place and the film behaves like pure MBPVA system. So the DE decreased on using it 8-10 times. After that the only contribution is from the change in absorbance. The DE also decreases further on reusing it and also the reconversion back to the original state is not observed. On reusing the sample, a shift in the absorption spectra was observed (Fig. 4.2.12). On reusing it for about 20 times, there was a strong shift in the absorption spectrum showing the conversion to the thionine state.

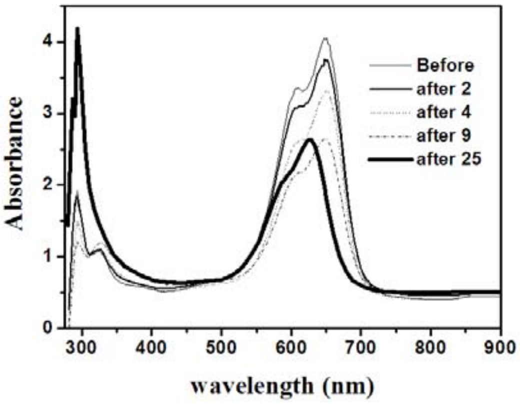


Fig. 4.2.12 Absorption spectra on reusing the sample

To study the effect of repetitive laser exposure on the material sensitivity, the film was exposed to a power density of 5mW/cm^2 and the real time transmittance was monitored for 5 min. The real time transmittance on repetitive exposure is shown in Fig. 4.2.13. Where 'Rx' denotes the transmittance on xth exposure. On reusing the sample the transmittance decreased and the decrease in transmittance may be due to the conversion of dye molecule to the thionine state.

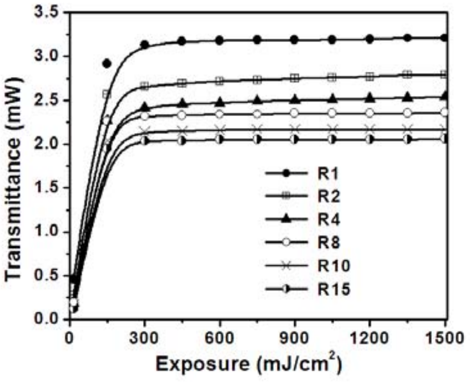


Fig. 4.2.13 Real time transmittance on reusing the sample

4.2.10. Film Fabrication- Modified Procedure

The storage life of the grating recorded on MBPVA film with VAc monomer was one week whereas it was only 24 hrs while using partially polymerized VAc (section. 4.1.7.5). In order to improve the storage life of the grating, the preparation steps were modified and VAc was polymerized in ethanol medium. To prepare partially polymerized vinyl acetate solution, ethanol (10ml) and benzoyl peroxide (0.1g) was taken in a two-necked round bottom flask fitted with an additional funnel, reflux condenser, thermometer and a stirrer and heated to 85°C and it was kept for 2 minute. Then the solution was cooled to 55°C, methanol (10 ml) and inhibitor freed VAc (20 ml) was added and continuous stirring was given for 30 minutes. This partially polymerized VAc solution thus obtained was mixed with 10% PVA solution and films were fabricated by varying the PVA:VAc ratio. The film composition was optimized as explained above and 6.4% efficiency (750mJ/cm^2) was obtained for PVA: VAc ratio of 5:2.5 (v/v). Though the efficiency decreases on storage, the storage life can be extended to 48 hr with the modified procedure. And these films also reused by recording grating at an exposure of 750mJ/cm^2 and 500 mJ/cm^2 in an interval of 48 hr. Fig. 4.2.14 is the plot of DE on reusing the MBPVA/VAc prepared in ethanol medium. These films can be reused with better efficiency than the MBPVA/VAc prepared in methanol medium.

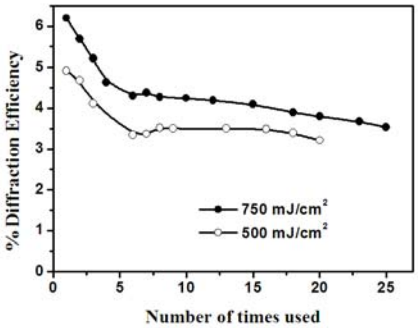


Fig. 4.2.14 Diffraction efficiency on reusing of the sample (MBPVA/VAc/ethanol)

The reusability property of MBPVA/VAc is a self property of its composition and the user has no control over that. Hence the material cannot be considered as an ‘erasable’ material. Though attempts were made to make it erasable, the efforts went in vein.

4.2.11. Resolution of the material

Highest DE of 6.4% obtained on this material was for a spatial frequency of 120 lines/mm, where the gratings were recorded using single beam method. To find out the resolution of this material, gratings were recorded using double beam interferometry (section 2.9.2) by varying the inter-beam angle. Fig. 4.2.15 is the plot of DE with spatial frequency. On increasing the spatial frequency, the system resulted in poor efficiency.

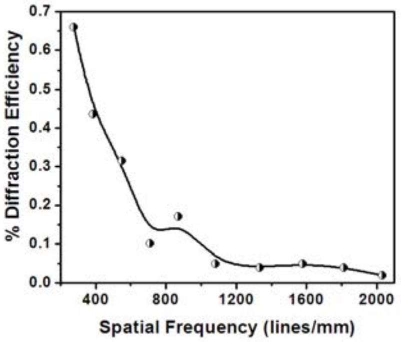


Fig. 4.2.15 Variation of diffraction efficiency with spatial frequency.

4.2.12. Conclusion

Vinyl acetate based holographic recording media showed a DE of 6.4% at 750mJ/cm^2. The recorded gratings were found to remain in the material for 48 hr with a decrease in DE. The major attraction of this material is its reusability. From the experimental studies it is evident that the MBPVA/VAc system can be reused more than 20 times. Being an inexpensive, nontoxic material with high environmental stability and good optical clarity this material can contribute a lot to holography. Usually in holography, photorefractive materials that are used as rewritable media are very expensive and its synthesis is very difficult. The use of reusable photopolymers in this regard is very advantageous due to its low cost and eases of fabrication. Hence the development of MBPVA/VAc as a reusable media will be a major achievement.

PART III

Effect of Additional Monomers on the Storage Life of MBPVA-Vinyl acetate

4.3.1.Introduction

Though a photopolymerizable system basically consists of a monomer, a photoinitiator, and a coinitiator in a suitable polymeric film which acts as binder, systems containing two or more monomers are also reported [20, 25, 79-80]. When acrylamide (AAm) is used as a monomer, methylene bisacrylamide (MBA) is often used as an additional monomer to speed up the polymerization reaction and to obtain stable gratings. Where index modulation is produced when molecular space lattices of the AAm chains are formed, and MBA builds cross-links in that lattices to form copolymer. The additional monomer in the PVA/AAm system produces crosslinked polymers with higher density and lower mobility than the linear poly (acrylamide) and improves the sensitivity and efficiency. Besides the polymer film containing a mixture of similar monomers, two or more monomers of different reactivity rates and molecular polarizabilities (eg., cyclohexyl methacrylate as the high-reactivity monomer and vinylcarbazole as the low-reactivity monomer) were also reported [27]. The use of such a combination of monomers results in a two-way diffusion of the monomers during exposure, giving a modulation of the chemical composition of the final material. The resulting modulation of the molecular polarizability of the polymer can give a larger RI modulation than is possible with the density modulation (by the diffusion of monomer into the highly exposed regions) alone. When these films are exposed to an interference pattern, the polymer will be formed preferentially from the high-reactivity monomer, producing a concentration gradient that will cause additional high-reactivity monomer to diffuse into the high-intensity areas. However, as the polymerization proceeds the volume fraction of polymer in the high-intensity areas increases, and monomer will tend to be excluded from these areas. Since the remaining monomer mixture has been enriched in the low- reactivity monomer, the low-intensity areas- will then contain an excess of low reactivity monomer, and the high-intensity areas will contain a polymer with an excess of the high-reactivity monomer. The modulation of the chemical composition of the final fully polymerized material is achieved in this way. The RI modulation resulting from this modulation of chemical composition tends to be much larger than that resulting from the density effect (for single monomer system) and can predominate even if the two effects should be in opposite directions.

Among different PVA based systems, MBPVA/VAc could be reused more than twenty times with considerable readability [73]. Though 6.5% DE was obtained, a sharp decrease in efficiency was observed on storage; and no diffraction pattern was observed after 48 hrs. This decrease in efficiency is due to the migration of monomer in the unexposed region to that of the exposed region and the deexcitation of dye molecule from leucoform to the original form. As an attempt to improve the storage life of the gratings recorded on MBPVA/VAc additional monomers were incorporated to the system. As acrylic acid (AA) and its esters undergo reactions at the double bond which readily combine with themselves or other monomers (eg., amides, methacrylates, acrylonitrile, vinyl, styrene and butadiene) to form homopolymers or co-polymers, the additional monomers selected were AA and methacrylic acid (MAA). The effect of additional monomers on different holographic parameters such as sensitivity, efficiency, storage life and shelf life is explained here.

4.3.2.Film Preparation

Partially polymerized VAc solution was prepared in ethanol as explained in section 4.2.10. MBPVA/VAc solution also was prepared. To this different volume of AA or MAA was added and continuous stirring was done for 30 min. The AA concentration was varied from 0.02 to 0.2 M and that of MAA was varied from 0.015 to 0.15 M. Films were casted using this solution and the drying period was 48 hr. The drying period for films with 0.1M or above AA was more than 2 days.

4.3.3. Effect of Acrylic Acid on MBPVA/Vinyl Acetate

To study the effect of AA incorporation on the holographic performance of MBPVA/VAc film, different studies were done on theses films and the results are explained in the following sections.

4.3.3.1. Real Time Transmittance

To come across how the additional monomer affects the sensitivity of MBPVA/VAc film, real time transmittance was monitored by exposing the films to a power density of 5mW/cm^2 and it is depicted in Fig.4.3.1. The material sensitivity was found to be decreased with AA concentration. This decrease in sensitivity was found to be an inherent property of AA (section 4.1.3.2) [22, 42]. As the films with AA concentration above 0.14M was of poor quality and less sensitivity, further studies were not done on those films.

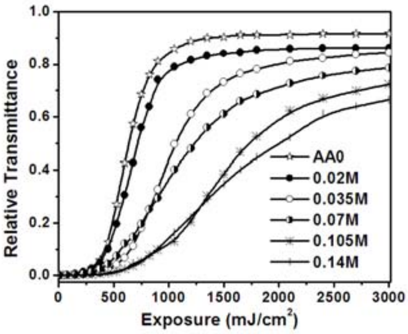


Fig.4.3.1 Relative transmittance of MBPVA/VAc films with different acrylic acid content

4.3.3.2. Optical Absorption Studies

The absorption spectra of the films were recorded before and after exposure. The spectra were recorded on storage also. Fig.4.3.2 shows the absorption spectra of MBPVA/VAc film with 0.035M AA. Though the leucoform is not stable, the recovery of dye is very slow compared to MBPVA/VAc films.

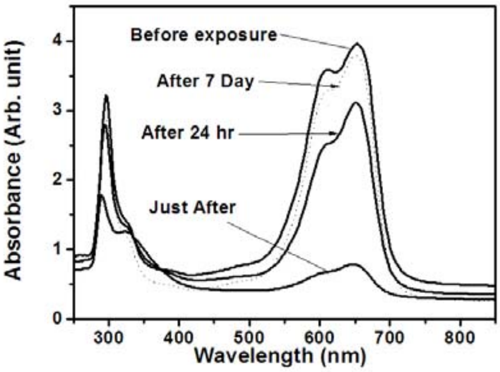


Fig. 4.3.2. The absorption spectra of MBPVA/VAc film with 0.035M acrylic acid.

4.3.3.3. Refractive Index Measurements

In two-monomer system, the increase in efficiency with additional monomer is due to the increase in index modulation. To analyze how the additional monomer affects the RI modulation, change in RI on laser exposure was measured (Fig. 4.3.3). At high concentration of AA, the index modulation was very less and it may be due to the low sensitivity with higher concentrations of AA.

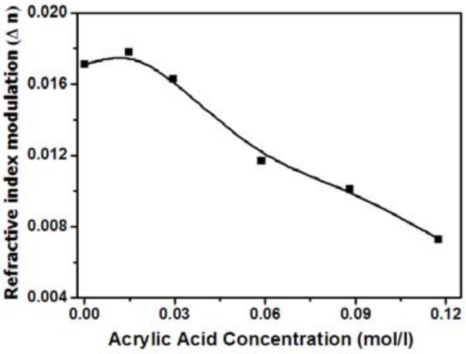


Fig. 4.3.3 Refractive index modulation on laser exposure (MBPVA/VAc)

4.3.3.4. Diffraction Efficiency Measurements

To study the influence of AA on the DE, gratings were recorded (using single beam method) on the above prepared film at 750mJ/cm^2 and the efficiency was determined. The efficiency decreased with AA content and maximum efficiency obtained for AA doped film was 5.6% (AA concentration was 0.02M) and was less than that of the undoped film. The variation of DE with AA concentration is shown in Fig.4.3.4. As expected, no improvement in DE and sensitivity was observed with the incorporation of additional monomer [20]. Though no significant change in the index modulation was observed at low concentrations of AA, the variation of DE was notable at even low concentrations. Though gratings were recorded at different fluence, no improvement in DE was observed.

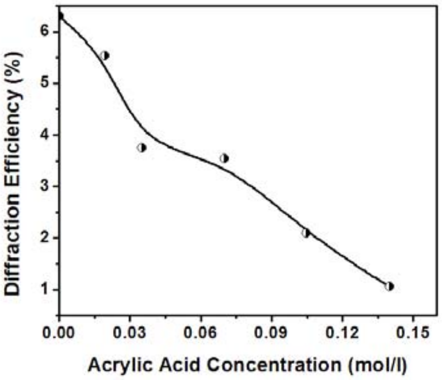


Fig. 4.3.4 The variation of DE with AA concentration

4.3.3.5. Storage Life of Grating

The efficiency of the gratings was monitored on storage and it was found that DE decreased for all films. With the incorporation of AA, the storage lives were improved and the life of the grating is found to be directly proportional to AA concentration. For films with AA concentration less than 0.035M, the gratings vanished within two week. In the case of films with 0.035M AA, within 24 hrs, the efficiency decreased from 3.54% to 0.15% and the grating exist (0.07%) in the film for 45 days. At higher concentrations also the same behaviour was observed. But at higher concentration, the film lost it transparency after three weeks of preparation and the scattering was too high. The efficiency on storage for AA concentration of 0.035M is shown in Fig.4.3.5.

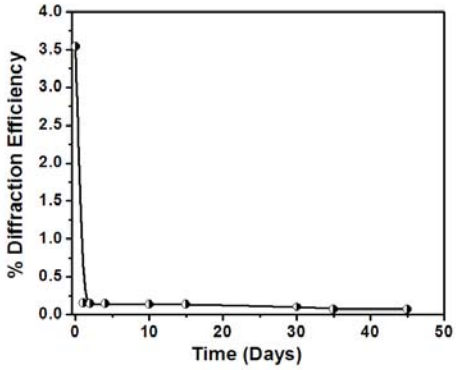


Fig. 4.3.5 The efficiency on storage for AA concentration of 0.035M

4.3.3.6. Shelf Life

On storage the films (unexposed) became sticky because of the oozing out of AA from the film and the film lost it transparency and quality. The shelf life of the film is inversely proportional to the AA content. The shelf life of the optimum film (with more stability and efficiency) is limited to two months.

Though the storage life was improved with AA incorporation, the shelf life of the film was poor. Therefore in order to have better shelf life another monomer, MAA, was incorporated into the MBPVA/VAc system.

4.3.4. Effect of Methacrylic Acid on MBPVA/Vinyl Acetate

Films were fabricated by varying the MAA concentrations and characterized as above. Like AA doped films, here also the film properties were poor at higher concentrations of MAA.

4.3.4.1. Real Time Transmittance

Like AA doped films, here also the material sensitivity was found to be decreased with MAA concentration. But the films were more sensitive than AA doped films. The relative transmittance for a power density of 5mW/cm^2 is depicted in Fig. 4.3.6.

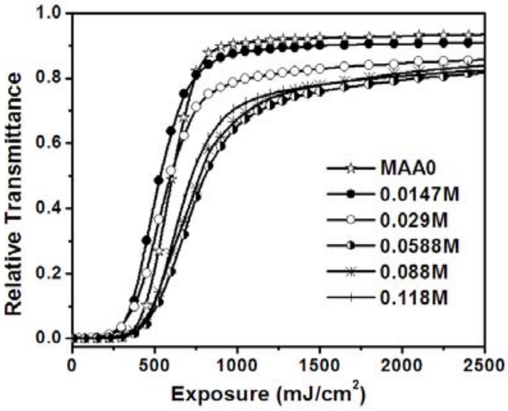


Fig. 4.3.6. The relative transmittance of MBPVA/VAc/MAA films

4.3.4.2. Optical Absorption Studies

Fig. 4.3.7 shows the absorption spectra of MBPVA/VAc/MAA film on storage. The absorption spectra showed the same behavior as that of AA doped films. Here the recovery of dye is slow compared to undoped films. On storage, a slight shift in the absorption peak was observed and it implies that the dye molecules are converted to more stable thionine state.

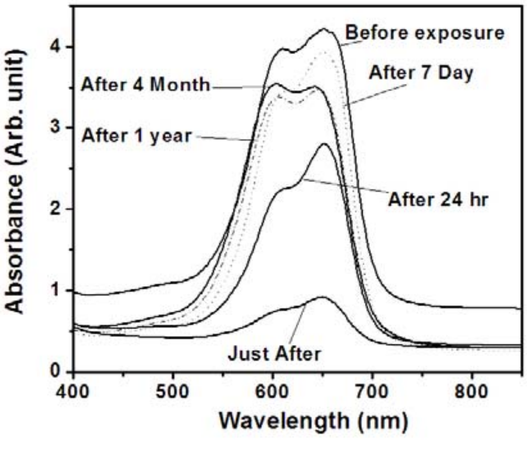


Fig. 4.3.7. The absorption spectra of MBPVA/VAc/MAA film on storage

4.3.4.3. Refractive Index Measurements

The RI modulation on laser exposure was determined for different MAA concentrations and is plotted in Fig. 4.3.8. Like AA doped films, the index modulation decreased with increase of additional monomer.

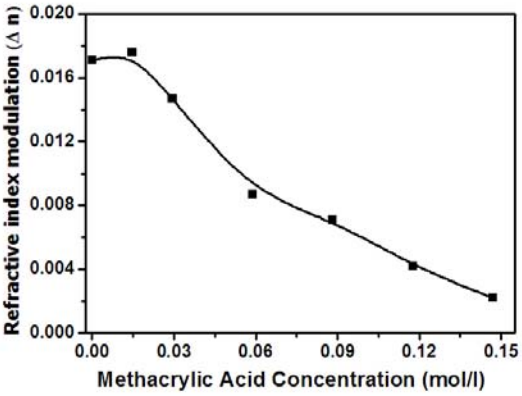


Fig. 4.3.8. The refractive index modulation on laser exposure

4.3.4.4. Diffraction Efficiency Measurements

To study the influence of MAA on the DE, gratings were recorded (using single beam method) at 1000mJ/cm^2 and the efficiency was determined. Though the efficiency was better than that of AA doped films, the efficiency was not improved on MAA doping. The efficiency decreased with MAA concentration and maximum efficiency obtained for MAA doped film was 6.1% (MAA concentration was 0.015M). The variation of DE with MAA concentration is shown in Fig. 4.3.9. The decrease in DE with MAA concentration is due to the decrease in index modulation. The reason for decrease in RI modulation can be the inactivity of MAA for the given exposure or the formation of new molecular structures which prevents further diffusion of monomers.

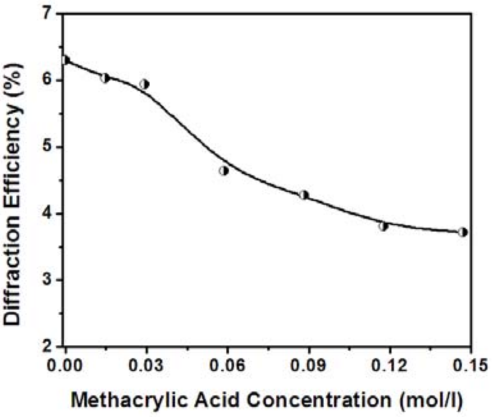


Fig. 4.3.9. The variation of DE with MAA concentration

To find out the spatial resolution of the material, gratings were recorded on these films using double beam interferometry, by varying the inter-beam angle. The efficiency obtained at higher spatial frequencies (>150 lines/mm) was less than that achieved using single beam method. When 200 lines/mm were recorded, the efficiency obtained was only 1.23% at 250mJ/cm^2.

