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Enhancement of Diffraction Efficiency and Storage Life of Poly (Vinyl Chloride) Based Optical Recording Medium with the Incorporation of an Electron Donor

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Abstract

The diffraction efficiency, sensitivity and storage life of Methylene blue sensitized poly (vinyl chloride) film was improved by the addition of an electron donor in the matrix. The addition of pyridine enhanced the diffraction efficiency by two times and storage life of the gratings was increased to 2-3 days.

OCIS Codes: 090.2900, 050.1950, 160.2900, 160.5470, 210.4810

1. Introduction

The development of suitable recording media is one of the challenges in the area of holographic data storage. The main advantage of using photopolymers for holography is the 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 [1-6]. Polymeric materials such as polymethyl methacrylate (PMMA), Polydiacetylene (PDA), polyvinyl carbazole (PVK), polyvinyl alcohol, (PVA), polyacrylic acid (PAA), polythiophene, etc have been widely investigated for holographic applications[7-8]. Another important material is poly vinyl chloride (PVC) on account of its properties like dimensional stability, ease of fabrication, non-toxicity, stability against UV radiations, transparency in the visible spectral region etc. It can also be fabricated to any desired thickness and it is not influenced by the humidity. The feasibility of using this matrix as an optical recording medium has been reported earlier by making this as copper acetate doped methylene blue sensitized polyvinyl chloride (CMBPVC) films.[9]

Unlike in other matrices, the change of state occurring to the dye molecules (Methylene blue) on laser irradiation is permanent in PVC and it exists in the leuco form itself [10]. 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.[10-11] 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.[12] Also in CMBPVC films, 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 and storage life of the gratings recorded in the CMBPVC system. Initially CMBPVC films were prepared by dissolving suspension grade PVC in cyclohexanone to get 13.5% PVC solution. The sensitizer solution was prepared by dissolving methylene blue and copper acetate (2:1 ratio) in glacial acetic acid. The PVC solution was sensitized with the so prepared sensitizer solution[9]. To improve the shelf life of the material, copper acetate was avoided. Even without copper acetate the film showed almost the same behavior in the transmittance curve. The relative transmittance of both the CMBPVC and MBPVC films on exposing to an expanded laser beam (632.8 nm) having an incident intensity of 5mW/cm^2 is shown in figure 1. In this case also the change of state occurring to the dye molecule on laser exposure was stable on storage but the storage life of the grating was only few hours. In order to improve the storage life of the gratings recorded on MBPVC the material has to be modified and intended to make it as a photopolymerizable material. A photopolymerizable recording medium generally consists of a photosensitizer (photoinitiator that is sensitive to the visible wavelengths and an electron donor) and one or two monomers dissolved in a polymer matrix. The photoinitiators could be dye or metal ions. The grating formation in a photopolymer recording medium is due to the refractive index modulation resulting from the polymerization of monomers and its diffusion and the absorbance modulation caused by the excitation of photoinitiators. The authors' intention is to improve the storage life of MBPVC films by establishing a refractive index modulation due to polymerization and diffusion of monomers. Due to the less solubility of monomers and electron donors, the efforts made to incorporate a monomer or electron donor in MBPVC solution prepared as described above went in vein. So the preparation technique was modified and by the modified procedure monomers and electron donors could be easily incorporated to the MBPVC solution. The MBPVC films fabricated with electron donors gave an enhancement of diffraction efficiency and the gratings recorded on such films could be stored for 2-3 days.

2. Methodology

Instead of sensitizing the PVC solution by adding methylene blue as in the earlier case, MB solution was prepared by dissolving methylene blue (Qualigens) in cyclohexanone (Qualigens) to have a dye concentration of 1.59 $x10^{-2}$ mol/l. 15% MBPVC solution was prepared by dissolving 15 g suspension grade PVC powder (supplied by Reliance India, Mumbai) having k value 70 in 100 ml of MB solution. This MBPVC solution was casted on micro slides using gravity settling method and the drying period was 24 hours.

The samples were exposed to the expanded beam from a 15 mW, CW He-Ne laser (Melles Griot) having emission at 632.8nm. The real time transmittance studies and recording of grating were done on this material as explained in our earlier reports [8-11]. Diffraction efficiency was calculated as the ratio of first order diffracted beam intensity to that of incident beam intensity. The effect of laser exposure was studied by taking the absorption spectra before and after laser exposure with a Hitachi U-3410 UV- visible-NIR spectrophotometer. The refractive index before and after exposure was measured using an Atago DR-M2 refractometer. Change in refractive index was obtained by taking the difference between the refractive indices of exposed and unexposed samples.

3. 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 then 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. From the relative transmittance, rate of bleaching was found out by taking the slope of the relative transmittance Vs time curve at different time intervals. Figure 2 shows the relative transmittance Vs exposure for MBPVC films prepared by the conventional procedure and that by the new procedure for an incident intensity of 5mW/cm^2. In figure 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 new method. So the material sensitivity of MBPVC$_2$ is low compared to that of MBPVC$_1$.It is not fully clear why there is a considerable difference between the optical properties of the films prepared by two procedures. It may probably because, by changing the sequence of addition of PVC and methylene blue, the distribution of methylene blue in the PVC matrix is made more uniform while following the latter method, ie. Adding PVC to a solution of methylene blue in cyclohexanone. The change of state occurring to methylene blue 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 diffraction efficiency of 0.2% and the storage life of the grating was extended to 24 hours. The comparison of both MBPVC1 and MBPVC 2 are shown in Table 1.

