Synthesis of Mechanoresponsive Healable Polymers through Diels–Alder Unclick/Click Chemistry via Single Electron Transfer-Living Radical Polymerization

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Ph.D. Thesis, Under the Faculty of Technology

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Certificate

This is to certify that the thesis entitled **"Synthesis of Mechanoresponsive Healable Polymers through Diels–Alder Unclick/Click Chemistry via Single Electron Transfer-Living Radical Polymerization"** is a genuine record of research work carried out by **Ms. Nishad K. M.**, under my supervision, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, to the Cochin University of Science and Technology, and further that no part of the work reported in this thesis has been presented before for the award of any other degree. All the relevant corrections and modifications suggested by the audience and recommended by the doctoral committee of the candidate during the presynopsis seminar have been incorporated in the thesis.

Dr. Rani Joseph
(Supervising Guide)

Declaration

I hereby declare that the work presented in this thesis entitled **"Synthesis of Mechanoresponsive Healable Polymers through Diels–Alder Unclick/Click Chemistry via Single Electron Transfer-Living Radical Polymerization"** is my own unaided work under the guidance of Dr. Rani Joseph, Emeritus Professor, Department of Polymer Science and Rubber Technology, and the same has not been submitted elsewhere for the award of any other degree.

Cochin - 22
30/12/2017

Nishad K. M.


بِسْمِ اللهِ الرَّحْمٰنِ الرَّحِيمِ

To my dear family…

"Everybody is a Genius. But If You Judge a Fish by Its Ability to Climb a Tree, It Will Live Its Whole Life Believing that It is Stupid."

-Albert Einstein

"Everything will be okay in the end. If it's not okay, it's not the end."

-John Lennon

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At any cost I have finished, but not alone...,and now feel ecstatic. After five years of long journey through different phases of misery, hectic laughter, and tragedy, now I am near to the wrapping up stage. The moment is here to look back to pen the gratitude from my heart to all people who have supported me and assisted me directly or indirectly in exploring the expanses of knowledge . Without their untiring support, I may not be there where I am today, obviously not lucidly. So to express gratitude in a proper way is difficult. Certainly I will strive to do my best. I would like to reveal that I am not at all good at expressing gratitude but good at keeping it in mind.

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Journey took a different path when Dr. S. Prathapan Sir decided to include me in his wonderful research group when my work demanded organic synthesis. From that moment onwards, I have been there in the Dept. of Applied Chemistry till now utilising all the facilities and also financial assistance. I consider myself as fortunate to be a part of both Dept. of Polymer Science & Rubber Technology and Dept. of Applied Chemistry, Cochin University of Science & Technology since this collaboration made me capable to build the thesis around the title "Synthesis of Mechanoresponsive Healable Polymers through Diels–Alder Unclick/Click Chemistry via Single Electron Transfer-Living Radical Polymerization." Right from the beginning of my research itself, Prathapan Sir is there in the every nook and corner of my work. With the

realization that mere 'thank you' is inadequate to express my indebtedness, "Sir,...Thank you Sir, for all benevolent support you have given, infinite patience that you have shown, guidance that you have rendered, sacrifices that you have made, confidence that you have instilled in me, consistent encouragement that you have provided etc. Sure! Without these I could not have been reached this far. My memories in CUSAT will be around the unforgettable day 09-10-2013, the day when I have started mechanophore synthesis under your guidance. Sir, I cannot simply imagine a better advisor. You are the best conductor of blessings from God to me that's why I am adorned with the official address of Assistant Professor in Chemistry."

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The thing is that I didn't find any boundary and compartmentalization all along my doctoral research span. I humbly express my sincere thanks to former and the current Faculty members who were adorned the post of H.O.Ds in both PS & RT and DAC along with all other Faculty members and non-teaching staff of both Dept. of Polymer Science & Rubber Technology and Dept. of Chemistry for their timely help and co-operation whenever I approached.

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HRMS analysis was carried out in NIIST, Thiruvananthapuram. A word of thanks to Ms. Santhini who carriedout HRMS analysis and also to Thahira Madam who has helped in LCMS analysis with out any delay. I also acknowledge Saji, CUSAT who has meticulously carried out NMR analysis. I also remember Vishnu (Late) who supplied chemicals and apparatus in time.

No thesis is possible without the support of library. I take this time to appreciate library staff who have always done their best to render whatever service they could.

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I will always rejoice the wonderful time with roommates Anjali, Renjana, Reshma and Beena. "Thank you for your love and caring and also for making my days in Athulya hostel memorable."

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The last but precious phrase of gratitude that I have conserved is for my dear family, who is my backbone and have supported all along my life more than I deserve and longed to see my dreams come true. Of course my Bava and Amma showed the way although they were not familiar and gave all the support and arrangement they could to reach my dream securely. My brother is responsible for my thrust for chemistry. As time goes on, I understood that I have selected right scholastic career. They took a lot of pain to clear the official hurdles to complete my research when I was blessed with the Job as Assistant Professor. My sister whom I used to call bety has helped me in every possible way she could.

"Bava, Amma, Rayu, Pappa, Baby, Bety, Popu, Aashif, Sharaf, Sajeen,... Your prayers and support for me built the platform on which I am staying and also sustained me so far. I know you have been suffering, but..., I hope I can make you proud of me in return. I am not separate from you and you are not separate from me. So let us thank all the people who have supported us throughout our journey."

In the name of Allah, The Most Gracious, the Most Merciful, we express sincere gratitude to all who, guided, inspired and supported us throughout our journey.

Nishad K. M.

Preface

The default mechanochemical response of polymers to external mechanical stress is unselective bond scission which ultimately results in mechanical degradation of polymers. The early recognition of damage or failure is of high importance since we can take preventive measures before the material reach mechanical failure. Polymer mechanochemistry, wherein chemical transformations are triggered by mechanical force with the help of mechanophores, presents unique opportunities to create functions including damage sensing, healing and stress induced strengthening by the productive channeling of mechanical energy from the applied stress to activate chemical reactions. The main focus of our work was to synthesize a polymer having the stress responsive and self-healing capability and also to analyse the possibility of mechanically induced chemical reactions. So in this thesis we introduce stress responsive and self-healing mechanophore incorporated polymers by employing Diels–Alder Unclick/Click chemistry and Single Electron Transfer-Living Radical Polymerization (SET-LRP) protocol.

Stress responsive unit called mechanophore was incorporated to polymers using Single Electron Transfer-Living Radical Polymerization. The mechanophore was based on Diels–Alder Unclick/Click chemistry. Living Radical Polymerization (LRP) is a particularly powerful method for the synthesis of polymers with precisely controlled molecular weight, functionality and dispersity. But most of the LRP reactions require stringent anaerobic conditions, which limit its application. Here we report a modified method for SET-LRP that could be successfully carried out in the presence of air without deoxygenating the reaction mixture.

Analysis of stress responsive behavior was carried out by mechanochemical activation studies using ultrasonication. The initial mechanochemical studies with GPC and NMR didn't give any evidence for the Unclick reaction with no appreciable change in the corresponding spectra. But the studies with UV-Vis and PL spectroscopy gave evidence for the retro Diels–Alder reaction. To probe possibility of the mechanically

induced Diels–Alder reaction which is responsible mechanically induced reforming property, model Diels–Alder reaction were carried out by sonicating chloroform solution of diene and dienophile. Results of the experiment confirmed mechanically induced Diels–Alder and thus the utility Diels–Alder for the synthesis of stress induced strengthening of material. Both Diels–Alder and retro Diels–Alder reactions are feasible during ultrasonication and the equilibrium depends up on concentration of reactants, ultrasound intensity, etc.

Self-healing ability of synthesized polymers were analyzed using ^{1}H NMR spectroscopy, UV-Vis spectroscopy and PL spectroscopy by carrying out Diels–Alder reaction at room temperature between anthracene end capped polymer and maleimide in the solid state.

Summary of the thesis

The thesis is divided into five chapters. A short summary of each chapter is as follows.

Chapter 1

Introduction

Chapter 1 is divided in to two sections. In the first section, an overview pertaining to polymer mechanochemistry is outlined with primary focus on self-healing and stress-sensing applications. Diels–Alder Click/Unclick chemistry is also explained in the context of self-healing as well as stress responsive behavior.

In the second section efficiency of SET-LRP to synthesize mechanophore attached polymers is discussed. Special emphasis is given to the tolerance of SET-LRP towards oxygen in the presence of reducing agents.

The motivation of the present study and the major objectives are also included at the end of the chapter.

Chapter 2

Synthesis of a few initiators for Single Electron Transfer-Living Radical Polymerization.

Chapter 2 begins by laying out the background on Diels–Alder reaction and then go on to the synthesis and characterization of mechanophore and mechanophore initiator. The characterization of physical properties of synthesized compounds using IR spectroscopy, NMR spectroscopy and mass spectroscopy is summarized. Structures of a few synthesized mechanophore and mechanophore initiators are given in **Chart 1** and **Chart 2** respectively.

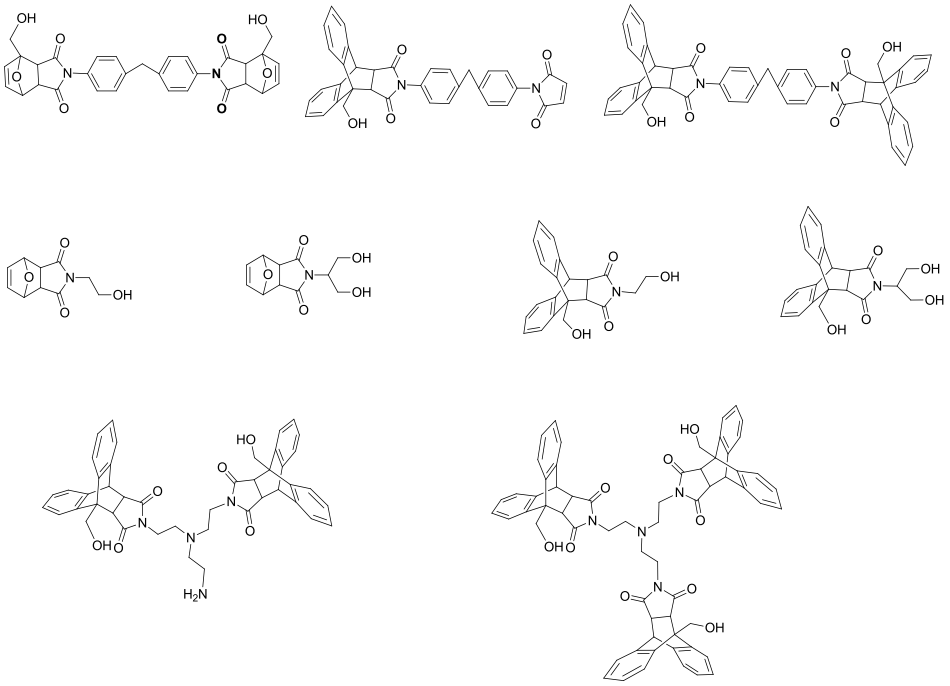


Chart 1

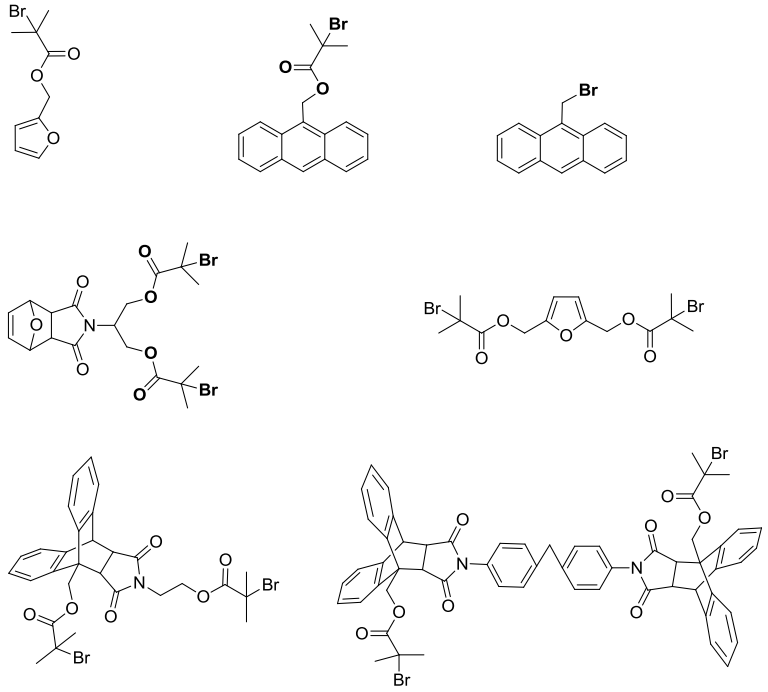


Chart 2

Chapter 3

Synthesis of polymers via SET-LRP

In this chapter, we report a modified method for SET-LRP reaction. Polymerization was carried out without using standard deoxygenation procedures such as Freeze-Pump-Thaw cycle and nitrogen purging. Nevertheless, high molecular weight block polymers could be synthesized using macroinitator. Experimental methods for the synthesis of mechanophore attached polymers through modified Single Electron Transfer-Living Radical Polymerization are included in this chapter. Characterization of synthesized polymers by IR, NMR and GPC gave evidence for a nearly symmetrical living block polymer. The active chain end groups were then exploited for chain extension reaction. CBABC type block polymer was also synthesized by this method. Structures of synthesized polymers by our modified Single Electron Transfer-Living Radical Polymerization (SET-LRP) is given in **Chart 3**.

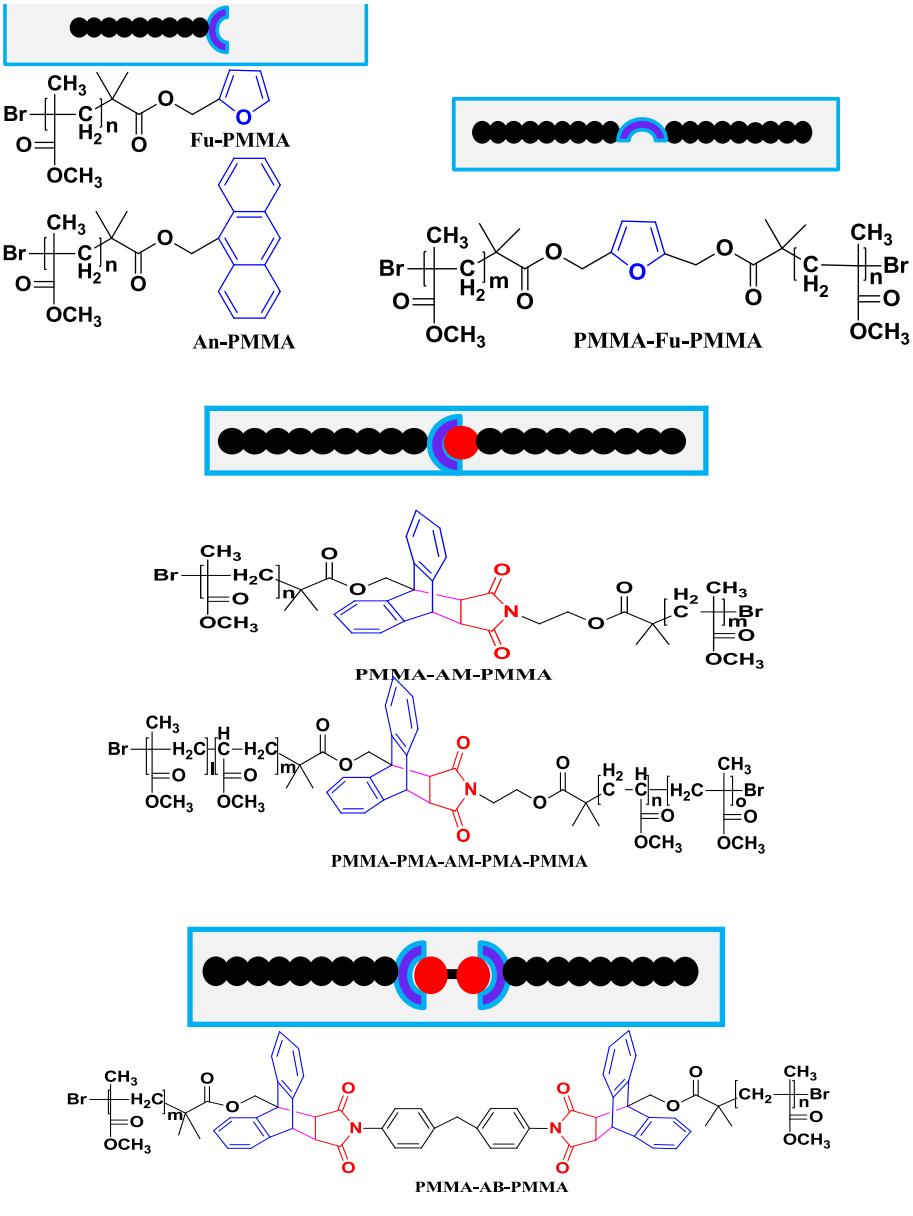

Fu-PMMA
An-PMMA
PMMA-Fu-PMMA
PMMA-AM-PMMA
PMMA-PMA-AM-PMA-PMMA
PMMA-AB-PMMA
PAN-AB-PAN

Chart 3

Chapter 4
Mechanochemical Activation Studies

The fourth chapter is devoted to the investigations on mechanochemical activation of novel mechanophore attached PMMA by ultrasonication experiments. Upon subjecting a chloroform solution of polymer to ultrasound irradiation, an increase in the UV-Vis absorption characteristic of anthracene was observed indicating the stress induced retro Diels–Alder reaction. It means that this mechanophore is a potential candidate as force sensor since there is a direct correlation between fluorescence intensity and intensity of ultrasound irradiation. Effect of position of mechanophore as well as dependence of molecular weight of polymer on mechanochemical activation were studied. It was found that retro Diels–Alder reaction occurred only when mechanophore unit is centrally located in the polymer chain. Measurement of mechanochemical transduction with polymers of different molecular weight revealed that molecular weight of polymer is the key descriptor of mechanochemical activity. Interestingly sonicated polymer solutions did not exhibit the characteristic absorption spectrum of anthracene after keeping the film for 12 h at room temperature, an evidence for the room temperature healing. The synthesized mechanophore attached polymer was found to have outstanding cleavage and healing behavior under mechanical stimulus.

Self healing studies were independently carried out. Maleimide group was clicked on anthracene end capped polymer film at room temperature in order to independently prove the self healing ability. These results promise to open way for the design and synthesis of self-healing and/or stress induced strengthening materials using anthracene bismaleimide mechanophore.

Force induced chemical reaction could enable material to avoid catastrophic failure by inducing stress induced crosslinking reaction. So this chapter begins with discussing mechanically induced chemical reactions and then goes on to mechanically induced Diels–Alder reaction that is responsible for stress induced strengthening behavior. Here we have carried out Diels–Alder reaction mechanically using ultrasonic irradiation

and the products were characterized on the basis of IR, ^{1}H and ^{13}C NMR spectroscopy.

Chapter 5

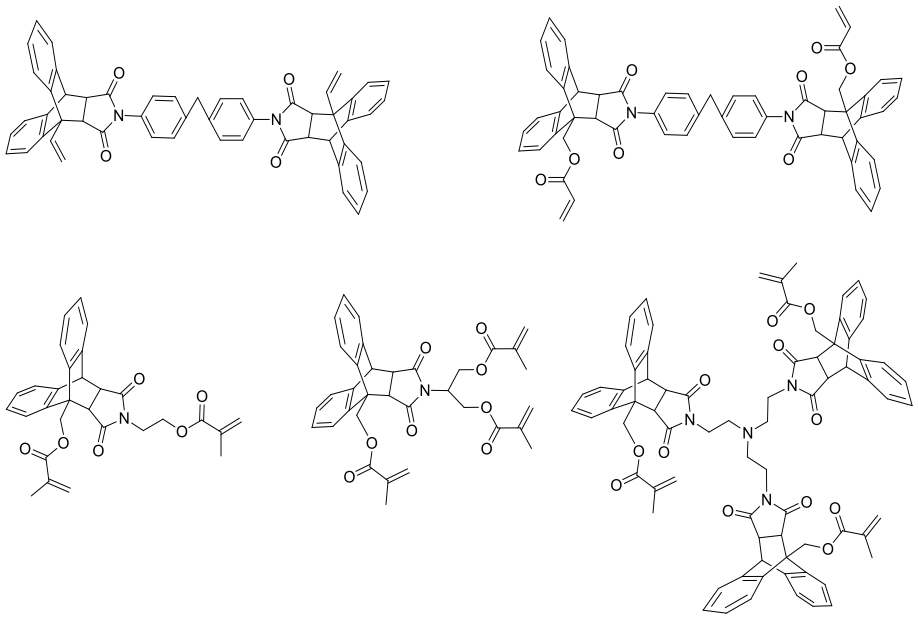
Summary and Conclusions

It consolidates research findings and proposes future directions of the work.

Chapter 6

Future Outlook

Here the mechanochemical activation studies were carried out using ultrasonication experiments in solution. But in actual situations the force is not given through ultrasonication and also not in solution state. So in order to study mechanochemical activation study in solid state mechanophore attached polymers, following crosslinkers were synthesized and the synthesized compounds were characterized by IR, NMR, GCMS and LCMS analysis and the studies are underway.



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Chapter **4**

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List of Publications

[1] Expeditious synthesis of novel mechanophore-linked poly(methyl methacrylate) by Cu(0)-mediated single-electron transfer living radical polymerization under mild condition, **Nishad, K. M.**; Rani, J.; Philip, K.; Prathapan, S. Proceedings of Prof. K V Thomas Endowment "International Symposium on New Trends in Applied Chemistry" (NTAC–2017), Research and Postgraduate Department of Chemistry, Sacred Heart College, Thevara, Kochi, Kerala, India. **ISBN 978-81-930558-2-3**

[2] Synthesis of Photochromic Dibenzobarrelenes, Saumya, T. S.; Aswathi, C. S.; **Nishad, K. M.**; Prathapan, S; Unnikrishnan, P. A. Proceedings of "International Conference on Materials for the Millennium" MATCON 2016, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, Kerala, India. **ISBN 978-93-80095-738**

[3] Cost Effective Synthesis of a Biologically Active Decapeptide on Hydrophilic Polymer Support by Solid Phase Peptide Synthesis, Rohini, K, C.; **Nishad, K. M**.; John, V, D.; Subashchandran, K. P. Proceedings of "International Conference on Materials for the Millennium" MATCON 2016, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, Kerala, India. **ISBN 978-93-80095-738**

Published abstracts and professional presentations

[1] Self-healing polymeric materials:– A review, **Nishad, K. M**.; Philip, K.; Rani, J. International Conference on Advances in Material science, ICAMS-2013, Post Graduate Department of Chemistry, Sree Sankara College, Kalady, Ernakulam, Kerala, India.

[2] Site selective Diels-Alder reaction of 9-(2-furylmethoxymethyl) anthracene, Saumya T.S.; **Nishad K. M**.; Prathapan, S.; Unnikrishnan P. A. National Seminar on Current Trends in Chemistry CTric-2013, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, Kerala, India.