4.3.4.5. Storage Life of Grating

The efficiency of the gratings was monitored on storage and it was observed that the DE decreased in all cases within 24 hr. For films with higher MAA concentrations (above 0.15M), the films lost its properties on storage. In the case of films with 0.015M MAA, the grating vanished after one week of formation. In the case of films with 0.029M MAA, the initial DE was 6% and after one week it came down to 0.5% but the gratings could be stored for more than 2 years with considerable readability (0.1% efficiency). The efficiency on storage for MAA concentration of 0.029M is shown in Fig. 4.3.10. Because of the low efficiency, the holograms recorded on these films were not photographed.

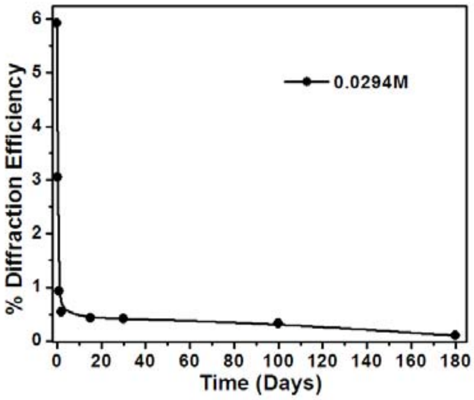


Fig. 4.3.10. The efficiency of MBPVA/VAc/MAA film on storage (MAA= 0.029M)

4.3.4.6. Surface Analysis

The material resolution was not improved with the incorporation of additional monomers and the maximum resolution of MBPVA/VAc /monomer is limited to 150 lines/mm. The surface mapping of the grating was done using Dektak 6M stylus Profilometer. The surface mapping of gratings recorded on MBPVA/VAc/MMA film with 33 lines/mm is shown in Fig.4.3.11. Where the fringe spacing was 30µm and the depth of each fringe was 108 nm. The film thickness was 50 µm.

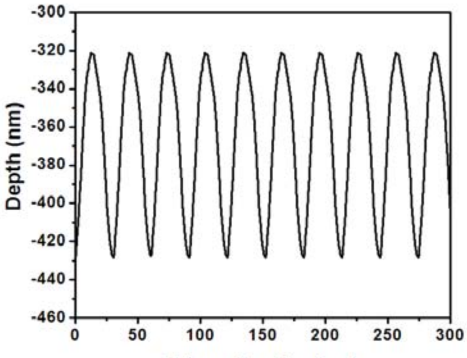


Fig.4.3.11 The surface profile of gratings recorded on MBPVA/VAc/MMA film

4.3.4.7. Shelf Life

MAA did not affect the shelf life of MBPVA/VAc film and the optimum film (with 0.029M MMA) could be stored for more than 2 years. Even after two years, gratings could be recorded on those films with an efficiency of 4%. Like the MBPVA/VAc films, the MAA doped films also were free of scattering centers and hence the monomer incorporation did not affect the SNR.

4.3.5. Conclusion

MBPVA/VAc film was fabricated with two different monomers AA and MAA. Though the additional monomer badly affected the sensitivity and efficiency, the storage life of the grating has ameliorated. The gratings recorded on films with 0.029M MAA could be stored for 2 years with decrease in efficiency.

References

1. R.W. L. Wilson , K. Curtis , M Tackitt , A . Hill , A Hale, M.Schilling ,C . Boyd, S. Campbell , L . Dhar , A. Harris, Opt. Quant. Elect., 32, 393 (2000)
2. H. Sherif, I. Naydenova, S. Martin, C. Mc Ginn , V. Toal, J. Opt. A: Pure Appl. Opt., 7, 255 (2005)
3. C.Garcia, I. Pascual, A.Fimia, Appl. Opt., 38, 5548 (1999)
4. S. Blaya, L. Carretero, R. Mallavia, A. Fimia, R. F. Madrigal, Appl. Opt., 38, 955 (1999)
5. D.A.Waldman, R.T.Ingwall, Proc.SPIE, 2689, 127 (1996)
6. R.L.Colvin, R.G.Larson. A. L. Harris, M. L. Schilling, J.Appl.Phys.,81, 5913 (1997)
7. S. Lelievre, J. J. A. Couture, Appl. Opt., 29, 4384 (1990)
8. G. Manivannan, R. Changkakoti, R. A. Lessard, Opt. Eng., 32, 671 (1993)
9. M. Barikani, E. Simova, M. Kavehrad, Appl. Opt., 34, 2172 (1995)
10. R. Grazymala, T. Keinonen, Appl. Opt., 37, 6623 (1998)
11. G. Manivannan, G. Mailhot, M. Bolte, R. A: Lessard, Pure Appl. Opt., 3,845 (1994)
12. Y.Liu, H.Wang, M. Tian, J.Lin, X. Kong, S. Huang, J. Yu, Opt.Lett., 20, 1495 (1995)
13. S. Blaya, L. Carretero, R. Mallavia, A. Fimia, R. F. Madrigal, M.Ulibarrena, D. Levy, Appl. Opt., 37, 7604 (1998)

14. F. Djouani, Y. Israëli, L. Frezet, A. Rivaton, R. A. Lessard, M. Bolte, J. Polym. Sci. Part A: Polymer Chem., 44, 1317 (2006)
15. G. Manivannan, P. Leclere, S. Semal, R. Changkakoti, Y. Renotte, Y. Lion, R. A. Lessard, Appl. Phys. B: Lasers Opt., 58, 73 (1994)
16. M. Bolte, G. Agarwal, C. Pizzocaro, C. Lafond, R. A. Lessard, Proc. of SPIE, 4087, 671 (2000)
17. M. Bulinski, V. Kuncser, C. Plapcianu,S. Krautwald, H. Franke, P. Rotaru, G. Filoti, J. Phys. D: Appl. Phys., 37, 2437 (2004)
18. M. C. Valsangiacom, M. Bulinski, I. Iova, G. Schinteie, C. Kuncser, G. Filoti, D. Bejan, Roman. Reports. Phys., 55, 283 (2003)
19. V. Kuncsery, G. Filotiy, R. Podgorsekz, M. Biebricherz, H. Frankez, J. Phys. D: Appl. Phys., 31, 2315 (1998)
20. S. Blaya, L. Carretero, A. Fimia, R. Mallavia, R. F. Madrigal, R. Sastre, F. A.Guerri, J. Mod. Opt., 45, 2573 (1998)
21. I. Naydenova, E. Mihaylova, S. Martin, V. Toal, Opt. Exp., 13, 4878 (2005)
22. M. Ortuño, E. Fernández, S. Gallego, A. Beléndez, and I. Pascual, Opt. Exp., 15, 12425 (2007)
23. C. Solano, G. M. Ponce, C. Castaneda, Appl. Opt., 17, 5207 (2006)
24. V.Weiss, E Millul, Appl. Surf. Sci., 106, 293 (1996)
25. S. Blaya, L.Carretero, R.F Madrigal, A.Fimia, Jpn. J. Appl. Phys., Part 1 - Regul. Pap. Short Notes Rev. Pap., 41, 3730 (2002)
26. R.T.Ingwall, M.Troll, Opt. Eng., 28, 586 (1989)
27. W.J. Tomlinson, E.A Chandross, H.P. Weber, G.D. Aumiller, Appl.Opt., 15, 534 (1976)
28. S. Blaya, R. Mallavia, L. Carretero, A. Fimia, R. F. Madrigal, Appl. Phys. Lett., 73, 1628 (1998)
29. G. Q. Xia, W. S.Lian, H. M.Ju, G. F.Xi, Chin. Phys., 14, 2004 (2005)
30. K Pavani, I Naydenova, S Martin, V Toal, J. Opt. A: Pure Appl. Opt., 9, 43 (2007)
31. R.H. Kayser, R.H Young, Photochem.Photobiol., 24, 395 (1976)
32. S. Cohen, A.Parola, G.H. Parson, Chem. Rev., 73, 141 (1973)
33. M. Ushamani, K. Sreekumar, C. S.Kartha, and R. Joseph, Appl. Opt., 43, 3697 (2004)

34. L.P.Krul, V. Matusevich, D. Hoff, R. Kowarschik, Y.I Matusevich, G.V.Butovskaya1, E.A.Murashko1, Opt.Exp., 15, 8543 (2007)
35. J.H. Liu, F.T. Wu, J.Poly. Research, 11, 1022 (2004)
36. B. M. John, Ushamani M, K.Sreekumar, R. Joseph, C.S. Kartha, Appl. Opt., 46, 346 (2007)
37. M. L. Schilling, V. L. Colvin, L. Dhar, A. L. Harris, F. C. Schilling, H. E. Katz, T. Wysocki, A. Hale, L. L. Blyler, C. Boyd, Chem. Mater., 11, 247 (1999)
38. C. Pizzocaro, R.A. Lessard, M Bolte, Can. J. Chem., 76, 1746 (1998)
39. T. Galcera, X. Jouan, M. Bolte, J. Photochem. Photobiol.A, 45, 249 (1988)
40. M.Bolte, R.A.Lessard, Y.Israeli , A.Rivaton , Proc. Holography 2005, Materials for holographic and optical data storage, CLOSPI – BAS (2005)
41. C.G.Stojanoff, P. Froning, Proc. SPIE, 3417, 154 (1998)
42. M. Ushamani, K.Sreekumar, C.S. Kartha, R. Joseph, J. Mod. Opt., 51, 743 (2004)
43. M.Ushamani, K.Sreekumar, C.S. Kartha, R. Joseph, Proc. SPIE 5290, 352 (2004)
44. B. M. John, M.Ushamani , V.S.Nisha, R. Joseph, K.Sreekumar, C. S. Kartha, Proc. of Intl. Conf. APT- 04 , Cochin. India (2004)
45. R.A.Lessard, M. Bolte, Y. Israeli, A. Rivaton, Proc. Intl. Conf. on Optics and Optoelectronics -ICOL 2005, Dehradun, India (2005)
46. R. M. Beaulieu , R A. Lessard, Proc. SPIE, 4087, 1298 (2000)
47. S. H. Lin, K. Y. Hsu, W. Z. Chen, W. T. Whang, Opt. Lett., 25, 451 (2000)
48. J. Mumbru, I. Solomatine, D. Psaltis, Opt. Commn., 194 ,103 (2001)
49. D. Sankar, P.K. Palanisamy S. Manickasundaram , P. Kannan, Opt. Mater., 28 ,1101 (2006)
50. A. Baum, P. J. Scully, M. Basanta, C. L. P. Thomas, P. R. Fielden, .N. J. Goddard, Opt.Lett., 32,190 (2007)
51. W. S. Kim, H.S. Chang, Y.C. Jeong, Y.M. Lee, J.K. Park, Opt. Mater., 27, 1190 (2005)
52. W. S. Kim, H.S. Chang, Y.C. Jeong, Y.M. Lee, J.K. Park, C.W.Shin, N. H. Tak, Opt. Commn., 249, 65 (2005)
53. F.M. Li ,Q.Y.Gao , L.Wang , J.X. Zhang , S.J. Chen , Z.C.Li , J. Polym. Sci., Part A, Polym. Chem., 35, 1087 (1997)

54. C. H. Bamford, A. D. Jenkins , Proc. Royal Soc. of London. Series A, Mathematical and Physical Sciences, 216, 515 (1953)
55. G. H. Li, S. J.Hua, L. R.Ming , G. Q.Yu, Y. Xianda, J.Henan Univ.30, 44 (2000)
56. H. J.Dong, W. Juan, J. Qingdao ,Univ. Engg. &Tech. Edn., 15, 17 (2000)
57. I. Capek, J. Barton, J. Polym. Sci.: Polym. Lett. Edn., 12, 327 (2003)
58. I.A.Banerjee, G.A.Epling, N.K. Modukuru , Euro. Polym. Jnl**,** 38 , 2383 (2002)
59. D. R. Boswell, US patent. 5753349 (1998)
60. D. R. Boswell, US patent. 5464690 (1995)
61. O. Junichi, O.Shigeru, US patent , 5236809, (1993)
62. S. Yao, X. Qin, X. Yu, Q. Zhang , G. Xu, Z. Wang, Y. Dong, X. Jing, Y. Sun, B. Huang, Trans. Nonferrous Met. Soc. China, 15, 88 (2006)
63. D R. Schoenfeld, V. Krneta, M. C. Cole, P. A. Whiteside, US Patent, 71737449 (2007)
64. D. J. Mickish, S. R. MacKara , T. J. Trout, US Patent, 5633100 (1997)
65. A.M. Weber, US Patent,5013632 (1991)
66. V.Weiss, A.A Friesem, J.Opt.Soc.Am.A ,11, 2004 (1994)
67. Ushamani M, “Studies on photosensitive polymers for optical recording” PhD Thesis, Cochin University of Science and Technology, India (2002)
68. G. Mannivannan , R Changkakotti , R.A.Lessard, J.Phys. Chem., 97, 7228 (1993)
69. B. Jeff ,Appl. Opt., 30, 1598 (1991)
70. R. P.S. Rao , K.S.Narayana, S.M. Shanker , J.Opt., 28, 15 (1999)
71. M.Ushamani, N.G. L. Deenja, K.Sreekumar, C.S. Kartha, R. Joseph, Bull. Mater. Sci., 26, 343 (2003)
72. K. Kazumasa, S. K. N. Sinji, M. Toru, K. Toshihiro , Appl. Opt., 37, 3038 (1998)
73. B. M. John, M.Ushamani, R. Joseph, K.Sreekumar, C.S.Kartha, J. Mod. Opt., 53, 343 (2006)
74. V.Weiss, E.Millul, A.A. Friesem , Proc. SPIE, 2688, 11 (1996)
75. M. Ushamani, V.S.Nisha, B. M. John, K. Sreekumar C.S. Kartha, R. Joseph, Proc. of MACRO-2004 , Trivandrum, India (2004)
76. M.Ushamani, K.Sreekumar, C.S. Kartha, R. Joseph, Appl. Opts., 41,1984 (2002)
77. G. Pradeep, S.Cyriac, S. Ramkumar , C Sudha Kartha, Jpn. J. Appl. Phys., 38, (1999)

78. S.Gallego, C.Neipp, M.Ortuno, A .Marquez, A. A.Belendez, I.Pascual, Appl. Opt., 42, 5839 (2003)
79. H. Yao, M.Huang, Z. Chen, L. Hou, F. Gan, Mat. Lett., 56, 3 (2002)
80. L. Carretero, A. Murciano, S. Blaya, M. Ulibarrena , A. Fimia, Opt. Exp., 12, 780 (2004)

Chapter 5

Studies on Dye Sensitized Poly(vinyl alcohol)/ Acrylamide Films

This chapter deals with the fabrication and characterization of methylene blue sensitized poly(vinyl alcohol)/acrylamide (MBPVA/AAm) films. Though MBPVA/AAm is an already studied holographic material, its composition was optimized to have better efficiency. The preparation technique is also different and no pre-exposure, UV curing or thermal treatment was employed. The feasibility of using MBPVA/AAm as a panchromatic material is also evaluated.

5.1. Introduction

Photopolymerization based processes have been used in many fields such as the fabrication of integrated circuits, microlithography, optical data storage and holography. Photopolymerizable materials are good media for holographic interferometry and non-destructive holographic testing [1]. The mechanism of recording holograms in these materials implies photopolymerization processes in the illuminated zones that produce a modulation in the refractive index (RI). The advantage of these systems is that they can be treated as pure volume holograms with high diffraction efficiency (DE) and can be monitored in real time. Acrylamides (AAm) have been widely used in holography for the late 70's onwards and an improvement was achieved when methylene bisacrylamide (MBA) was added to speed up the polymerization reaction [2-7]. Acrylamide-based PVA films constitute a low-cost organic material, and a great deal of attention has been given to the composition of an acrylamide-based photopolymer system initiated by triethanolamine (TEA) and methylene blue (MB) [8-9]. The reported efficiency for MBPVA/AAm system is 60% for an exposure of 50 mJ/cm^2 [10]. In the reported works, the films were prepared by spin coating and all the film constituents were of the highest grade available [11]. In the present work the chemicals used were of ordinary laboratory grade and the films were fabricated using gravity settling method. As each composition of the photopolymer will influence its characters greatly, it is important to optimize the compositions [12]. As explained in the reported works, no pre-exposure or UV curing were done on this material [13].

5.2. Film Fabrication

The photopolymer solution used in the present study comprises of PVA, AAm, MB and TEA. AAm crystals were dissolved in the PVA solution and it was sensitized with MB and TEA. The films were prepared using gravity settling method at room temperature. To optimize the film composition, the concentrations of the constituents were varied and the composition which gave highest DE was selected as the optimum value. The thickness of the film was varied by changing the wt. % of PVA solution used for film fabrication.

As the technology of film preparation is transferred to M/S. Light Logics Holography & Optics. Pvt. Ltd., Trivandrum, India, the finer details of the film composition is not included in the thesis.

5.3. Experimental Details

The absorption spectra of the MBPVA/AAm films were recorded using JASCO V-570 spectrophotometer. A glass plate coated with PVA /AAm was used as the reference plate. As the film shows highest spectral sensitivity in the red region, a 15 mW, CW, polarized He-Ne laser having emission at 632.8 nm was used for the optimization of film constituents. The film composition was optimized by grating recording and DE measurements as explained in section 2.9.2 and 2.10. The recording parameters like beam- ratio, inter-beam angle and exposure energy were also optimized so as to have highest efficiency.

5.4. Optimization of Acrylamide

MBPVA/AAm films were fabricated by keeping MB and TEA concentration as constant. AAm concentration was varied from a_1 to a_7. The films were labeled as $A_1, A_2, \ldots A_7$; where the AAm concentration $a_1<a_2<\ldots<a_7$. A_0 is the MBPVA film without AAm. In all cases, films with good optical quality were obtained. Above a_7 concentration, AAm crystallize and the film losses its properties. The thickness of the films was 120µm. The AAm concentration was optimized by characterizing the films as follows.

Real time transmittance studies were carried out by exposing the samples to a power density of 5mW/cm^2 for 5 minute and the relative transmittance is plotted in Fig.5.1. Films with higher concentration of AAm showed higher values of relative transmittance. At 700 mJ/cm^2, all films reached the saturation state and above which the transmittance remained the same.

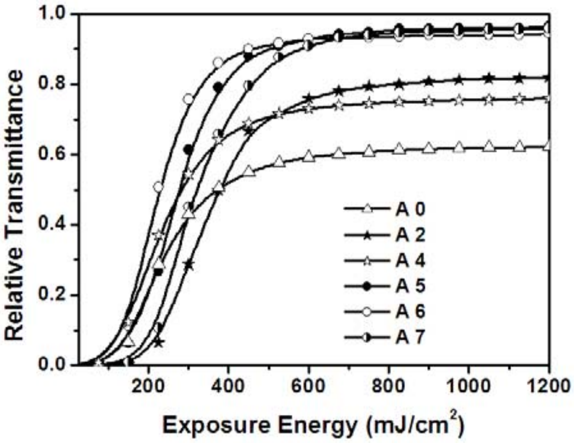


Fig. 5.1 Real time transmittance of films with different AAm concentration

To optimize the AAm concentration, gratings were recorded on these films at a fluence of 500 mJ/cm^2 by keeping the beam intensity ratio as 1:1 and spatial frequency as 625 lines/mm. The variation of DE with AAm concentration is plotted in Fig.5.2. As the AAm concentration increased, the DE increased and reached a maximum of 36% (A_5 sample). This is because, as the monomer concentration increases, the number of monomers getting polymerized increases, which results in a large RI modulation and the DE increased. However, it is impossible to increase the concentration of AAm indefinitely because the compatibility and solubility of this monomer in the polymer film are limited. At high concentration of AAm, this monomer precipitates on the surface of the film; this gives rise to the observation of noise gratings, which are produced by the interference of the scattered light of these solid particles with the incident laser beam in the process of hologram formation. Moreover, high concentration of AAm makes the film shrink greatly [11]. The decrease in efficiency at higher concentration may be due to the noise gratings.