4. 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 electron donor produced during laser exposure initiates the polymerization reaction. Usually in PVA based based recording systems like PVA/acrylamide [4] and PVA/vinyl acetate [13], triethanolamine was used as charge transfer agent. The sensitivity of eosin PVA/acrylamide was improved with the incorporation of diphenyliodonium chloride [14]. Even though several electron donors were tried to be incorporated in the MBPVC solution, due to the less solubility in cyclohexanone, only Dimethyl formamide (DMF), Pyridine, Triethylamine (TEA) and Dimethylamino benzaldehyde (DBA) were found to be compatible with MBPVC. The relative transmittance of these films on exposing to a laser beam of intensity $7mW/cm^2$ is shown in figure 3. In all cases the dye molecules in the exposed regions remained in the leucoform. But the shelf life was poor as the dye in the unexposed regions fades on storage in all cases except for pyridine doped samples. So pyridine was selected as the electron donor for further study.

5. Electron donating mechanism of pyridine

Pyridine is the nitrogen containing aromatic analogue of benzene and the structure is shown in figure 4.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 electron donor.

When the MBPVC films were exposed to red wavelength, MB molecules absorb light and get excited ($^1MB^*$) and it is transferred to triplet state ($^3MB^*$) by an intersystem crossing[15]. An 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. If a monomer is incorporated to the system, the pyridine radicals formed could be added to the C=C of monomer molecules and hence initiates the polymerization reaction.

6. Optimization of Pyridine concentration

MBPVC solution was sensitized with pyridine (Qualigens) and films were prepared with pyridine concentration varying from 0.59 mol/l to 3.54 mol/l. At higher concentrations of pyridine, 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 Px (X= 0.5 to 3). The relative transmittance of these films for an incident intensity of 7mW/cm^2 is shown in figure 5. The relative transmittance is highest for P1 samples i.e. for films with pyridine concentration 1.126mol/l. The rate of bleaching of the P_1 film is shown in figure 6. Within 2 minutes the transmittance became constant and further bleaching was not taking place. Thus, within this time all the dye molecules were transferred to the leuco form.

To optimize the pyridine concentration, gratings were recorded on the samples at a fluence of 2000mJ/cm^2 and diffraction efficiency was determined. 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 mol/l (sample P_1). The variation of diffraction efficiency with pyridine concentration is shown in figure 7. The refractive index of these samples was determined before and after exposing to the laser beam and the change in refractive index was calculated. The change in refractive index with pyridine concentration is plotted in figure 8. Highest refractive index modulation was obtained for P1 sample

The change in absorbance on laser exposure (2100 mJ/cm^2) was determined as in our earlier works[8] and plotted in figure 9. Highest absorbance modulation also occurs for P1 sample. The film that showed highest refractive index and absorbance modulations gave maximum diffraction efficiency. Like CMBPVC, here also the change of state (leuco form) occurring to the dye molecule is permanent. Figure 10 shows the absorption spectra of the sample P1 storage.

To optimize the energy required for the grating formation, gratings were recorded on sample P_1 at different exposures. Maximum diffraction efficiency was obtained for exposure energy of 1500 mJ/cm^2 and it remains constant (0.46%) from to 1500 to 3000 mJ/cm^2. The grating recorded on these films could be read for 2-3 days. The comparison of both MBPVC2 films and MBPVC films with optimum pyridine (P1) are shown in Table 2.

Though the diffraction efficiency obtained was low, the storage life of the recorded grating and shelf life of the MBPVC films were improved with the incorporation of pyridine. The Diffraction efficiency of the material could be improved with the incorporation of suitable monomers. The sensitivity and efficiency of the MBPVC/Pyridine could be improved by the use of some complexing agents and attempts are being made to improve the sensitivity efficiency.

7. Conclusion

The preparation technique of the MBPVC system developed in our lab was modified and pyridine was incorporated to the PVC matrix as charge transfer agent. The diffraction efficiency and storage life of the gratings recorded on MBPVC was improved with the incorporation of pyridine. Maximum Diffraction efficiency obtained for an exposure of 1500 mJ/cm^2 was 0.465 and the grating could be stored for 2-3 days.