[3] Expeditious synthesis of novel mechanophore-linked poly(methyl methacrylate) by Cu(0)-mediated single-electron transfer living radical polymerization under mild condition, **Nishad, K. M.**; Rani, J.; Philip, K.; Prathapan, S. Proceedings of Prof. K V Thomas Endowment "International Symposium on New Trends in Applied Chemistry" (NTAC–2017), Research and Postgraduate Department of Chemistry, Sacred Heart College, Thevara, Kochi, Kerala, India. **ISBN No. 978-81-930558-2-3**

[4] Synthesis of Thermally Reversible Ethanoanthracene/Trismaleimide Trifunctional Cross-Linker for Self Healing Polymer through Diels-Alder Click-Unclick Tool, **Nishad, K. M.;** Philip, K.; Rani, J.; Prathapan, S. National Seminar on Current Trends in Chemistry CTric-2017, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, Kerala, India.

[5] Single Electron Transfer-Living Radical Polymerisation of methyl methacrylate with activated Cu(0) wire in the presence of air under mild condition, **Nishad, K. M.;** Rani, J.; Philip, K.; Prathapan, S. Science Academies' Lecture Workshop on Advances in Supramolecular Chemistry and Nanoscience-2017, Research and PG Department of Chemistry, St. Joseph's College, Irinjalakkuda, Thrissur, Kerala, India.

[6] Stress–responsive Poly(methyl methacrylate) via covalently embedding novel mechanophore based on anthracene and bismaleimide, **Nishad, K. M.**; Rani, J.; Philip, K.; Prathapan, S. National Seminar on Emerging Trends in Chemical Research-2017, Research and Post Graduate Department of Chemistry, Christ College, Irinjalakkuda, Kerala, India. (Best Oral Presentation Award)

[7] Investigation of ultrasound-induced mechanochemical transduction of novel mechanoresponsive healable three arm star poly(methyl methacrylate), **Nishad, K. M.**; Rani, J.; Philip, K.; Prathapan, S. International conference on emerging frontiers in chemical science-2017, Post Graduate and Research Department of Chemistry, Farook College, Kozhikode, Kerala, India. **ISBN No. 978-93-5279-617-5**

List of Abbreviations and Symbols

ACN	acetonitrile
ATRP	atom transfer radical polymerization
Bipy	2,2'-bipyridine
br	broad
$CDCl_3$	deuterated chloroform
C	centigrade
CRP	controlled radical polymerization
CuLRP	copper-catalysed living radical polymerization
DCM	dichloromethane
DCP	dicumyl peroxide
DMF	*N,N*-dimethyl formamide
DMSO	dimethyl sulfoxide
DMSO-*d6*	deuterated dimethylsulfoxyde
d	doublet
DP	degree of polymerization/kinetic chain length
ESI-MS	electrospray ionisation mass spectrometry
FRP	free radical polymerization
FT-IR	fourier transform infrared
g	gram
GC-MS	gas chromatography-mass spectrometry
GPC	gel permeation chromatography
h	hour
Hz	hertz
I	initiator
IR	infrared
ISET	inner sphere electron transfer

K_i	rate constant of initiation
K_p	rate constant of propagation
K_t	rate constant of termination
LRP	living radical polymerization
m	multiplet
M	monomer
Me	Methyl
Me_6TREN	*N,N,N',N',N'',N''*-Hexamethyl-(aminoethyl)amine
min	minute
mg	milligram
mL	milliliter
mp	melting point
MMA	methyl methacrylate
MALDI	matrix assisted laser desorption ionisation
MS	mass spectrometry
M_n	number average molecular weight
$M_{n,NMR}$	M_n by nuclear magnetic resonance
$M_{n,GPC}$	M_n by gel permeation chromatography
$M_{n,th}$	theoretical number average molecular weight
Mp	peak molecular weight
Mw	molecular weight
nm	nanometre
M_w	weight average molecular weight
MWD	molecular weight distribution
NMP	nitroxide-mediated polymerization
NMR	nuclear magnetic resonance
OSET	outer sphere electron transfer
PDi	polydispersity index
PL	photo luminescence

PMMA	poly(methyl methacrylate)
ppm	parts per million
RAFT	reversible addition fragmentation chain transfer
RDA	retro diels–alder
RI	refractive index
ROMP	ring opening metathesis polymerization
rt	room temperature
s	singlet
SEM	scanning electron microscopy
SET-LRP	single electron transfer-living radical polymerization
t	triplet
TEA	triethylamine
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	tetramethylsilane
TPP	triphenylphosphine
UV	ultraviolet
UV-Vis	ultraviolet-visible

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Chapter 1
Introduction

Contents

Part A

Mechanoresponsive Healable Polymers

***Conspectus**: The inevitable mechanical stress on polymeric materials leads to polymer degradation resulting in the deterioration of material quality and consequently limit material's lifetime. With the advancement in polymer mechanochemistry, chemists sought to redirect the destructive mechanical energy to productive form that makes it possible for the material to perform stress induced strengthening, stress responsive and self-healing functions. This chapter provides a perspective on the fundamental aspects of polymer mechanochemistry along with key advancements in the area with special emphasis on mechanoresponsive, stress induced strengthening and self-healing applications.*

1.A.1 Mechanochemistry - Force triggered chemical reaction

Thanks to their unique combination of mechanical properties such as high strength, elasticity, processability, etc., polymers and their structural composites are used in a variety of applications. Even so, polymers are prone to catastrophic failure and aging due to the unavoidable stress experienced by materials during their service life.[1,2] Biological materials overcome this crisis by their acquired ability to sense damage, heal and even become stronger in response to mechanical forces.[3] So stress responsive and self healing materials are considered to be very significant since if damages are detected in the early stages they can be healed before the material reaches catastrophic failure. Inspired by mechanotransduction in biological systems such as hearing[4], tissue growth,[5] wound healing,[6] etc., polymer mechanochemistry has provided a route to redirect the destructive mechanical energy to constructive form by incorporating structural motifs called mechanophores which respond to mechanical force in a constructive manner. Mechanophores induce site selective cleavage **(Figure 1.1)** preferentially by mechanical activation followed by subsequent chemical changes that modify or augment material properties.

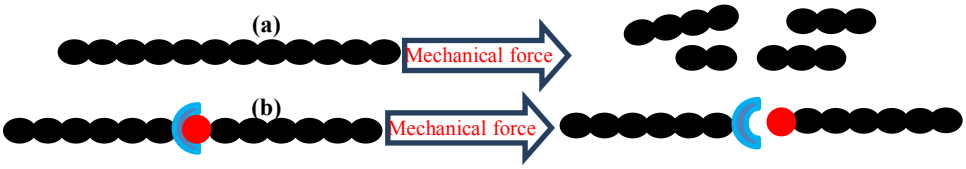


Figure 1.1 Mechanical force induce (a) random cleavage across the polymer chain and (b) site selective cleavage across the mechanophore incorporated polymer

1.A.2 Mechanophore - Force sensitive molecule

In a nutshell, mechanophore is a force sensitive functional moiety that undergoes some structural changes selectively over all other bonds in the polymer chain and provides molecular scale reading of mechanical stress through color change, fluorescence change etc., followed by subsequent chemical changes to augment material properties.

Need of mechanophore originated from the fact that it can provide a mechanism by which mechanical stress is directed to constructive activity. To this end, mechanophores are incorporated at the center of polymer chain and polymer chains act as the link between exogenous forces and mechanophore. Mechanophore facilitate productive chemical change that enables color change, catalytic release, self healing, cross linking etc. in the polymer prior to cleavage in the polymer backbone.

Suitability of a molecule to act as mechanophore depends upon the presence of a weak bond, strained ring, or isomerizable bond. Mechanically induced chemical change may be conformational change, bond-bending, bond stretching, bond scission, etc. Here the thesis focuses on mechanically induced bond stretching and bond scission. Polymer mechanochemistry has progressed considerably and has been explored in areas of drug delivery, mechanoresponsive materials, self-healing, catalysis,[7] chemiluminescence, stress induced strengthening etc.

1.A.3 Methods for mechanochemical activation

Several techniques are available to study the mechanical reactivity of polymers in solution, solid state and also at the single molecular level.

Discrepancy among these techniques is due to their disparity in the accessible range of strain rate and applied force (**Figure 1.2)**. The mechanochemical activation in solid state polymer is carried out by compression, tension, mastication, ball milling, solvent swelling,[8] crystallization,[9] laser generated acoustic waves[10] etc.

Mechanochemical reactivity at the single molecule level can be studied using single molecule force spectroscopy (SMFS) such as AFM and optical tweezers. The solution based mechanochemical activation studies employ ultrasound irradiation, cross slots,[11] contraction flows,[12] etc.

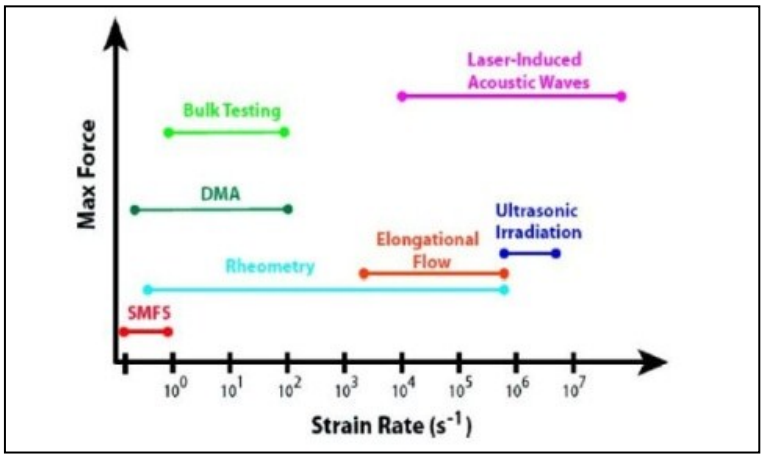


Figure 1.2 Techniques used for mechanochemical activation studies with accessible strain rate

Of these, ultrasound irradiation of dilute polymer solution is the most widely used method for the preliminary investigation of mechanochemical reactivity of mechanophore since the relatively high strain rates of the order of 10^6 to 10^7 $s^{-1}$are attainable by this technique.

1.A.4 Mechanism of mechanochemical activation

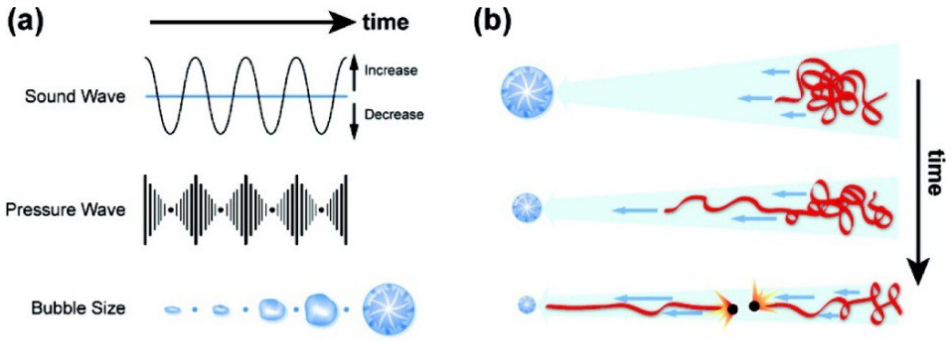


Figure 1.3 Mechanism for mechanochemical activation using ultrasound radiation

Application of sound waves creates nucleation, growth and collapse of bubbles in solution (**Figure 1.3**).[13] When the bubble collapses, the volatile species are affected by high temperature and pressure hotspots and the polymer chains remains unaffected by these thermal factors but are affected by the mechanical shear field.[14] Polymer segments located near the shear field of a collapsing bubble experience a velocity gradient. This velocity gradient stretches the polymer chain and the polymer chain uncoils. Thus strain energy is converted into chemical energy by increasing the bond distance. When the bond is stretched mechanical potential energy of the system decreases with increase in chemical potential energy (**Figure 1.4**). As a result, energy of reactant increases and the activation energy decreases as given by the equation $\Delta(\Delta E_{act}) = F.\Delta d$ where F is the force and Δd is the geometry change along the force direction[15] - finally leading to chain scission.[16]

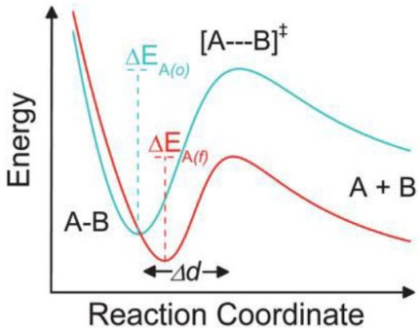


Figure 1.4 Morse potential energy diagram for reaction in the presence and absence of mechanical force

1.A.5 Factors influencing ultrasound mechanochemistry

Ultrasound induced polymer scission is affected by nature of solvent, polymer concentration, polymer molecular weight, chemical structure of polymer, temperature as well as ultrasound intensity.[17] These factors are concisely discussed in the following sections.

1.A.5.1 Solvent

Vapor pressure, viscosity, surface tension and viscosity of the solvent can influence chain scission rate of polymers in solution. Madas and co-workers reported a decrease in chain scission rate constant for poly(vinyl acetate) with increasing solvent vapor pressure during ultrasonication.[18] Compared to the effect of solvent vapor pressure, the effect of viscosity on chain scission rate is lower.[19] Increase in solvent viscosity generally decreases the rate of scission.

1.A.5.2 Polymer concentration

Polymer concentration has an effect on polymer chain scission rate in solution. Increasing the polymer concentration leads to decrease in the

rate of chain scission.[20] Price and Smith studied the effect of polymer concentrations on rate of chain scission using different concentration of polystyrene in toluene and found lower limiting molecular weight (M_{lim}) in less concentrated solutions.

1.A.5.3 Ultrasound Intensity

With increase in ultrasound intensity, rate of chain scission increases and M_{lim} for chain cleavage decreases. But when the ultrasound intensity is too high it decreases chain scission. Mostafa studied the effect of ultrasound intensity on mechanochemical activation using polystyrene solution in benzene having concentration 1 wt/vol%.[21] They found a decrease in weight average chain length from 3240 to 1004 when the ultrasound intensity was 4.89 Wcm^{-2} while the molecular weight decreased to 380 when higher ultrasound intensity was used keeping the polymer concentration and sonication time constant (15.8W cm^{-2}).

1.A.5.4 Temperature

The ultrasound induced chain scission rate decreases with increase in temperature.[22] This is due to high vapor pressure at high temperature. Hence at high temperature large amount of solvent enters in to the cavitation bubbles. This solvent exerts a cushioning effect when bubble collapse and decreases shear field intensity and hence also the velocity gradient. In effect, the force experienced by the polymer decreases with increase in the temperature and chain scission rate decreases.

1.A.5.5 Initial molecular weight

Rate coefficient of ultrasound induced chain scission depends upon molecular weight of the polymer[23] and limiting molecular weight as given by the proportionality equation:

$$k \propto (M - M_{lim})^x$$

where k is the rate coefficient, M is the molecular weight of the polymer, $M_{lim}$is the limiting molecular weight and x, depending on experimental conditions, varies from 0 to 3.

Ultrasound mechanochemistry depends up on the aforementioned properties, so all these variables are kept constant throughout the mechanochemical studies.

1.A.6 Historical developmentof polymer mechanochemistry

Encina demonstrated the increase in the rate of chain scission of poly(vinylpyrrolidone) (**Figure 1.5**) by incorporating peroxide bond in thepolymer chain.[24] Since the bond dissociation energy of peroxide bond is 50 kcal/mol which is less than those for C-C (88 kcal/mol) and C-O (91 kcal/mol) bonds. Encina raised the possibility of site selective cleavage by incorporating weak bonds in polymer chain.

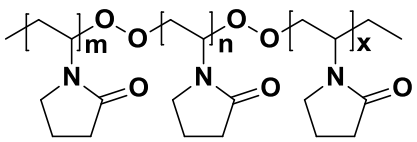


Figure 1.5 Poly(vinylpyrrolidone) with randomly incorporated labile peroxide linkages.

Moore and co-workers[25] demonstrated remarkable selectivity in the cleavage at the weak azo linkage on subjecting acetonitrile solution of azo-centered link-functionalized polymer to pulsed ultrasound at 20 kHz and 8.7 W cm^{-2}.GPC analysis showed a decrease in the intensity of peak characteristic of polymer having molecular weight 40 kDa and corresponding increase in the intensity of peak characteristic of polymer having molecular weight 20 kDa indicating cleavage at midpoint on ultrasound irradiation (**Figure 1.6**).

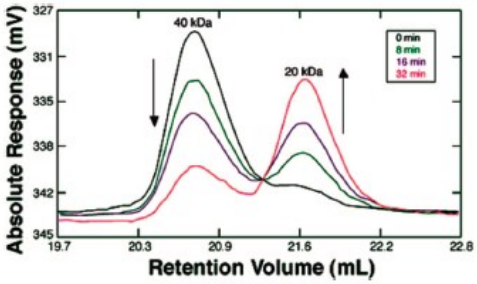
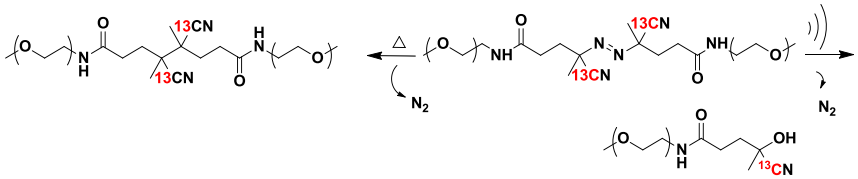


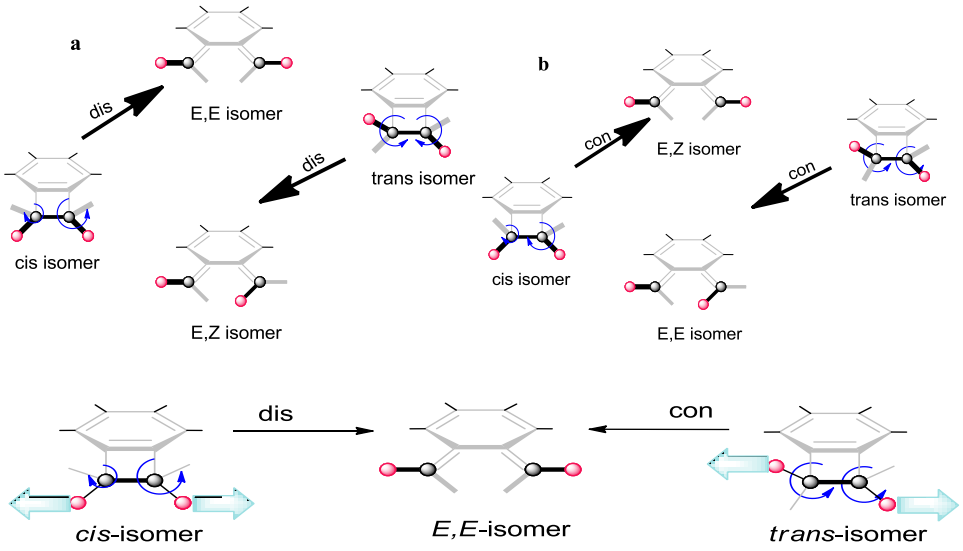
Figure 1.6 GPC traces of azo linked poly(ethylene glycol) having molecular weight 40 kDa showing cleavage

This result was confirmed by ^{13}C labeling experiments.^{13}C labeling experiments gave evidence for a homolytic cleavage at C-N bond with formation of radical intermediate followed by the reaction with hydroxyl radical to form cyanohydrins, whereas thermolysis is resulted in radical combination **(Scheme (1.1)**.



Scheme 1.1 Poly(ethyleneglycol) functionalized with a single azo moiety at the center selectively cleaves at the weak azo linkage when subjected to an acoustic field generated by ultrasound.

Hickenboth et al. reported a seminal work demonstrating potential of polymer mechanochemistry to bias reaction pathways that are not accessible by thermal or photochemical pathways.[26] They found that ultrasonication of solutions of cis and trans substituted benzocyclobutene (BCB) centered poly(ethyleneglycol) polymers resulted in the electrocyclic ring opening of the BCB to give the same product regardless of the stereochemistry of the mechanophore (**Scheme1.2**).



Scheme 1.2 Electrocyclic ring opening reaction of benzocyclobutene mechanophore attached poly(ethylene glycol) induced by a) light, b) heat c) stress

Thermally or photochemically induced electrocyclic ring opening reactions of spiropyrans has been known since 1950's.[27] Mechanically induced 6π electrocyclic ring opening reaction was demonstrated using poly(methyl methacrylate) with centrally incorporated bis functionalized

spiropyran by Moore and co-workers.[28] Upon subjecting this polymer solution to ultrasound irradiation they observed an increase in the UV-Vis absorption peak characteristic of merocyanine with increase in time.

The possibility of thermal cleavage was eliminated by carrying out a control experiment with terminally linked spiropyran. The absence of characteristic peak of merocyanine in the UV-Vis spectrum after sonication of polymer with spiropyran end capped polymer confirmed that the ultrasound induced 6πelectrocyclic ring opening reaction was mechanically induced (**Figure 1.7**).

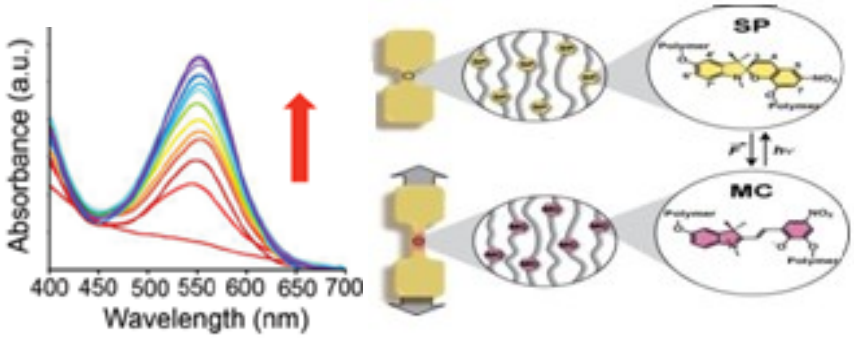


Figure 1.7. Stress induced change of spiropyran into merocyanine

Subsequently a number of mechanophores chemistries have are reported to date. Some of these (which are related to the present work) are given below (**Figure 1.8**).