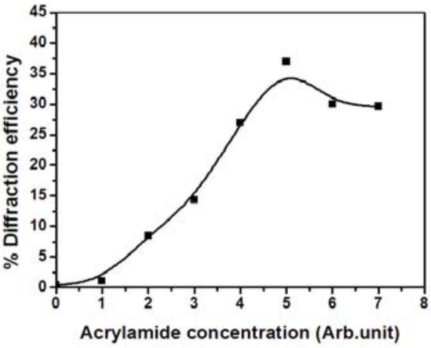


Fig.5.2 The variation of DE with acrylamide concentration

On laser exposure, the monomers in the exposed region get polymerized and there exist a change in the RI values of the unexposed regions and exposed regions. The RI modulation arises when the films were uniformly illuminated to a fluence of 500 mJ/cm^2 is determined using an Atago refractometer and is plotted in Fig.5.3. The change in RI also is found to be highest (0.042) for A_5 sample, which showed highest efficiency. Because of the monomer diffusion, there can be slight variation in the RI modulation when illuminated with fine fringes.

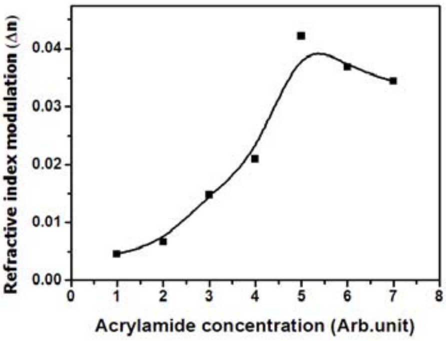


Fig.5. 3 The refractive index modulation arises on laser exposure

5.5. Optimization of Beam Ratio

The intensity ratios of two beams were varied by placing attenuators in the path of one beam. To find out the optimum beam ratio, gratings were recorded on film with optimum AAm concentration by maintaining the exposure energy as

500 mJ/cm^2. The DE for different beam ratios is plotted in Fig.5.4. Maximum efficiency was obtained for a beam ratio of 1:1, where the fringe visibility is nearly unity.

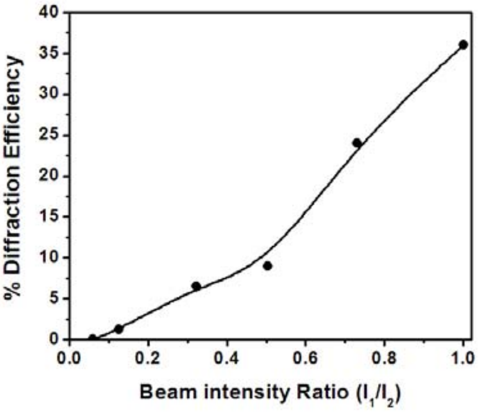


Fig.5.4 The plot of DE with different beam ratios

5.6. Optimization of Dye Concentration

MBPVA/AAm films were fabricated with optimum AAm concentration (A_5 sample) and the MB concentration was varied from c_1 *to* c_9. The films were labeled as C_1, C_2, ….. ,C_9 where the dye concentration of $C_1 < C_2 < …. < C_8 < C_9$. Real time transmittance was monitored by exposing the samples to a power density of 5 mW/cm^2 for 5 minute and Fig.5.5 is the plot of relative transmittance Vs exposure energy. Relative transmittance was highest for films with lower dye concentration. In the case of films with higher dye concentration, the given exposure may be insufficient to convert all the dye molecules to leucoform and hence the decrease in relative transmittance. In the case of films with lower dye concentration, there exists considerable increase in relative transmittance even at 50 mJ/cm^2. Hence further studies were carried out by exposing the samples to an energy density of 50 mJ/cm^2.

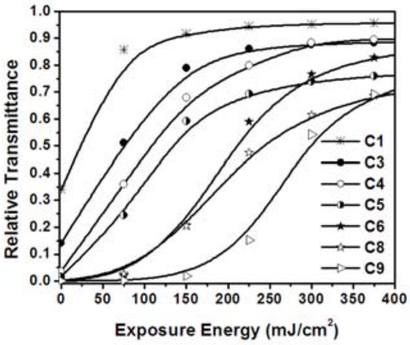


Fig. 5.5 Relative transmittance Vs exposure energy for samples with different MB

Each film was exposed to an energy density of 50 mJ/cm^2 and the absorption spectra of the exposed regions and that of the unexposed regions were recorded. When the films were exposed to laser beam, the dye molecules get excited and undergo intersystem crossing and converted to leuco form. Hence the absorbance decreases on laser exposure. Fig.5.6 shows the absorption spectra of C_1 film. The change in absorbance or absorbance modulation on laser exposure was determined for each MB concentration and was plotted in Fig.5.7. The absorbance modulation is highest for C_4 films.

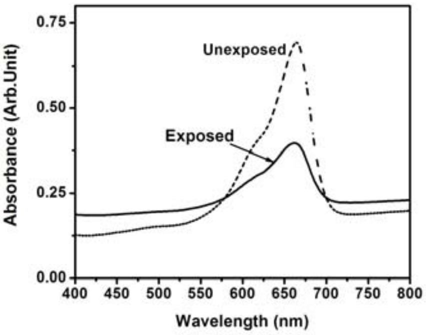


Fig.5.6 The absorption spectra of C_1 film

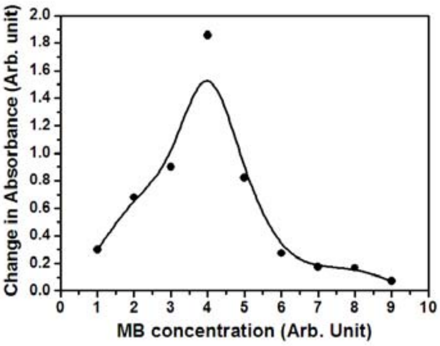


Fig. 5.7 Absorbance modulation on laser exposure for films with different MB concentration

RI of films having different dye concentration was measured for both exposed and unexposed regions. The RI modulation on laser exposure (50 mJ/cm^2) was determined for each case and the plot of RI modulation with dye concentration is shown in Fig.5.8. The highest RI modulation was obtained for C_3 films.

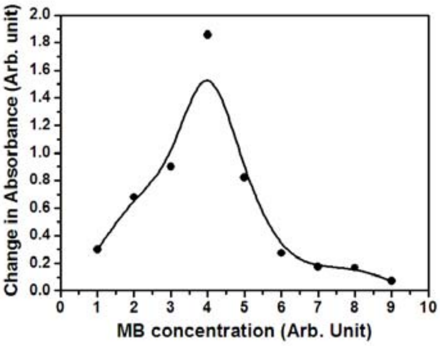


Fig. 5.8 Plot of refractive index modulation with dye concentration

In order to optimize the dye concentration, gratings were recorded on the films by keeping the beam intensity ratio as 1:1 and spatial frequency as 1100 lines/mm. The variation of DE with MB concentration is plotted in Fig.5.9. The efficiency initially increased with dye concentration and showed highest efficiency of 54% for C_3 films. When the dye molecules are more, more photons will be absorbed, thus increasing the number of excited states of the dye, which will increase the monomer's polymerization rate [11]. This increase in the polymerization rate and absorbance modulation leads to an increase in efficiency with dye concentration. The efficiency was decreased for films with dye concentration above c_3. The decrease in DE is due to the possible competitive polymerization mechanism that is produced when high concentrations of the dye are used [14]. Because at high concentration, the dye forms dimeric state, which is involved in a polymerization termination reaction, resulting in a decrease in the overall rate of polymerization. After those dye molecules participating in the polymerization have been consumed, the dimeric molecules of the dye will decompose; the monomers in the material will polymerize perfectly as long as the exposure time is long enough. The decomposition process of the dimeric dye influences the polymerization rate, leading to the decrease in the sensitivity of material. In other words, at high dye concentration, the given exposure is insufficient. However, the films with highest RI modulation showed highest efficiency and hence it is clear that the RI modulation contributes more to DE rather than the absorbance modulation.

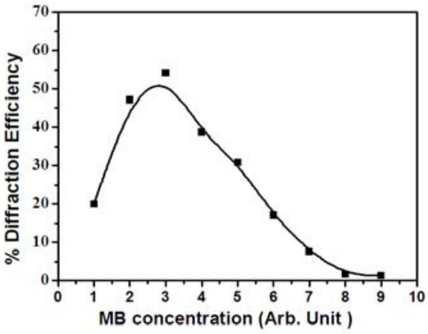


Fig. 5.9 The variation of diffraction efficiency with MB concentration

5.7. Optimization of Electron Donor

To observe the photoreduction in MB an ED is necessary and certain types of amines can provide electron to photoexcited MB via the transitory formation of a charge transfer complex, which is believed to be produced [15-17]. Amine groups can cause the fastest photobleaching effect on MB, as they contain a nitrogen atom attached to at least two alkyl groups and these groups have an electron donating inductive effect on the nitrogen atom. To find the effect of different EDs, MBPVA/AAm films were fabricated with TEA, triethylamine, dimethyl formamide (DMF) and hexamine. The concentration of each co-initiator was kept similar (say, x). Gratings were recorded on all these films by varying the exposure energy at a spatial frequency of 1100 lines/mm and the efficiency is plotted in Fig.5.10. Among the different films, TEA doped films showed high efficiency. DMF and hexamine doped films showed poor efficiency and it was less than that of the films without ED. It has been investigated that EDs do not always favor the redox process [18-19]. And the electron donating power of TEA is higher than that of triethylamine due to the lone pair of electrons in the oxygen atom. As the TEA doped films showed highest efficiency and sensitivity, the concentration of TEA was varied and the efficiency is plotted in Fig.5.11. Films with different TEA are labeled as T_1, T_2, T_3 and T_4 and the film without TEA is labeled as T_0, where the concentration of $T_1 < T_2 < T_3 < T_4$.

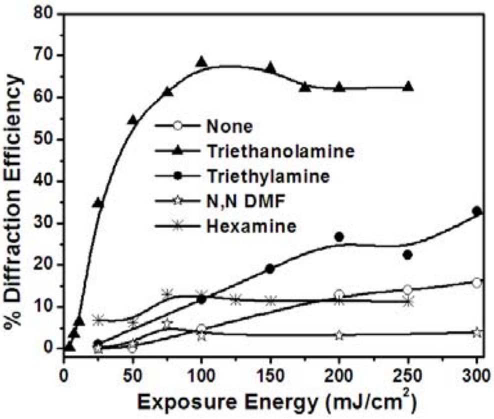


Fig. 5.10 DE of MBPVA/AAm film with different electron donors

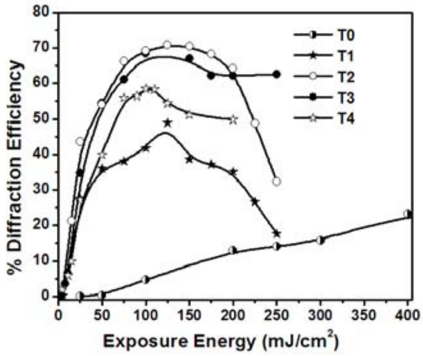


Fig. 5.11 Optimization of TEA concentration: DE with exposure

T_2 films showed highest efficiency of 70% for an exposure of 120 mJ/cm^2. The DE remained almost constant with change in the concentration of TEA, but the sensitivity at low exposure is influenced greatly by the concentration of TEA. At high concentration of TEA, the film becomes sticky and the drying period is long and it makes the film shrink more.

5.8. Optimization of Exposure

The variation of absorbance modulation and RI modulation on laser exposure was determined for the optimized film and are plotted in Fig.5.12 and Fig.5.13 respectively. With the increase in exposure, both the modulations which contribute to DE were found to be increased and remained constant at 120 mJ/cm^2. When gratings were recorded on the optimized film by varying the exposure energy, highest efficiency of 70% was obtained for an exposure of 120 mJ/cm^2 (Fig.5.11). The efficiency initially increased with exposure and remained constant and thereafter decreased. The decrease in DE at higher exposure might be caused by the cross-talk of gratings. The main sources of noise are the surface deformation of the recording material, random scatter caused by the granularity of the recording material and nonlinear recording of the signal wave. When the exposure increased, the cross talks increase much quicker resulting in more output signal being scattered, and the DE decreased [11]. Though films were fabricated with thickness ranging from 60 to 130μm, the efficiency and sensitivity were not improved.

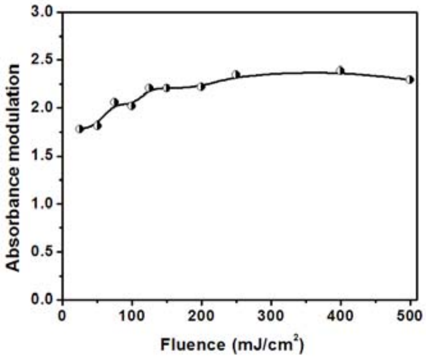


Fig. 5.12 The variation of absorbance modulation with exposure

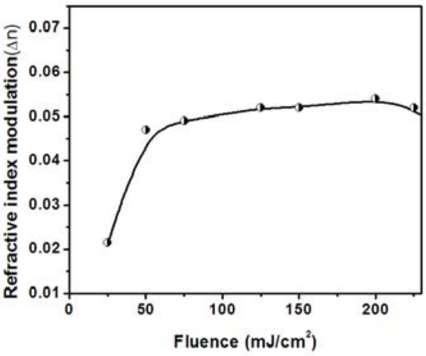


Fig. 5.13 The variation of refractive index modulation with exposure

5.9.Thickness Modulation

When the polymer films are exposed to laser beam, the thickness of the exposed regions is less than that of the unexposed region. Fig.5.14 is the surface profile of MBPVA/AAm film, when illuminated with a laser beam of uniform intensity. It is evident that a grove is formed in the exposed region. On laser exposure different polymer chains come closer and the exposed regions get compressed and the groove formation may be due to this phenomenon. The thickness modulation was found to be increased with exposure. The thickness modulation at different exposure was determined and is plotted in Fig.5.15.

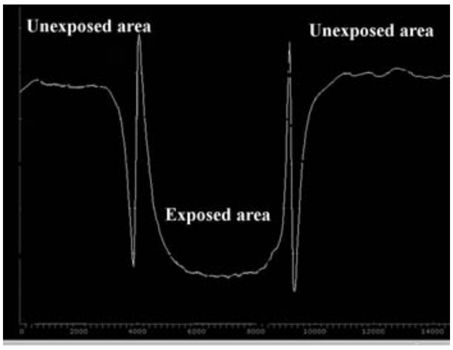


Fig. 5.14 The surface profile of MBPVA/AAm film on uniform illumination

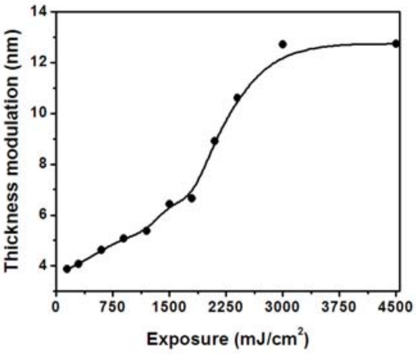


Fig. 5.15 The thickness modulation at different exposure

5.10. Efficiency on Storage

The DE of the gratings recorded on the optimized film at 125 mJ/cm^2 was monitored for days and the variation of efficiency is plotted in Fig.5.16. The films were kept in dark and no pre or post exposure was applied as in the reported works [13, 20]. And the reconstructed power was 0.8µW. It was observed that the gratings are not stable in MBPVA/AAm film and the DE was decreased on storage. Though the efficiency was decreased from 70% to 10% within 6 days, the gratings could be read for months with low efficiency. The decrease in efficiency is due to the diffusion of unreacted monomers from destructive to constructive interference region and the polymerization may continue even in the dark. Another reason is the instability of leuco state. From the plot of the absorption spectra (Fig.5.17) on storage, it is evident that the leuco dye is not stable. When the gratings were illuminated, the dye molecules absorb a portion of the reconstruction beam and as a result the efficiency decreases. The efficiency was found to be decreased, irrespective of the dye concentration and the drop in efficiency was more prominent at higher dye concentrations.

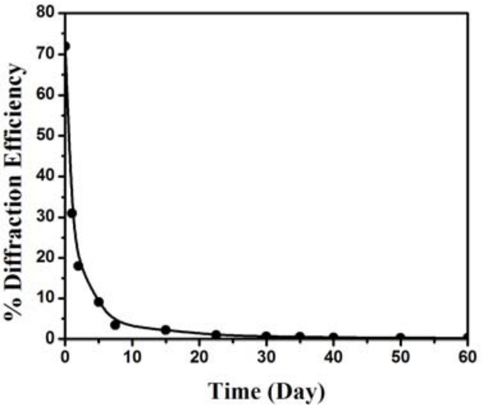


Fig. 5.16 The DE of MBPVA/AAm on storage

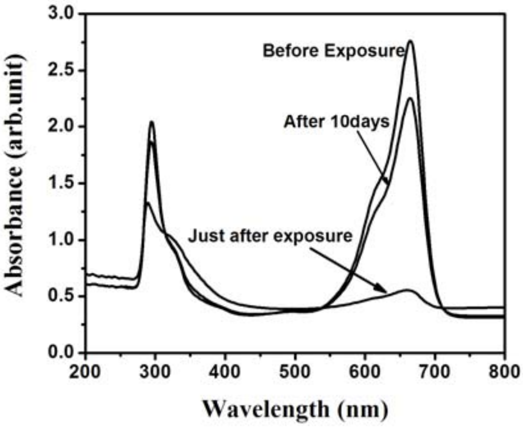


Fig. 5.17 The absorption spectra on storage

5.11. Shelf Life of the Film

To determine the shelf life of the film, gratings were recorded on the MBPVA/AAm film on each day after preparation (drying) of the film. The films were kept in a dark box at room temperature. The films showed the highest efficiency of 70% only for few days after preparation. The efficiency was found to be decreased on ageing of the film and gratings could not be recorded on films prepared 6 months before. Fig.5.18 is the decrease of DE with ageing of the samples. The decrease in efficiency with ageing is due to the polymerization of monomer with ageing of the film. The film quality was unaffected on ageing and the dye is not faded on ageing. The variation of maximum absorbance of films with ageing is plotted in Fig.5.19 and it remained the same on ageing. The variation of RI modulation on ageing is determined and depicted in Fig.5.20. The index modulation decays on ageing and it is the reason for the decrease in efficiency on ageing of the samples. The shelf life of the commercially available polymer solution, Polygramma, is also limited to less than 6 months when the solution is kept at below 20°C [21].

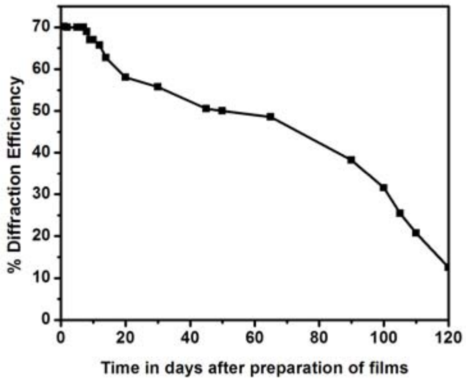


Fig. 5.18 the DE on ageing of the sample

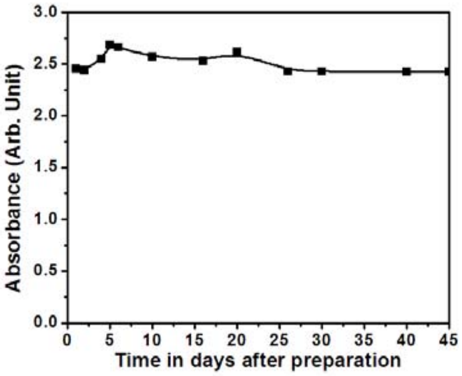


Fig. 5.19 The maximum absorbance of unexposed films on ageing

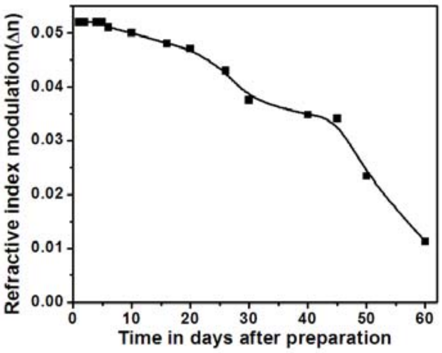


Fig. 5.20 The refractive index modulation on ageing of the film

5.12. Resolution of the Film

To find out the resolution of the material, gratings were recorded on the optimized film at different inter-beam angles by keeping the exposure energy as 120 mJ/cm^2. Spatial frequency of each grating was determined using Bragg equation. Fig.5.21 is the plot of variation of DE with spatial frequency. The efficiency was almost constant when the inter-beam angle changed from 25^0 to 50^0. This corresponds to a spatial frequency of 625-1350 lines/mm. At higher spatial frequencies, the DE decreased.