Acknowledgement

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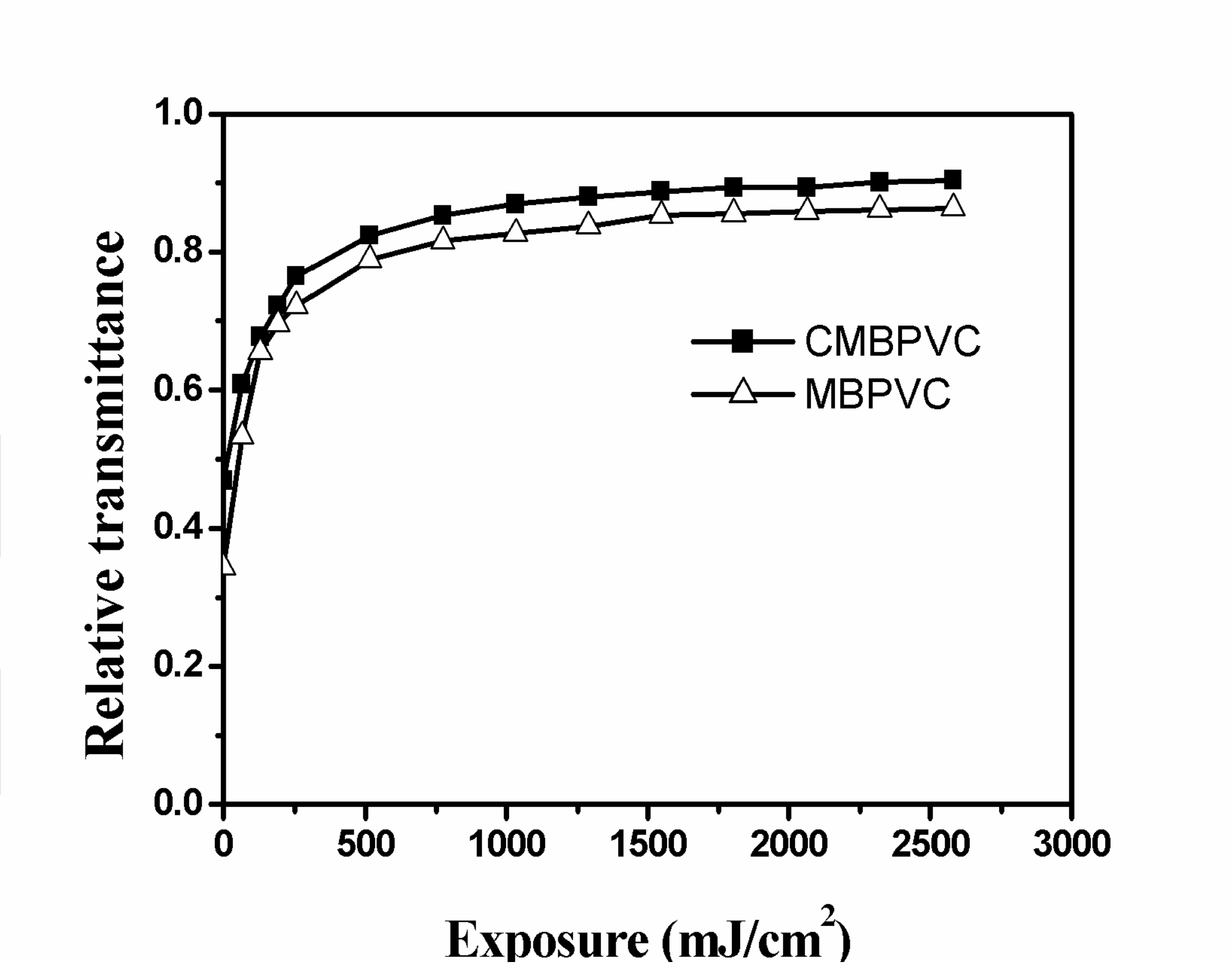
Figure Captions

1. Figure1. Relative transmittance of CMBPVC and MBPVC films
2. Figure2.Relative transmittance of MBPVC films fabricated using both the old and new procedure
3. Figure(3) Relative transmittance of MBPVC films with different electron donors
4. Figure 4. Structure of pyridine
5. Figure 5. Relative transmittance of samples with different pyridine concentrations.
6. Figure 6. Rate of bleaching of sample with pyridine concentration 1.126 mol/l (sample P_1)
7. Figure 7. Variation of diffraction efficiency with pyridine concentration
8. Figure 8. Change in refractive index with pyridine concentrations
9. Figure 9. Change in absorbance with pyridine concentrations
10. Figure 10. The absorption spectra of the sample P1 on storage.

Table Captions

1. Table 1. Comparison of MBPVC prepared using old and new procedures; MBPVC1 and MBPVC 2
2. Table 2. Comparison of MBPVC2 films and MBPVC2 films with optimum pyridine concentration (P1)



Relative transmittance
Exposure (mJ/cm^2)
CMBPVC
MBPVC
0.0
0.2
0.4
0.6
0.8
1.0
0
500
1000
1500
2000
2500
3000

Figure1.