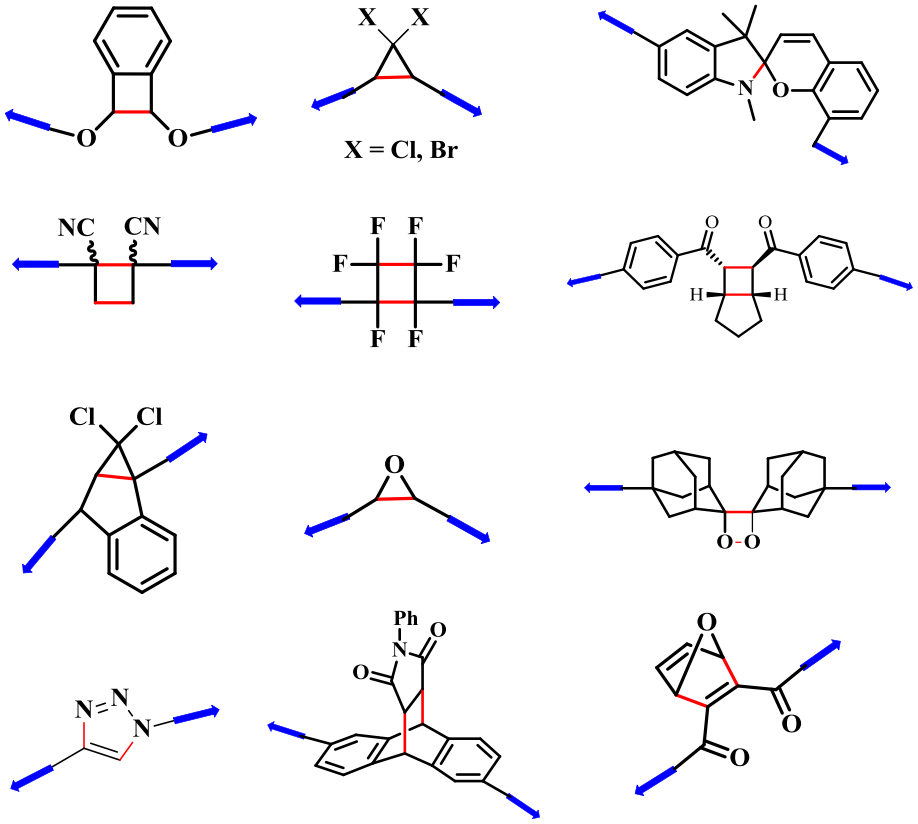


Figure 1.8. A few of the reported mechanophores

1.A.7 Structure–Mechanochemical activity relationship

Efficiency of mechanical to chemical energy transduction depends upon mechanophore orientation, polymer chain alignment and relaxation, temperature, solvent swelling, activation time dependences, loading conditions etc.

The effect of change in polymer attachment point to mechanophore on mechanochemical activation threshold force was studied by Johnathan

and co-workers using 1,4- and 1,5-disubstituted 1,2,3-triazolebased mechanophore attached polymer (**Figure 1.9**).[29] Subjecting acetonitrile solution of both aforementioned polymers to ultrasonication resulted in [3+2] cycloreversion. But the rate of [3+2] cycloreversion was found to be 20% greater for 1,5-substituted triazole compared to the 1,4-congener.

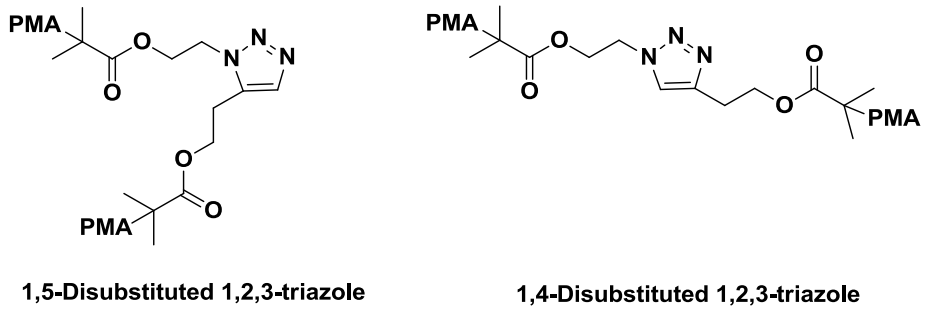


Figure 1.9.

Both point of attachment of mechanophore in the polymer chain as well as molecular geometry influence mechanochemical activation. Following this, Maxwell J. Robb introduced naphthopyran based mechanochromic mechanophore and the influence of molecular geometry on mechanochemical actvation was studied using naphthopyran regioisomers substituted at the 5-, 8-, and 9-positions (**Figure 1.10**).[30]

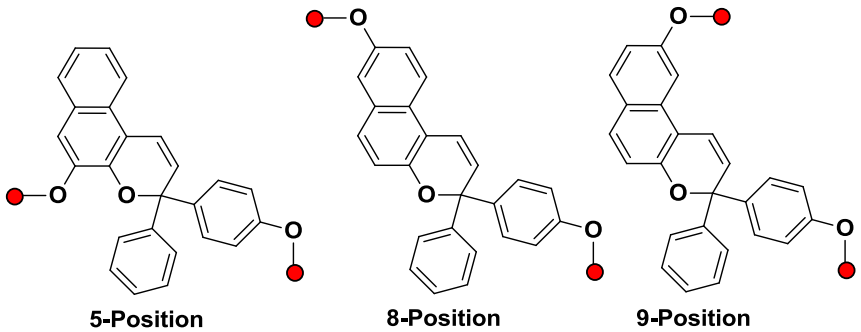
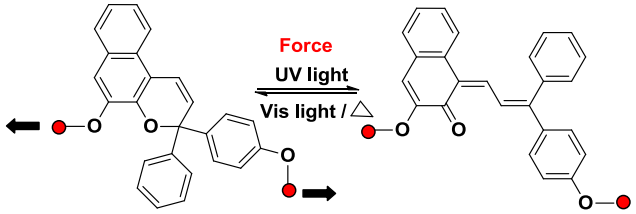


Figure 1.10Naphthopyran regioisomers substituted at the 5-, 8-, and 9-positions

Under stress, only naphthopyran regioisomer substituted at the 5-position underwent 6π electrocyclic ring opening reaction to transform into colored merocyanine, while other regioisomers remained mechanochemically inactive (**Scheme 1.3**).



Scheme 1.3 Transformation of naphthopyran into a colored merocyanine using mechanical force

Brett A. Beiermann et al investigated the effect of orientation of polymer chains with respect to the direction of stress using spiropyran mechanophore. The orientation of mechanophore is a key factor for effective transfer of energy across the polymer to mechanophore unit.[31] The orientation of force-sensitive chemical species (mechanophores) in bulk polymers was measured via the anisotropy of fluorescence polarization. Mechanophores aligned along the tensile direction were shown to be preferentially activated by force **(Figure 1.11)**.[32]

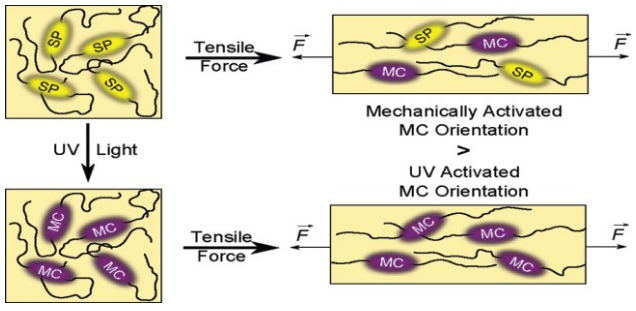


Figure 1.11 Mechanophores oriented along the force direction were preferentially activated by mechanical force.

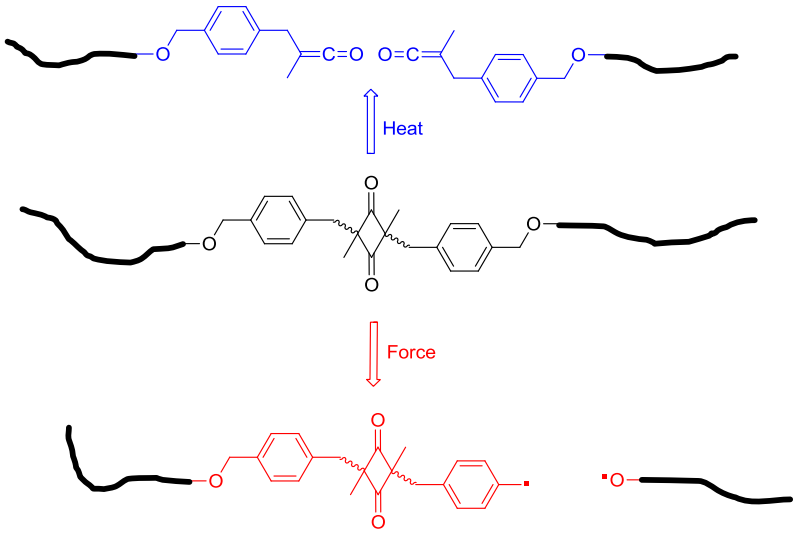
Given that mechanical degradation is unavoidable, stress sensitive materials or force sensors have potential application in a broad range of scenarios from study of biological materials to detection and prevention of fracture in synthetic materials. In this context, the aim of our work is to develop stress responsive self-healing polymer capable of reporting damage via mechanical process so that early detection of damage is possible and also structural integrity can be maintained. Potential of [4+2] cycloaddition based mechanophore attached polymer for stress induced strengthening application is also explored. Hence the following section is based on mechanophore assisted stress sensing, self healing and stress induced strengthening.

1.A.8 Stress induced strengthening

1.A.8.1 Stress induced strengthening of weakest bond

Contrary to the usual mechanically facilitated ring opening reaction where chemical bonds become weaker under external force, Ramon Groote and co-workers reported stress induced strengthening of bonds at the cyclobutane-1,3-diones mechanophore.[33] Both Density Functional Theory (DFT) based computational studies and mechanochemical scission experiments using sonication experiments showed that the activation energy of retro [2+2] cycloaddition increases for the cis-isomer and minimally affected in the case of trans-isomer. Contrary to the expected cleavage at the mechanophore via [2+2] cycloreversion, the chain scission was not observed at the mechanophore but elsewhere in the polymer chain (benzylic C-O bond) (**Scheme 1.4**). This result emphasize that all weak chemical bonds should not be presumed applicable as mechanophores and

the study also underscored the importance of theoretical calculations for evaluating mechanophores.

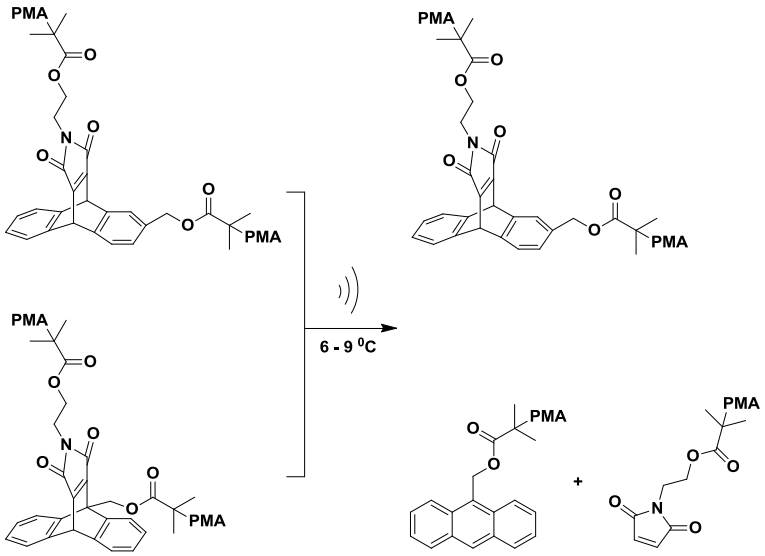


Scheme 1.4 Mechanically and thermally induced cleavage.

1.A.8.2. Mechanical suppression of reactivity-Anti-Hammonds effect

Point of attachment of mechanophore in the polymer has great effect on the mechanochemical activation. Sai Sriharsha and co workers report Mechanical suppression of reactivity[34] (**Figure 1.12**). Mechanophores based on Diels–Alder adducts derived from 2-substituted anthracene and 9-substituted anthracene were used for the study. Only the adduct derived from 9-substituted anthracene derivatives underwent *retro* Diels–Alder reaction during the ultrasonication of the mixture of polymer solution. As opposed to mechanically accelerated chemical reaction, authors here observed catch bond behavior or mechanically suppressed reactivity upon mechanochemical activation in the 2-substituted anthracene derived mechanophore attached polymer. Hence change in the mechanophore

design can lead to catch bond behavior (as opposed to slip bond). The experimental result was supported by theoretical and computational studies where they observed anti–Hammond behavior in the 2- substituted anthracene mechanophore attached polymer.



Scheme 1.5 During the ultrasonication of mixture of polymer solution only the adduct derived from 9-substituted anthracene derivatives underwent *retro* Diels–Alder reaction

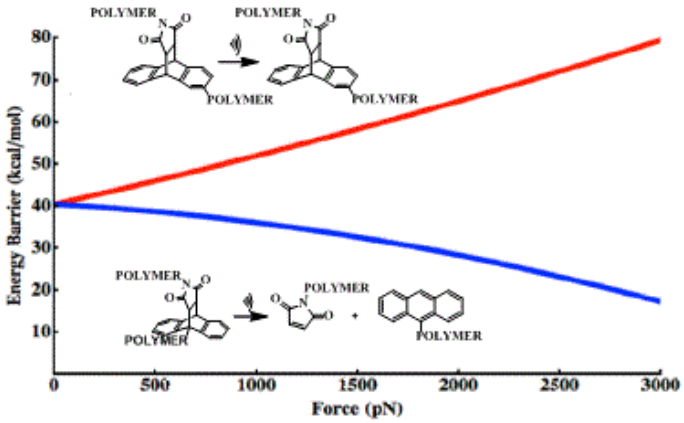
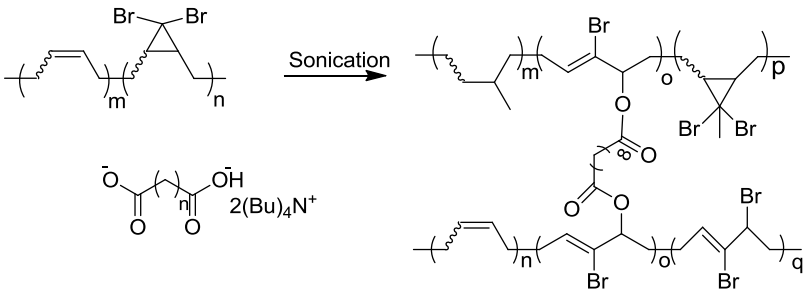


Figure 1.12 Energy barrier for ultrasound induced *retro* Diels–Alder reaction

1.A.8.3 Mechanochemical strengthening of polymer

Ramirez and co-workers reported first example of mechanically induced cross linking reaction in *gem*-dibromocyclopropane mechanophore incorporated polybutadiene[35]. On subjecting the polymer solution to large destructive force generated by ultrasonication, the mechanophore underwent electrocyclic ring opening reactions to give 2,3-dibromoalkenes. The intermolecular reaction of 2,3-dibromoalkenes with carboxylate nucleophile led to stress induced cross linking reactions (**Scheme 1.6** and **Figure 1.13**).



Scheme 1.6 Mechanochemical activation of *gem*-dibromocyclopropane mechanophore incorporated polybutadiene and subsequent crosslinking.

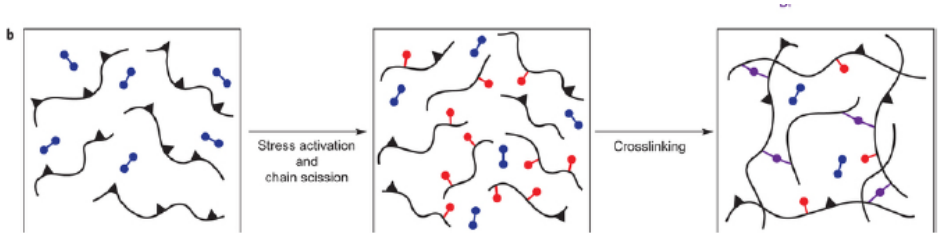
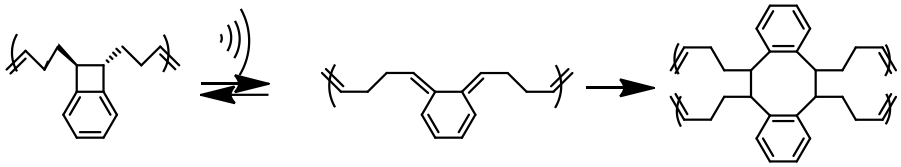


Figure 1.13 Mechanochemical activation of *gem*-dibromocyclopropane mechanophore incorporated polybutadiene and subsequent crosslinking.

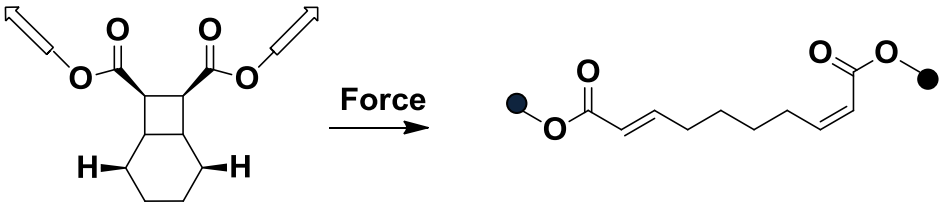
However 2,3-dibromoalkene is less reactive and also gem-dibromocyclopropane ring opening is irreversible in the absence of crosslinking, and in the presence of ionic reactants. In order to overcome this, Junpeng Wang and co-workers prepared mechanochemically strengthened polymer by incorporating highly reactive benzocyclobutene mechanophore along its backbone.[36] When polymer solution was exposed to pulsed ultrasonication, benzocyclobutene mechanophore was activated to an ortho-quinodimethide.[37] The highly reactive *ortho*-quinone methide participated in [4+4] dimerization which resulted in stress induced strengthening **(Scheme 1.7).**



Scheme 1.7 Mechanochemical strengthening of benzocyclobutene mechanophore incorporated polybutadiene during sonication

The above reported mechanophores are based on scissile activation in which mechanochemical activation results in chain rupture and molecular weight degradation. In sharp contrast, Zachary and coworkers reported mechanophore based on nonscissile activation[38]. Authors synthesized stress responsive high molecular weight polyester having approximately 700 bicyclo[4.2.0]octane mechanophores per unit chain. When subject to ultrasonication, these mechanophores elongated by ~7 Å per monomer to form α,β-unsaturated esters and thereby providing molecular level stress-relief under load. The unveiled α, β-unsaturated esters are reactive enough to form cross linked polymer through thiol-enol conjugate addition thus

expanding the scope for stress induced strengthening of materials **(Scheme 1.8)**.



Scheme 1.8 Stress responsive behaviour of bicyclo[4.2.0]octane mechanophore incorporated polymer.

1.A.9 Polymer mechanochemistry at the service of stress responsive materials.

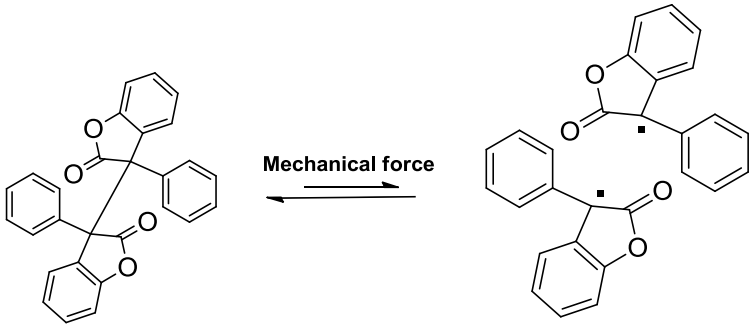
Polymer mechanochemistry introduces three types of optical feedback pathways to screen the stress concentration points in a material and are based on change in absorption (mechanochromism), fluorescence generation (mechanofluorochromism) and chemiluminescence (mechanoluminescence). In mechanochromism a chromophore is generated or changed mechanically and can be monitored by UV-Vis absorption spectroscopy and quantified by applying Beer-Lambert law. But it is the least sensitive method and cannot be used for systems having concentration below 10^{-5} M. Both mechanofluorochromism and mechanoluminescence are closely related and offer good level of sensitivity. In the present context, we are concentrating only on mehanochromism and mechanofluorochromism and omitting mechanoluminescence since our selected system is capable of exhibiting both mehanochromism and mechanofluorochromism.

1.A.9.1 Mechanofluorochromism

Both covalent incorporation of mechanophore as well as noncovalent incorporation of mechanophore can be used to endow mechanofluorochromism in polymeric materials. Renecker and Kim developed a mechanochromic polymer by covalentlyincorporating E isomer of azobenzene chromophore onto linear polyurethane chain. E to Z isomerization was mediated by light induced reaction. The polymer responded to mechanical stress by the transition from Z to E isomer with accompanying color change.[39] But difference in absorption was very low which limits its application.

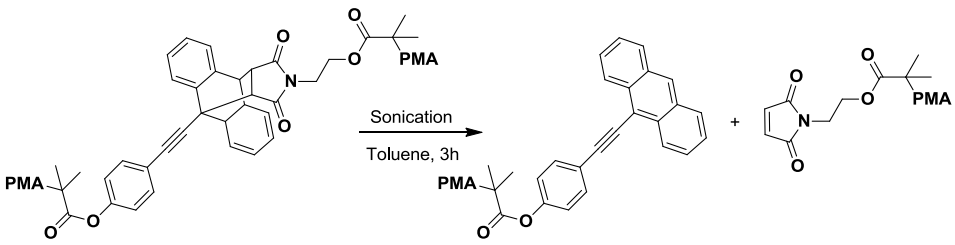
The most widely used and potential mechanostress probe is the spiropyran. The mechanochemical activation was first demonstrated by White and co-workers in 2007. Mechanically induced 6π electrocyclic ring opening of colorless spiropyran to colored merocyanine allowed the sensing of latent failure.

Stress responsive behavior of both the aforementioned mechanophores is based on mechanically induced isomerization. Stress responsive behavior can also be brought about by mechanically induced covalent bond scission. Hironori Oka used diarylbibenzofuranone based mechanophore to study the effect of polymer molecular weight on mechanoresponsiveness in the bulk state and they observed enhanced mechanoresponsiveness in the star-shaped polymer compared to the linear analogue of similar molecular weight arm segment.[40] The observed mechanoresponsive behavior is due to the generation of colored radicals by mechanically assisted C-C bond cleavage **(Scheme 1.9)**.



Scheme 1.9 Mechanical force induced cleavage of Diarylbibenzofuranone

Makarov, Bielawski and co-workers introduced a mechanophore based on anthracene-maleimide Diels-Alder adduct which is optically transparent. Mechanically induced retro Diels-Alder reaction regenerated π conjugation and the stress responsive behavior can be studied by following absorption and fluorescence emission.[41] R. Göstl substantially improved stress-reporting capability of the above system by replacing anthracene with π-extended anthracene and observed release of anthracene with high fluorescence quantum yield **(Scheme 1.10)**.



Scheme 1.10 Ultrasound induced scission of mechanophore incorporated PMA

A rhodamine based mechanochromic elastomer having high sensitivity to stress and also ability to show three primary colors during continuous uniaxial extension and relaxation process was reported by

Taisheng Wang and co-workers.[42] Here both mechanochemistry and bond bending conformational change were used to bring the three primary color fluorescence emission (**Figure 1.14**). The reversibility and fastness of the color change along with high quantum yield make this system a potential force sensor.