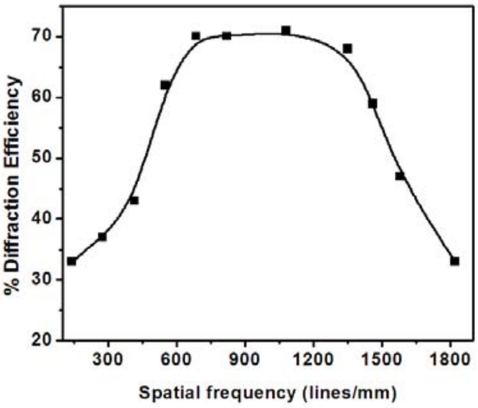


Fig. 5.21 The variation of diffraction efficiency with spatial frequency

5.13. Surface Profile of the Material

The surface mapping of the gratings was done using Dektak 6-M stylus Profilometer. The surface mapping of both unexposed film and grating recorded film is shown in Fig.5.22. Here 'A' is the unexposed region and 'B' is the region where grating with 100 lines/mm is recorded. Fig.5.23 is the surface profile of the gratings recorded with a spatial frequency of 1600 lines/mm (fringe spacing~0.63µm). Here the depth of each fringe is 4 nm. As it is negligible compared to the recording wavelength, the grating formed is not a surface relief.

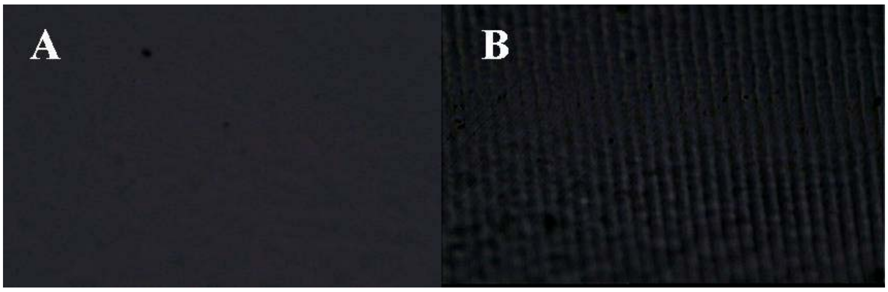


Fig. 5.22 The surface mapping of unexposed film (A) and grating recorded film (B)

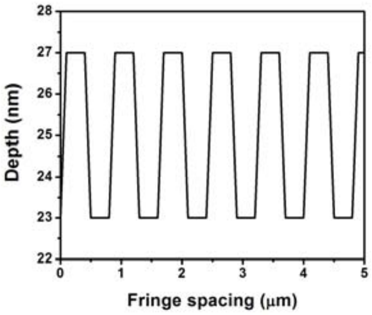


Fig. 5.23 The surface mapping of the gratings recorded with 1600 lines/mm

5.14. Bragg Detuning

Bragg detuning effect and asymmetry of DE are serious problems if a photopolymer is used as a holographic recording material. The critical reasons are bulk RI change and shrinkage of the recording materials [22-23]. To find out the Bragg detuning of the grating and hence the shrinkage of the photopolymer material, angular response of the grating was monitored. This is done by varying the angle of reconstructed beam and by monitoring the diffracted beam intensity. As it was easier to control, the film was rotated instead of the laser beam. The angular response was monitored for days after recording of the grating and is shown in Fig.5.24. Just after recording, the films showed a DE of 73% and the lateral lobes (second order diffracted beam) are having an efficiency of ~7%. As the first order diffracted peak was not very sharp (width is 1°), great care should be given during angular multiplexing. On storage a shift in the diffracted peak was observed and is due to the shrinkage of the material. One week after recording, the efficiency decreased to 10% and the central maximum was shifted. The corresponding shift was 0.35degree which is a measure of the shrinkage of the polymer material.

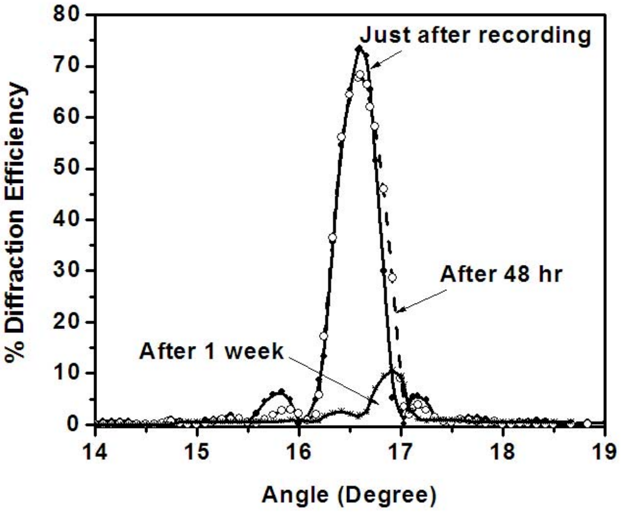


Fig.5.24 The angular response of MBPVA/AAm on storage

5.15. Angular Multiplexing

To find out the dynamic range of the material, gratings were multiplexed on the optimized film using angular multiplexing. The dynamic range refers to the total response of the medium when divided up among many holograms multiplexed in a common volume of material. Physically, it depends on thickness, modulation depth and sample geometry. The dynamic range has a strong impact on the data storage density that can be achieved in a material. Angular multiplexing was done by recording a number of gratings on the same area by varying the angle.

For this gratings were recorded on the films at four different angles (30°,25°, 20°,15°) separated by 5° between recordings for an exposure of 25mJ/cm^2. This angle was chosen so that the first order diffracted peak of each grating would not contribute to the DE of neighboring gratings. Though the first order diffracted peak spread only 1°, the 2nd orders also have considerable efficiency. Therefore in order to avoid the cross talk, the angular separation was selected as 5°. Gratings were multiplexed on freshly prepared film, one month and three month old films. The efficiency of each grating on multiplexing with the corresponding angle (inter beam angle) is plotted in Fig.5.25. The efficiency of each grating on the freshly prepared sample was 50%, 6.6%, 0.29 % and 0.09 % respectively. As the efficiency decreased with the number of multiplexed gratings, further recordings were not carried out. The decrease in efficiency with the number of multiplexed gratings is due the less RI modulation on each recording. The majority of the diffracted energy is concentrated in the first grating and to increase the uniformity of multiplexed gratings, it is necessary to progressively increase the exposure energy for the successive gratings. It is already reported that the dynamic range is not shared equally among gratings recorded with equal exposure energy within the polymer layer [7].

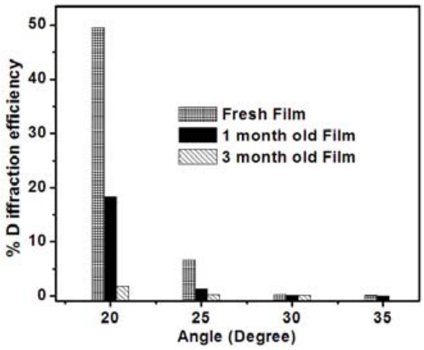


Fig. 5.25. The efficiency of gratings multiplexed with an exposure of 50mJ/cm^2

So in order to obtain gratings of equal efficiency; a number of trials have been done by varying the exposure energies for each recording. Finally gratings with ~4% efficiencies were obtained for the exposure energies 4 mJ/cm^2, 8 mJ/cm^2, 16 mJ/cm^2 and 32mJ/cm^2. The efficiency of each grating on multiplexing to have same efficiency is plotted in Fig.5.26. The dynamic range (M#) of films with optimized film constituents (thickness =120μm) is calculated as 0.826. The dynamic range of a recording medium highly depends on the film thickness and hence it could be improved by increasing the film thickness. The M# of an erythrosine B doped PVA/AAm film with thickness of 160μm was 3.6 (where 30 gratings with ~1% efficiency were multiplexed using angular and peristrophic multiplexing) [7]. The polymer developed by InPhase Technology (formulations 523 530) with film thicknesses 200μm and 1.5mm showed M# of 6.7 and 50 respectively [24].

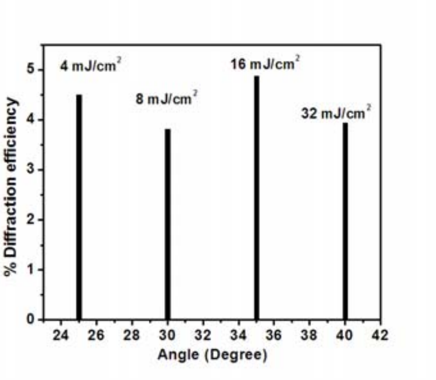


Fig. 5.26The diffraction efficiency of gratings multiplexed to have equal efficiency

5.16. Recording of FT Hologram

In holographic data storage devices, data pages are recorded using fourier transform (FT) holography. By using this technique, two dimensional holograms can be recorded on the material with diminutive consumption of sample area and the noise in the image could be reduced by incorporating suitable filters in the fourier plane. Usually, in storage devices the object beam is allowed to pass through a spatial light modulator (SLM), but in the present study the object beam was passed through a transparency containing few letters. FT holograms were recorded using the experimental setup illustrated in section 2.13 [25]. The FT of the letters was constructed using lenses and was allowed to interfere with an unexpanded beam (reference beam). This interference pattern was recorded on the film. After recording, the images were reconstructed by illuminating with the reference beam. The reconstructed image was photographed using a CCD camera (Pixelfly PCO 225x7346). Fig.5.27 shows the FT hologram of letter ‘A’ recorded on MBPVA/AAm doped film, where (A) is the object, (B) FT and (C) the reconstructed image.

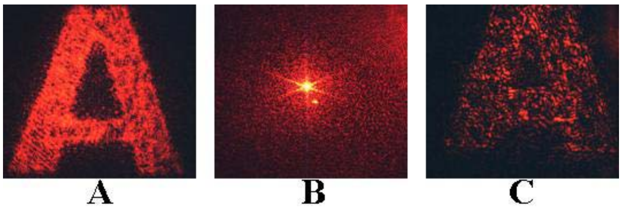


Fig.5.27. FT hologram of letter ‘A’

5.17. Recording of Hologram

Possibly the most exciting art of laser is in recording holograms and it has wide application in various fields. Transmission holograms were recorded on MBPVA/AAm films using the experimental setup described in section 2.14. The photograph of the recorded hologram is shown in Fig.5.28. Though the holograms were recorded using a He-Ne laser (632.8 nm), the holograms could be reconstructed with other wavelengths also. Fig.5.29 is the photograph of the hologram reconstructed using a Frequency doubled Nd:YAG laser.

Fig.5.28 The photograph of the hologram recorded and reconstructed using He-Ne laser

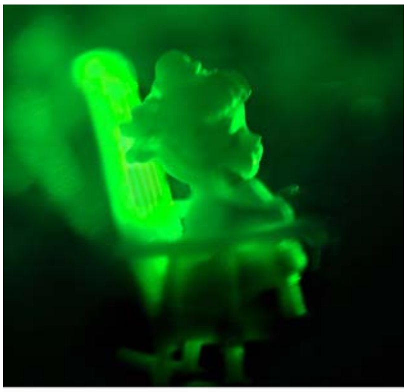


Fig.5.29 The photograph of the hologram recorded using He-Ne laser and reconstructed using Freq. doubled Nd:YAG laser

Most of the photopolymers commercialized for display applications are available in liquid form and one of them marketed in solid form, DuPont films, are denied to our country for last couple of years. As the material is economic, possessing high efficiency and having considerable storage life, it finds applications in display holography, holographic interferometry, holographic optical elements etc.

5.18. Using Lower Wavelength Lasers

Though the spectral sensitivity of MB is highest in the red region, it has sensitivity in the entire visible region [26]. So gratings could be recorded on these films using wavelengths lower than 632.8 nm. The lasers used for characterization include frequency doubled Nd: YAG laser (532 nm, 20mW), 43 series Ar^+ laser (488 nm, 140 mW) and blue emission from a switchable He-Cd laser (442 nm). As the storage capacity is inversely proportional to the recording wavelength, the storage capacity could be improved with lower wavelength lasers.

The absorption spectra shown in Fig.5.30 enlighten the spectral sensitivity of the material. The absorption spectra were recorded by exposing the films to a power density of 5 mW/cm^2 for 5 minutes by using four different wavelengths.

Highest absorbance modulation of 1.695 was obtained while using a He-Ne laser, whereas that obtained using 442 nm He-Cd laser was only 0.953.

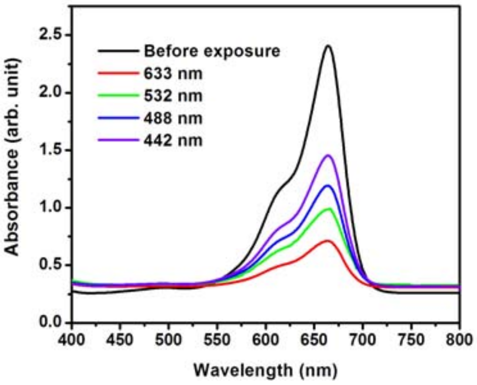


Fig. 5.30 The optical absorption spectra of the polymer film before and after exposing to different wavelengths.

Gratings were recorded using four different lasers by maintaining the inter-beam ratio as 1:1 and the inter beam angle as 50°. The spatial frequencies while using He-Ne, Nd:YAG, Ar^+ and He-Cd lasers are 1350 lines/mm, 1590 lines/mm, 1730 lines/mm and 1920 lines/mm respectively. The DE measurements were done by illuminating the gratings with a 1µW He-Ne laser beam. While recording with a He-Ne laser, 70% efficiency was obtained for an exposure of 120 mJ/cm^2. The exposure required to have the highest efficiency (70%) while using a 532 nm laser is 250 mJ/cm^2 and for 488 nm laser the optimum exposure requirement is 900 mJ/cm^2. Whereas the efficiency obtained while using He-Cd laser 442 nm) was only 23% for an exposure of 3200 mJ/cm^2. Fig.5.31 shows the variation of DE with exposure for different wavelengths. As the absorbance (Fig.5.30) of the film at 400 nm is same as that at 442 nm, it is expected to have the same efficiency (~20%) upto 400 nm. Hence the material could be used in the entire visible region. When the gratings were reconstructed using the recording wavelengths itself, almost the same efficiencies were obtained.

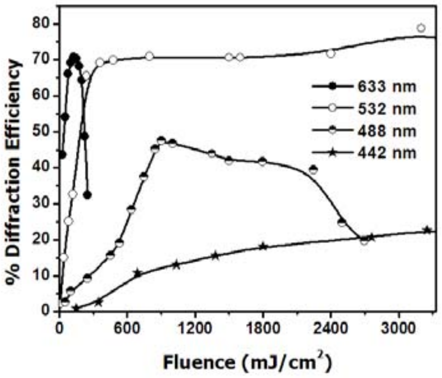


Fig. 5.31 Variation of DE with recording fluence using four different wavelengths

Transmission holograms were recorded on MBPVA/AAm films using the experimental setup described in section 2.13. The photographs of the holograms recorded using He-Ne, Nd:YAG, Ar^+ and He-Cd lasers are shown in Fig. 5.32.(a), 5.32.(b), 5.32.(c) and 5.32.(d) respectively. The holograms were reconstructed with the recording wavelengths itself.

(a) (b) (c) (d)

Fig. 5.32. Transmission hologram recorded using He-Ne laser (a), Nd: YAG laser (b), Ar^+ laser (c) and He-Cd laser (d)

Fimia *et al.* reported a panchromatic photopolymer system (~20% efficiency) consist of three monomers (AAm, MBA and zinc acrylate), and two different dyes (4,5-diiodosuccinylfluorescein (2ISF) and MB in 1:1 molar ratio) and sodium *p*-toluenesulphinate as co-initiator [9,27]. Another panchromatic material consists of PVA and AAm, with a photo initiator system formed by a 1:1 molar mixture of the Rose Bengal and MB [28]. Under irradiation with 514 or 633 nm wavelengths, those films showed 35-64% DE and the spatial resolution was 1000 lines/mm. A Chinese research group has improved the efficiency of PVA-AAm system containing RB-MB photoinitiator system with the incorporation of MBA. The efficiency obtained using 633nm was ~80% where it was 40% when gratings were recorded using 488 nm Ar^+ laser [29]. Though DuPont has developed a panchromatic photopolymer material, after hologram formation the film has to be exposed to strong white or UV light (100 mJ/cm^2 exposure at 350-380) followed by a baking at a temperature of 120^oC for two hours in order to increase the brightness of the image [30]. Though few photopolymer films are reported as panchromatic recording media, the photopolymer system described here is important on account of its wide spectral sensitivity, efficiency and ease of fabrication.

5.19. Conclusion

MBPVA/AAm films were fabricated with gravity settling method and the composition was optimized. Gratings recorded in the optimized film for exposure energy of 120 mJ/cm^2 could give more than 70% efficiency. The dynamic range of the material is 0.8 when four holograms were angularly multiplexed on that. Both transmission holograms and fourier transform holograms were recorded on these films. The feasibility of using MBPVA/AAm as a panchromatic recording material is reported. This material is interesting on account of its efficiency, sensitivity, low cost, easiness of fabrication etc.

References

1. S. Blaya, L. Carretero, A. Fimia, R. Mallavia, R. F. Madrigal, R. Sastre , F. A.Guerri, J. Mod. Opt., 45, 2573 (1998)

2. J. Jeudym, D. J. Robillarj , Opt. Commn.,13, 25 (1975)
3. S. Calixto , Appl. Opt., 26, 3904 (1987)
4. S.Martins, A. Feelyc, V.Toal , Appl. Opt., 36, 5757 (1997)
5. I. Naydenova, E. Mihaylova, S. Martin, V. Toal , Opt. Exp., 13,4878 (2005)
6. C. Neipp, A. Belendez, S. Gallego, M. Ortuno, I. Pascual. J. T. Sheridan, Opt.Exp.,11, 1635 (2003)
7. H. Sherif, I. Naydenova, S. Martin, C.M.Ginn, V. Toal, J.Opt.A:Pure Appl. Opt.,7, 255 (2005)
8. S. Blaya , R. Mallavia, L. Carretero, A. Fimia, R. F. Madrigal, App.Phys.Lett., 73, 628 (1998)
9. A. Fimia, F. Mateos, R. Mallavia, S. Blaya, A. Beleâ andez, R. Sastre, F. A. Guerri, J. Mod. Opt., 46, 1091 (1999)
10. S. Blaya, L. Carretero, R.F. Madrigal, A. Fimia, Jpn. J. Appl.Phys., 41, 3730 (2002)
11. H. Yao, M. Huang, Z. Chen, L. Hou, F. Gan, Mater Lett., 56, 3 (2002)
12. S. Gallego, M. Ortuñno, C. Neipp, A. Marquez, A. Belendez, E. Fernandez, I. Pascual, 14, Opt. Exp., 5121 (2000)
13. J. A. Jenney, J. Opt. Soc. Am., 60, 1155 (1970)
14. C.S.H. Chen, J. Polym. Sci., A55, 1107 (1965)
15. W. Nickerson, J.R Merkel, Bio. Chim. Biophys. Acta., 14,303 (1954)
16. R.Kayser, R. Yong, Photochem. Photobiol., 24,395 (1976)
17. S.G. Cohen, A. Parola, G. H. Parsons, Chem. Rev., 73, 141 (1973)
18. G. Martínez-Ponce, C. Solano, 14 , Opt. Exp., 3776 (2006)
19. M. Barikani, E. Simova, M. Kavehrad, Appl. Opt., 34, 2172 (1995)
20. M.S. Donovan, T.A. Sanford, A.B. Lowe, B.S. Sumerlin, Y. Mitsukami, C.L. Mccormick, Macromol., 35, 4570 (2002)
21. http://www.polygrama.com
22. Y.Y. Kwon, K. Y. Kim, J.Y. Park, J. Y. Park, Proc. SPIE, 6488, 09 (2007)
23. H. Coufal, D. Psaltis, G. T. Sincerbox, Holographic data storage, (Springer) (2000)
24. M. Schnoes, B. Ihas, A. Hil., L.Dhar , D. Michaels , S. Setthachayanon , G. Schomberger,W.L. Wilson , www.inphase-technologies.com/technology
25. B.M. John, R. Joseph, C.S. Kartha, Proc. 19th Kerala Science Congress, 4-6 (2007)

26. B.M. John, V. Pramitha, K.P. Nimmi, K.Sreekumar, R. Joseph , C.S. Kartha, Proc. 31st OSI Symp. on Contemporary Optics and Applications,171 (2007)
27. A. Fimia, F. Mateos, R. Mallavia, S. Blaya, A. Beleandez, R. Sastre, F. A.Guerri, Proc. SPIE, 2951, 69 (1996)
28. R. Mallavia, A. Fimia, C. Garcia, R. Sastre, Proc. SPIE, 4296, 328 (2001)
29. M. Huang, S.Wang, A.Wang, Q.Gong, F.Gan, Chin. Opt. Lett., 3, 268 (2005)
30. T. H. Jeong , E.Wesley, Holosphere 16, 20 (1989)

Chapter 6

Effect of Chromium Doping on the Diffraction Efficiency of Methylene Blue Sensitized PVA/Acrylamide Films

The diffraction efficiency of methylene blue sensitized poly (vinyl alcohol)/ Acrylamide (MBPVA/AAm) films was found to be decreased on storage. The storage life of the grating was improved with the incorporation of ammonium dichromate. This Chapter details the effect of chromium doping on the efficiency, sensitivity and storage life of MBPVA/AAm films. Interestingly, a self enhancement in efficiency was observed for a particular ratio of methylene blue and ammonium dichromate.