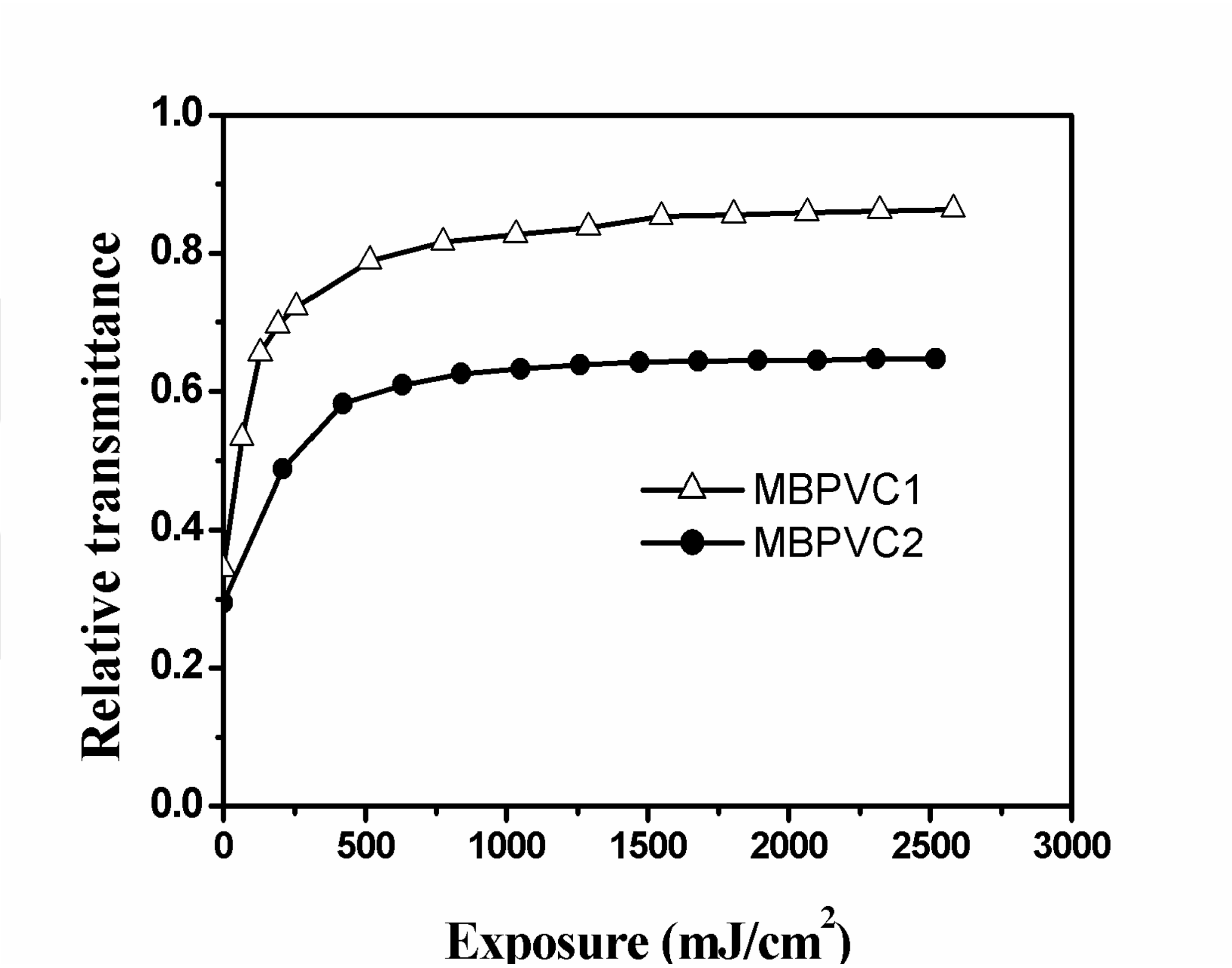

Relative transmittance
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
2500
3000
MBPVC1
MBPVC2
Exposure (mJ/cm2)

Figure2.

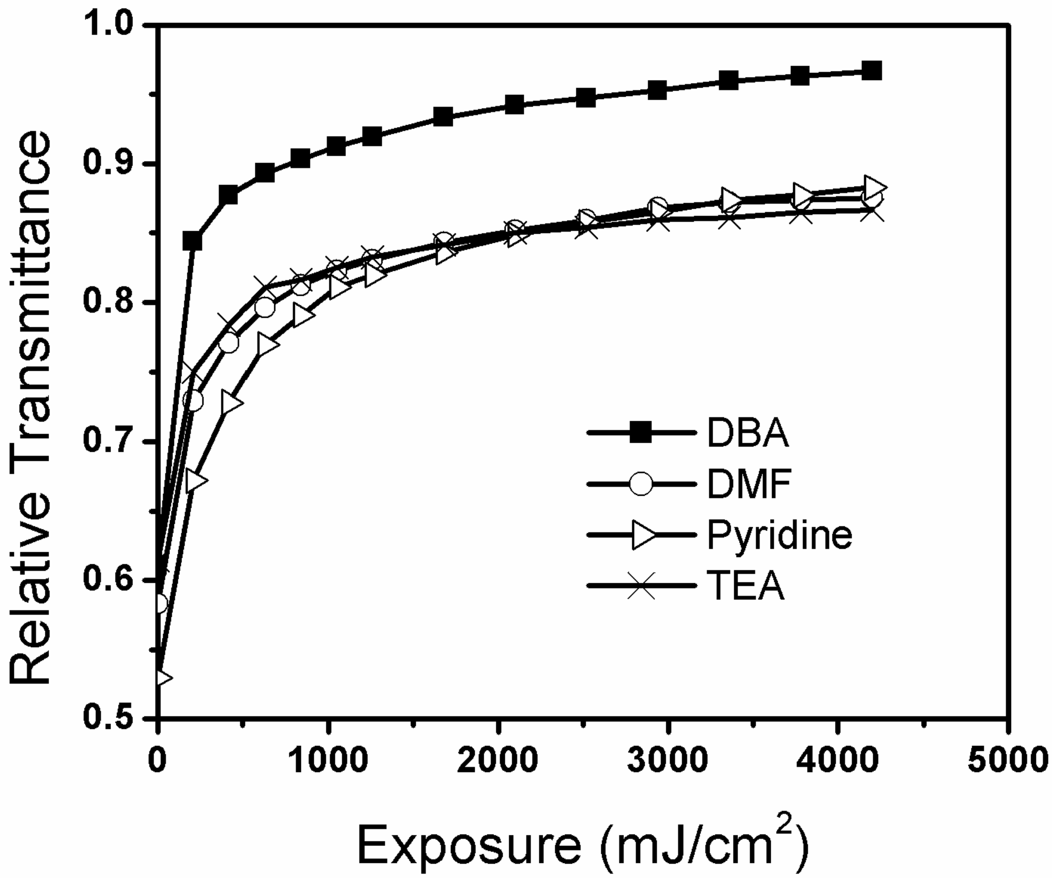

1.0
0.9
0.8
0.7
0.6
0.5
Relative Transmittance
0
1000
2000
3000
4000
5000
Exposure (mJ/cm^2)
DBA
DMF
Pyridine
TEA

Figure 3

.