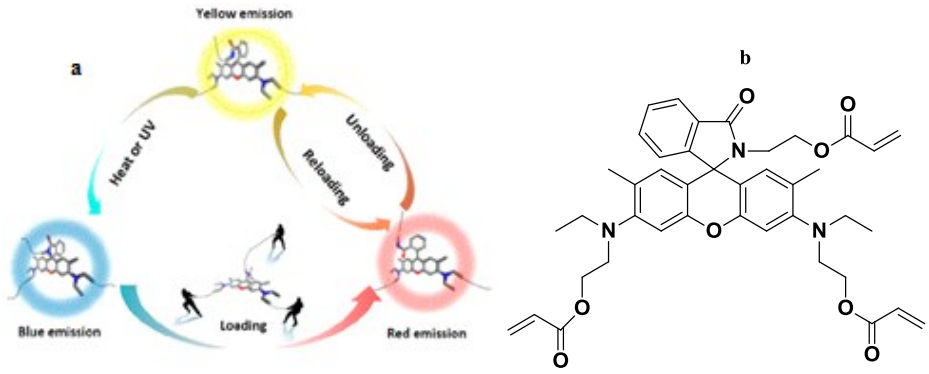


Figure 1.14 (a) Depiction of mechanically induced ring-opening reaction and bond-bending-induced secondary fluorescent color change (b) rhodamine based mechanophore

Both cyclobutane and cyclooctane mechanophores were used as crack sensors.[43] Cyclobutane and cyclooctane moieties were incorporated in to an epoxy matrix. Under stress when crack formed both mechanophores cleaved and showed fluorescence (**Figure 1.15** and **Figure 1.16**).

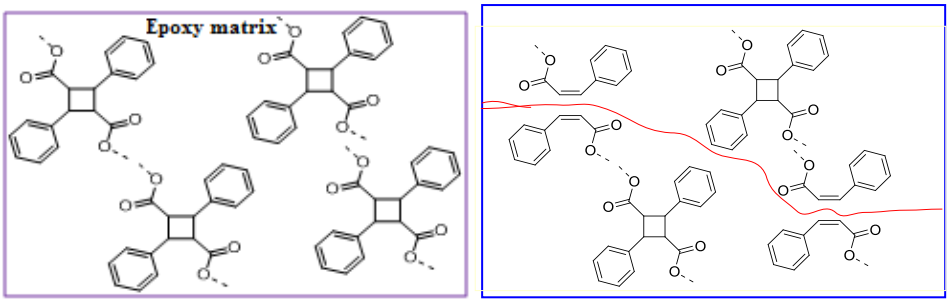


Figure 1.15 Depiction of mechanoresponsive behavior of cyclobutane mechanophore

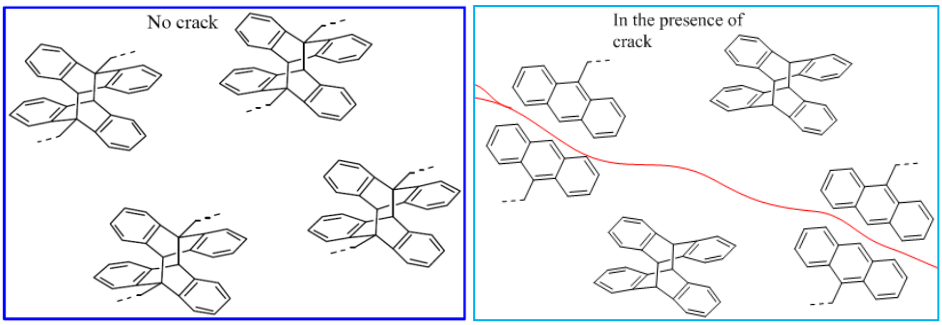
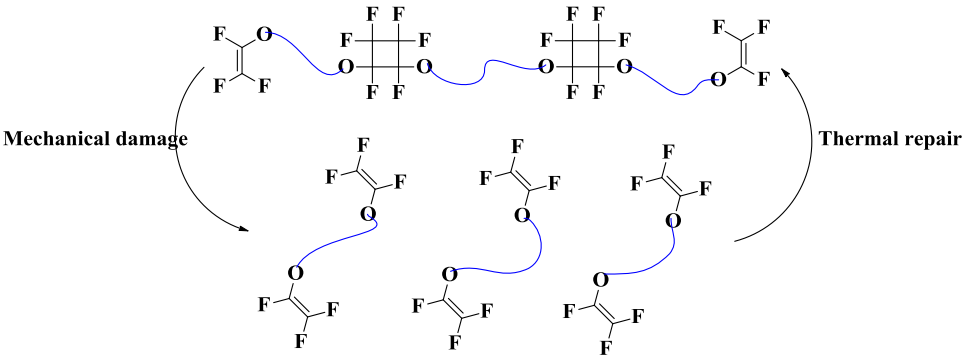


Figure 1.16 Depiction of mechanoresponsive behavior of cyclooctane mechanophore attached polymer

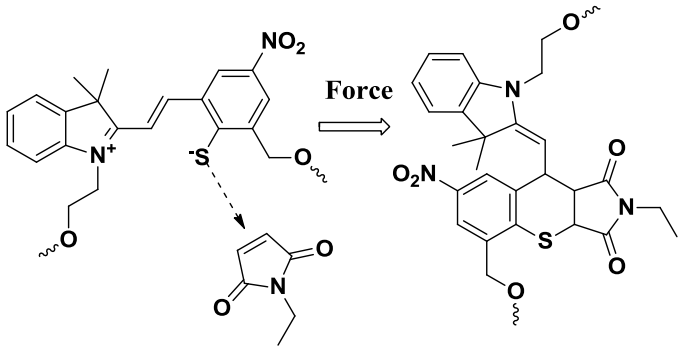
1.A.10 Mechanophore for self healing application

Hope M. Klukovich et al reported a thermally remendable perfluorocyclobutane (PFCB) polymer.[44] Under stress, trifluorovinyl ether end groups were formed by [2+2] cycloreversion. The polymer remended into original perfluorocyclobutane form by heating its solution to a temperature greater than150 ºC (**Scheme 1.11).**



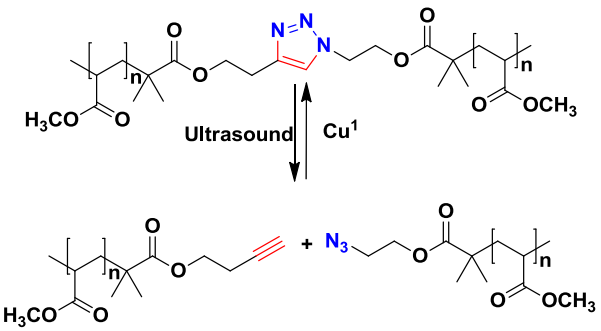
Scheme 1.11 Mechanochemical activation of perfluorocyclobutane and subsequent thermal repair

Yuan Lin reported the first example of a polymer composite having both mechanochromism and load induced cross linking reaction using spirothiopyran mechanophore.[45] at the initial stage of loading, spirothiopyran converted into green colored thiomerocyanine and served the function of stress sensing. On removing the load it reverted back to original spirothiopyran. When the load was too high such that it exceed the thiomerocyanine to spirothiopyran isomerization threshold, it induced reaction of C=C bonds of maleimide group via Thiol-ene click reactions to form a cross linked polymer (**Scheme 1.12).** .



Scheme 1.12 Stress induced thiol–ene click addition between spirothiopyran and *N*-ethylmaleimide.

Bielawski and co-workers mechanically "unclicked" the triazole ring by incorporating the same in to the center of poly(methyl acrylate)[46].



Scheme 1.13 Stress induced *retro* [3+2] cycloaddition reaction and Cu^1 induced [3+2] cycloaddition.

Ultrasound induce *retro* [3+2] cycloaddition reaction and Cu^1 induce [3+2] cycloaddition. But the unclicked components are capable to reclick in to the original polymer by Cu^1 catalysis condition (**Scheme 1.13**).

Part B

Single Electron Transfer Living Radical Polymerization (SET-LRP) for mechanophore incorporated polymers.

Conspectus: The scope of this section is to highlight the importance of Single Electron Transfer-Living Radical Polymerization (SET-LRP) over other Controlled Living Radical Polymerizations (CLRPs) as an efficient method for the synthesis of mechanophore incorporated polymers. Various types of controlled living radical polymerizations are explained highlighting their major potential and limitations. In the second part of this section, versatility of Cu(0)-mediated Single Electron Transfer-Living Radical Polymerization is included. Special emphasis is given to the tolerance of SET-LRP towards oxygen.

1.B.1 Single Electron Transfer-Living Radical Polymerization for mechanophore incorporated polymers

Our major aim is to demonstrate the stress responsive behavior of mechanophore attached polymer by mechanochemical activation studies using ultrasound radiation. It is found that solvodynamic forces are greatest at the middle of the chain during sonication and consequently probability of chain scission and mechanoactivation are highest at the middle of the chain.[47] Accordingly in order to study the mechanochemical activation using ultrasound irradiation, we need polymer having mechanophore at the centre or at the end of the chain and also the polymer should have low polydispersity index. So we have selected

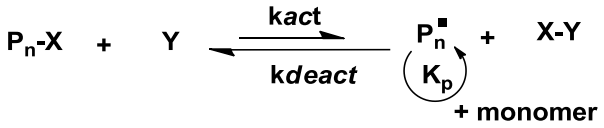
controlled radical polymerization methods. Hence the following section is centered on discussion around various Controlled Living Radical Polymerizations.

1.B.1.1 Towards Controlled Living Radical Polymerization (CLRP)

Free radical polymerization (FRP) is one of the extensively used polymerization protocol since its inception by Flory in 1937.[48] More than 50% of all synthetic polymers are manufactured using free radical polymerization process.[49] Its tolerance towards large number of chemicals, impurities and water along with the availability of a variety of polymerization methods such as bulk, solution, emulsion, dispersion and suspension are the major reason for its wide accessibility and for being dominant polymerization technique in the industrial field. Despite these virtues, it has some disadvantages such as poor control over molecular weight resulting in polymer featuring broad molecular weight distribution and difficulty to incorporate end group functionalities. These limitations are due to the chain termination and chain transfer processes that do exist along with the polymerization.

Efforts to overcome these limitations paved the way for Living Polymerization (LP) introduced by Swarc in 1956.[50] They reported the polymerization of styrene in THF via sodium naphthalide and were able to reduce the chain termination drastically. Observed negligible chain transfer and termination are probably due to electronic repulsion between like charges in the polymer chain.[51] It is difficult to commercialize this method since it demands extensively purified monomers and reagents and specially designed equipments in addition to the need of low temperature

making the process expensive. It is also limited to a narrow pool of monomers. So by combining the positive aspects of both FRP and LP, Controlled Living Radical Polymerization took its birth. Although CLRP cannot mimic FRP in purist's sense, it became a stepping stone towards the synthesis of polymers with precisely controlled molecular weight, high chain end group fidelity and relatively narrow polydispersity index. The basic mechanism of CLRP is given in **Scheme 1.B.1.** Livingness of CLRP relay on the reversible equilibrium between propagating species P_n-X and dormant species $P_n^{\cdot}$. The activation and deactivation equilibrium is maintained by adding mediating reagents or controlling reagents which reacts with propagating radical thus reducing the concentration of propagating radical much lower than that of dormant species and hence also the chain termination leading to polymers with controlled molecular weight and dispersity.



Scheme 1.B.1 Mechanism of CLRP

For a polymerization reaction to be classified as "Living", it should satisfy the following conditions.[52]

1) $k_i > k_t$; Rate constant of initiation (k_i) should be greater than the rate constant of termination (k_t).
2) A plot of M_n versus % conversion should be linear.

3) A plot of $\ln([M]_0/[M]_t)$ against time should be linear.

4) Synthesized polymer should have active chain end enabling iterative chain extension.

5) Polymer should have narrow molecular weight distribution.

6) Termination should be largely reduced or negligible.

7) Molecular weight of the polymer should be controllable.

Matyjaszewski derived a kinetic criterion for living polymerization as[53]

$$k_p/k_t > 10^4 \text{ mol}^{-1}\text{L}$$

$$k_p/k_{tr} > 10^4 \text{ mol}^{-1}\text{L}$$

$$1/k_{t/tr} > 10^4 \text{ s}$$

Where k_p is the propagation rate constant, k_t is the termination rate constant and k_{tr} is the chain transfer rate constant.

1.B.1.2 Types of Controlled Living Radical Polymerization (CLRP)

Of the different controlled radical polymerizations, the most widely used are Nitroxide Mediated Polymerization (NMP), Atom Transfer Radical Polymerization (ATRP), Reversible Addition Fragmentation Chain Transfer polymerization (RAFT) and Single Electron Transfer-Living Radical Polymerization (SET-LRP).

1.B.1.2.1 Nitroxide Mediated Polymerization (NMP)

Nitroxide Mediated Polymerization also called stable free radical polymerization was invented and patented by Solomon and Rizzardoin

1985.[54] 2,2,6,6-Tetramethylpiperidynyl-1-oxy (TEMPO) (**Figure 1.B.1**) was the first mediator in NMP and was introduced by Georges when they polymerized styrene at 123 °C.[55]

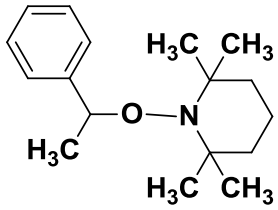
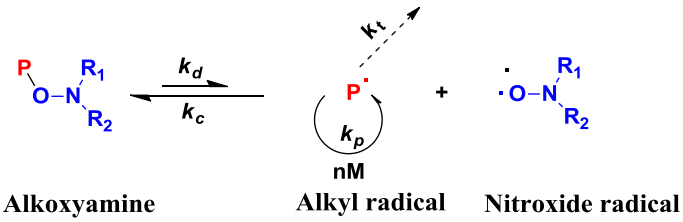


Figure 1.B.1 TEMPO

The mechanism of NMP is given in **Scheme 1.B.2**. Controllability of NMP is based on the dynamic equilibrium involving dormant alkoxyamines, active alkyl radical and nitroxides. The NMP mediator (R_1R_2NOP) decomposes into active alkyl radical ($P^{\cdot}$) and stable nitroxide radical ($R_1R_2NO^{\cdot}$). Polymerization is initiated by active alkyl radical. The nitroxide radical although unreactive by itself, react with the propagating radicals thus reducing the concentration of propagating radicals to much lower than that of dormant alkoxyamine species and thus reduces chain termination and thereby offers control over molecular weight and dispersity.



Scheme 1.B.2 Mechanism of NMP

The following TEMPO derivatives (**Figure 1.B.2)** were developed as mediators with a view to reduce the high temperature required while using TEMPO in NMP.[56]

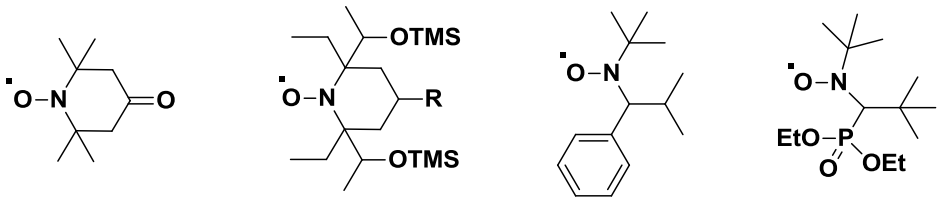


Figure 1.B.2 TEMPO derivatives used in NMP

In order to synthesize a mechanophore incorporated polymer, it is necessary to start from NMP initiator. To synthesis NMP initiator, NMP initiating site has to be attached to mechanphore. One of the NMP initiators used for the synthesis of star polymers is shown below[57] (**Figure 1.B.3**).

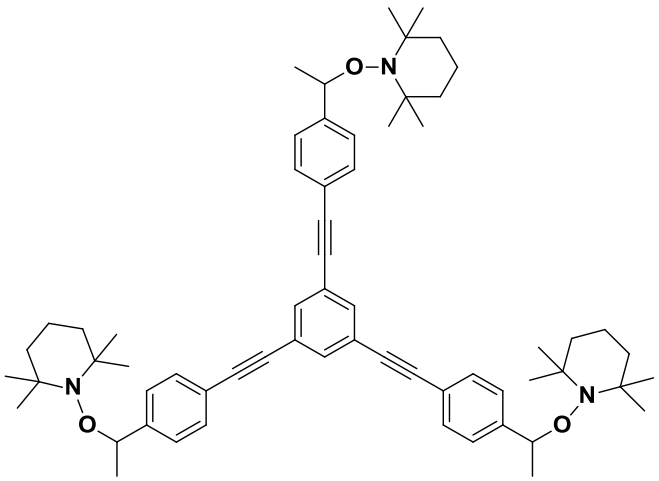
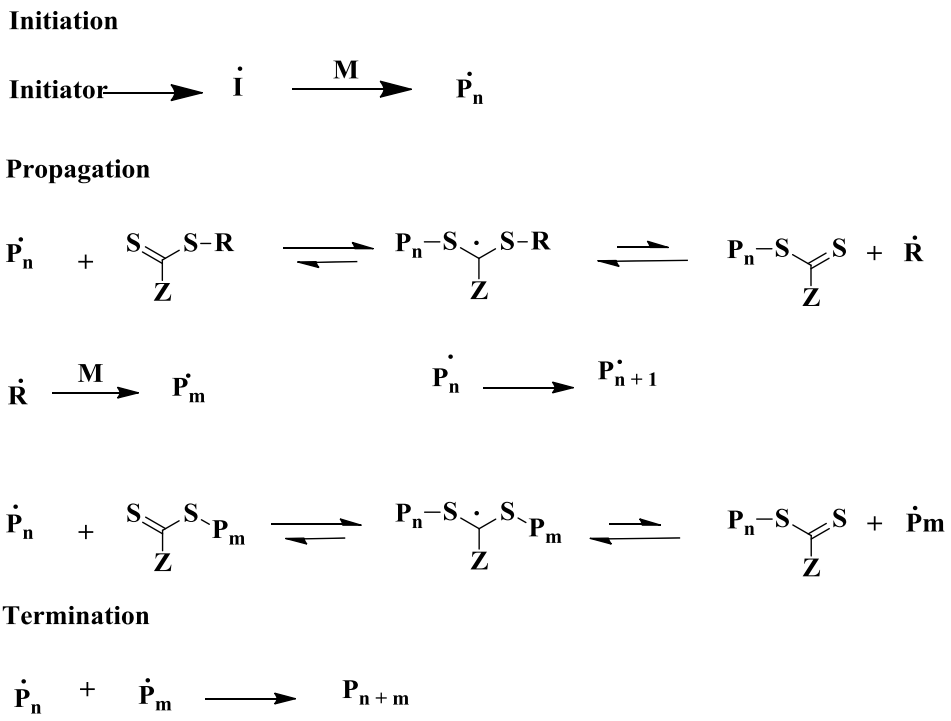


Figure 1.B.3 Initiator used in NMP

Though effective, need for high reaction temperature (125-140 ºC) and long reaction time (2-3 days) makes NMP technique less attractive.

1.B.1.2.2 Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization

The RAFT method was proposed by Rizzardo and Thang and the mechanism is given in **Scheme 1.B.3**.[58] Here the chain termination is diminished by reversible chain transfer process using chain transfer reagent based on di/trithioester which rapidly exchanges between propagating radical and dormant species.

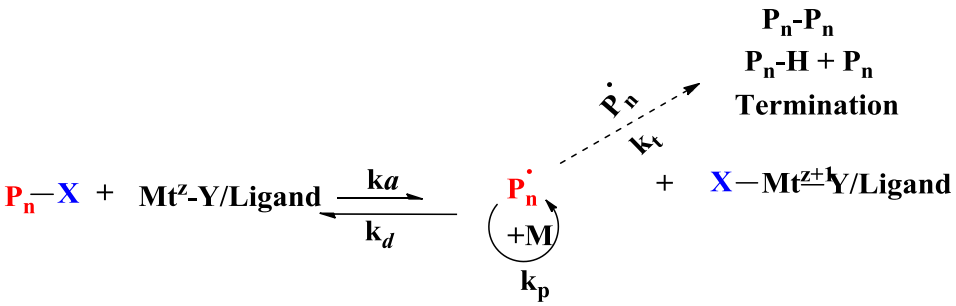


Scheme 1.B.3 Mechanism of RAFT

On the upside, RAFT is a versatile system since it is simple to carry out and it does not use any metal catalyst. Also it is compatible with both more activated monomers such as methacrylate and less activated monomers such as vinyl acetate, *N*-vinylpyrrolidone, *N*-vinylcarbozole etc.,[59] On the downside all RAFT reagents are not commercially available and also it demands multiple stages. The color and unpleasant odor of the polymer due to the incorporated dithioester also limit its merit.

1.B.1.2.3. Atom Transfer Living Radical Polymerization (ATRP).

ATRP was reported independently by Sawamoto[60] and Matyjaszewski groups. It is based on the reversible equilibrium between dormant species and transition metal catalyst. Contrary to both NMP and RAFT, here alkyl halides are used as initiators. Proposed mechanism of ATRP is outlined in **Scheme 1.B.4.** Here the equilibrium between dormant species and active radical is established by the reversible transfer of halogen (Cl or Br) between transition metal complex and dormant species. Transition metal complex exists in two oxidation states. Mt^z-Y/Ligand which is in lower oxidation state cleave carbon halogen bond in R-X homolytically to generate $P_n^{\cdot}$ and convert itself into Mt^{z+1}-Y/Ligand. The generated $P_n^{\cdot}$ can either combine with monomer to generate growing polymer chain with rate constant k_a or be deactivated by maintaining a reversible equilibrium with Mt^z-Y/Ligand with rate constant k_d. In ATRP, k_t, the rate constant for termination and radical concentration are diminished appreciably by Persistent Radical Effect (PRE).[61] Here the propagating radicals are irreversibly terminated to further reduce their amount and hence control the polymerization.



Scheme 1.B.4 Proposed mechanism of ATRP

The common ATRP initiators used to mediate polymerization are based on α-halo ester based compounds such as ethyl 2-bromoisobutyrate and methyl 2-bromopropionate.[62] Commonly used ligands for ATRP are 2-pyridylmethanimine, *N,N,N′,N′*-tris(2-aminoethyl)amine (TREN), *N,N,N',N'', N'',N''*-hexamethyl-[tris(aminoethyl)amine] (Me_6TREN) and (tris(2-pyridylmethyl)amine (TPMA) which are all nitrogen based ligands[63] (**Figure 1.B.4**).