6.1. Introduction

To date, many photopolymers have been investigated for their suitability as holographic recoding media. Among those, dye sensitized PVA/Acrylamide films are important on account of its high diffraction efficiency (DE), high SNR, ease of fabrication etc [1-8]. The acrylamide (AAm) based films generally consist of a binder, one or two monomer, an electron donor (ED), and a dye. When a dye molecule absorbs a photon in the presence of an ED, free radicals are produced that cause local polymerization of AAm. A corresponding variation occurs in the local refractive index (RI) of the material [9]. This variation is not only attributed to bond conversion in the polymerization process, but also to the secondary effect, whereby the local density is modulated as mass transport occurs during the recording. Though the AAm-based photopolymer is a self-developing dry layer, the stability of gratings depends strongly on small variations in laboratory conditions (relative humidity and temperature) and the efficiency decreased on storage [5, 9-10]. To a great extend, the stability of the grating depends on the reconstructing wavelength also. This is because when the same wavelength is used for reconstruction, the residual dye and monomer react, which results the lowering of RI modulation and hence the DE [5, 11]. Often, the gratings recorded on PVA/AAm films were stabilized by UV curing, incoherent or coherent illumination, thermal treatment etc. [12-15]. Since heating the film (~80°C) causes problems due to the change in thickness of the hologram, it is not recommended. During UV curing special attention has to be made and hence of the different methods used, the most effective are illuminating the grating with incoherent or coherent light. Of the two types of illumination, coherent light cannot be considered more effective (a great deal of energy is needed to stabilize the plate) and so stabilizing the plate with ambient light is recommended because of its low cost. In the case of methylene blue (MB) sensitized films, the leucodye is not stable even after coherent or incoherent illumination. Due to this problem, during reconstruction, the dye molecules absorb the incident intensity and which results in a decrease of efficiency. The stability of leucostate is also equally important in this regard.

When a photopolymer is used in holographic data storage, the stability of recorded data is a major challenge and the media should be free from all fixing process. Though 70% efficiency was obtained for MBPVA/AAm films fabricated in our laboratory, the efficiency was found to be decreased on storage (Section 5.10). The efficiency drop is mainly due to the reconversion of dye molecules from leucoform and the monomer diffusion after the recording process. In the case of dye sensitized films the addition of organic crosslinkers like methylene dimethyl acrylamide (MBA) were reported to be not successful as the efficiency decreased [5]. As an attempt to improve the storage life, another organic crosslinker gluteraldehyde (GA) is incorporated. As metal ion doped polymers have made significant impact in holography, as an attempt to improve the storage life of the gratings, few metallic salts were incorporated during preparation [16-19]. Among these the dichromated films showed better storage life [20-21].The following sections explain the effect of different crosslinkers on the storage life of MBPVA/AAm films.

6.2. Effect of Different Crosslinkers on MBPVA/Acrylamide Film

Cross-links are covalent bonds linking one polymer chain to another and due to this the molecular mobility of crosslinked structure is restricted. Cross-links are formed by chemical reactions that are initiated by heat, pressure, or by the mixing of an unpolymerized or partially polymerized resin with specific chemicals called crosslinking reagents. If the material is of photocrosslinking type, when the polymer is exposed to suitable radiation, the sensitizer undergoes photochemical changes leading to RI modulation [22]. Here two types of crosslinkers, one is organic and the other is metal ions, are used. MBPVA/AAm solution was prepared as optimized in Chapter 5. To this different crosslinkers were added and the holographic performance of the modified material was studied by DE measurements, real time transmittance and optical absorption studies. He-Ne laser having emission at 632.8 nm was used for characterization and the gratings were recorded on these films as explained in section 2.9.2.

6.2.1. Organic Crosslinker

Though MBPVA/AAm films were fabricated with MBA as in the reported works, the efficiency was decreased from 40% to 32% within 24hrs [23-24]. Hence MBA was replaced by another organic crosslinker GA ($C_5H_8O_2$), which is a colorless liquid with a pungent odor often used as a bactericide as well as a fungicide. GA is frequently used in biochemistry applications as an amine reactive homo bifunctional crosslinker [25]. GA-crosslinked gelatin is having great importance in photolithography [26-27]. MBPVA/AAm films were fabricated with different concentrations of GA and gratings were recorded on these films. Of the different GA doped films, one with 0.15M GA showed better storage life. Though there was a sudden decrease in efficiency, the efficiency remained the same (~12%) after 3 days of recording. Fig.6.1. is the plot of DE of both undoped and GA doped MBPVA/AAm films on storage. As the aimed storage life was not achieved, metal ions were incorporated as crosslinkers.

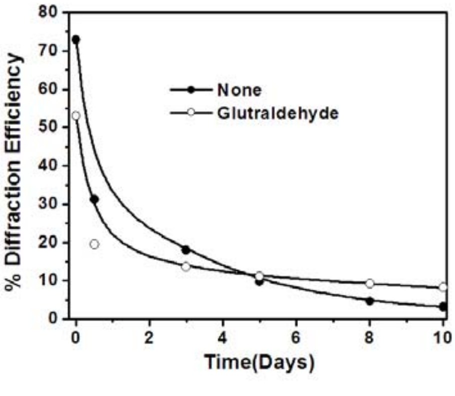


Fig.6.1 DE of both undoped and GA doped MBPVA/AAm films on storage.

6.2.2. Metal Ions

Metal ions such as ferric (Fe^{+3}) and dichromate (Cr^{+4}), stannous (Sn^{+2}) have been used in conjunction with PVA for recording holograms in real time [19, 28-31]. As the transition metals show variable oxidation states, there is possibility of photocrosslinking. With this assumption different metal ions were incorporated to the MBPVA/AAm solution. The metallic salts selected were ammonium dichromate (ADC), cadmium acetate, stannous chloride, zinc acetate, lead nitrate and ferric chloride. All except Fe^{+3} doped films were of good quality. Films were fabricated by varying the concentration of each metallic ion. The absorption spectra of different films showed that the leucoform of dye was not stable in all cases. But the reconversion of dye molecules was slow in the case of dichromated films. The sensitivity of dichromated films was less than that of undoped and other metal ion doped films (Fig.6.2). Gratings were recorded on these films at 400mJ/cm^2 and DE was monitored on storage. Fig.6.3. is the plot of DE of different metal ion doped (ADC-5.33x10^{-4}M, Cadmium Acetate-1.17x10^{-3}M, $SnCl_2$-3.96x10^{-4}M, Zinc acetate-1.226x10^{-3}M, lead nitrate-9.06x10^{-4}M) MBPVA/AAm films on storage. In all cases the efficiency was found to be decreased. Though the efficiency decreased, the dichromated films showed better storage life than the undoped films. Hence further studies were done on dichromated films.

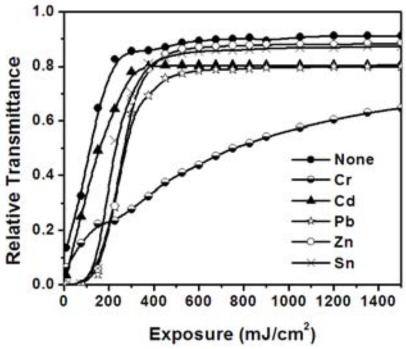


Fig. 6.2 Relative transmittance of different metal ion doped films

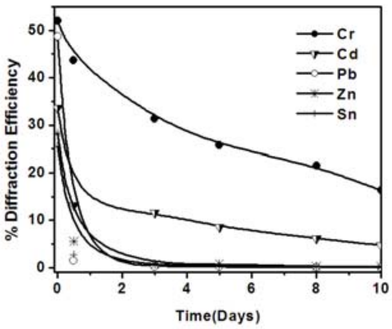
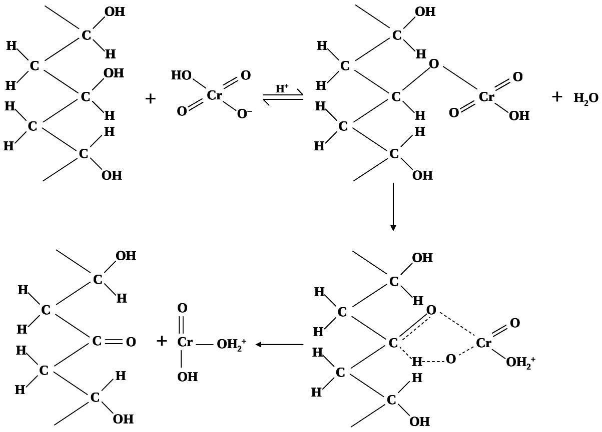


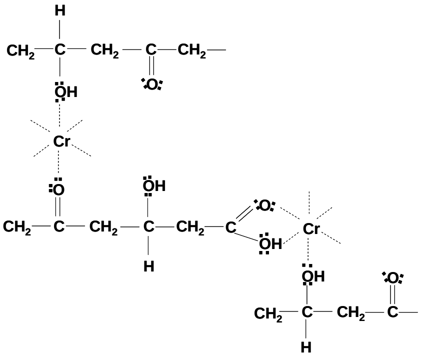
Fig. 6.3 DE of different metal ion doped films on storage.

6.3. Importance of Chromium Doping

Dichromated PVA (DCPVA) as a real time holographic recording material has been studied during the past few decades by several researchers [19, 28, 32]. The sensitizer of dichromated light-sensitive systems, Cr^{+6}, is considered to be reduced to Cr^{+3} through the intermediate ionic stages, Cr^{+5} and Cr^{+4}. Cr^{+4} are very labile and transfers to Cr^{+5} quickly [33-34]. This Cr^{+5} react with PVA and produces crosslinked PVA and Cr^{+3}. The Crosslinking should be attributed to the coordination of the hydroxyl group of PVA and the chromic ions produced in the film in the absence of water by reduction of the dichromate [35]. Approximately one C-C bond is broken for every five molecules of dichromate reduced [36]. The over all reaction can be summarized as follows [37].



The photocrosslinked PVA-configuration could be schematically represented as follows [19, 38].



The improved storage life of dichromated MBPVA/AAm is due to the crosslinking phenomenon. The crosslinking may prevent further diffusion of monomer and the recovery of dye molecules. It is expected that optimization of dichromate concentration could achieve a stable efficiency on storage and with this goal the concentration of MB and ADC were varied and optimized to have stable efficiency.

6.4. Film Fabrication

The films were fabricated using gravity settling method at room temperature (≅30°C). The film constituents are 10% PVA, acrylamide (as optimized in section 5.4), triethanolamine (TEA), MB and ADC. MB concentration was varied from 0.7×10^{-4} to 4.16×10^{-4} M and ADC concentration was varied from 0.5×10^{-3} to 2.106×10^{-3} M. Though there were no reports on MB sensitized dichromated PVA (MBDCPVA), MB sensitized dichromated gelatin (MBDCG) is a well-known holographic recording material [39-41]. It is reported that MB separates in an acidic state when the product of the concentration of ADC and MB is larger than the solubility product of 2×10^{-6} $(\text{mol/l})^2$ [42-43]. So in order to avoid the precipitation of MB and to eliminate the complicated steps, the concentration of ADC was selected such that the product of the concentrations of

MB and ADC should be less than the solubility product 2x10^{-2} (mol/l)^{2}. The films were prepared using gravity settling method and the drying period was 48hrs.

6.5. Effect of Chromium on Samples with Different MB Concentrations

Gratings were recorded on films with various combinations of MB and ADC at different exposures by keeping the spatial frequency as 1100 lines/mm. The efficiency was monitored by illuminating the grating with a 0.8µW He-Ne laser beam. The DE of films with MB concentrations 0.7x10^{-4}M, 1.47x10^{-4}M, 2.17x10^{-4}M, 2.79x10^{-4}M, 3.57x10^{-4}M and 4.27x10^{-4}M are shown in Fig. 6.4, 6.5, 6.6, 6.7, 6.8 and 6.9 respectively. In call cases, the efficiency and sensitivity of MBPVA/ AAm films were found to be decreased on chromium doping. But an anomalous behavior in DE was observed in the case of films with 2.79 x10^{-4} M MB. From the graph (Fig.6.7) it is evident that, the DE and sensitivity is least for films with 1.59x10^{-3} M ADC. In this particular case, both DE and sensitivity were improved for higher concentration of ADC. In all cases except for films having 2.79x10^{-4}M dye concentration, DE was found to be decreased on storage. So the films with 2.79x10^{-4}M MB shows a unique behaviour.

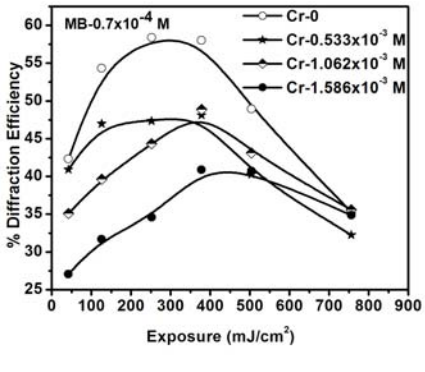


Fig.6.4 Diffraction efficiency of films having 0.7x10^{-4} M methylene blue

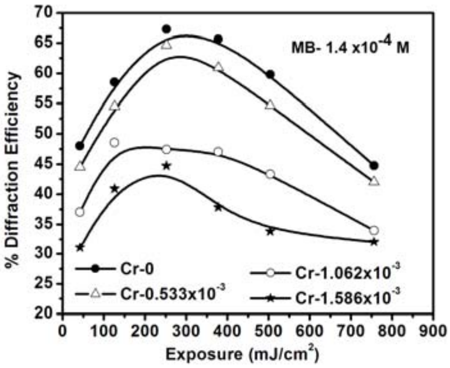


Fig.6.5 Diffraction efficiency of films having 1.4x10^{-4} M methylene blue

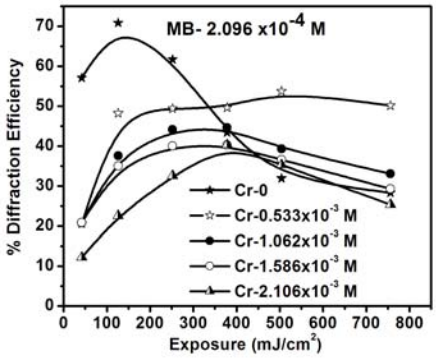


Fig.6.6 Diffraction efficiency of films having 2.1 x10^{-4} M methylene blue

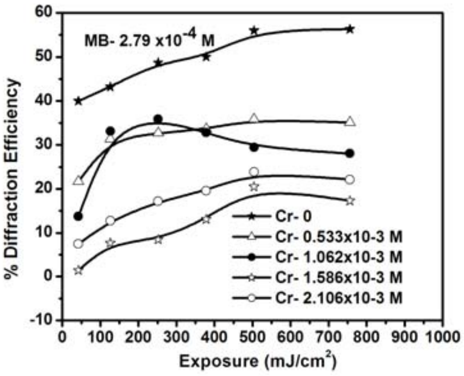


Fig.6.7 Diffraction efficiency of films having 2.79x10^{-4} M methylene blue

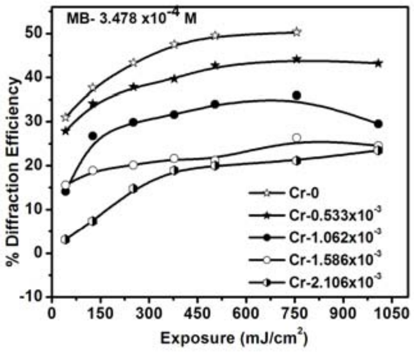


Fig.6.8 Diffraction efficiency of films having 3.5x10^{-4} M methylene blue

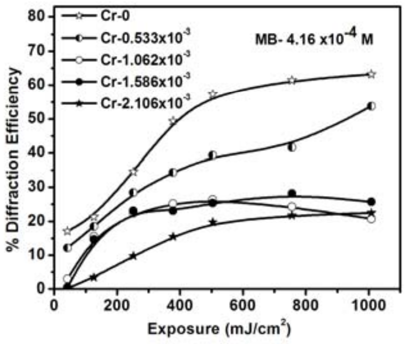


Fig.6.9 Diffraction efficiency of films having 4.16x10^{-4} M methylene blue

6.6. Efficiency on Storage

Diffraction efficiencies of both undoped films and dichromated films were monitored on storage. The efficiency was found to decrease on storage except for two combinations of ADC and MB. Unlike other films, those with 2.106x10^{-3} M ADC and 2.79 x 10^{-4} M MB showed stable efficiency (20%) on storage. Whereas the films with 2.79 x 10^{-4} M MB and 1.59x10^{-3} M ADC showed a self enhancement of DE on storage. These samples (just after recording) showed highest efficiency of 20% at 500mJ/cm^2 without any pre exposure and chemical fixing. The DE was found to slowly increase to 40% by 3 months. It remained the same for months and then the efficiency gradually decreased and reached the initial efficiency of 20%. Thereafter it remains the same for more than one year the grating gave the same DE. The DE of films (with 2.79x10^{-4}M MB) on storage is plotted in Fig.6.10.

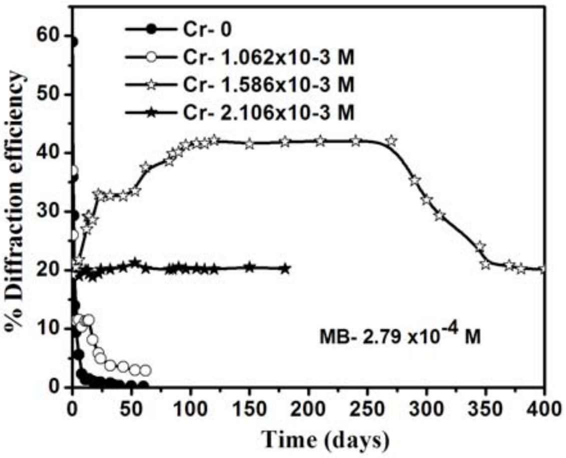


Fig.6.10. DE of both undoped and chromium doped films on storage (MB- 2.79x10^{-4} M)

6.7. Self Enhancement of Diffraction Efficiency

The self enhancement (SE) of a hologram is the increase in its efficiency over time under light illumination or in the dark. SE, both during and after the recording can together be regarded as a two stage holographic recording method, which is profitable when the recording energy or the exposure time is limited at the first stage. Such a recording method has the advantage of large vibration stability at the second stage. Though SE of DE was reported in $LiNbO_3$: Fe crystals, KBr crystals with F centers, amorphous AS_2S_3 films, thionine-PVA layers, DCPVA and dichromated gelatin (DCG) (after chemical fixing), this is the first observation of SE in AAm films [44-50]. According to the mechanism and properties of the effect, enhancement can be of coherent, incoherent and dark. In the case of dichromated polymers, that are less sensitive and need long exposure times, Dark SE is more important. Dark or relaxational SE is due to the transmission increase of a hologram by thermo-stimulated relaxation process. In thionine- PVA, the effect is due to the Borrmann effect or the effect caused by excited dye molecules [47]. In this a transient grating made of metastable molecules interferes destructively with a permanent grating made of final photochemical products. Loughnot *et al.* observed that after recording, the thermal polymerization enhances the spatial modulation of segment density between bright and dark areas [51]. This goes along with an increase of the modulation of RI in dark and an improvement of the DE. The key phenomenon is the balance between the chemical initiation of the polymerization and the diffusion of unreacted species. In DCPVA, the SE increases with pH, but it decreases with dichromate concentration and exposure energy [49]. The SE which was observed in DCG gratings (after chemical fixing) was much higher than that observed in DCPVA [50]. This increase may be due to the hardening of gelatin during chemical fixing. But the increase is a little slower for higher pH values than for lower pH values. A slight SE at low energy was observed in acrylic acid-Cr^{+6} solution kept in dark due to the formation of Cr^{+3}[52]. In DCPVA, it was reported that the efficiency increases within 1-3 days depending on the pH and then it decrease [49]. But in the case of MBDCPVA/AAm films, it takes around four months to complete the SE [20-21].