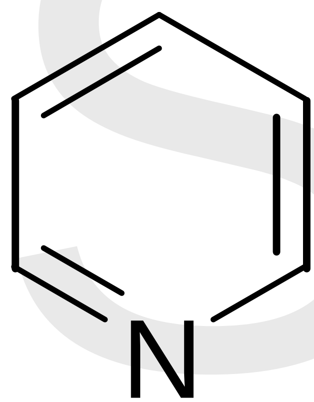
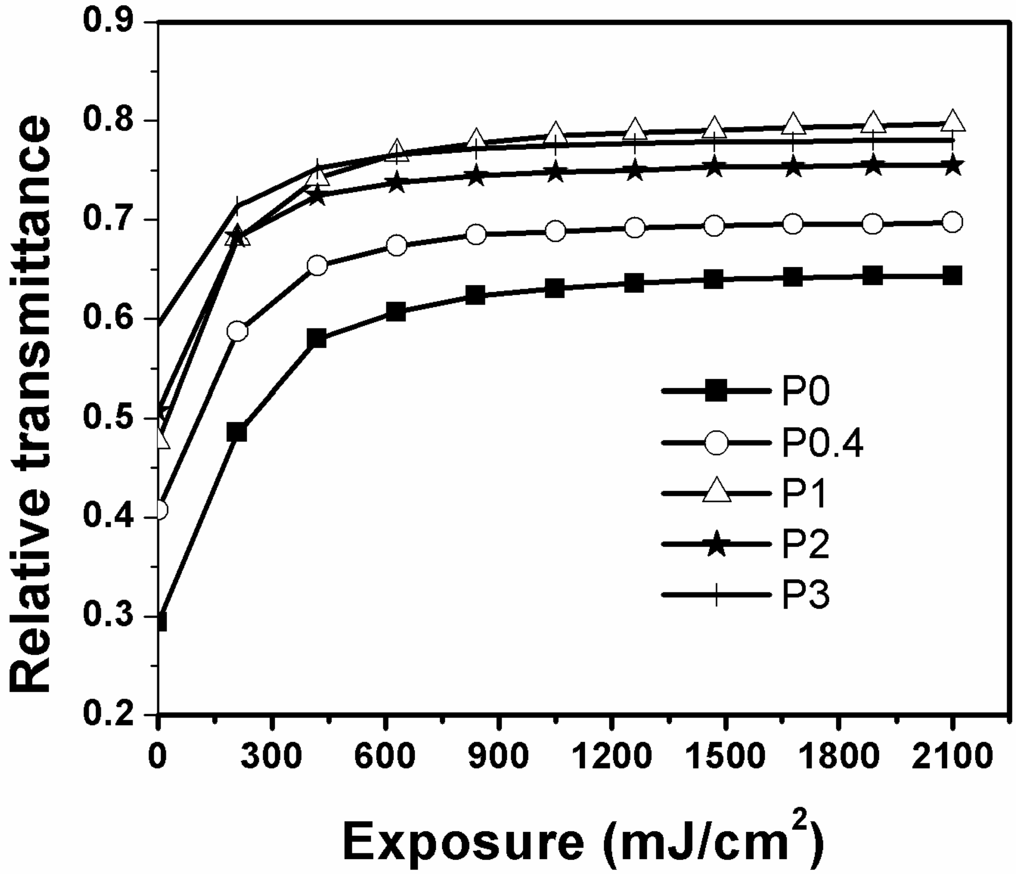
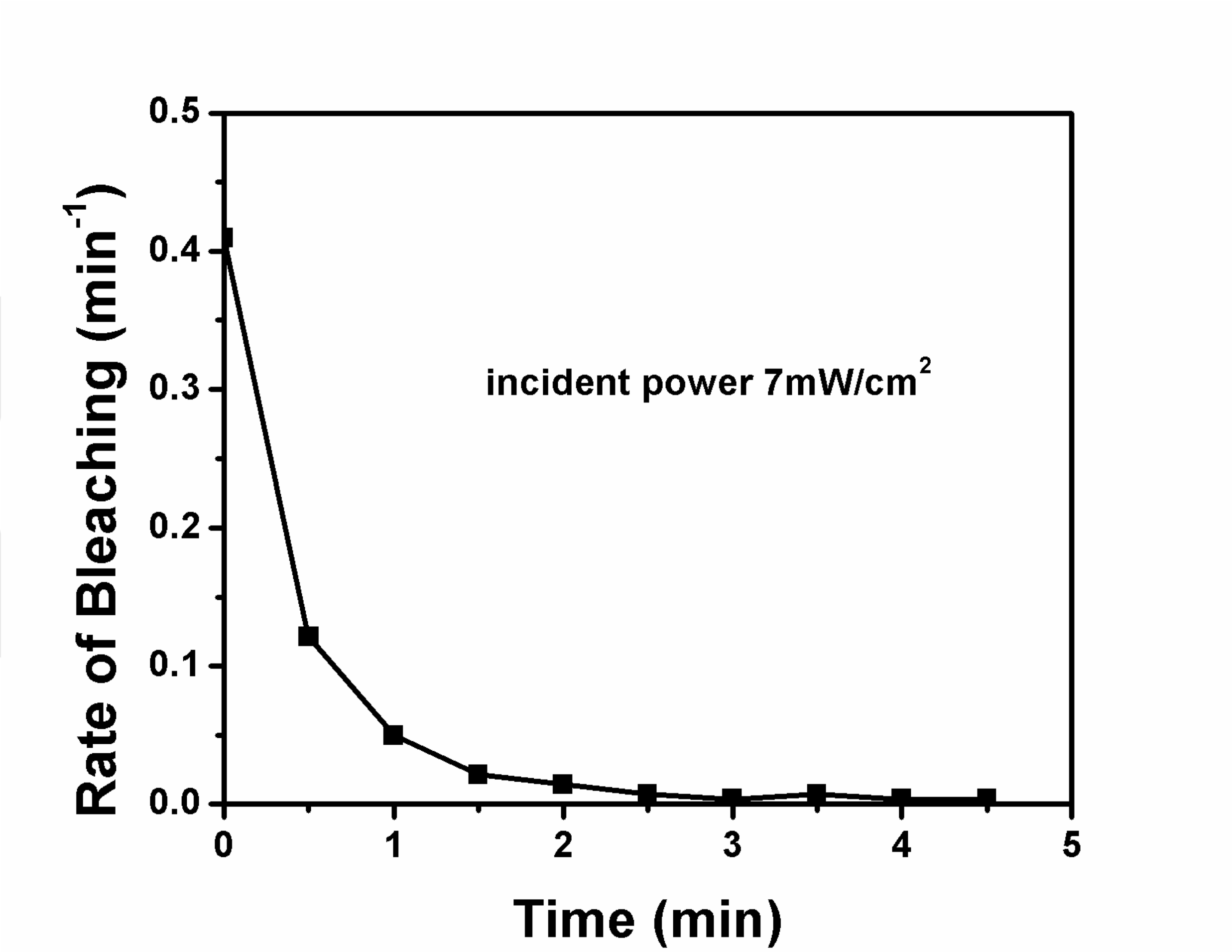