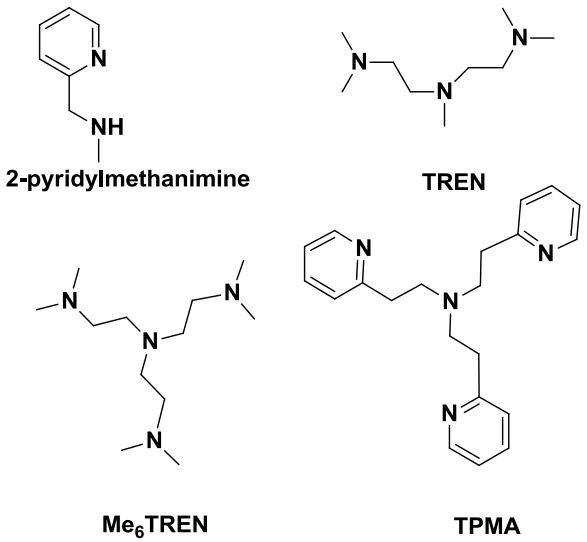
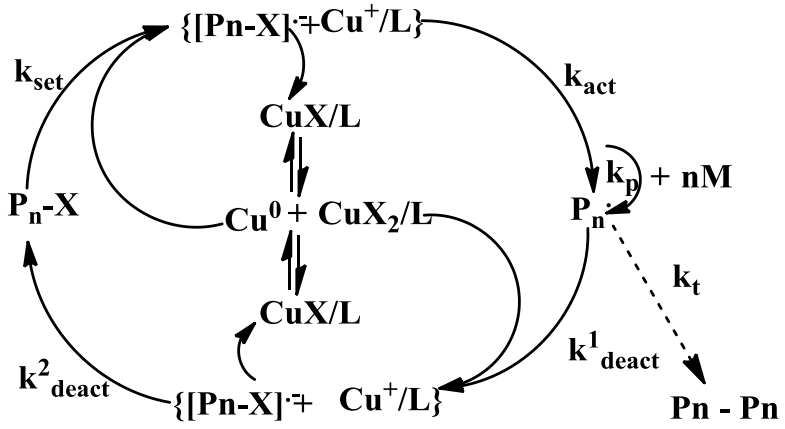


Figure 1.B.4 Commonly used ATRP ligands

ATRP also suffers the following limitations such as high sensitivity to air, need for maintaining stoichiometric amount of copper and high temperature. Efforts to overcome these limitations ultimately led to SET-LRP.

1.B.1.2.4 Single Electron Transfer-Living Radical Polymerization (SET-LRP)

SET-LRP was first reported by Percec and co-workers in 2006.[64] Here Cu(0) acts as electron donor. P_n/P-X accept electron from Cu(0) and convert itself into radical anion $[P_n/P\text{-}X]^{\cdot-}$. Cu(I) formed from Cu(0) disproportionate itself into Cu(I) and Cu(II)X_2/L. The radical anion $[P_n/P\text{-}X]^{\cdot-}$undergoes heterolytic cleavage to generate $P_n^{\cdot}/P^{\cdot}$**.** Cu (II)X_2/L mediate both initiation and reversible termination.



Scheme 1.B.5 Mechanism of SET-LRP proposed by Percec

One of the outstanding features of SET-LRP is that it is simple and easy to perform as it can be carried out at or below ambient temperature. The low temperature is ascribed to outer electron transfer process involved in the mechanism in contrast to inner electron transfer process associated with ATRP.

1.B.1.2.4.1 Versatility of SET–LRP

1.B.1.2.4.1.1 Monomer compatibility

SET-LRP has been used successfully for the polymerization of acrylates,[65] methacrylates,[66] acrylamides,[67] and methacrylamides[68] with good controllability over molecular weight and high end group fidelity. Even vinyl chloride[69] and acrylonitrile[70] which are reported to be inert towards ATRP are compatible with SET-LRP.

1.B.1.2.4.1.2 Initiator compatibility

The initiators used for ATRP can also be used in SET–LRP. Several mono-initiators are found to be compatible with SET-LRP.[71] The most commonly used one for the polymerization of acrylate is methyl 2-bromopropanoate. Some of the monofunctional initiators based on α-bromo ester used for the SET-LRP are given in **Figure 1.B.5**. Halo alkanes such as chloroform and carbon tetrachloride, nitrile initiators such as 2-bromopropiononitrile have also been demonstrated to be effective for SET-LRP.

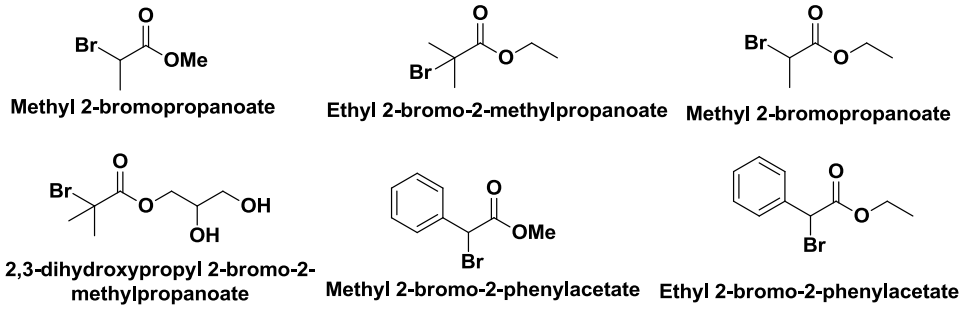


Figure 1.B.5 Monofunctional initiators

Figure 1.B.6 depicts a few bi-functional initiators used in SET-LRP.[72]

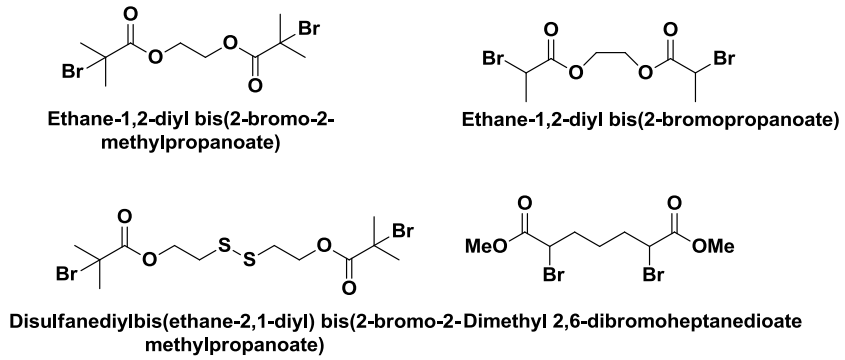


Figure 1.B.6 Bifunctional initiators

1.B.1.2.4.1.3. Multifunctional initiators

Multifunctional initiators are of great interest as they are useful for the synthesis of star polymers having high degree of functionality compared to their linear counterparts. Four-arm initiators such as pentaerythritol, tertrakis(2-bromopropionate), 2,2-dibromomethyl-1,3-dibromopropane,1,2,3,4,6-penta-O-isobutyryl bromide-α-D-glucose and octa-*O*-isobutyrylbromide lactose have been used for the synthesis of star polymers using SET-LRP.[73]

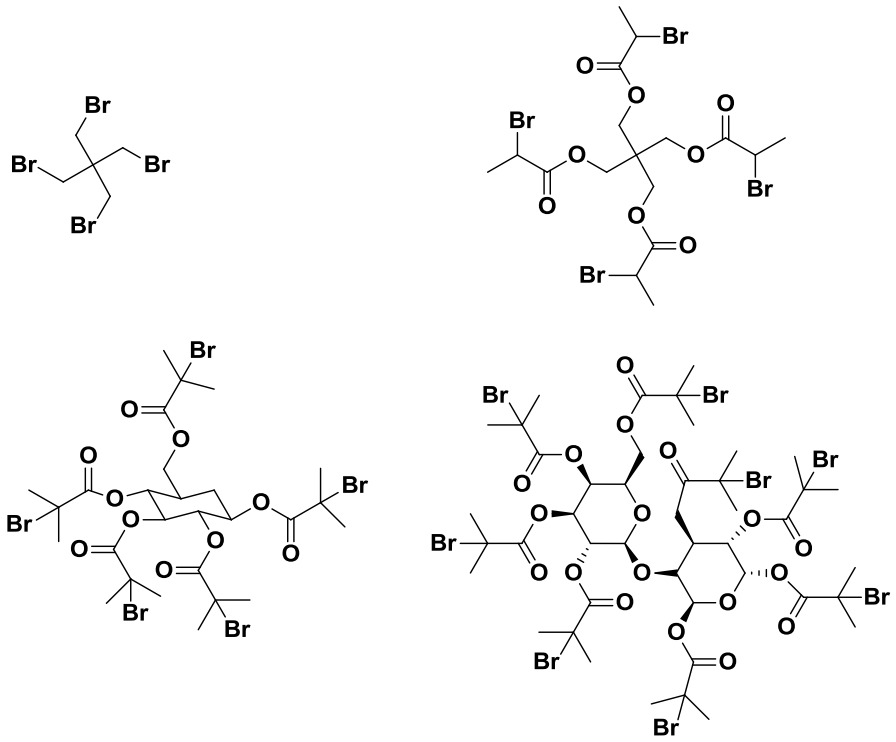


Figure 1.B.7 Multifunctional initiators

1.B.1.2.4.1.4. Solvent compatibility

Disproportionation of Cu(I)X to Cu(0) and Cu(II)X_2 is the controlling process in SET-LRP. So any solvent which facilitates the disproportionation of Cu(I)X can be used as a medium for SET-LRP.[74] Of the different polar solvents used in SET-LRP such as methanol, ethanol, and, isopropanol, DMSO and H_2O have been the most widely used since these favor SET-LRP to proceed through first order kinetics with 100% end group fidelity.[75] While nonpolar solvents such as toluene and acetonitrile give a polymer with less chain end group fidelity.[76] Highly polar 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) solvent for SET-LRP of

methacrylates has proven to give dual control over both molecular weight and tacticity.[77]

1.B.1.2.4.1.5. Catalyst compatibility

Cu(0) as both powder and wire has been reported to give SET-LRP with first order rate kinetics throughout the reaction. The rate of propagation is directly proportional to surface area of the copper irrespective of its morphology.[78] Cu(0) wire is the most widely used catalyst since it provides several advantages such as easy removal of catalyst, recyclability, greater control over MWD and facile tuning of reaction rate. Recently feasibility of SET-LRP with other metal catalyst such as iron (Fe),[79] nickel (Ni),[80] magnesium (Mg),[81] ytterbium (Yb),[82] lanthanum (La),[83] tin (Sn),[84] silver (Ag),[85] gadolinium (Gd)[86] and samarium (Sm) [87]have been widely explored.

1.B.1.2.4.1.6. Ligand compatibility

In a similar vein to ATRP, it also uses nitrogen based ligands. During polymerization, ligand remains associated with both Cu(I) and Cu(II). Hence both nature (nature of the nitrogen atom, denticity, length of the linker between nitrogen atoms, topology) and concentration of ligand affect reaction rate, end group fidelity and controllability of SET-LRP. Studies show that minimal ligand concentration is good enough for a good level of control over polymer molecular weight.[88] The typical N-containing ligands used are tris(2-(dimethylamino)ethyl)amine(Me_6TREN),[89] (tris(2-aminoethyl)amine (TREN),[90] N,N,N',N",N"-pentamethyldiehylenetriamine (PMDETA),[91] 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA),[92]

2,2'-bypiridine (Bipy),[93] 4,4'-dinonyl-2,2'bipyridine (diNbpy)[94] etc., with Me_6Tren being the most commonly used one.

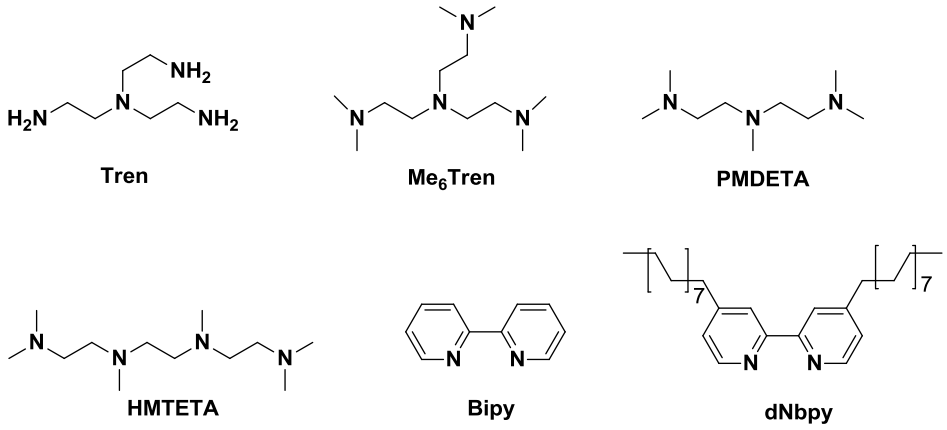


Figure 1.B.8 Ligands used in SET-LRP

1.B.1.2.4.2 Activation methods for copper

1.B.1.2.4.2.1 Activation via reducing agents

An initial period of slow rate is observed in SET-LRP while using copper wire. Copper wire is usually covered with copper oxide due to atmospheric oxygen. Initial slow rate could be due to the low efficiency of copper oxide for initiation compared to copper. So copper wire activated using hydrazine hydrate in a strictly oxygen free condition was utilized for SET-LRP.[95] SET-LRP with preactivated copper wire proceeded with no induction period and with high rate of acceleration while maintaining low polydispersity index and high chain end group fidelity.

The activation of Cu(0) wire carried out using other reducing agents such as $NaBH_4$,[96] phenol, phenolates,[97] and ascorbic acid[98] have also been reported.

1.B.1.2.4.2.2 Activation via acids

Concentrated sulfuric acid and hydrochloric acid were also used to activate Cu(0) wire by dissolving Cu_2O from its surface.[99]

No appreciable difference in k_p^{app} values was observed on replacing nonactivated copper wire with activated one but the polymerization proceeded with no induction period and also good correlation between theortical and experimental molecular weight was observed.

1.B.1.2.4.2.3 Activation via solvents

Solvents such as 2,2,2-trifluoroethanol and 2,2,3,3-tetrafluoropropanol have the ability to actvate copper wire.[100] Polymerization of methyl methacrylate carried out in DMSO using activated copper resulted in increase in k_p^{app} with no induction period and the polymer retained high end group fidelity and low polydispersity index.

1.B.1.2.4.3 SET-LRP in the presence of air

CLRP are less tolerant towards air or oxygen. Small amount of oxygen will lead to an induction period, retarded chain growth as well as loss of control over molecular weight. Compared to SET-LRP, in ATRP elimination of oxygen is vital since Cu(I) is the activator in ATRP which is prone to reversible oxidation. Consequently CLRP demands elaborate deoxygenation procedures such as Freeze-Pump-Thaw cycle and nitrogen purging. From an industrial application point of view, it is highly desirable to be able to carry out the reaction in the presence of air.

Catalyst used in SET-LRP was Cu(0) wire. In the presence of oxygen, Cu is oxidized into copper oxide which is a deactivator and hence termination occurs readily.

Nguyen reported a method for activation of copper wire using reducing agent hydrazine hydrate.[101] Hydrazine hydrate effectively reduces Cu_2O on the Cu surface to Cu(0) and reactivated Cu(0) acts as an efficient scavenger for oxygen[102]. This process would continue until all oxygen is consumed and eliminate time consuming deoxygenation procedures such as Freeze-Pump-Thaw cycle. So activation of Cu(0) is a proficient tool to carry out the reaction in less time and also to polymerize less activated monomers. Both methods helped to get rid of the induction period and to gain polymer with controlled molecular weight.

1.B.1.2.4.4 SET-LRP for mechanophore incorporated polymers

In contrast to other CLRP, versatility of this method is due to low catalyst loading, being able to synthesis ultra-high molecular mass polymer in shorter reaction time with high end group fidelity, control of MWDs and low polydispersity index, no need of cleanup process, high compatibility with solvents and catalyst, tolerance towards both activated monomers and non activated monomers. These features together with moderate reaction condition and colorless product make SET–LRP suitable for the commercial production of polymers.

Out of the prevalent controlled living polymerization protocols such as NMP, RAFT, ATRP and SET-LRP we have selected SET-LRP as the tool, not only to synthesize mechanophore attached polymers but more

importantly to enable polymerization with exceptional controllability and end group fidelity, where by termination has been significantly reduced.

Polymer mechanochemistry has utilized the potential of SET-LRP to place the mechanophore at the centre of the polymer chain to study the mechanoresponsive behavior of novel mechanophores. Moore and co-workers utilized SET-LRP to study the mechanoresponsive behavior of cyanoacrylates[103] by synthesizing cyanoacrylates mechanophore incorporated polymer.

1.2.5 Objectives of the study

Material having stress responsive, self-healing, as well as stress induced strengthening behavior is very attractive since these can extend material life time. Our initial attempt is to design a mechanophore having all these properties. It is already known that Diels–Alder reaction is thermally reversible and has previously been used for self-healing applications. So we have decided to synthesize novel mechanophores based on Diels–Alder click chemistry and then to analyze its mechanoresponsive and self-healing ability followed by probing the feasibility of Diels–Alder unclick chemistry using mechanical force so that the mechanophore based on Diels–Alder click chemistry would exhibit three distinct behavior such as self-healing, stress induced strengthening as well as stress-sensing. Overarching Objectives of the study are listed below.

- *Synthesis of novel mechanophores.*
- *Synthesis of intiators for SET-LRP.*

- *Synthesis of mechanophore incorporated polymers through modified SET-LRP.*
- *Investigation of mechanically induced site selective cleavage in mechanophore incorporated polymer.*
- *Investigation of self-healing ability of synthesized polymers*
- *Exploration of Diels–Alder click chemistry for stress induced strengthening of materials.*

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Chapter 2

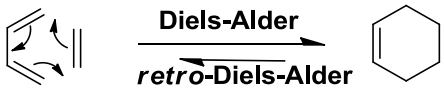
Synthesis of a few Initiators for Single Electron Transfer-Living Radical Polymerization

Contents

Conspectus:- *This chapter describes the synthesis of a few initiators that could be used in Single Electron Transfer-Living Radical Polymerization to investigate the tolerance of SET-LRP towards air and also a few mechanophore initiators that are relevant to force sensing and self-healing applications. Importance of Diels–Alder click chemistry in the context of stress-sensing and self-healing is outlined. Structural authenticity of the synthesized mechanophores and initiators using FT-IR, UV-Vis,* ^{1}H *NMR,* ^{13}C *NMR, GC-MS and LC-MS analyses is also included.*

2.1 Diels–Alder click chemistry for mechanophore synthesis

Diels–Alder (DA) chemistry described by Otto Paul Hermann and Diels and Kurt Alder is a [4π+2π] cycloaddition reaction between electron rich diene and electron deficient dienophile to give a six-membered cyclic product *via* carbon–carbon bond making.[1] Typically this reaction has been driven thermally or photochemically.



Scheme 2.1. General representation of the Diels–Alder/*retro* Diels–Alder reaction

One attractive feature of DA chemistry is its thermal reversibility as DA adduct at appropriate temperature range undergo reversible reaction called *retro* Diels–Alder (rDA) reaction to regenerate diene and dienophile components. This reversibility has been successfully employed in self-healing of polymeric materials.[2]

Diels–Alder reaction is mechanically reversible. Mechanically induced *retro* Diels–Alder reaction was demonstrated by sonicating centrally located DA adduct based mechanophore attached PMMA polymer.[3]

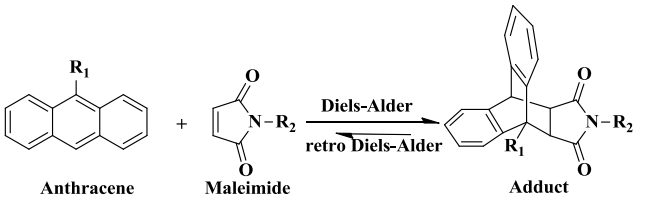
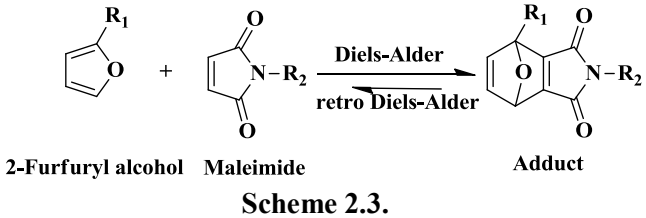
Diels–Alder reaction meets the criteria of click processes[4] since the reaction is modular and stereospecific, and the reaction can be carried out in a simple step with readily available reagents without solvent or solvent that is benign to get the products in high yield without chromatographic separation. Diels–Alder reaction meets all the aforementioned properties such as as thermal reversibility, mechanical reversibility as well as click/unclick

concept. Hence we thought about the possibility of using Diels–Alder chemistry in the design of mechanophore attached polymers so that we could combine self-healing[5], stress-sensing as well as stress induced strengthening in a polymer.

Efficient Diels–Alder reaction demands electron rich diene and electron deficient dienophile. Commonly used dienes in self healing materials are anthracene and furan and the dienophile is maleimide. Compatibility of maleimide is due to highly electron poor C=C and also the presence of nitrogen atom providing access to substituent attachment.

Anthracene reacts with maleimide at temperature around 110 ºC to form adduct and it is highly stable compared to furan maleimide adduct for which DA reaction is feasible between 25 and 120 ºC. The condition for DA/rDA reaction of anthracene/furan-maleimide system is given in Table 2.1.

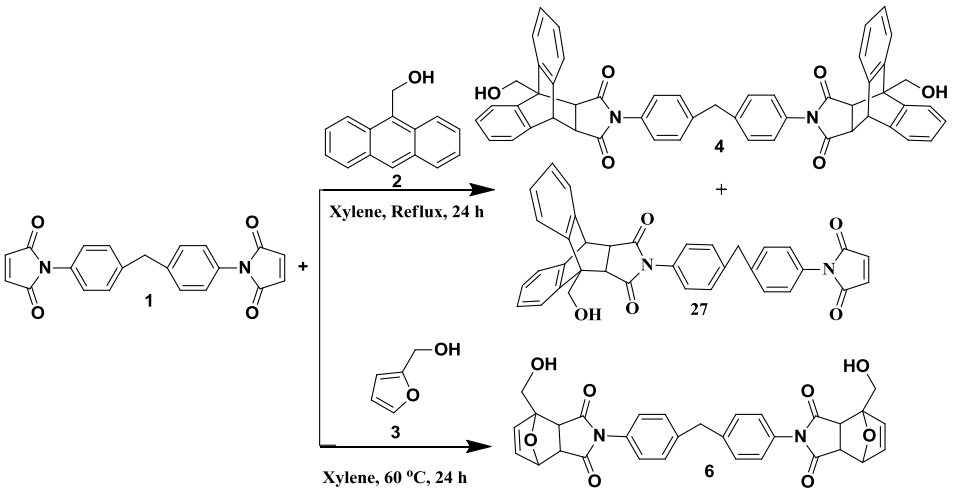
Table 2.1

Selected Diels–Alder reactions	Reaction condition
 **Scheme 2.2.**	DA:- 120 ºC heating for 2 days without a catalyst. rDA:- at temperatures higher than 120 ºC
 **Scheme 2.3.**	DA:- between 25 and 120 ºC without a catalyst rDA:- temperatures higher than 120 ºC

So our aim is to synthesise some mechanophores based on Diels–Alder click/unclick chemistry. Diene selected were 2-substituted furan and 9-substituted anthracene and the dienopile used were mono and bismaleimides. Here [4+2] Diels–Alder reaction was used to synthesise mechanophores. Resultant mechanophores were then functionalized with α-bromo ester group with a view to attach these into the polymer *via* SET-LRP.