The SE process can be characterized by the self-enhancement coefficient, $\xi=\eta_t/\eta_0$ and by the self enhancement rate, $\beta= d\xi/dt$. Where η_0 is the initial DE immediately after the recording and η_t is the DE after time t. Highest value of self-enhancement coefficient, ξ =2.082 was observed on 120th day after recording. The SE coefficient and rate is determined and plotted in Fig.6.11 and 6.12 respectively. An increase in the rate is observed during the first month after recording and after that it remained constant for nine months. After that the rate decreased and became constant after 12 months.

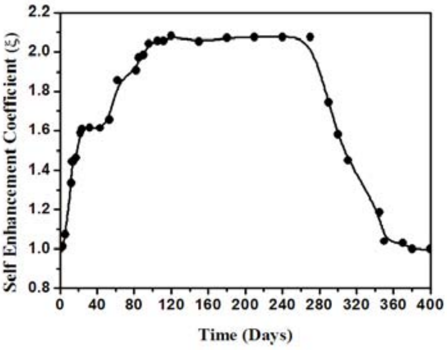


Fig.6.11. The self enhancement coefficient with time

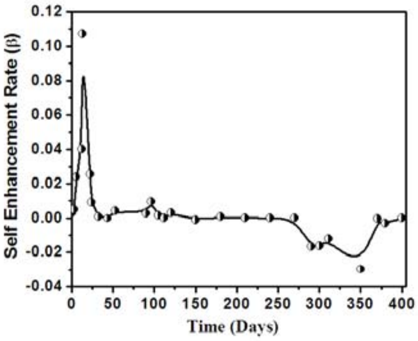


Fig.6.12. The self enhancement rate with time

The SE observed in this case may be due to the dark reaction, diffusion, polymerization and internal stresses as observed in DCPVA [48]. Cr^{+6} is consumed slowly during photochemical reaction induced during the exposure. All the Cr^{+5} (produced by the reduction of Cr^{+6}) are not reduced to Cr^{+3} during exposure and this reduction continue in the dark. This reduction is large in the more exposed regions than in the less exposed region. The number of crosslinkage between Cr^{+3} and the PVA increases and thus the index modulation also increases which induces an increase in DE. This dark reaction may be the major reason for the SE. Cr^{+3} or unreacted Cr^{+5} may diffuse from the less exposed regions to the more exposed regions. Diffusion of Cr^{+3} ions is possible only if all the Cr^{+3} ions are not bound in the crosslinkage. The polymerization was not finished during the recording period. Polymerization continues bringing new cross-linkages together with Cr^{+3} ions, which is responsible for the grating formation. The internal stress in the coating increases during drying and exposure times. But when the coating expands by absorbing moisture at room temperature, the internal strain is relaxed and this also contributes to the increase in DE.

6.8. Behavior of Dye

The films were exposed to an expanded laser beam of intensity 5mW/cm^2 for 10 minutes and the relative transmittance of both Cr doped and undoped samples were measured. The relative transmittance of films having 2.8×10^{-4}M dye with different dichromate concentration is plotted in Fig.6.13. From the graph it is evident that on Cr doping, the MBPVA/AAm films became less sensitive to laser and the energy requirement is high. This is because of the photocrosslinking caused by the dichromate. Fig. 6.14 shows the absorption spectrum of Cr doped sample (2.8×10^{-4} M dye and 1.59×10^{-3} M ADC). In the case of undoped samples, the recovery of the dye molecule from the leucoform is very fast and it is almost fully recovered within two weeks (section 5.10, Fig.5.17). But in the case of Cr doped samples, the recovery is very slow and it remains the same leucoform on storage. In this case, the leuco MB formed is crosslinked in the PVA matrix and so further oxidation of leuco dye is not possible as observed in the dye sensitized polymers.

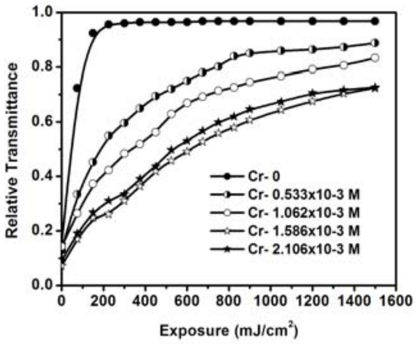


Fig.6.13. Relative transmittance of both undoped and Cr doped films (MB- 2.79×10^{-4} M)

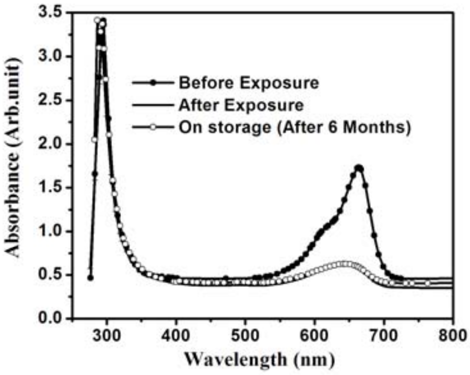


Fig.6.14. Absorption spectrum of the dichromated sample on storage

6.9. Mechanism of Grating Formation

The mechanism of grating formation can be explained as follows. On exposing to the interference pattern, the MB molecules get excited and electron transfer takes place between MB and TEA [3].This reaction produce leuco MB and the amine radical and this radical initiates the polymerization reaction. Polymerization takes place at the region of constructive interference and as a result a monomer concentration gradient occurs which allows the diffusion of monomer from the unexposed to the exposed region. At the same time, the Cr^{+3} ions obtained by the reduction of Cr^{+6} crosslink with PVA. Both polymerization and crosslinking contribute to the RI modulation, which leads to the grating formation. The RI modulation in undoped sample was 0.0463 and that for Cr doped sample (which showed SE) was 0.0507. The absorbance modulation occurs during exposure also contribute to the grating formation.

6.10. Hologram Recording

Transmission holograms were recorded on MBDCPVA/AAm films using the experimental setup described in section 2.14. The photograph of the recorded hologram is shown in Fig.6.15.

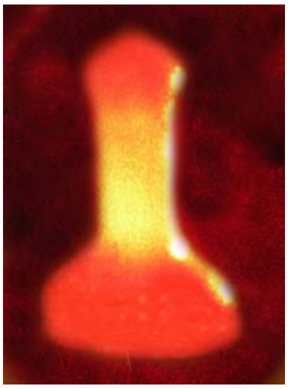


Fig.6.15. The photograph of the hologram recorded on MBDCPVA/AAm film

The MBDCG films described in the literature were sensitive to both red and UV-green region [39, 53]. But the sensitivity of MBDCPVA/AAm described here is limited to the red region only and this is due to the low concentration of ADC. DCPVA/AAm films were fabricated to know the feasibility of using the material in lower wavelengths.

6.11. Dichromated PVA/AAm Films

Dichromated polymer materials have made a significant impact on optical storage technology [16, 19, 28, 32, 52-55].Generally a dichromated system consists of ADC embedded in a polymer matrix. Though dichromated systems were investigated by incorporating different EDs and dyes, no reports were made on the monomer incorporation [22, 41, 56-60]. Here the holographic performance of DCPVA containing a photopolymerizable monomer (AAm) is evaluated.

6.11.1. Triethanolamine as Electron Donor

Polymer solution was prepared with 10%PVA, AAm (as optimized in section 5.4) and TEA. This solution was sensitized with ADC. Films were fabricated with ADC concentration ranging from 0.001M to 0.05M. Golden yellow films were obtained in all cases, but on storage the films were turned to grayish colour. Gratings were recorded on these films using a 488 nm Ar^+ laser. But the efficiency obtained was less than 2% even at an exposure of 1500 mJ/cm^2. Though TEA is suitable for xanthene dye doped DCPVA and dye sensitized

PVA/AAm systems, it is not suitable for DCPVA/AAm films [58, 61-63]. The EDs influence significantly the DE of recorded holograms. From all different nitrogen containing compounds, dimethyl formamide (DMF) showed the best performance while using with dichromated systems [22, 30]. Hence films were fabricated with dimethyl formamide DMF as electron donor.

6.11.2. DMF as Electron Donor

Polymer solution was prepared with 10%PVA, AAm (as optimized in section 5.4) and 0.13M DMF. ADC concentration was varied from 0.0034 to 0.068M. Good quality films with 110μm thickness were obtained after a drying period of 48hrs. A 488 nm Ar$^+$ laser was used for characterization. Though the material is more sensitive in the UV region, it has slight sensitivity in the blue region also. Optical absorption spectra of DCPVA/AAm film (AD-0.0068M) on laser exposure (2000mJ/cm^2) are shown in Fig. .16.

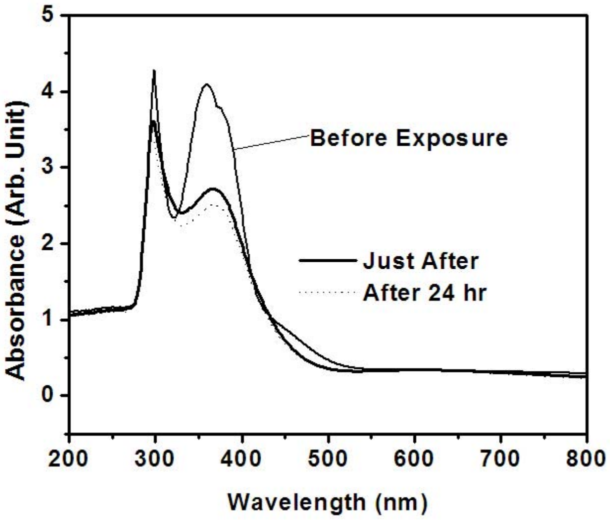


Fig. 6.16. Absorption spectra of DCPVA/AAm on laser exposure (2000mJ/cm^2)

The real time transmittance of DCPVA/ADC films on exposing to a power density of 7mW/cm^2 is shown in Fig.6.17. Unlike dye sensitized polymers, photodarkening occurs in dichromated polymers. The photobleaching is also reported in dichromated systems. During photochemical reaction, a chemical species that absorbs light is produced. If the molar absorption coefficient of the product is higher than that of the reactive dye (photosensitizer), photodarkening takes place and if the coefficient is smaller, then partial photobleaching occurs [64]. In the present case photodarkening is observed at higher dichromate concentrations, whereas photobleaching was observed at low concentrations of dichromate. The films with 0.0068M ADC showed photobleaching followed by photodarkening. Here the photochemical reaction is principally between dichromate and ED. If DMF is fully consumed, the photochemical reaction will stop by itself and causes partial photobleaching [64].

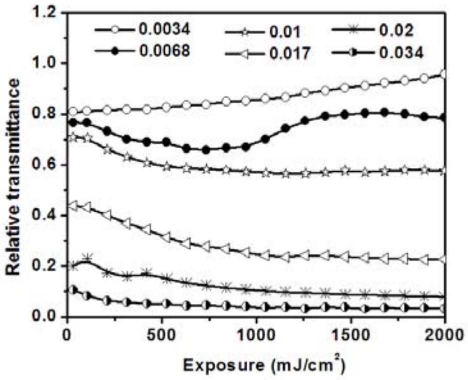


Fig. 6.17 The relative transmittance of DCPVA/ADC films

6.11.3. Diffraction Efficiency Measurements

To optimize the ADC concentration, gratings were recorded on these films using 488 nm Ar$^+$ laser by keeping the beam ratio as 1:1 and spatial frequency as 1400 lines/mm. The variation of DE with ADC concentration is plotted in Fig.6.18. Highest efficiency of 43% was obtained (exposure of 840 mJ/cm^2) for 0.017M ADC. The efficiency obtained for DCPVA/AAm is much higher than that of DCPVA. In conventional DCPVA, the efficiency without fixing process is less than 1% [48]. After thermal fixing, the efficiencies of DCPVA and DCPVA-DMF are 45% and 65% respectively, where the recording fluence is 1000 mJ/cm^2.

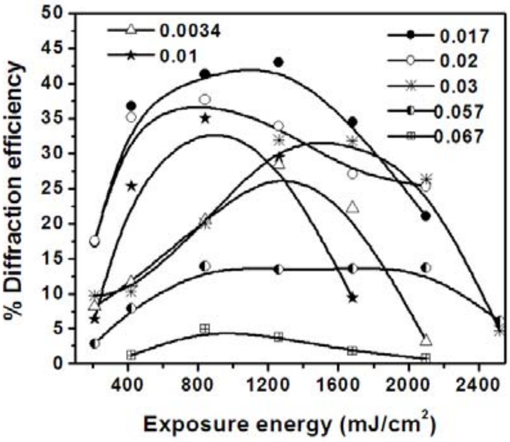


Fig. 6.18. Diffraction efficiency of DCPVA/AAm films

The DMF concentration also was optimized (0.21M) and an efficiency of 51% at a recording fluence of 750 mJ/cm^2 was obtained. The advantage of this formulation is that, unlike the conventional DCPVA films, it does not require a thermal development after recording [19,65]. The efficiency of the material was found to decrease on storage and within one month it was reduced to 20%. The storage capacity of this material is much better than that of MB doped films (*storage capacity α 1/ λ*) and is 2350 lines/mm. Holograms were recorded on this material using the experimental setup explained in section 2.13. Photograph of the hologram recorded on the optimized film is shown in Fig.6.19.

Fig. 6.19 Photograph of the hologram recorded on DCPVA/AAm

6.12. Conclusion

The storage life of the gratings recorded on MBPVA/AAm film was improved with the addition of crosslinkers. Addition of ADC makes the MBPVA/AAm films more stable and helps in storage. Unlike MBPVA/AAm, a self enhancement of efficiency was observed for a particular combination of dye and dichromate. Even though the initial efficiency of dichromated films was low (20%), the self-enhancement observed makes the system regain the DE (42%) and helps in maintaining the efficiency constant for several months. Dichromated PVA/AAm films were also fabricated and it showed an efficiency of 51% for an exposure of 750 mJ/cm^2. The efficiency and sensitivity achieved in this case is much higher than that of conventional DCPVA films (without thermal treatment).

References

1. H. Sherif, I. Naydenova,S. Martin, C. M.Ginn, V. Toal, J.Opt.A:Pure Appl. Opt.,7, 255 (2005)
2. F. R. Ling, B. H. Tong, S. J. Jiang, B.Wang, Y. Li Zhang, J. Opt. Soc. Am. A , 24, 1945 (2007)
3. S. Blaya, L. Carretero, R. F. Madrigal , A.Fimia: Jpn. J. Appl. Phys., 41, 3730 (2002)
4. V. Weiss and E. Millul: Appl. Surf. Sci., 106, 293 (1996)
5. S. Gallego, M. Ortuno, C. Neipp, C. Garcia, A. Belendez , I. Pascual, Opt. Exp., 11, 181 (2003)
6. S. Blaya , L. Carretero, R. Mallavia, A.Fimia, M.Ulibarrena, D. Levy, Appl. Opt., 37, 7604 (1998)
7. C. Garcia, A. Fimia, I.Pascual, Appl. Opt., 38, 5548 (1999)
8. C. Garcia, A. Fimia, I.Pascual, Appl. Phys., 72, 311 (2001)
9. S.Martin, P. Leclere , Y. Renotte , V.Toal Y.Lion Opt.Eng,. 33, 3942 (1994)
10. S. Blaya, M. Murciano, P. Acebal, L. Carretero, M. Ulibarrena , A. Fimia, Appl. Phys. Lett., 84, 4765 (2004)
11. J. A .Jenney, J. Opt. Soc. Am., 60, 1155 (1970)
12. R.K. Kostuk, Appl. Opt., 38, 1357 (1999)

13. M.S.Donovan, T.A. Sanford, A.B. Lowe, B.S. Sumerlin, Y. Mitsukami, C.L. Mccormick, Macromol., 35, 4570 (2002)
14. G. Q. Xia, W. S.Lian, H. M.Ju, G. F.Xi, Chin. Phy., 14, 2004 (2005)
15. S. Gallego, C. Neipp, M. Ortuno , A. Belendez ,I. Pascual, J.Mod.Opt., 51, 491(2004)
16. S. Savic, D. Pantelic, D. Jakovijevic, Appl. Opt., 41, 4484 (2002)
17. A. D. Kirk, Chem. Rev., 99, 1607 (1999)
18. V. Kuncsery, G. Filotiy, R. Podgorsekz, M. Biebricherz, H .Frankez, J.Phys. D: Appl. Phys., 31, 2315 (1998)
19. S. Lelievre ,J. J. A. Couture, Appl.Opt., 29, 4384 (1990)
20. B. M. John, R. Joseph, K. Sreekumar, C. S. Kartha, J.Mater. Sci: Mater. Electron., (article in press) (2008)
21. B. M. John, R. Joseph, K. Sreekumar, C. S. Kartha, Optoelectronic materials and thin films, M.K.Jayaraj, Ed., Allied Publications 592 (2005)
22. R.A.Lessard, M.Bolte, R.Beaulieu, J.J.A. Couture, G.Manivannan, Proc. of ICLAOM-03, Delhi, 959 (2003)
23. L. Carretero, S. Blaya, R. Mallavia, R. F. Madrigal , A. Fimia, J.Mod.Opt., 45, 2345 (1998)
24. C.Nisha , Study on MBPVC and MBPVA films by incorporating electron donors and monomer, M.Phil Dissertation, Cochin Univ. of Sci. & Tech.(2005)
25. K. D. Seo, S.D. Oh, S.-H. Choi, S.H. Oh, J.C. Woo, H.-J. Park, http://www.scientific.net
26. L.J. Yang , Y.C.Ou, Lab Chip, 5, 979 (2005)
27. W. G. Liu, K.De Yao, G. C. Wang , H. X. Li, Polym. Commn., 41, 7589 (2000)
28. M. Barikani, E. Simova, M. Kavehrad, Appl.Opt., 34, 2172 (1995)
29. R. Changkakoti, G Manivannan, A.Singh, R.A Lessard, Opt. Eng., 32, 2240 (1993)
30. G Manivannan, R. Changkakoti, R.A Lessard, Opt. Eng., 32,671 (1993)
31. M. C. Valsangiacom, M. Bulinski, I. Iova, G. Schinteie, C.Kuncser, G. Filoti, D. Bejan, Romn. Reports in Phy., 55, 283 (2003)
32. G. Manivannan, R. Changkakoti, R. A. Lessard, J. Phys. Chem., 97, 7228 (1993)
33. K. Wang, L. Guo, L. Zhou, J. Zhu, Appl. Opt., 35, 6369 (1996)