Figure 4



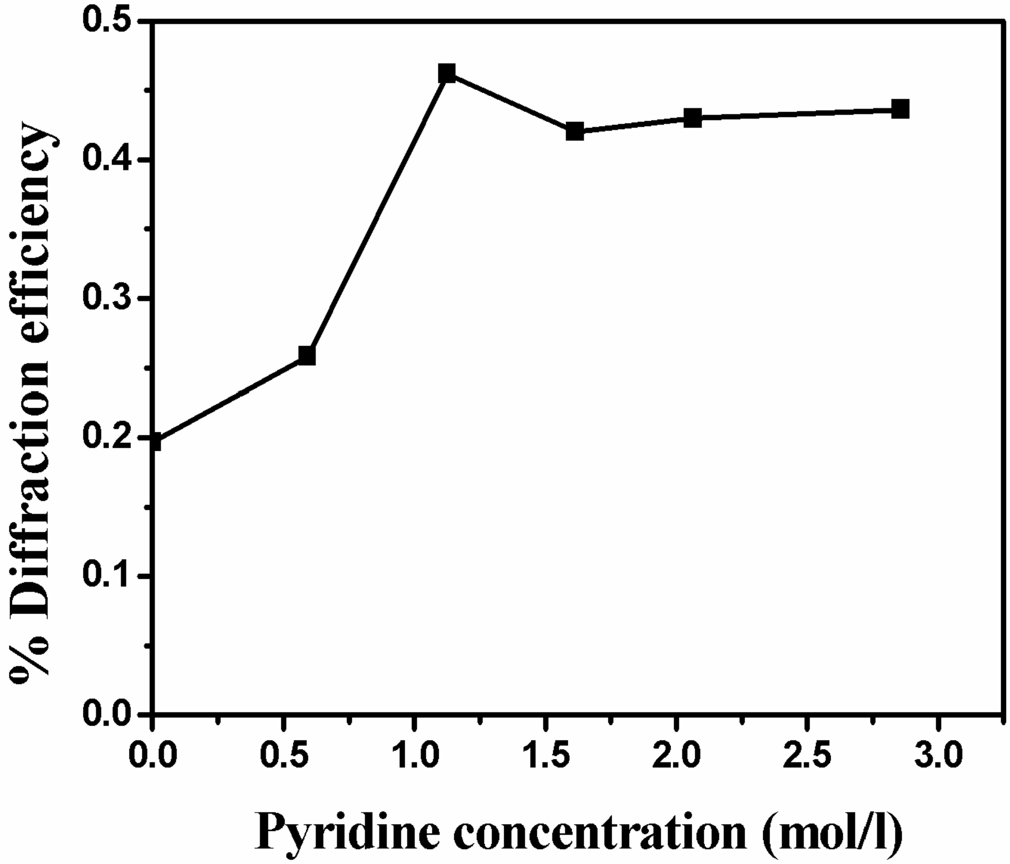
Relative transmittance
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0
300
600
900
1200
1500
1800
2100
Exposure (mJ/cm2)
P0
P0.4
P1
P2
P3

Figure 5.