2.2 Results and Discussion

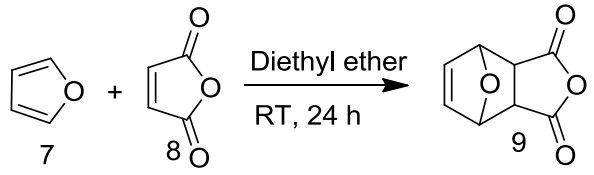
Mechanophores **4** and **27** were synthesized *via* [4+2] Diels–Alder reaction by refluxing 1,1'-(methylenebis(4,1-phenylene))bis(1*H*-pyrrole-2,5-dione) (**1**) and anthracen-9-ylmethanol (**2**) in xylene solvent for 24 h. Both 1:1 adduct and 1:2 adducts were isolated with a view to synthesise polymer having mechanophore at the end or at the centre of polymer respectively. Mechanophore **6** was synthesized by heating furan-2-ylmethanol (**3**) and 1,1'-(methylenebis(4,1-phenylene))bis(1*H*-pyrrole-2,5-dione) (**1**) in xylene at 60 ºC for 12 h (Scheme 2.4).



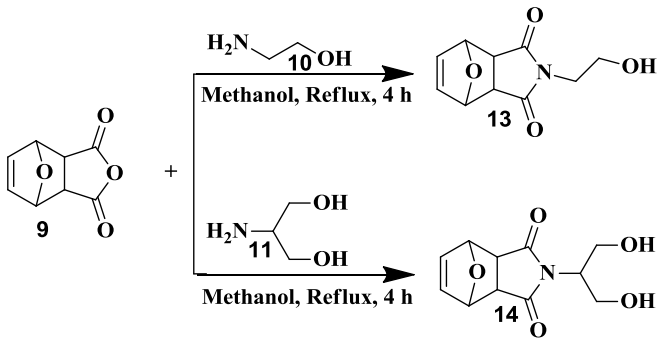
Scheme 2.4.

More attention was given to bismaleimide and trismaleimide mechanophores compared to monomaleimide as the former have two and three active mechanophore sites per unit respectively.

Mechanophores **13** and **14** were synthesized by the reaction of furan protected maleic anhydride, 3a,4,7,7a-tetrahydro-4,7-epoxyisobenzofuran-1,3-dione (**9**) with 2-aminoethanol (**10**) and 2-aminopropane-1,3-diol (**11**) respectively. Reaction was carried at around 60 ºC in methanol solvent for 6 h (Scheme 2.6). Lower temperature was used for furan based mechanophore synthesis. The C=C of maleic anhydride (**8**) is very reactive towards amine, hence double bond of maleic anhydride was protected by furan (**7**) by using a known protocol given in Scheme 2.5.



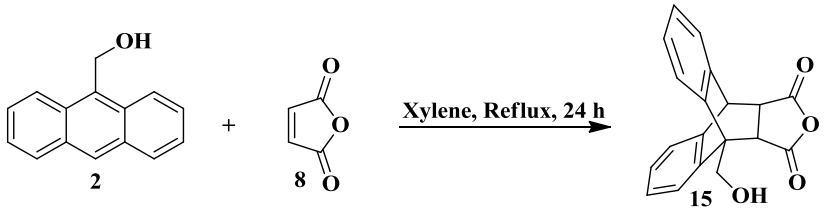
Scheme 2.5.



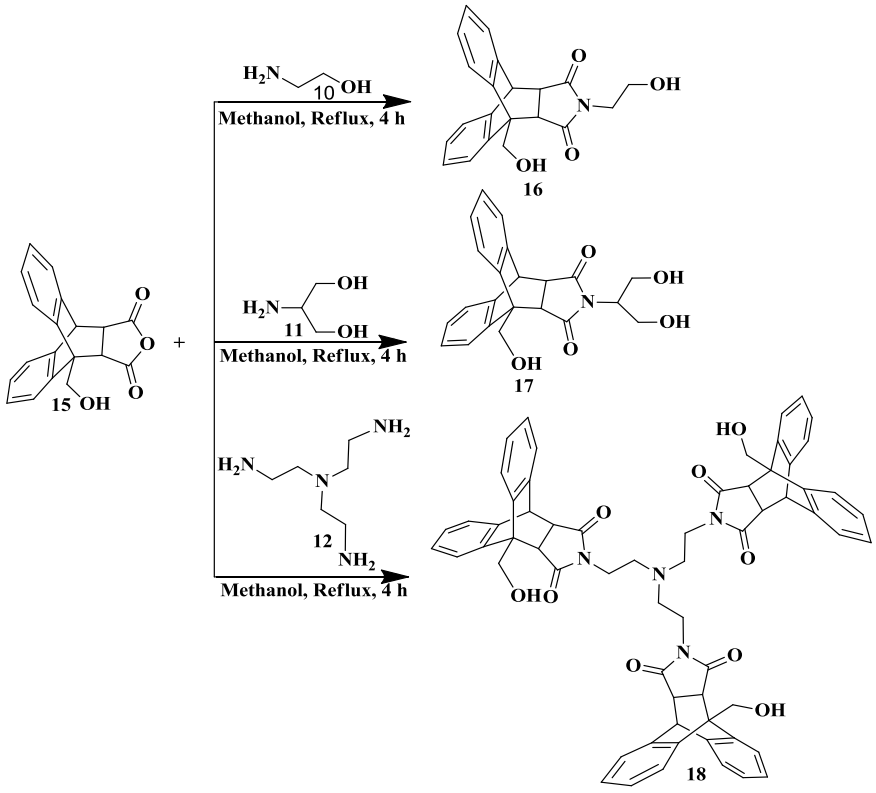
Scheme 2.6.

In a similar vein, mechanophores **16**, **17**, and **18** were synthesized by the reaction of **15** with corresponding aminoethanol (Scheme 2.8).

Precursor **15** was yielded via the Diels–Alder reaction anthracen-9-ylmethanol (**2**) with maleic anhydride (**8**) (Scheme 2.7).



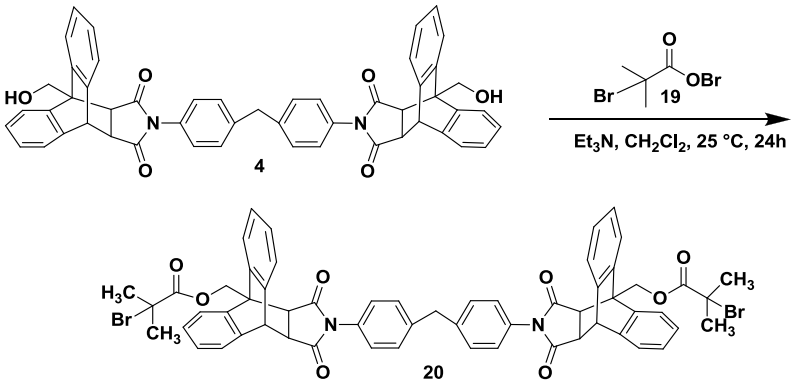
Scheme 2.7.



Scheme 2.8.

Purification was achieved by chromatography and recrystallization. All products were obtained in good yield (> 80%). Chemical structures and purity of all synthesized compounds were confirmed by TLC, ^{1}H

NMR, ^{13}C NMR, GC-MS and LC-MS. The FTIR spectra of anthracene maleimide mechanophores (**4**, **6**, **16**, **17**, **18**, **27**) bearing amide groups showed the carbonyl doublet characteristic peak in the range of 1780-1770 and 1725-1705 cm^{-1} due to C=O from imide group. Hydroxyl group attached to methylene group of parent DA adduct of compounds **4**, **6**, **13**, **14**, **15**, **16**, **17**, **18** and **27** showed absorption band between 3350 and 3500 cm^{-1}. Compounds **4**, **15**, **16**, **17**, **18**, **27** showed diasteriotopic hydrogens as doublet of doublet in the range δ 4.78-5.08. In all these compounds bridgehead hydrogen appeared as singlet in the range δ 4.65-4.72 which is charecteristic of barrelene system. In ^{13}C NMR spectrum of aforementioned compounds, carbonyl group indicated its presence by the appearance of peaks in the range δ 170 to 178. Initiators were synthesized[6] by incorporating α-bromo ester functionality using 2-bromoisobutyryl bromide (**19**) in the presence of triethylamine using a protocol given in Scheme 2.9.

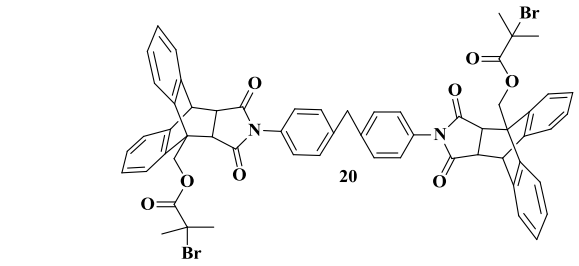


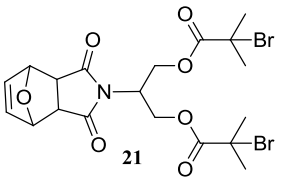
Scheme 2.9.

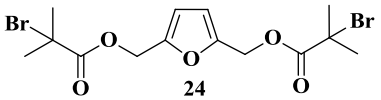
Yield of the reaction varied between 70 and 98 %. Unfortunately, a few of the initiators decomposed over silica and alumina. Hence we purified initiators by fractional recrystallization from methanol. They are

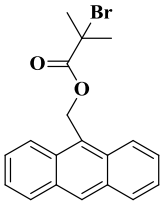
soluble in common solvents such as DCM, toluene, $CHCl_3$ and THF. FT-IR, ^1H NMR, and ^{13}C NMR, GC-MS and LC-MS of compounds indicated successful incorporation of ester functionalty. IR spectrum of compounds **20-25** indicated the presence of α-bromo ester functionality by the appearance of an absorption band in the range 1738-1727 cm^{-1} which is attributed to ester carbonyl. In ^{13}C NMR spectrum of aforementioned compounds, carbonyl group indicated its presence by the appearance of peaks in the range δ 170 to 179. Initiators synthesized are given in Table 2.2.

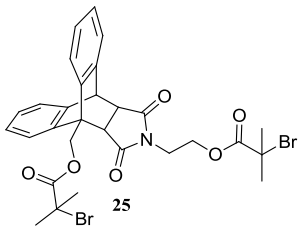
Table 2.2. Initiators synthesized

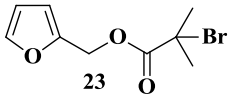


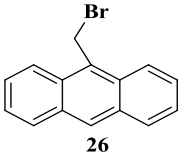












2.3 Conclusion

We have synthesized a few novel mechanophores using Diels–Alder reaction. Some of these were functionalized successfully to convert them into initiators. With a view to synthesise mechanophore responsive healable polymers having the potential of stress induced strengthening, we have synthesised mechanophores primarly based on [4+2] DA reactions. Here we selected anthracene and furan as dienes and maleic anhydride and maleimide derivatives as dienophiles for the synthesis of mechanophores. Successful synthesis of these mechanophores were authenticated by the characterization using FT-IR, ^{1}H NMR, ^{13}C NMR, GC-MS and LC-MS. Unfortunately during purification by column chromatography some of the initiators decomposed over silica and/or alumina surface and hence we had to resort to repeated recrystallization for their purification. We have synthesized seven initiators that could initiate SET-LRP. Out of these three are novel compounds. We also envision the use of these mechanophore as an effective probe for sensing damage and also for repairing of the same.

2.4 Experimental Section

2.4.1 Materials and methods

Unless and otherwise stated, all commercially available materials were purchased from either Spectrochem or Sigma Aldrich and were used as received without further purification. Solvents were dried and purified using known protocols.

2.4.2 Instrumentation

Melting points were determined on a *Neolab* melting point apparatus and are uncorrected. Infrared spectra were recorded on *Jasco*

4100 and *ABB Bomem (MB Series)* FT-IR spectrometers. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz *Bruker AvanceIII* FT-NMR spectrometer using deuterated chloroform or deuterated dimethyl sulphoxide as solvent with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) were reported in parts per million (ppm) downfield of TMS. Multiplicities were designated as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q) and multiplet (m). Elemental analysis was performed using *Elementar Systeme (Vario EL III)*. Molecular mass was determined by electron impact (EI) method using GC-MS (*Agilent GC-7890A, Mass-5975C*) and fast atom bombardment (FAB) using *JMS 600 JEOL* mass spectrometer.

2.4.3 General procedure for synthesis

2.4.3.1 Synthesis of anthracen-9-yl methanol (2)

9-Anthracenemethanol was prepared using a known protocol.[7] (Yield: 60%; mp: 158-162 °C).

2.4.3.2 Synthesis of furan-2,5-diyldimethanol (5)

Furan-2,5-diyldimethanol was prepared using a known protocol.[7] (Yield: 98%; mp: 74 °C).

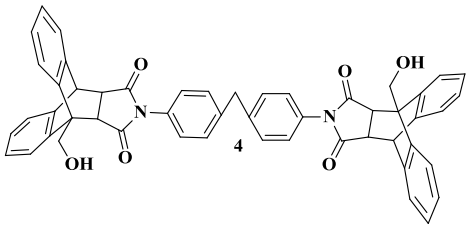
2.4.3.3 Synthesis of mechanophores

2.4.3.3.1 Synthesis of anthtracene derived mechanophores

2.4.3.3.1.1 Synthesisof9-(hydroxymethyl)-13-(4-(4-((9,10)-9-(hydroxymethyl)-12,14-dioxo-11,12,14,15-tetrahydro-9*H*-9,10-[3,4]epipyrroloanthracen-13(10*H*)-yl)benzyl)phenyl)-10,11-dihydro-9*H*-9,10-[3,4]epipyrroloanthracene-12,14(13*H*,15*H*)-dione (4)

In a 50 mL round-bottom flask anthracen-9-ylmethanol (0.1 g) was

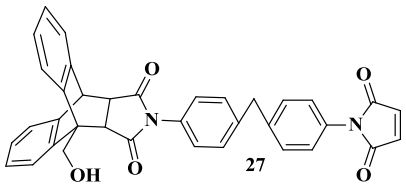
dissolved in a minimum amount of xylene. 1,1'-(methylenebis(4,1-phenylene))bis(1H-pyrrole-2,5-dione) (**1**) was added to this and refluxed for 24 h . The product was purified by column chromatography using ethyl acetate/hexane (3:2) solvent mixture to give **4** and **27**



White crystalline solid; Yield: 60%; mp: 236 ^{0}C; IRν_{max} (KBr): 3459, 1772, 1704, 1512, 1467 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.2 Hz, 1H), 7.29 -7.34 (dd, *J* = 18.4, 4.8 Hz, 1H), 7.11-7.28 (m, 5H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.33 (d, *J* = 8.0 Hz, 2H), 5.08 (d, *J* = 8.4 Hz 1H), 4.92 (d, *J* = 10 Hz 1H), 4.78 (d, *J* = 3.2 Hz, 1H), 3.77 (s, 1H), 3.44 (d, *J* = 8.4 Hz, 1H), 3.34-3.37 (dd, *J* = 8.4 Hz, 3.2 Hz, 1H), 2.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 176.1, 176.0, 141.8, 141.0, 139.3, 138.9, 129.6, 129.4, 127.1, 127.1, 126.7, 126.6, 126.4, 125.4, 124.1, 123.4, 122.3, 60.2, 49.8, 47.9, 46.1, 45.9, 41.0; MS: *m/z* 775 (*M* + *1*); Elemental analysis calculated for $C_{51}H_{38}N_2O_6$: C: 79.05, H: 4.94, N: 3.62; Found C: 79.03, H: 4.92, N: 3.61.

2.4.3.3.1.2 Synthesis of (9,10)-13-(4-(4-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)benzyl)phenyl)-9-(hydroxymethyl)-10,11-dihydro-9*H*-9,10-4]epipyrroloanthracene-12,14(13*H*,15*H*)-dione (27)

Compound **27** was synthesized using a protocol described in 2.4.3.3.1.1.

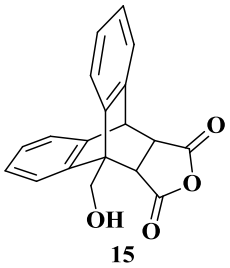


27

Yellow solid; Yield: 30%; mp: 146 ^{0}C; IRν_{max} (KBr): 3471 cm^{-1}, 1707 cm^{-1}, 1514 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.57 (d, *J* = 7.2 Hz, 1H), 7.33-7.35 (m, 1H), 7.28-7.30 (m, 1H), 7.13-7.18(m, 9H), 7.02-7.04 (d, *J* = 8.4 Hz, 2H), 6.78-6.79 (s, 2H), 6.35-6.37 (d, *J* = 8.4 Hz, 2H), 5.07-5.11 (dd, *J* = 11.6, 5.6 Hz 1H), 4.91-4.95 (d, *J* = 11.6 Hz, 1H), 4.77-4.78 (d, *J* = 3.2 Hz, 1H), 3.87 (s, 2H), 3.43-3.45 (d, *J* = 8.8 Hz, 1H), 3.36-3.39 (dd, *J* = 8.6, 3.4 Hz, 1H), 2.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 175.0, 168.5, 140.8, 140.2, 139.0, 138.3, 137.9, 133.1, 128.7, 128.6, 128.4, 126.1, 126.0, 125.7, 125.6, 125.4, 125.1, 124.4, 123.1, 122.3, 121.3, 59.2, 48.7, 46.9, 45.2, 44.9, 40.0; MS: *m/z* 567 (*M* + *1*), 589 (*M* + *Na*); Elemental analysis calculated for $C_{36}H_{26}N_2O_5$: C: 76.31, H: 4.63, N: 4.94; Found C: 76.30, H: 4.60, N: 4.92.

2.4.3.3.1.3 Synthesis of (9,10)-9-(hydroxymethyl)-9,10,11,15-tetrahydro-9,10-[3,4]furanoanthracene-12,14-dione (15)

Compound **15** was synthesized using a protocol described in 2.4.3.3.1.1



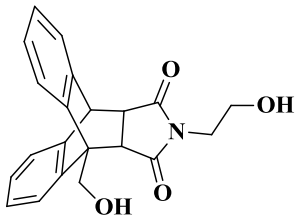
15

White crystalline solid; Yield: 90%; mp: 182 °C; IRν_{max} (KBr): 3563 cm^{-1}, 1834, 1777, 1233, 1078 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.63-7.65 (m, 1H), 7.34-7.39 (m, 2H), 7.17-7.26 (m, 5H), 5.11-5.14 (d, *J* = 11.2Hz, 1H), 4.98-5.01 (d, *J* = 10.8 Hz,1H), 4,78-4.79 (d, *J* = 3.2Hz,1H), 3.74-3.76 (d, *J* = 9.6 Hz, 1H), 3.59-3.62 (dd, *J* = 9.4, 3.4 Hz,1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.1, 141.4, 141.1, 138.6, 138.4, 127.6, 127.0, 126.8, 125.5, 124.1, 123.6, 122.1, 59.4, 49.5, 48.7, 46.7, 45.5; MS: *m/z* 306 (*M*+) 307(*M*+1); Elemental analysis calculated for $C_{19}H_{14}O_4$: C: 74.50, H: 4.61; Found C: 74.48, H: 4.60.

2.4.3.3.1.4 Synthesis of (9,10)-13-(2-hydroxyethyl)-9-(hydroxymethyl)-10,11-dihydro-9*H*-9,10-[3,4]epipyrroloanthracene-12,14(13*H*,15*H*)-dione (16)

In a 50 mL round-bottom flask fitted with a condenser and dropping funnel, (9r,10r)-9-(hydroxymethyl)-9,10,11,15-tetrahydro-9,10-[3,4] furanoanthracen-12,14-dione (**15**) (0.1 g) in 5 mL methanol was

added . To this stirred solution, ethanolamine (0.02 g) in 5 mL methanol was added dropwise. After the addition, the solution was heated at 60 ºC for 6 h. Product was purified by column chromatography and repeated recrystallization from methanol.

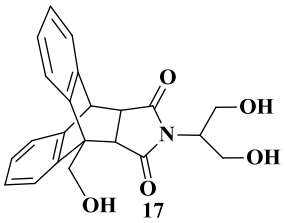


16

White crystalline solid; Yield: 96%; mp: 182 °C. IRν_{max} (KBr): 3444, 1777, 1705, 1516, 1463 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.56 (d, *J* = 7.2, 1H), 7.30-7.32 (dd, *J* = 7.0, 0.6 Hz, 1H), 7.09-7.27 (m, 6H), 5.05-5.08 (d, *J* =11.6 Hz, 1H), 4.89-4.92 (d, *J* =11.6 Hz, 1H), 4,69-4.70 (d, *J* =3.2Hz, 1H), 3.32-3.35 (d, *J* = 8.4 Hz, 1H), 3.24-3.28 (m, 3H), 3.03-3.05 (t, *J* =10Hz 2H), 2.90 (s, 1H), 1.18(s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.27, 177.22, 141.8, 141.7, 139.5, 139.3, 126.95, 126.90, 126.7, 126.6, 125.3, 124.1, 123.4, 122.4, 60.2, 60.0, 49.5, 47.8, 46.1, 45.7, 41.2; MS: *m/z* 349 (M^+); Elemental analysis calculated for $C_{21}H_{19}NO_4$: C: 72.19, H: 5.48, N: 4.01; Found : C: 72.12, H: 5.42, N: 3.98

2.4.3.3.1.5 Synthesis of (9,10)-13-(1,3-dihydroxypropan-2-yl)-9-(hydroxymethyl)-10,11-dihydro-9*H*-9,10-[3,4]epipyrroloanthracene-12,14(13*H*,15*H*)-dione (17)

Compound **17** was synthesized using a protocol described in 2.4.3.3.1.4 using compound **15** and **11**.

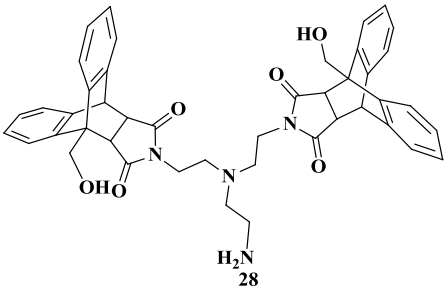


17

White crystalline solid; Yield: 80%; mp: 236 $^{\circ}$C; IRν_{max} (KBr): 3459, 1772, 1704, 1512, 1467 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.63 (d, 1H) 7.38-7.40 (m, 1H), 7.32-7.34 (m, 1H), 7.19-7.24 (m, 5H), 5.29 (s, 3H), 5.11-5.14 (d, 1H), 4.96-4.98 (d, 1H), 4.76-4.76 (d, *J* = 3.2 Hz, 1H), 3.91-3.94 (m, 1H), 3.25-3.49 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 177.8, 141.6, 139.4, 139.1, 127.07, 127.02, 126.8, 126.7, 125.3, 124.1, 123.4, 122.4, 60.2, 60.2, 60.0, 55.3, 53.4, 49.6, 47.6, 45.8, 45.7; δ MS: *m/z* 379 (M^+), 398 (M+19); Elemental analysis calculated for $C_{22}H_{21}NO_5$: C: 69.64, H: 5.58, N: 3.96; Found C: 69.62, H: 5.55, N: 3.94.

2.4.3.3.1.6 Synthesis of 13-(2-((2-aminoethyl)(2-((9,10)-9-(hydroxymethyl)-12,14-dioxo-11,12,14,15-tetrahydro-9*H*-9,10-[3,4]epipyrroloanthracen-13(10*H*)-yl)ethyl)amino)ethyl)-9-(hydroxymethyl)-10,11-dihydro-9*H*-9,10-[3,4]epipyrroloanthracene-12,14(13*H*,15*H*)-dione (28)

Compound **28** was synthesized using a protocol described in 2.4.3.3.1.4 using compound **15** and **12**.