34. C. Pizzocaro, C. Lafond, M. Bolte, J. Photochem. Photobio. A: Chem., 151, 221 (2002)
35. B. Duncalf ,A.S. Dunn, J.Appl.Polym.Sci., 8, 1763 (1964)
36. I. Sakurada , S. Matsuzawa, K. Kagaku, 18, 252 (1961)
37. K.B. Wiberg, Ed., Oxidation by chromic acid and chromyl compounds in oxidation in Organic chemistry, Academic Press, New York, (1965)
38. M. Sasaki, K. Honda, Kikuchi, Rep. Inst. Ind. Sci. Univ. Tokyo, 27,1 (1978)
39. K. Wang, L. Guo, J. Zhu, W. Zhang, B. Cheng, Appl. Opt.,37 ,326 (1998)
40. R. Changkakoti ,S. V. Pappu, Opt. Laser Technol., 21, 259 (1989)
41. T. Mizuno, T. Goto, M. Goto, K. Matsui, T. Kubota, Appl. Opt., 29, 4757 (1990)
42. A. Graube, Opt. Commn., 8, 251 (1973)
43. K. Kurokawa, S. Koike, S.Namba, T.Mizuno, T. Kubota, Appl. Opt.,37, 3038 (1998)
44. T.K.Gaylord, T.A Rabson, F.K.Tittel, C.R. Quick, J.Appl. Phys., 44, 896 (1973)
45. A. Ozoles, Latv, J.Phy.Tech.Sci., 5,45 (1979)
46. A. Ozoles, O. Salminen, M.Reinfelde, J.Appl. Phys., 75, 3326 (1994)
47. S.Caron, J.J.A Conture, R.A.Lessard, Appl. Opt., 29, 599 (1990)
48. R .Grazymala, T. Keinonen, Appl. Opt., 37, 6623 (1998)
49. T.Keinonen, R. Grazymala, Appl.Opt., 38, 7214 (1999)
50. R. Grazymala, T.Keinonen, Appl. Opt., 38, 7222 (1999)
51. D.J. Loughnot, C.Turch, Pure Appl. Opt., 1, 269 (1992)
52. T Galcera, X.Jouan, M.Bolte, J.Photochem. Photobio. A, 45, 249 (1988)
53. J. Zhu, G.G Dong, X. Guo, L. Chen , J. Li, J. Opt. A: Pure Appl. Opt., 6, 132 (2004)
54. S. Calixto ,R. A. Lessard , Appl. Opt., 23, 1989 (1984)
55. C. Pizzocaro, R.A. Lessard, M. Bolte, Can. J. Chem., 76,1746 (1998)
56. D. Pantelic, B.Muric, Appl. Opt., 40, 2871 (2001)
57. J. J. Couture ,G. Manivannan, R.A. Lessard, R. Changkakoti, Proc. SPIE, 2043, 37 (1994)
58. G.Manivannan, G. Mailhot, M. Bolte,R. A. Lessard, Pure Appl. Opt., 3, 845 (1994)
59. M.Mazakova, P.Sharlandjiev, M. Pantcheva, G. Spassov , Appl. Opt., 24, 2156 (1985)
60. R. Changkakoti, S.S.C Babu, S.V Pappu, Appl. Opt., 27, 324 (1988)

61. G.Manivannan, P.Leclere, S.Samal , R.Changkakoti, Y.Renotte, Y.Lion ,R.A. Lessard , Appl. Phys., B ,58, 73 (1993)
62. S. Blaya, L. Carretero, A. Fimia, R. Mallavia, R. F. Madrigal, R. Sastre , F. Amat-Guerri, J. Mod. Opt., 45, 2573 (1998)
63. R.A. Lessard, C. Malouin, R. Changkakoti, G. Manivannan, Opt. Eng., 32, 665 (1993)
64. S. Carron, R.A Lessard, P C Roberge, Appl. Opt., 40, 707 (2001)
65. R.A Lessard, R Changakakoti, G. Manivannan, Proc.SPIE 1559, 438 (1991)

Chapter 7

Fabrication of a Self-developing and Stable Copper Doped Photopolymer System

A self developing and self processing red sensitive material, copper doped methylene blue sensitized poly (vinyl alcohol)/acrylamide, which could be used as a permanent holographic recording material has been developed. The optimized film composition shows 32% diffraction efficiency for an exposure of 600mJ/cm^2. The efficiency remains the same for years without any fixing process. The material is important on account of its self processability, long storage life, low cost and easiness of fabrication. This chapter deals with the effect of copper doping on the storage life, sensitivity and efficiency of MBPVA/AAm films.

7.1. Introduction

Holographic digital data storage is positioned to be a serious competitor in the next generation of optical storage devices with ultra-large storage capacity of 1TB cm^{-3} and ever-faster data transfer rate of 10 GBs^{-1} [1]. Holographic data storage has the advantage that the entire volume of the recording medium is used. And data pages are multiplexed into the same volume, allowing for parallel recording and reading of data and this leads to high data transfer rate and short access times. Though several companies and academic institutions like IBM, Bell Labs, NEC, Rockwell, MEI, were trying to realize this goal for the past decades, the major obstacle has been the lack of an adequate recording media [2]. Compared with other holographic materials, photopolymers have great advantage of recording and reading holograms in real time and the spectral sensitivity could be easily shifted to the type of recording laser. Though ‘Aprilis’, ‘Optware’ and ‘InPhase Technologies’ have released polymer-based holographic discs, the cost is not attractive to customers [3]. In this context, indigenous development of photopolymer systems that satisfies the media requirements for both display and storage applications have become a growing challenge.

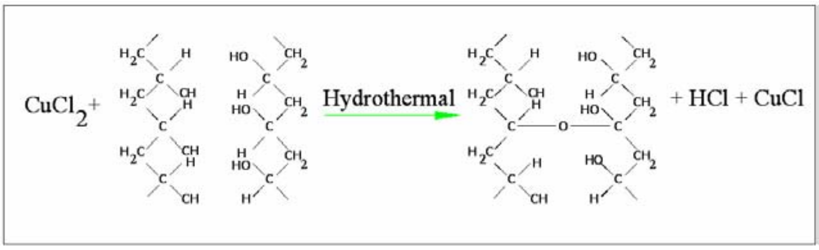
The major drawbacks of dye sensitized PVA/AAm is the decrease in diffraction efficiency (DE) on storage (section 5.10) [4- 6].Therefore usually UV curing and post exposure techniques were employed to stabilize the recorded data. If any type of fixing process is adopted, it may adversely affect the stored information and chemical or thermal fixing is not welcomed in storage applications. There comes the demand for the development of a recording media which sustain the stored information without any type of fixing process, UV curing and post exposures.

It was found that the DE of MBPVA/AAm films on storage could be stabilized with the incorporation of cupric chloride [7-8]. As no fixing process is required, the Cu doped MBPVA/AAm films described in this chapter could satisfy the media requirement for both display and real time applications.

7.2. Why Copper Doping

The decrease in DE of MBPVA/AAm is due to the diffusion of residual monomer from the region of destructive interference to that of the constructive interference. This diffusion causes distortion of the recorded grating and hence decrease in efficiency. The reconversion of dye molecule from leucoform is another reason for the decrease in DE. Due to the reconversion of dye molecule, during reconstruction, the dye molecules absorb major portion of the incident energy and as a result, the efficiency decreases. In certain conditions the efficiency decreases to a fraction of its original value in a matter of hours due to humidity. Moisture makes the PVA layer more permeable to migrating species and this induces a decrease in DE [6].

If a crosslinker is added to the system, it can inhibit further diffusion of molecules and as a result, the recorded grating becomes undisturbed and hence constant DE can be obtained on storage. But in the case of dye sensitized films the addition of organic crosslinkers like methylene dimethylacrylamide were reported to be not successful as the efficiency decreased [4-6, 9]. In this study efforts were made to crosslink the matrix with a metal ion as there are reports that in metal ion (Cr^{+6} and Fe^{+3}) doped PVA, on absorbing suitable energy, the metal ions crosslinks with PVA matrix [10-15]. To maintain the spectral sensitivity of the material unaffected, cupric chloride was selected as the crosslinker. Gong *et.al* explained the formation of crosslinked PVA with $CuCl_2$ (at 200^0C) and the schematic representation of the reaction process is as follows [16].



In the present study, experiments were performed by exploiting the photocrosslinking of PVA. On laser exposure, Cu^{+2} ions in the cupric chloride get reduced to Cu^{+1} resulting in ionic crosslink between PVA chains [8]. The following sections analyze how cupric chloride influences the holographic performance of MBPVA/AAm films.

7.3. Experimental Procedure

MBPVA/AAm solution was prepared as optimized in Chapter 5. To this homogeneous solution, copper chloride was added. This homogeneous solution was casted on micro slides using gravity settling method. The drying period was 48 hr. In all the cases, films with good optical clarity were obtained. The samples with different Cu- concentrations were named as *Cu-1, Cu-2,……, Cu-30.* where the concentration of cupric chloride in *Cu-1<Cu-2,…., <Cu-30*

As the technology of film preparation is transferred to M/S. Light Logics Holography & Optics. Pvt. Ltd., Trivandrum, India, the finer details of the film composition is not included in the thesis.

Gratings were recorded on these films as explained in section 2.9.2 by keeping the beam intensity ratio as 1:1. For this a 15 mW, CW, polarized He-Ne laser (Melles Griot) having emission at 632.8 nm was used. The sensitivity of the material was studied by measuring the real time transmittance by exposing to an expanded laser beam of intensity 5mW/cm^2 for 10 min. The refractive index (RI) before and after exposure was measured using an Atago DR-M2 refractometer and change in RI was calculated. The absorption spectra of the samples were recorded using JASCO V-570 spectrophotometer and the change in absorbance is also calculated. The surface mapping of the recorded gratings were carried out using AFM and Dektak stylus profiler.

7.4. Material Sensitivity with the Incorporation of Copper Chloride

To find out the material sensitivity on Cu doping the real time transmittance measurements were carried out. The relative transmittance T/T_0 was determined; where T is the real time transmittance of the sample on laser exposure and T_0 is the transmittance of the PVA/AAm films without dye and $CuCl_2$. The relative transmittance of both undoped (*Cu-0* or samples without $CuCl_2$) and Cu doped samples are plotted in Fig. 7.1. Here the sensitivity is defined as the increase in transmittance on laser exposure. As the material sensitivity increases, the transmittance increases at low exposures. This is because even at low exposure, the dye molecules were getting excited and initiate photochemical reaction and then it is converted to the leucoform. Here the relative transmittance of the undoped sample is much higher than that of Cu doped samples and it remained constant after an exposure of 150 mJ/cm^2. The relative transmittance of Cu doped samples increased slowly and high energy is required to bleach the samples. So the sensitivity of the undoped sample is much higher than that of Cu doped samples. As the copper concentration increases, the material sensitivity decreases. Samples with higher Cu concentrations (*Cu-25* and above) were almost insensitive to laser. This is because, on laser exposure, Cu^{+2} ions in the cupric chloride get reduced to Cu^{+1} resulting in ionic crosslink between PVA chains. The MB molecules may be trapped inside this crosslinked chain and it prevents further reaction of the dye molecules which could have results in decrease of material sensitivity. Thus it was observed that the addition of copper chloride decreased the material sensitivity or higher exposures are needed for this material [8].

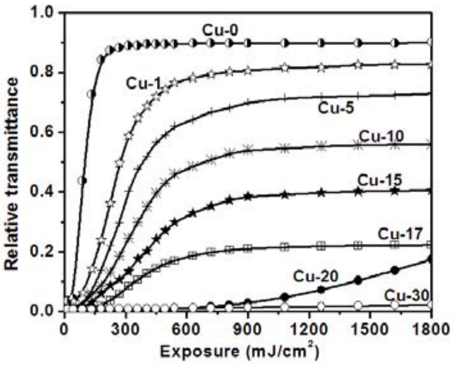


Fig. 7.1 Relative transmittance of undoped and Cu doped films at different exposures

7.5.Effect of Copper Chloride on DE

Gratings were recorded on both undoped and Cu doped samples by varying the exposure energy and the efficiency was determined. Fig. 7.2 is the plot of variation of DE with exposure for different Cu doped films. The efficiency of Cu doped films was less than that of undoped films (70%) and the DE decreased with increase in $CuCl_2$ concentration.

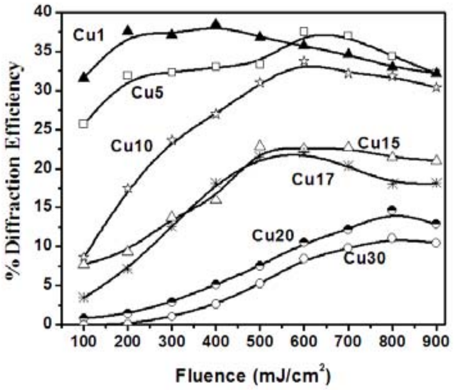


Fig.7.3 Variation of DE with copper chloride concentration.

In Cu doped films, the grating formation is due to the RI modulation produced by both the monomer diffusion resulting from the photopolymerisation and the photocrosslinking. The RI modulation of the films was determined for an exposure of 500mJ/cm^2 and it is plotted in Fig.7.4. The RI modulation is higher for Cu-10 samples which showed 32.8% efficiency for an exposure of 600mJ/cm^2. As the Cu concentration increases, the monomer diffusion decreases and photo-crosslinking increases. At low Cu concentration, the RI modulation is due to the monomer diffusion and at high concentration it is due to photocrosslinking [8, 17].

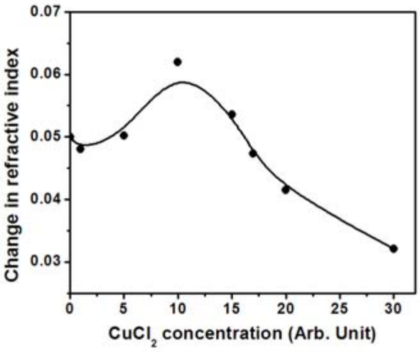


Fig.7.4 Change in refractive index for different Cu doped samples

7.6. Diffraction Efficiency on Storage

In the case of undoped films, a drastic fall in efficiency was observed within 24hrs. (Section 5.10). To find the storage life of the gratings recorded on Cu doped films, the efficiencies of all the films were determined on each day after recording. The reconstructed power used was less than 1µW. The variation in DE of the samples on storage is plotted in Fig.7.5. The efficiencies of samples with Cu-concentration below *Cu-10* were found to be decreased on storage. But the decrease is slow compared to that of the undoped samples. (Fig. 5.16) One of the major observations that could be made is that DE of *Cu-10* and samples with higher Cu remained the same for more than two years. But there was a decrease in the value of DE on increasing Cu concentration. So *Cu-10* was selected as the optimized sample, where a constant DE of 32% (for an exposure of 600mJ/cm^2) was maintained for more than two years. This constant efficiency could be obtained due to the absence of monomer diffusion and crosslinking effect of $CuCl_2$

that makes the leucoform more stable. The stability of grating may also be due to the stability of change of state (leucoform) occurred to the dye molecules [7-8, 17].

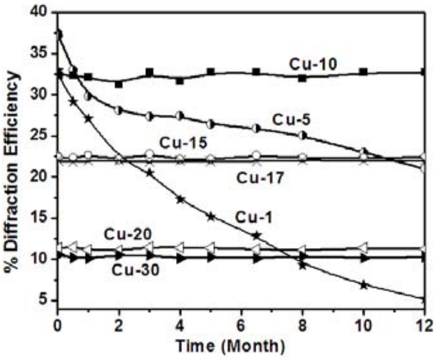


Fig.7.5. The DE of different Cu doped films on storage

The $CuCl_2$ concentration required to maintain stable efficiency is directly proportional to the MB concentration. If the dye concentration is increased, the amount of $CuCl_2$ required for crosslinking also increased; accordingly the sensitivity and efficiency decreased. At high dye concentration, 24% stable DE was observed for a higher Cu concentration. But to achieve this efficiency, the energy requirement was very high (1300mJ/cm^2).

7.7.Stability of Leucoform

If the dye molecules remain in its leucoform on storage, there will be less absorption losses during reconstruction. As a result major part of the reconstructing beam gets diffracted resulting in better DE. The reconversion of MB from leucoform to initial state is already reported in the case of MBPVA-AAm films [18]. To check the stability of the leucodye in Cu doped films, the absorption spectra of the samples with different copper concentrations were recorded before and after exposing to the laser beam (5 mW/cm^2 for 10 min) .The change in absorbance on storage was determined for all samples and it is depicted in Fig.7.6.

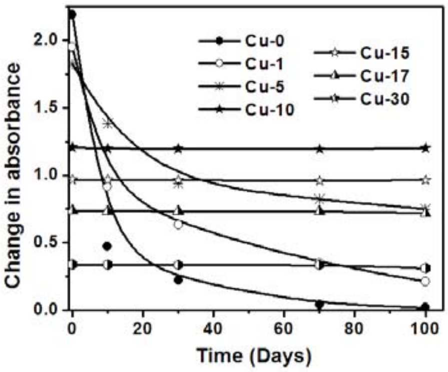


Fig. 7.6. The change in absorbance on storage.

At low Cu concentrations there is a change in absorbance on storage. But Cu-10 samples or higher Cu concentration did not show any decrease of change in absorbance on storage. Since the sensitivity of samples with higher $CuCl_2$ concentrations is lower than that of *Cu-10*, bleaching is less for these films and thus the change in absorbance is low compared to that of *Cu-10* films. In the case of *Cu-10* and samples with higher Cu concentrations, the dye molecules in the exposed regions remain in the leuco form for months as in CMBPVC films [19-20]. But unlike CMBPVC, in Cu doped MBPVA/AAm films the gratings could be stored for years with stable efficiency. On Cu doping, the dye molecules may trap inside the crosslinked PVA and which results in the stability of leucoform. The stability of the leucoform may be the major reason for obtaining a constant DE in Cu doped films [8].

7.8. Resolution of the Material

Gratings were recorded on the optimum sample *(Cu-10)* at different spatial frequencies. Constant DE could be obtained for gratings recorded with 625-1400 lines/mm. Above this spatial frequency, the efficiency decreased. The spatial resolution of the undoped MBPVA/AAm films was also the same. Thus with the incorporation of cupric chloride the resolution of the material remains unaffected. Fig.7.7 and Fig.7.8 shows the AFM image of the gratings (1 month after recording) recorded with 1100 lines/mm. The fringe spacing is 0.925µm. The thickness of the laser-exposed region is lower than that of the unexposed regions. The relief height (depth) was determined using a Dektak 6M stylus profiler and the surface profile is shown in Fig.7.9. The depth of the fringes recorded at various spatial frequencies was 3-4 nm. So the contribution of the surface relieves to total diffraction on adding to the RI modulation is negligible.

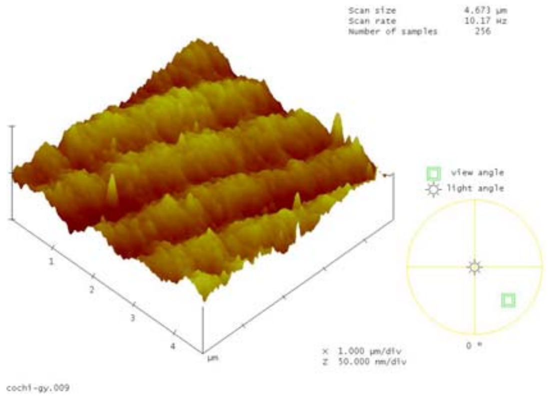


Fig. 7.7 AFM image of the gratings recorded with 1100 lines/mm (3D view)

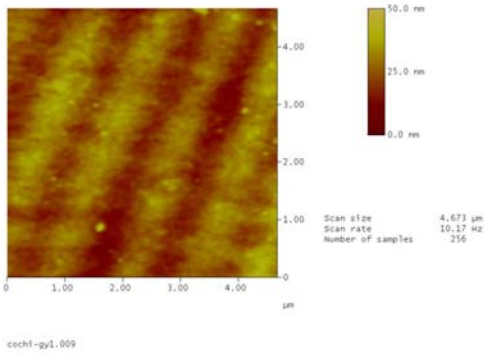


Fig. 7.8 AFM image of the gratings recorded with 1100 lines/mm (2D view)

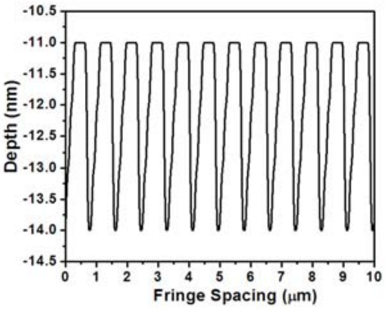


Fig. 7.9 Surface profile of the grating with a spatial frequency of 1200 lines/mm.

7.9. Shelf Life of the Material

To determine the shelf life of the film, gratings were recorded on *Cu-10* film on each day after preparation (drying) of the film. The films were kept in a dark box at room temperature. The films showed the highest efficiency of 32% only for few days after preparation. The efficiency was found to be decreased on ageing of the film and gratings could not be recorded on these films after 2.5 months of preparation. Fig.7.10 is the plot of DE on ageing the samples. The decrease in efficiency on ageing is due to the polymerization of monomer. As the shelf life of Cu doped film is poor than that of undoped films, photocrosslinking can also be another reason. The film quality was unaffected on ageing and the dye is not faded on ageing. But the RI modulation decays on ageing and it is the reason for the decrease in efficiency on ageing.