Rate of Bleaching (min⁻¹)
0.5
0.4
0.3
0.2
0.1
0.0
incident power 7mW/cm²
0
1
2
3
4
5
Time (min)

Figure 6.



% Diffraction efficiency
0.0
0.1
0.2
0.3
0.4
0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Pyridine concentration (mol/l)

Figure 7

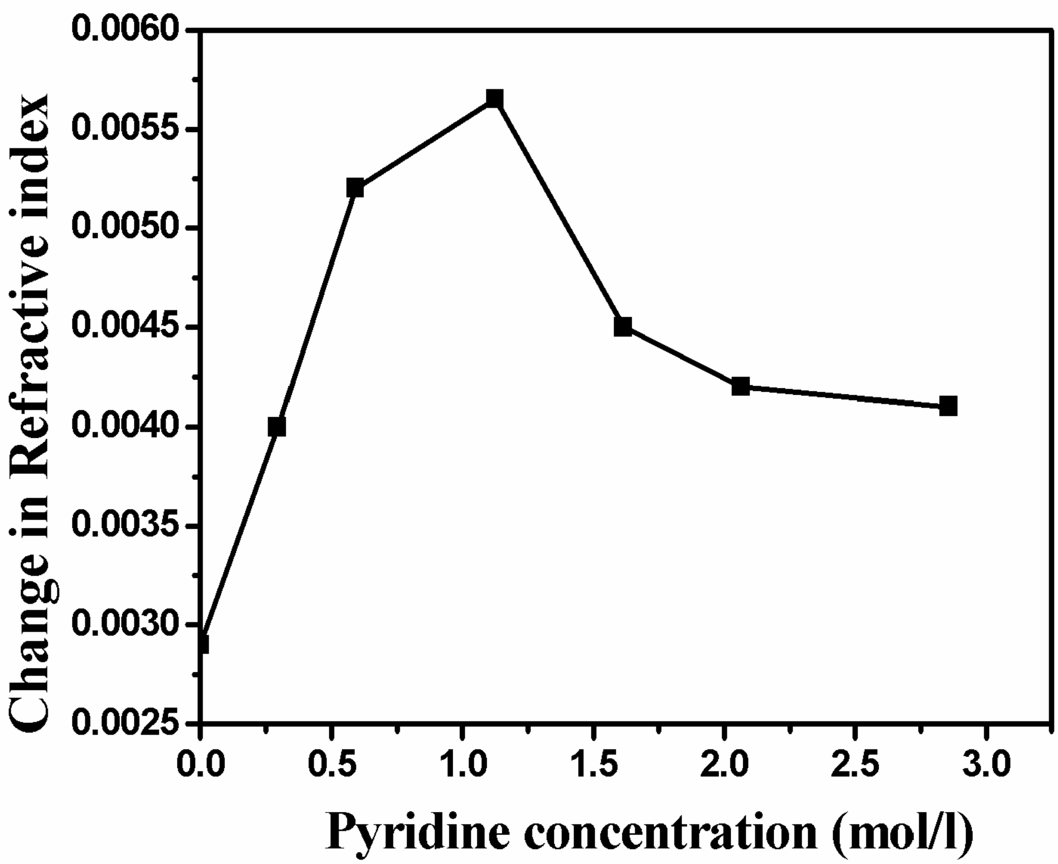

0.0060
0.0055
0.0050
0.0045
0.0040
0.0035
0.0030
0.0025
Change in Refractive index
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Pyridine concentration (mol/l)