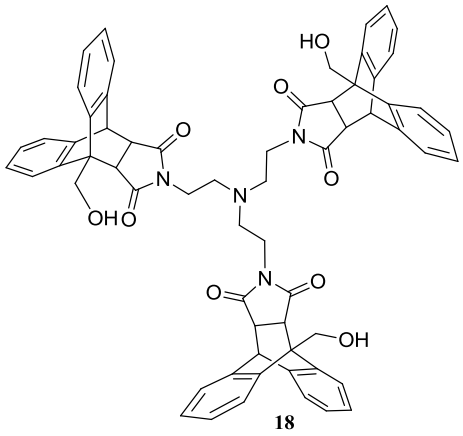
28

White crystalline solid; Yield: 60%; mp: 160 °C; IRν_{max} (KBr): 3330 cm^{-1}, 1774, 1686, 1590 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.58-7.60 (d,1H) 7.24-7.30 (d, 1H), 6.95-7.16 (m, 5H), 5.01-5.04 (d, 1H), 4.78-4.83 (m, 1H), 4.62-4.63 (d, 1H), 3.39-3.44 (m, 1H), 3.18-3.27 (m, 1H), 2.86-2.87 (d, 3H), 2.77 (s, 5H), 2.51 (s, 2H), 2.24 (s, 1H), 1.78-1.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 175.9, 141.1, 141.1, 138.4, 138.3, 125.8, 125.7, 125.6, 125.4, 124.1, 122.8, 122.7, 121.1, 58.8, 50.3, 50.0, 48.4, 46.9, 44.7, 37.1, 35.3, 35.2;

MS: *m/z* 723 (*M* + 1), 724 (M + 2), 745 (M + 23); Elemental analysis calculated for $C_{44}H_{42}N_4O_6$: C: 73.11, H: 5.86, N: 7.75; Found C: 73.10, H: 5.84, N: 7.73.

2.4.3.3.1.7 Synthesis of 9-(hydroxymethyl)-13-(2-((2-((11,15)-9-(hydroxymethyl)-12,14-dioxo-11,12,14,15-tetrahydro-9*H*-9,10-[3,4]epipyrroloanthracen-13(10*H*)-yl)ethyl)(2-((9,10)-9-(hydroxymethyl)-12,14-dioxo-11,12,14,15-tetrahydro-9*H*-9,10-[3,4]epipyrroloanthracen-13(10*H*)-yl)ethyl)amino)ethyl)-10,11-dihydro-9*H*-9,10-[3,4]epipyrroloanthracene-12,14(13*H*,15*H*)-dione (18)

Compound **18** was synthesized using a protocol described in 2.4.3.3.1.4 using compound **15** and **12**



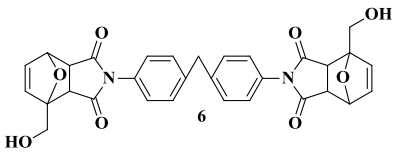
18

White crystalline solid; Yield: 80%; mp: 150 °C; IRν_{max} (KBr): 3522, 1841, 1764 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.54-7.57 (m, 1H), 7.29-7.31 (m, 1H), 7.08-7.18 (m, 4H), 7.01-7.05 (m, 2H), 4.94-5.07 (m, 1H), 4.76-4.88 (m, 1H), 4.62-4.64 (m, 1H), 3.20-3.36 (m, 2H), 2.77-2.80 (m, 2H), 1.75-1.78 (m, 1H), 1.51-1.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.8, 176.7, 142.4, 142.2, 124.0, 139.2, 139.2, 139.1, 139.0, 126.8, 126.8, 126.7, 126.6, 126.5, 125.2, 124.0, 124.0, 123.9, 123.5, 123.4, 123.3, 122.3, 122.3, 122.0, 60.3, 60.2, 60.0, 50.7, 50.2, 49.3, 49.2, 48.0, 47.8, 47.7, 45.9, 45.7, 45.6, 35.9. MS: *m/z* 1011 (M + 1), 1011 (M + 2); Elemental analysis calculated for $C_{63}H_{54}N_4O_9$: C: 74.83, H: 5.38, N: 5.54; Found C: 74.81, H: 5.36, N: 5.52.

2.4.3.3.2. Synthesis of furan derived mechanophores

2.4.3.3.2.1 Synthesis of 2,2'-(methylenebis(4,1-phenylene))bis(4-(hydroxymethyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione) (6)

Compound **6** was synthesized using a protocol described in 2.4.3.3.1.1.

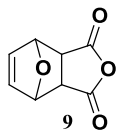


6

White crystalline solid; Yield: 80%; mp: 84 ºC; IRν_{max} (KBr): 3471, 1775, 1705, 1512 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.20-7.23 (m, 3H), 7.12-7.13 (dd, *J* = 4.6, 1.8 Hz, 2H), 6.59-6.60 (s, *J* = 5.6 Hz, 1H), 6.51-6.53 (dd, *J* = 6.1, 1.2 Hz, 1H), 5.30-5.31 (d, *J* = 1.6 Hz, 1H), 4.07-4.09 (d, *J* = 5.2 Hz, 2H), 3.97 (s, 1H), 3.04-3.09 (dd, *J* = 14.8 Hz, 2H), 2.64-2.68 (t, *J* = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 141.4, 138.5, 137.1, 129.7, 126.5, 96.1, 91.7, 81.3, 60.8, 49.9, 48.2; MS: *m/z* 572 (M+18), 577 (M+23); Elemental analysis calculated for $C_{31}H_{26}N_2O_8$: C: 67.14, H: 4.73, N: 5.05; Found C: 67.12, H: 4.71, N: 5.01.

2.4.3.3.2.2 Synthesis of Protected Maleic Anhydride – 3,6-Epoxy-1,2,3,6-tetrahydrophthalic Anhydride (9)

The synthesis was carried out following a modified literature procedure.[8] In a 50 mL round-bottom flask maleic anhydride (1.00 g) and furan (0.69 g,) were dissolved in 5 mL of diethyl ether. The mixture was stirred for 24 h at room temperature after which the white precipitate formed was collected by filtration and washed thrice with cold diethyl ether and dried under vacuum. The filtrate was reduced 3 mL and cooled to 4 °C overnight. Crystals formed were collected by filtration and washed with diethyl ether. Finally, the crystals were dried under vacuum.



9

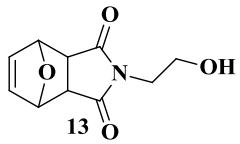
White solid; Yield: 90%; IRν_{max} (KBr): 3143 cm^{-1}, 3099 cm^{-1}, 1857 cm^{-1}, 1780 cm^{-1}.

2.4.3.3.2.3 Synthesis of 2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-epoxyisoindole-1,3(2*H*)-dione (13)

2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-epoxyisoindole-1,3 (2*H*)-dione (**13**) was synthesized by a known protocol[9]

In a 50 mL round-bottom flask fitted with a condenser and dropping funnel, 3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (1 g, 6 mmol) in 5 mL methanol was added . To the stirred solution of 3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride, ethanolamine (0.55 g, 6 mmol) in 5 mL methanol was added dropwise. After the addition, the solution was heated

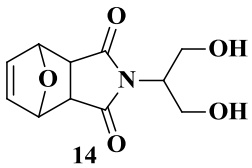
at 60 ºC for 6 h during which the solution turned light brown in color. Then the solution was concentrated to get brown oil.



White solid; Yield: 88%; IRν_{max} (KBr): 3143 cm^{-1}, 3099 cm^{-1}, 1857 cm^{-1}, 1780 cm^{-1}.

2.4.3.3.2.4 Synthesis of 2-(1,3-dihydroxypropan-2-yl)-3a,4,7,7a-tetrahydro-1*H*-4,7-epoxyisoindole-1,3(2*H*)-dione (14)

Compound **14** was synthesized using a known protocol using compound **9** and **11**.



White solid; Yield: 86%; IRν_{max} (KBr): 3147 cm^{-1}, 3096 cm^{-1}, 1856 cm^{-1}, 1784 cm^{-1}.

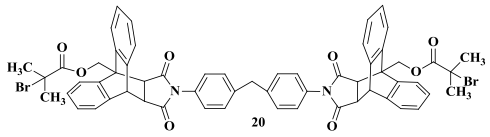
2.4.3.4 Synthesis of initiators

2.4.3.4.1 Synthesis of mechanophore functionalized initiators[9]

2.4.3.4.1.1 Synthesis of ((11,15)-13-(4-(4-((9,10,11,15)-9-(((2-bromo-2-methylpropanoyl)oxy)methyl)-12,14-dioxo-11,12,14,15-tetrahydro-9*H*-9,10-[3,4]epipyrroloanthracen-13(10*H*)-yl)benzyl)phenyl)-12,14-dioxo10,11,12,13,14,15-hexahydro-9*H*-9,10-[3,4]epipyrroloanthracen-9-yl)methyl 2-bromo-2-methylpropanoate (20)

Triethylamine (0.26 g, 2.60 mmol) was added to a solution of 9-anthracenemethanol–bismaleimide adduct **4** (2.1g, 2.00 mmol) in dry dichloromethane (DCM) (9 mL). The solution was stirred in an ice bath, and 2-bromoisobutyryl bromide **19** (5.99 g, 26.03 mmol) in dry dichloromethane (10 mL) was added dropwise over a period of 0.5 h while stirring. Then the reaction was left to reach completion for approximately

24 h. The solution was then precipitated in cold methanol and then filtered, washed thrice with HCl (0.5 M) followed by distilled water. Finally, the solution was passed through basic alumina column to remove unchanged 2-bromoisobutyryl bromide (**19**) followed by drying with anhydrous magnesium sulfate overnight, and then the solvent was removed under vacuum. The obtained crude product was purified by repeated recrystallization from methanol to give white solid. Yield 90%, R_f value 0.61 in 30% dichloromethane/hexane.

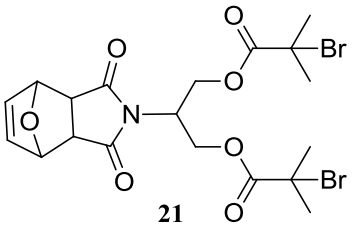


20

White crystalline solid; Yield: 80%; mp: 221 ^{0}C; IRν_{max} (KBr): 1745, 1714, 1509 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.45 (m, 6H), 7.00-7.02 (d, J = 8.4 Hz, 2H), 6.39-6.41 (d, J = 8.0 Hz, 1H), 5.63-5.66 (d, J = 11.6 Hz, d), 5.49-5.52 (d, J = 11.2 Hz, d) 4.884-4.887 (1H, J = 1.2 Hz, d), 3.84 (1H, s), 3.46 (1H, s), 1.99 (3H s), 1.97 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 174.5, 171.2, 141.6, 141.0, 140.8, 138.7, 138.0, 129.6, 129.3, 127.4, 127.3, 126.9, 126.8, 126.4, 125.5, 124.2, 123.2, 122.2, 63.1, 55.4, 48.1, 47.8, 45.9, 40.9, 30.8, 30.7; MS: *m/z* 1072 (M^+), 1090 (M+18); Elemental analysis calculated for $C_{59}H_{48}N_2O_8Br_2$: C: 66.05, H: 4.51, N: 2.61; Found C: 66.07, H: 4.53, N: 2.63.

2.4.3.4.1.2 Synthesis of 2-(1,3-Dioxo-3a,4,7,7a-tetrahydro-1*H*-4,7-epoxyisoindol-2(3*H*)-yl)propane-1,3-diyl bis(2-bromo-2-methylpropanoate) (21)

Compound **21** was synthesized using a protocol described 2.4.3.4.1.1

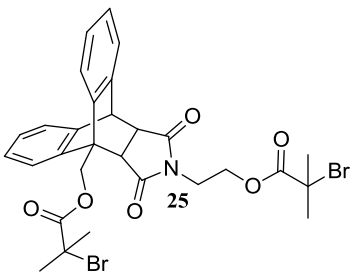


21

White crystalline solid; Yield: 80%; IRν_{max} (KBr): 1745 cm^{-1}, 1714 cm^{-1}, 1509 cm^{-1}.

2.4.3.4.1.3 Synthesis of ((9,10)-13-(2-((2-bromo-2-methylpropanoyl)oxy)ethyl)-12,14-dioxo-10,11,12,13,14,15-hexahydro-9*H*-9,10-[3,4]epipyrroloanthracen-9-yl)methyl-2-bromo-2-methylpropanoate (25)

Compound **25** was synthesized using a protocol described 2.4.3.4.1.1



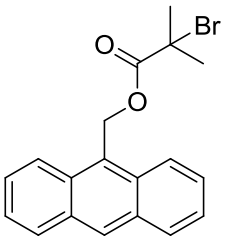
25

White crystalline solid; Yield: 80%; mp: 180 °C; IRν_{max} (KBr): 1743 cm^{-1}, 1712 cm^{-1}.

2.4.3.4.2 Synthesis of Diene functionalized initiators

2.4.3.4.2.1 Synthesis of Anthracen-9-ylmethyl-2-bromo-2-methylpropanoate (22)

Compound **22** was synthesized using a protocol described 2.4.3.4.1.1

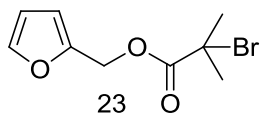


22

Pale yellow solid; Yield: 90%; mp: 84 °C; IRν_{max} (KBr): 2965, 1729, 1602, 1453, 1263 cm^{-1}; UV–Vis (chloroform)λ_{max}/nm : 334, 351, 368, 388 nm; PL (chloroform)λ_{max}/nm : 394, 417, 441nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 2H), 8.25-8.28 (d, 2H), 7.95-7.97 (d, 2H), 7.40-7.52 (m, 4H), 6.15 (s, 2H), 1.80 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 170.9, 130.3, 130.1, 128.4, 128.0, 125.7, 124.5, 124.1, 122.8, 59.7, 54.9, 29.7; MS: *m/z* 356 (*M*+), 358; Elemental analysis calculated for $C_{19}H_{17}BrO_2$: C: 63.88, H: 4.80 ; Found C: 63.84, H: 4.78.

2.4.3.4.2.2 Synthesis of Furan-2-ylmethyl 2-bromo-2-methylpropanoate

Compound **23** was synthesized using a protocol described 2.4.3.4.1.1

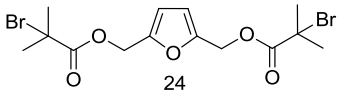


23

Pale brown liquid; Yield: 90%; IRν_{max} (KBr): 1736 cm^{-1}, 1590 cm^{-1}, 1268 cm^{-1}, 1152 cm^{-1}, 1106 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.35 (dd, *J* =1. 6, 0.8 Hz, 1H), 6.36-6.37 (d, *J* = 3.2, 1H), 6.28-6.29(dd, *J* = 3.2, 2 Hz, 1H), 5.07 (s, 2H), 1.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 164.6, 147.7, 142.3, 109.9, 109.5, 58.4, 54.5, 29.6; MS: *m/z* 245 (*M*+), 247; Elemental analysis calculated for $C_9H_{11}BrO_3$: C: 43.75, H: 4.49; Found C: 43.71, H: 4.48.

2.4.3.4.2.3 Synthesis of furan-2,5-diylbis(methylene)bis(2-bromo-2-ethylpropanoate) (24)

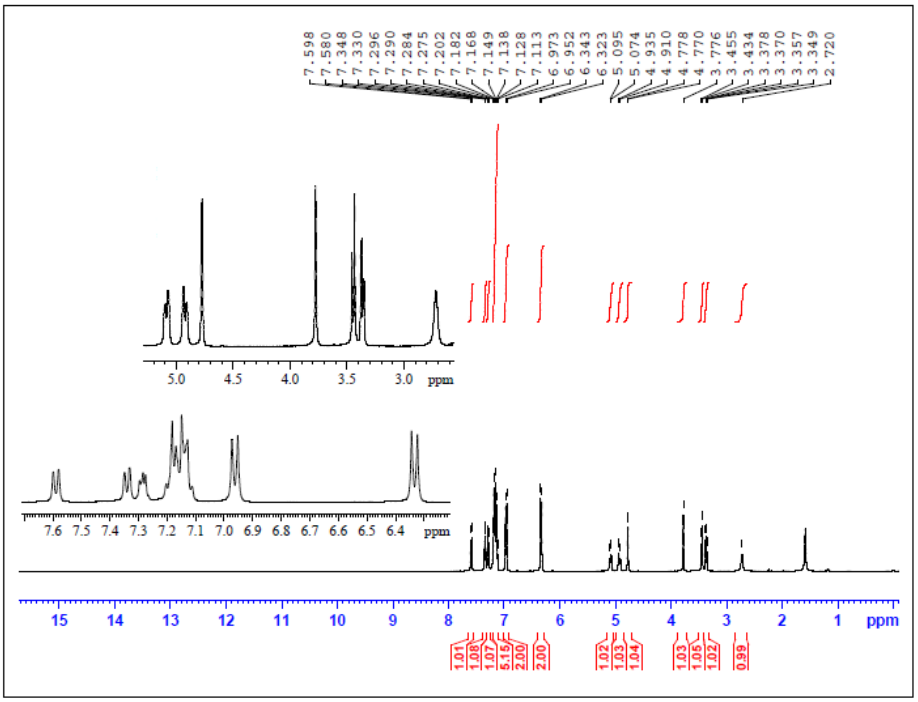
Compound **24** was synthesized using a protocol described 2.4.3.4.1.1



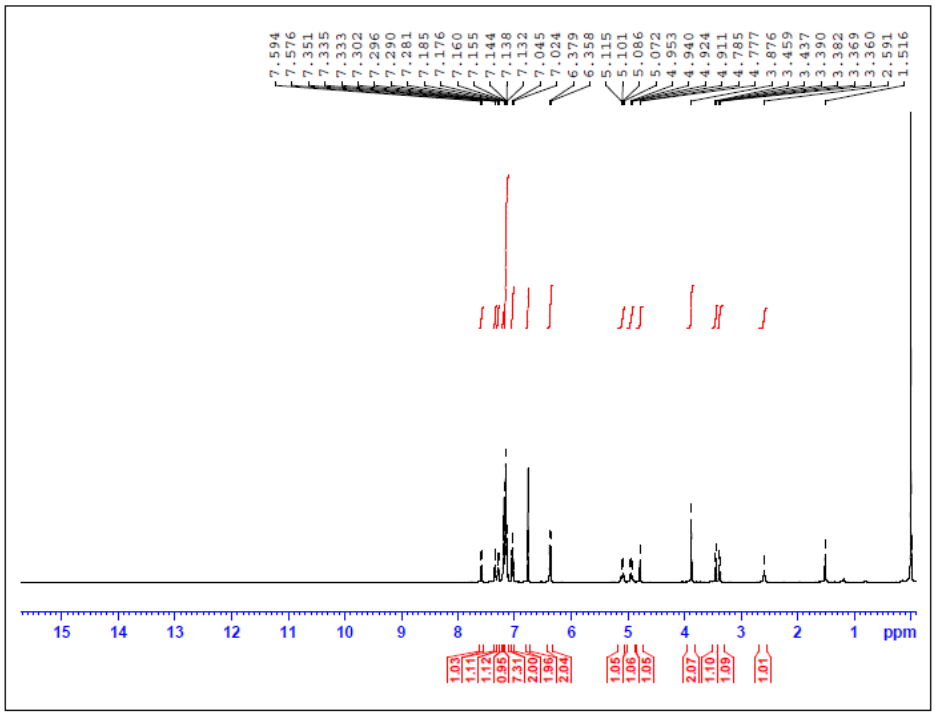
24

White solid; Yield: 90%; IRν_{max} (KBr): 1738, 1592, 1270, 1154, 1107 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.35 (1H, s), 5.07 (2H, s), 6.35 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 149.6, 111.8, 59.4, 55.4, 30.6; MS: *m/z* 425 (*M*+), 427; Elemental analysis calculated for $C_{14}H_{18}Br_2O_5$: C: 39.46, H: 4.26; Found C: 39.41, H: 4.23.