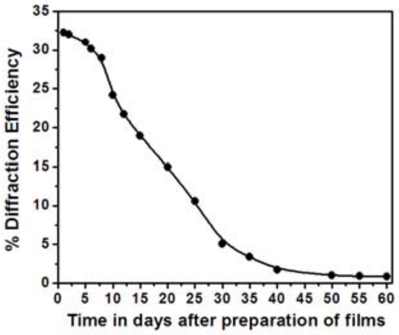


Fig. 7.10. The DE on ageing of the sample

7.10. Dynamic Range of the Material

The dynamic range of the *Cu-10* film was determined by angular multiplexing. For this gratings were recorded on the films at four different angles (30°, 25°, 20°, 15°) separated by 5° between recordings for an exposure of 600mJ/cm^2. This angle was chosen so that the first order diffracted peak of each grating would not contribute to DE of neighboring gratings. DE of each grating on multiplexing with the corresponding inter beam angle is plotted in Fig.7.11. The efficiency of each grating was 32%, 2.34%, 0.56 % and 0.08 % respectively. As the efficiency decreased with the number of multiplexed gratings, further recordings were not carried out. The decrease in DE with the number of multiplexed gratings is due to the less RI modulation on each recording [1]. This is because majority of the monomers are consumed during first recording and hence highest RI modulation occurred during first recording.

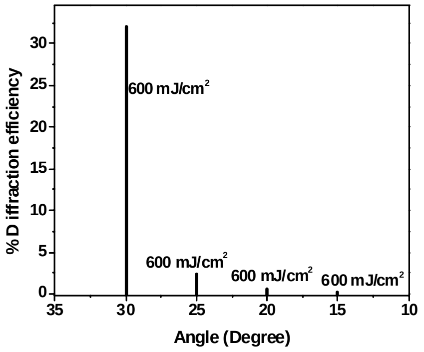


Fig.7.11. DE of gratings multiplexed with an exposure of 600mJ/cm^2

As the majority of the diffracted energy is concentrated in the first grating and to increase the uniformity of multiplexed gratings, the exposure energy for the successive gratings were progressively increased. So in order to obtain gratings of equal DE; a number of trials have done by varying the exposure energies for each recording. Among those, two trials are plotted in Fig. 7.12 and Fig.7.13; here also equal DE was not achieved for multiplexed gratings.

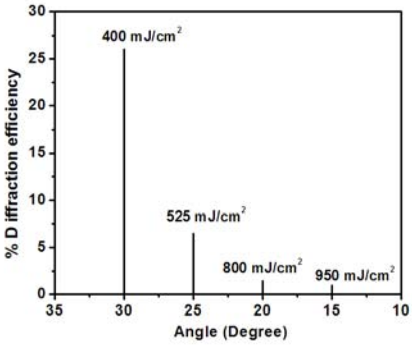


Fig.7.12. DE of gratings multiplexed by varying exposure

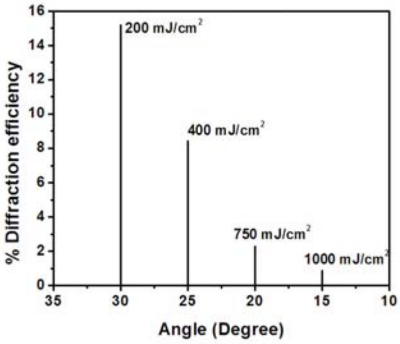


Fig.7.13. DE of gratings multiplexed by varying exposure

Finally gratings with equal efficiencies (~2%) were obtained for the exposure energies 50 mJ/cm^2, 200 mJ/cm^2, 500 mJ/cm^2 and 800mJ/cm^2 [21]. The efficiency of each grating on multiplexing is plotted in Fig.7.14. The dynamic range of Cu doped films (thickness =120µm) when four gratings were multiplexed is calculated as 0.57. The dynamic range of a recording medium highly depends on the film thickness and hence it could be improved by increasing the film thickness.

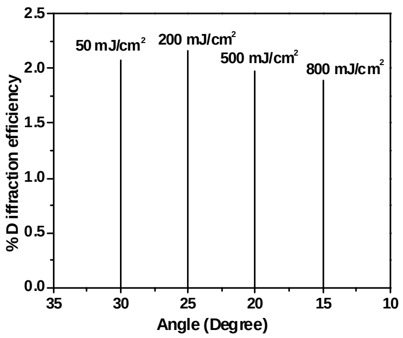


Fig.7.14. DE of gratings multiplexed to have equal efficiency

7.11. Recording of FT Hologram

FT holograms were recorded using the experimental setup illustrated in section 2.13 [21]. The FT of the letters was constructed using lenses and was allowed to interfere with an unexpanded beam (reference beam). This interference pattern was recorded on the film. After recording, the images were reconstructed by illuminating with the reference beam. The reconstructed image was photographed using a CCD camera. Fig.7.15. shows the FT hologram of letter ‘R’ recorded on *Cu-10* film where (A) is the object, (B) FT and (C) the reconstructed image.

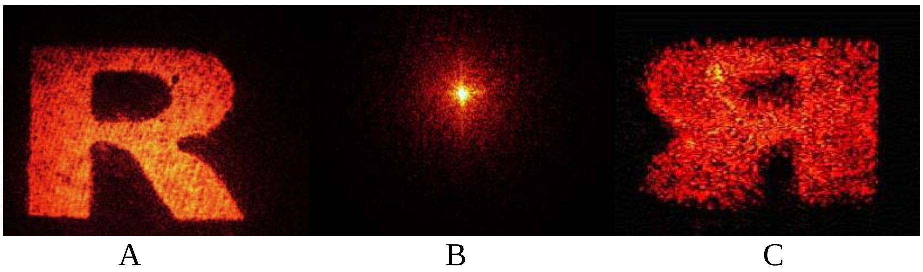


Fig.7.15. FT hologram of letter ‘R’ recorded on Cu doped film where (A) is the object, (B) FT and (C) the reconstructed image.

7.12. Recording of Hologram

Transmission holograms were recorded on Cu doped films and the photograph of the recorded hologram is shown in Fig.7.16. The importance of the photopolymer film described in the present work is that it needs no chemical or thermal treatment after recording. Silver halide emulsions (PFG, AgFa, Fuji etc) that are commonly used for recording requires tedious wet processing and special attention has to be given during the chemical fixing and drying processes.

Fig.7.16. The photograph of the hologram recorded and reconstructed using He-Ne laser

7.13. Comparison of Cu Doped and Undoped MBPVA/AAm Films

The gratings were stabilized by copper doping. Table 7.1 is the comparison of undoped and Cu doped *(Cu-10)* films fabricated under optimized conditions.

Table 7.1. Comparison of undoped and Cu doped films

	Undoped MBPVA/AAm	Cu doped MBPVA/AAm
Efficiency	70%	32%
Optimum Exposure	120 mJ/cm^2	600 mJ/cm^2
RI modulation	0.05	0.062
Storage life of grating	Decrease in efficiency on storage	Stable efficiency
Dye behaviour	Leucoform is not stable	Stable leucoform

7.14. Conclusion

A red sensitive material that can be used as a permanent recording medium, Cu doped MBPVA/AAm film, which is a promising candidate for both display holography and holographic data storage was developed. Copper chloride acts as a crosslinker in MBPVA/AAm films and helps to store gratings recorded on it for longer periods without any fixing process. There is an optimum $CuCl_2$ concentration required for keeping the DE constant. The optimum film shows 32% DE and 1400 lines/mm could be recorded on it. The efficiency of the optimum film remains unaltered even after two years of recording. The major advantage of the material is that it does not require any type of fixing or development process. Holograms were recorded on this economic, red sensitive permanent holographic material.

References

1. H. Sherif, I.Naydenova , S.Martin , C. McGinn C ,V.Toal , J.Opt.A:Pure Appl.Opt.,7, 255 (2005)
2. H. Coufal, D. Psaltis, G. T. Sincerbox, Holographic data storage , (Springer) (2000)
3. Kincade K, Laser Focus World, Oct. 68 (2003)
4. S. Gallego, M. Ortuno, C. Neipp, C. Garcia, A. Belendez , I. Pascual, Opt. Exp., 11, 181 (2003)
5. S. Blaya, M. Murciano, P. Acebal, L. Carretero, M. Ulibarrena , A. Fimia, Appl. Phys. Lett., 84, 4765 (2004)
6. S. Martin, P. E. L. G. Leclere, Y. L. M. Renotte, V. Toal ,Y. F. Lion, Opt. Eng., 33, 3942 (1994)
7. B. M. John, K. Sreekumar, R.Joseph, C. S.Kartha , Proc. Intl. Conf. ICOL- 05, Dehradun, India (2005)
8. B.M. John, R.Joseph, K.Sreekumar, C.S.Kartha, Jpn.J.Appl.Phys., 45, 8686 (2006)
9. S. Gallego, C. Neipp, M. Ortuno, A. Beléndez, I. Pascual, J.Mod.Opt., 51, 491 (2004)
10. R. Changkakoti, G. Manivannan, A. Singh and R. A. Lessard, Opt. Eng. 32, 2240 (1993)
11. S. Lelievre , J. A. Couture,Appl. Opt., 29, 4384 (1990)

12. M. Barikani, E. Simova, M. Kavehrad, Appl. Opt., 34, 2172 (1995)
13. R.A. Lessard, R. Changkakoti, G. Manivannan, Proc. SPIE 1559, 438 (1991)
14. R. Changkakoti, G Manivannan, A.Singh, R.A Lessard, Opt. Eng., 32, 2240 (1993)
15. G Manivannan, R. Changkakoti, R.A Lessard, Opt. Eng., 32, 671 (1993)
16. J. Gong, L. Luo, S.H. Yu, H. Qian , L. Fei, J. Mater. Chem., 16, 101 (2006)
17. B. M. John, R.Joseph , K. Sreekumar, C.S.Kartha Proc. Intl. Conf. on optoelectroncs, Fibre, Optics & Photonics(Photonics 2006), Allied publications, 2, 609 (2006)
18. G. Pradeep, S. Cyriac, S. Ramkumar , C. S. Kartha, Jpn. J. Appl. Phys., 39, 137 (2000)
19. M. Ushamani, K. Sreekumar, C. S.Kartha, R. Joseph: Appl. Opt., 41, 1984 (2002)
20. M. Ushamani, N. G. L. Deenja, K. Sreekumar, C. S. Kartha, R. Joseph, Bull. Mater. Sci., 26, 343 (2003)
21. B.M. John, R. Joseph, C.S. Kartha, Proc. 19th Kerala Science Congress, 4 (2007)

Chapter 8

Summary and Conclusion

More and more new ideas, emerging from basic research in holographic materials promise a break through that may change the profile of society in future. The goal of a material researcher is to develop new materials, produce and reproduce it and finally make it available to the prosperity of society. This chapter gives the summary of the thesis which has concentrated on the development of photopolymer holographic recording media.

In order to respond to the industry's growing demand for applications like holographic data storage, holographic optical elements, holographic displays, holographic interferometry, optical waveguides etc. much emphasis has been put on methods to develop new recording materials with high efficiency and high sensitivity. As holographic data storage enables a big leap towards the terabyte level, there is surging interest in the development of new cost effective, self developing and self processing recording materials with high dynamic range. Hence designing of highly light sensitive systems that polymerize at an ever faster rate have become a growing challenge. The discovery of new photosensitive mechanism or novel monomer formulae may lead to new materials hitherto unseen in the innovation of holography. Attempts have been made to develop new photopolymer formulations which can contribute a lot to the realm of holography. The thesis mainly aims at the development of various photopolymer films and its maximum exploitation. A summary of the results obtained from the experimental works are presented here.

A photopolymer system generally consists of a polymeric host matrix, photopolymerizable monomer, photosensitizing dye, charge transfer agent etc. For the present study, poly (vinyl alcohol) and poly (vinyl chloride) were selected as binder and methylene blue was used as the photoinitiator. Films were fabricated with different monomers and other matrix additives. The photopolymer films were fabricated using gravity settling method at room temperature. This technique is interesting on account of its easiness to set up, inexpensiveness etc. By this method, uniform films were obtained with good optical quality. The polymer films were characterized using different characterization tools and its composition was optimized to have highest efficiency, sensitivity, storage life etc. The most notable thing is that any type of fixing technique (chemical or thermal) and / or UV curing were not employed after grating formation. All the films were stored under normal laboratory conditions and were of good environmental stability.

Complexed methylene blue sensitized Poly (vinyl chloride) (CMBPVC) is a recording medium developed in our laboratory. Though only 0.26% efficiency was obtained, the material was attractive on account of the stability of the leucostate of the dye. Though the leuco form was stable, the stored data was found to be vanished within four hours of recording. Like conventional photopolymerizable systems, these films were not comprised of any monomer or electron donor and the shelf life of the system was also limited. In the present work, these limitations were more or less overcame. By eliminating the complexing agent, copper acetate, the shelf life was improved. With the incorporation of the electron donor, pyridine, the storage life of the gratings was extended to 3 days and the gratings were of 0.46% efficiency. Though two monomers, butyl acrylate and vinyl acetate were incorporated to improve the efficiency, none has given a good result. This may be due to the high threshold requirements of this monomer. Though the efficiency was not improved with the given recording power (5mW/cm^2), higher efficiency will be achieved with high power lasers.

Methylene blue sensitized poly (vinyl alcohol) (MBPVA) films were fabricated with different monomers like acrylic acid, methacrylic acid, butyl acrylate, acrylonitrile and vinyl acetate. Of these only vinyl acetate incorporated films showed considerable efficiency (5.5% at 420mJ/cm^2). But the shelf life of the film was poor. To overcome this, the fabrication steps were modified. Vinyl acetate was partially polymerized by solution polymerization to an oligomeric state and films were fabricated using the partially polymerized vinyl acetate. These films showed 6.3% efficiency for an exposure of 750mJ/cm^2. The gratings recorded on these films vanished within 24 hrs. From the optical absorption studies it became clear that the dye molecules have deexcited to the original state within 24hrs of storage. This resulted in the decrease in efficiency of the films. As the dye molecules get recovered to the original state, gratings were recorded on the same area for a number of times. It was found that the material can be reused more than twenty times with considerable efficiency. On reusing it around 20 times, there was a strong shift in the absorption spectrum showing the conversion of the dye molecules to thionine state. Usually the photopolymerizable materials are write-once-read-many (WORM) type and this is the first report of a reusable photopolymer system. As the material is reusable, it can be used in laboratories to build the experimental setups and to check whether the alignment is perfect or not.

The film fabrication steps of MBPVA/vinyl acetate films were modified by partially polymerizing the vinyl acetate in ethanol medium at 80°C. The storage lives of the gratings were improved to 48hrs. To enhance the storage life of the recorded grating, films were fabricated by incorporating two additional monomers, acrylic acid and methacrylic acid. The methacrylic acid doped MBPVA/vinyl acetate films showed a storage life of more than 2 years whereas that of acrylic acid doped films lasted only for one and a half months.

MBPVA/Acrylamide films were fabricated and film composition was optimized. Diffraction efficiency of 70% was achieved on these films at an exposure of 120mJ/cm^2. Using a He-Ne laser, 1350 lines/mm could be recorded on the optimized film with 70% efficiency. At higher spatial frequencies the efficiency was found to decrease. Fourier transform holograms, by which data pages are recorded on holographic data storage devices, were recorded. The dynamic range of the material is 0.8 when four holograms were angularly multiplexed on that. As the spectral sensitivity of methylene blue extends to the entire visible region, gratings were recorded on these films using lower wavelength lasers. The feasibility of using MBPVA/Acrylamide as a panchromatic material is studied. Holograms recorded on this material are of good quality. Since high efficiency can be obtained with low exposures, this medium is important in applications such as holographic interferometry and the fabrication of holographic optical elements.

To improve the storage life of the gratings recorded on MBPVA/ Acrylamide films, different crosslinking agents were incorporated. Though high efficiency was achieved in MBPVA/Acrylamide, the gratings recorded were not stable and the efficiency was found to decrease on storage. The storage lives of the recorded gratings were improved with the addition of crosslinkers. Among the different inorganic crosslinkers, cupric chloride and ammonium dichromate were found to be suitable to stabilize the data.

Addition of ammonium dichromate makes the MBPVA/Acrylamide films more stable and helps in storage. Unlike MBPVA/Acrylamide, a self enhancement of efficiency was observed for a particular combination of dye and dichromate. Even though the initial efficiency of dichromated films was low (20%), the self-enhancement observed makes the system regain the diffraction efficiency (42%) and helps in maintaining the efficiency constant for several months.

Dichromated PVA/Acrylamide films (sensitive to blue and green) were also fabricated and it showed an efficiency of 51% for an exposure of 750mJ/cm^2. Usually in dichromated PVA films, the efficiency just after recording is very low and it is stabilized and improved after thermal fixing. The efficiency and sensitivity achieved in this case is much higher than that of conventional dichromated PVA films.

On Cu doping, the gratings recorded on MBPVA/Acrylamide films were stabilized to have stable efficiency for more than two years. This self developing material which can be used as a permanent recording media showed an efficiency of 32% for an exposure of 600mJ/cm^2. As Cu doped films are free from all fixing techniques and the data is stable, it is a promising candidate for holographic data storage and other applications where real time monitoring is required.

Compared to the already existing recording media, photopolymer films described in the present study have many merits. The materials are important on account of their high efficiency, ease of fabrication, low cost and lack of fixing or development process. All the commercially available recording materials are very expensive. Photopolymers are also not exception for this. Its high cost makes people a distance away from holography. For the holographic technology to become popular for different applications, a cost effective recording medium is necessary. The polymers described in the present work deserve special attention as they are economically cheaper.

Major Achievements

The major achievements of the work presented in this thesis are listed below.

- Fabrication of red sensitive holographic material (MBPVA/Acrylamide) with 70% efficiency
- Possibility of using MBPVA/Acrylamide as a panchromatic material is introduced
- Red sensitive, self developing, permanent holographic material (Cu doped MBPVA/acrylamide) with more than 30% efficiency has been developed
- Red sensitive film (Cr doped MBPVA/Acrylamide) showing self enhancement of efficiency has been developed
- Development of a reusable recording medium MBPVA/vinyl acetate
- Fabrication of MBPVC films for the first time with the incorporation of electron donor and monomers

Future Outlook

MBPVC films fabricated were of low efficiency and sensitivity. An improved efficiency is expected with high recording powers and its sensitivity could be improved with proper choice of photosensitizers.

In MBPVA/vinyl acetate, the recovery of dye molecule and hence its reusability is not under the control of the experimentalist. The recovery of dye molecule may be due to its interaction with oxygen and hence by the use of suitable oxidizing agents, the ‘reusing’ property can be controlled.

On metal ion doping the initial efficiency and sensitivity of MBPVA/acrylamide films were lowered. The efficiency and sensitivity of the films could be improved by incorporating suitable monomers and electron donors. Instead of metal ions, different organic crosslinkers can be incorporated to MBPVA/acrylamide films and hence the efficiency could be improved. Replacing the monomers with multi-functionality, its performance can be improved. An antireflection coating if provided on the film will avoid the reflection losses and hence the efficiency could be improved. As thickness plays a crucial role in controlling the efficiency, sensitivity and dynamic range, the thickness of the film could be optimized for both display and storage applications. By adopting different multiplexing techniques like peristrophic or spatial multiplexing, the storage density could be improved. In the case of MBPVA/Acrylamide films, wavelength multiplexing can also be done.

Transmission holograms were already recorded on the photopolymer films. The next step is the recording of different types of holograms. White light viewable holograms and colour holograms (using red, green and blue wavelengths) could be recorded on the polymer films.

With the incorporation of nanoparticles, the resolution of the material is expect to be improved. The nanoparticles can also induce a threshold to the photopolymer films, which is profitable when a holographic disc is produced out of the polymer. The threshold requirement helps the disc to be handled under normal environmental conditions (without dark room storage).

Holographic optical elements (HOEs) are destined to re-define the role of optics in several areas. HOEs can function as gratings, lenses, aspherics or any other type of optical element. Different types of HOEs could be recorded on and its performance can be evaluated.

The environmental stability is an important factor when the film is going to be commercialized. So in order to commercialize the material, the effect on temperature and humidity on the film properties has to be studied.