Figure 8

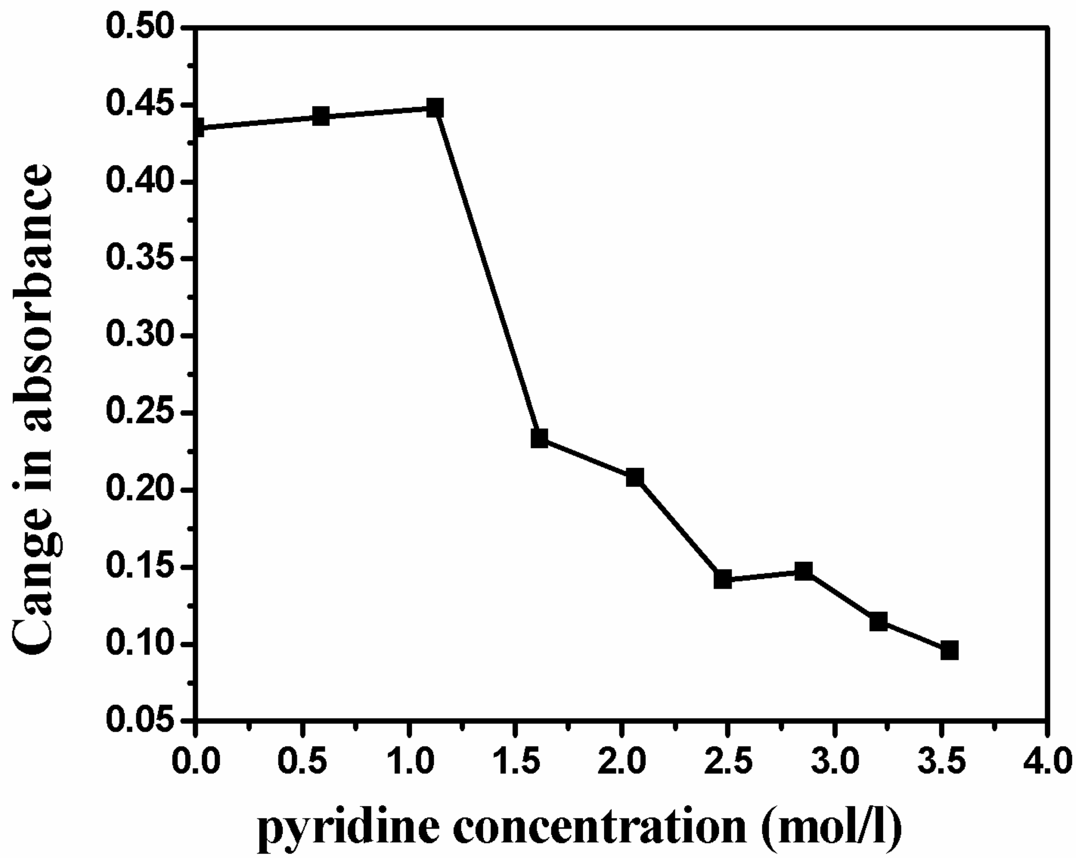

0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
Cange in absorbance
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
pyridine concentration (mol/l)

Figure 9

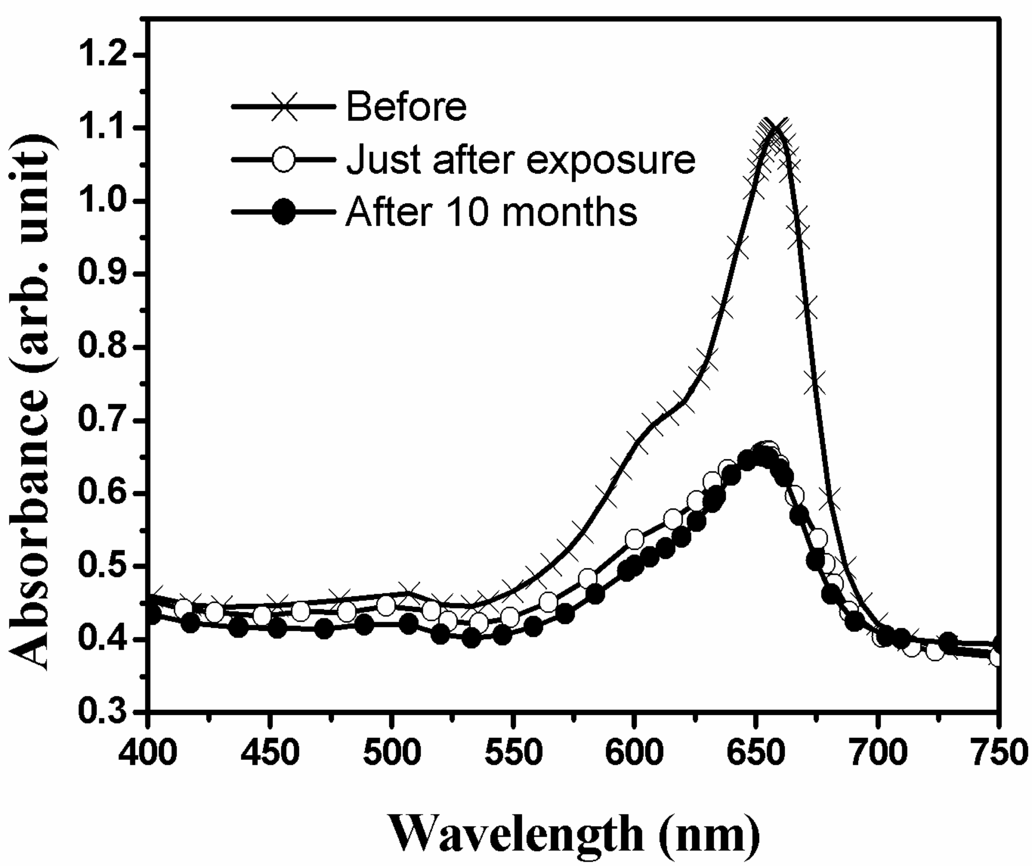

Before
Just after exposure
After 10 months
Absorbance (arb. unit)
Wavelength (nm)
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
400
450
500
550
600
650
700
750

Figure 10

Properties	MBPVC 1	MBPVC 2
Material sensitivity	High	Low
Diffraction Efficiency at 2000mJ/cm^2	0.24%	0.2%
Storage life	4 hour	24 hour
Possibility of incorporation of electron donor and monomer	No	Yes

Table1

Properties	MBPVC2	P1
Material sensitivity	Low	High
Diffraction Efficiency	0.2% at 2000mJ/cm^2	0.46% at 1500mJ/cm^2
Storage life	24 hour	2-3 days
Behaviour of leucoform	Stable	Stable

Table 2