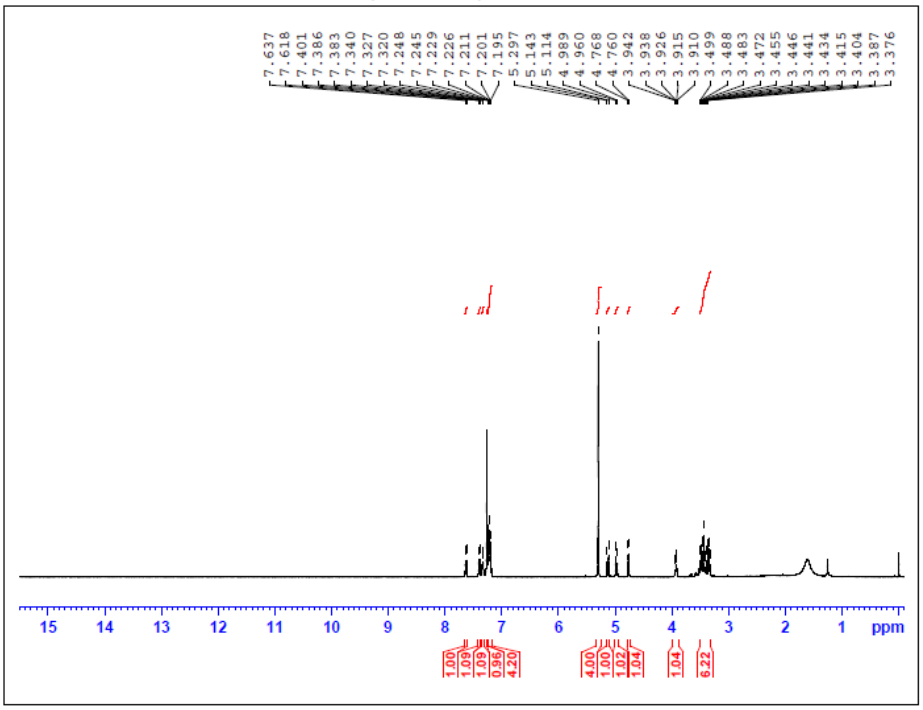
1. ^{1}H NMR spectrum of 9-(hydroxymethyl)-13-(4-(4-((9,10)-9-(hydroxymethyl)-12,14-dioxo-11,12,14,15-tetrahydro-9*H*-9,10-[3,4]epipyrroloanthracen-13(10*H*)-yl)benzyl)phenyl)-10,11-dihydro-9*H*-9,10-[3,4]epipyrroloanthracene-12,14(13*H*,15*H*)-dione (**4**)



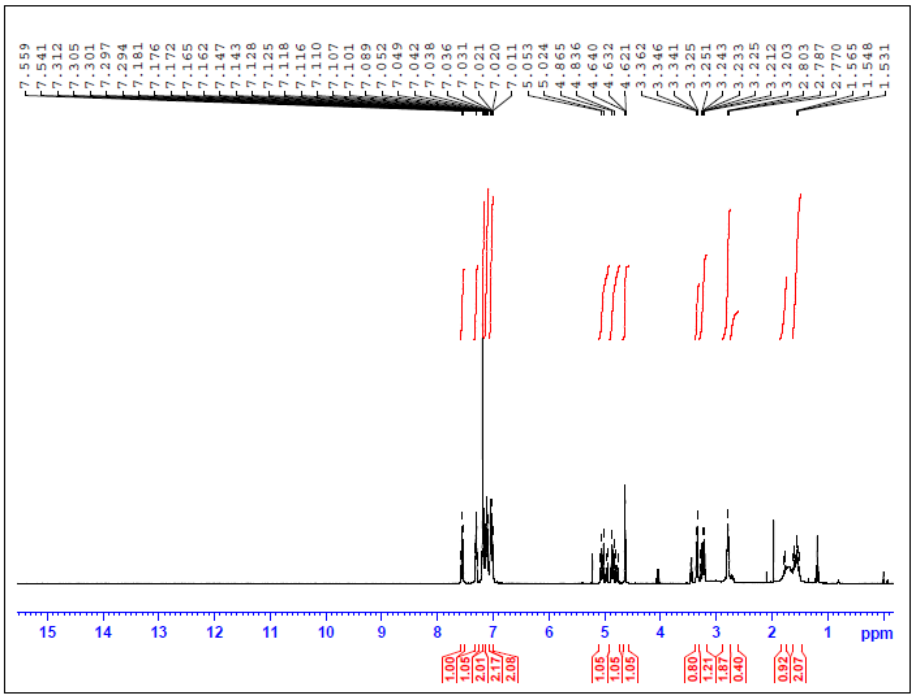
2. ^{1}H NMR spectrum of (9,10)-13-(4-(4-(2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)benzyl)phenyl)-9-(hydroxymethyl)-10,11-dihydro-9*H*-9,10-4]epipyrroloanthracene-12,14(13*H*,15*H*)-dione (**27**)



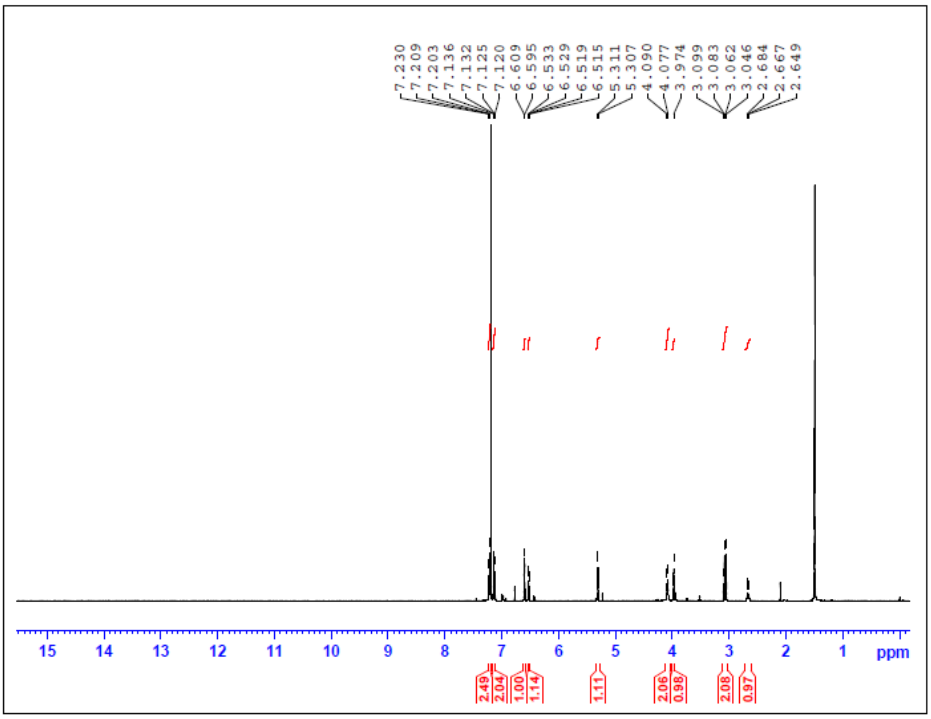
3. ^{1}H NMR spectrum of (9,10)-13-(1,3-dihydroxypropan-2-yl)-9-(hydroxymethyl)-10,11-dihydro-9*H*-9,10-[3,4]epipyrroloanthracene-12,14(13*H*,15*H*)-dione (**17**)



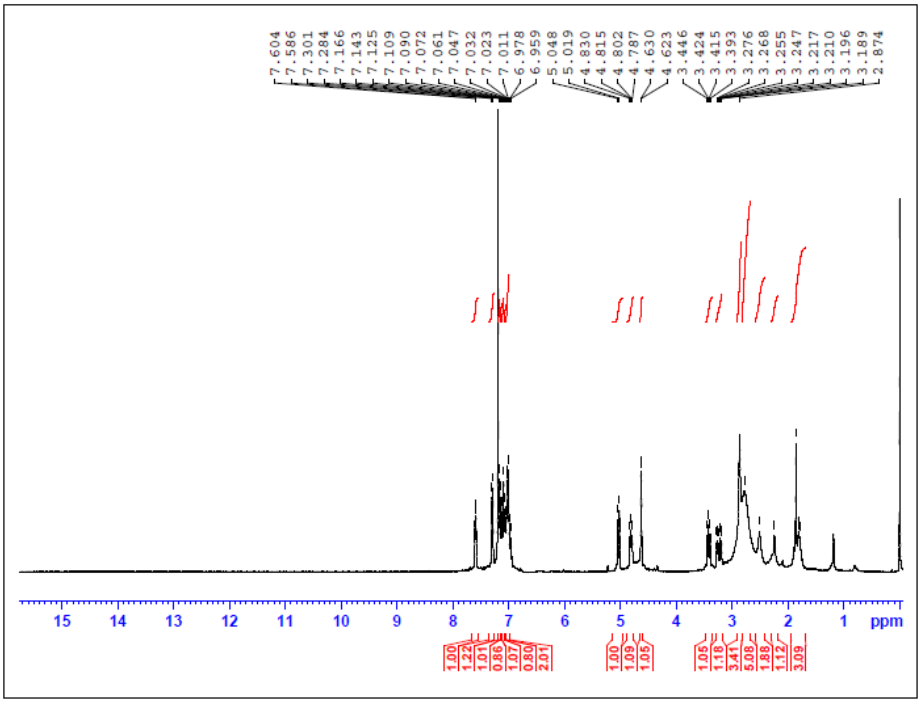
4. ^{1}H NMR spectrum of 9-(hydroxymethyl)-13-(2-((2-((11,15)-9-(hydroxymethyl)-12,14-dioxo-11,12,14,15-tetrahydro-9*H*-9,10-[3,4]epipyrroloanthracen-13(10*H*)-yl)ethyl)(2-((9,10)-9-(hydroxymethyl)-12,14-dioxo-11,12,14,15-tetrahydro-9*H*-9,10-[3,4]epipyrroloanthracen-13(10*H*)-yl)ethyl)amino)ethyl)-10,11-dihydro-9*H*-9,10-[3,4]epipyrroloanthracene-12,14(13*H*,15*H*)-dione (**18**)



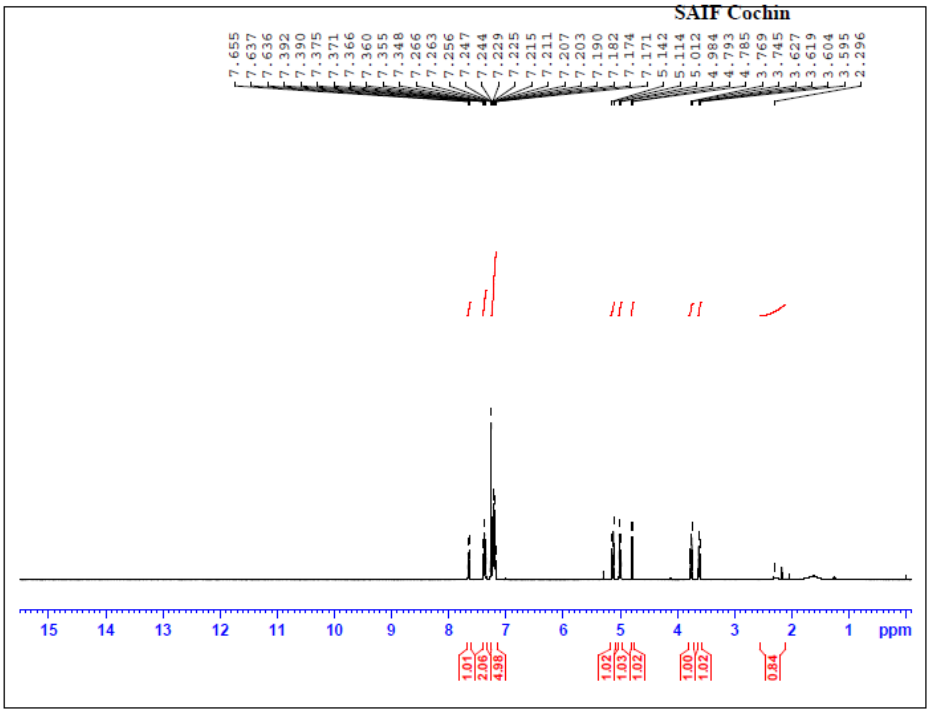
5. ^{1}H NMR spectrum of 2,2'-(methylenebis(4,1-phenylene))bis(4-(hydroxymethyl)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione) (**6**)



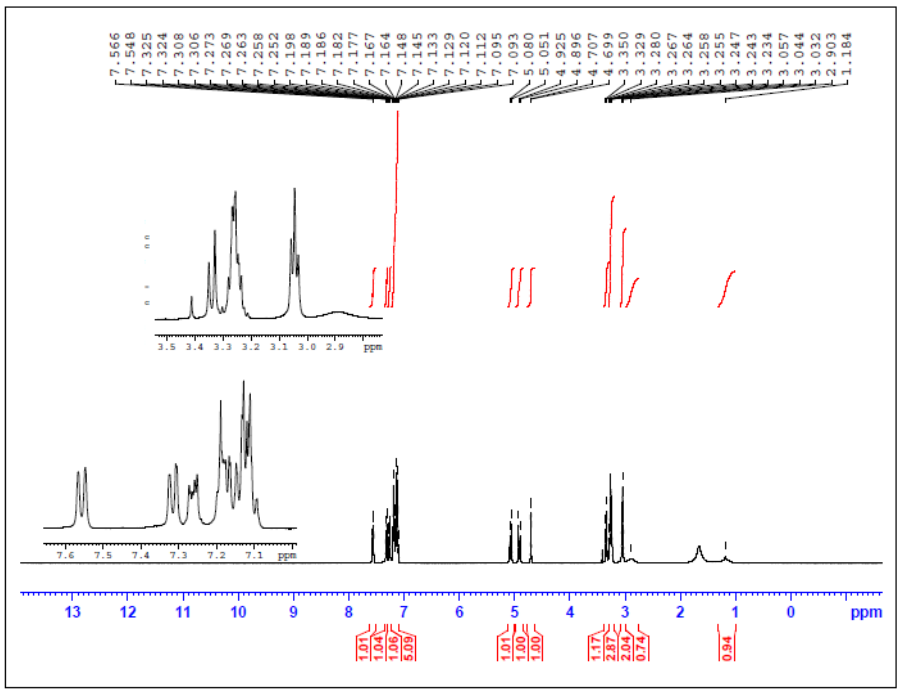
6. ^{1}H NMR spectrum of 13-(2-((2-aminoethyl)(2-((9,10)-9-(hydroxymethyl)-12,14-dioxo-11,12,14,15-tetrahydro-9*H*-9,10-[3,4]epipyrroloanthracen-13(10*H*)-yl)ethyl)amino)ethyl)-9-(hydroxymethyl)-10,11-dihydro-9*H*-9,10-[3,4]epipyrroloanthracene-12,14(13*H*,15*H*)-dione (**28**)



7. ^{1}H NMR spectrum of (9,10)-9-(hydroxymethyl)-9,10,11,15-tetrahydro-9,10-[3,4]furanoanthracene-12,14-dione (**15**)



8. ^{1}H NMR spectrum of (9,10)-13-(2-hydroxyethyl)-9-(hydroxymethyl)-10,11-dihydro-9*H*-9,10-[3,4]epipyrroloanthracene-12,14(13*H*,15*H*)-dione (**16**)



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Chapter 3

Synthesis of polymers via Single Electron Transfer-Living Radical Polymerization

Contents

Conspectus: This chapter describes the synthesis of a few dienes, dienophiles as well as mechanophore incorporated polymers via Single Electron Transfer-Living Radical Polymerization. Contrary to the usual SET-LRP, here a convenient and modified method of SET-LRP capable of being carried out in the presence of oxygen is reported. Efficiency of our modified method is inferred from characterization of polymers by FT-IR, ^{1}H NMR, ^{13}C NMR and GPC techniques.

3.1 Introduction

Single Electron Transfer-Living Radical Polymerization[1] has received considerable interest in the context of mechanophore incorporated polymer[2,3] as this method, performed under ideal conditions,

has been shown to generate high molecular weight polymer with narrow polydispersity having controlled MWD and high chain end group fidelity. Nevertheless, this technique presents a major limitation in terms of premature termination of growing chain as it is highly sensitive towards moisture and air and hence requires stringent reaction conditions and the use of *freeze pump thaw* cycle or nitrogen purging to eliminate the presence of oxygen. Efficiency of SET-LRP depends up on the disproportionation of the *in situ* generated Cu(I) to Cu(0), the activator and Cu(II), the deactivator[4-9]. Consequently, elimination of oxygen is crucial which may otherwise cause oxidation of copper to Cu(II), the deactivator. Studies showed that reducing agents such as phenol and phenolates[4], hydrazine and ascorbic acid[5] are efficient reducing agents towards Cu(II) species. Based on these findings, we hypothesized that triphenylphosphine (TPP) assisted SET-LRP could be a good strategy to enable oxygen tolerance. Successful polymerization in the presence of oxygen pushed us to investigate the compatibility of triphenylphosphine as ligand in SET-LRP. The efficiency of triphenylphosphine to act as ligand in SET-LRP has also been evaluated.

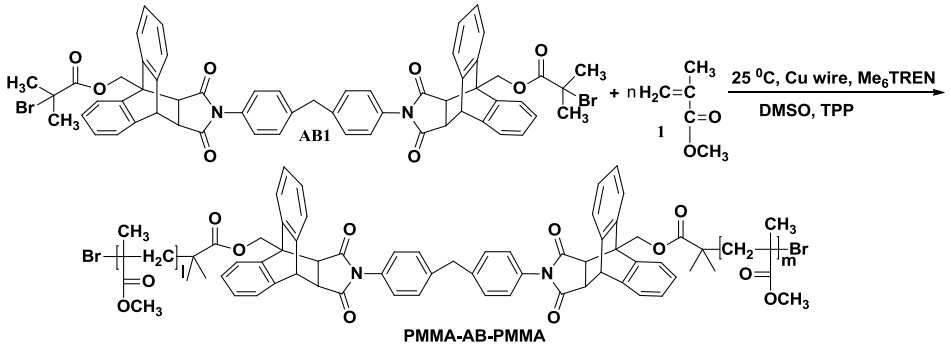
3.2 Results and Discussion

Diene, dienophile as well as mechanophore were incorporated in to polymer backbone using corresponding initiators via modified SET-LRP method developed by us.

3.2.1 Enhancing tolerance of SET-LRP towards air - Triphenylphosphine as an efficient reducing agent in SET-LRP

3.2.1.1 Synthesis of anthracene-bismaleimide mechanophore centered PMMA (PMMA-AB-PMMA) in the presence of air using triphenylphosphine as reducing agent.

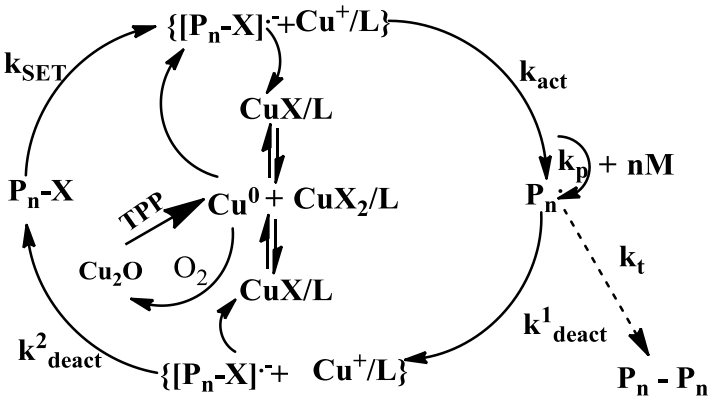
Bifunctional initiator (**ABI**) capable of initiating bidirectional SET-LRP, was used to produce PMMA-AB-PMMA with centrally located mechanophore. The protocol used for the synthesis is given in scheme 3.1.



Scheme 3.1. Synthetic route to PMMA-AB-PMMA

The reaction was carried out in polar solvent DMSO using the ligand Me_6TREN and the catalyst used was Cu(0) as a surface cleaned thin copper wire. Volume of solvent used was always half of that of monomer and the ratio of [MMA]/[I]/[TPP]/[Me_6TREN] was 250:1:0.1:0.1 and the reaction time was 30 minutes. Polymerization was performed at room temperature in DMSO with Cu(0) as catalyst and a hexamethylated tris(2-aminoethyl)amine (Me_6TREN) as ligand without deoxygenation. Addition of a reducing agent such as triphenylphosphine accelerated polymerization process most likely via the *in situ* reduction of the Cu_2O from the wire surface to Cu(0)

which is an activator in SET-LRP. The proposed mechanism for the modified SET-LRP is given in Scheme 3.2.



Scheme 3.2. Mechanism of SET-LRP in the presence of air and triphenylphosphine

Polymer PMMA-AB-PMMA was found to have good solubility in toluene, chloroform, dichloromethane (DCM) and dimethyl sulphoxide (DMSO). The polymer structure was confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR and GPC techniques.

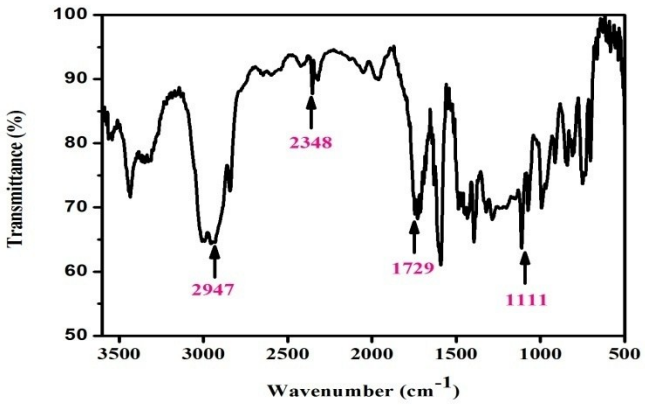


Figure 3.1. FT-IR spectrum of PMMA-AB-PMMA

In the FT-IR spectrum of PMMA-AB-PMMA (Figure 3.1.), the characteristic peaks at 1727 cm^{-1} corresponds to the ester carbonyl of PMMA. C-H stretching peak can be seen at 2947 cm^{-1}. No indication about the presence of mechanophore was obtained from FT-IR. It may be due to low amount of mechanophore in the polymer chain.

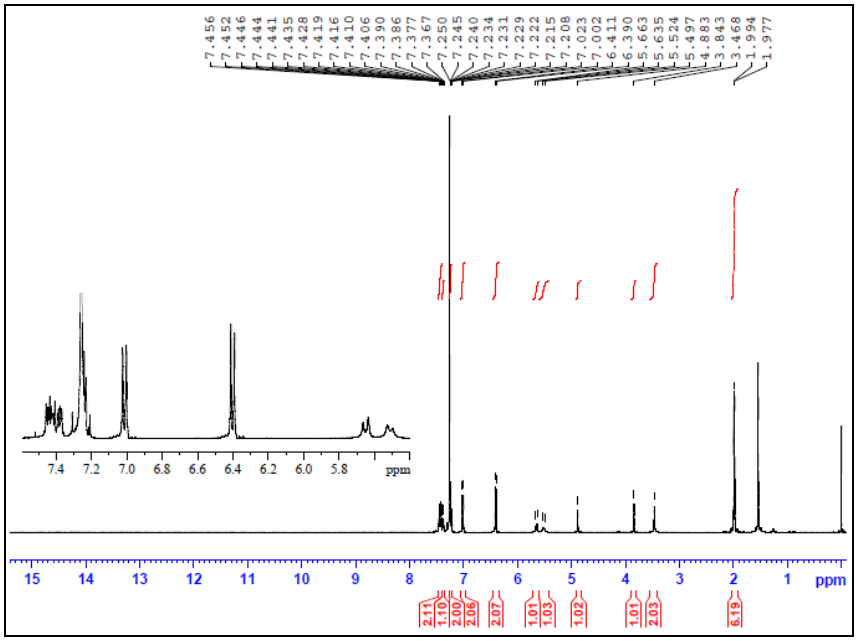


Figure 3.2. ^{1}H NMR spectrum of ABI

^{1}H NMR spectrum of initiator (**ABI**) is given in Figure 3.2. Peaks between δ 6.39 and 7.45 were assigned to aromatic protons in the initiator. The diastereotopic hydrogens appeared as two doublets in the δ 5.49-5.66 region. Presence of two methyl groups is evident by the signal appearing between δ 1.97 and 1.99.

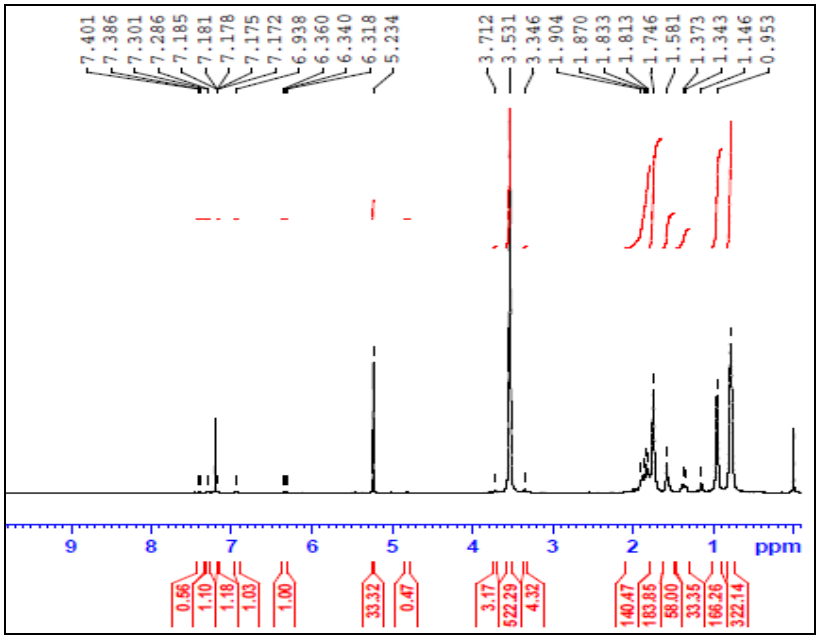
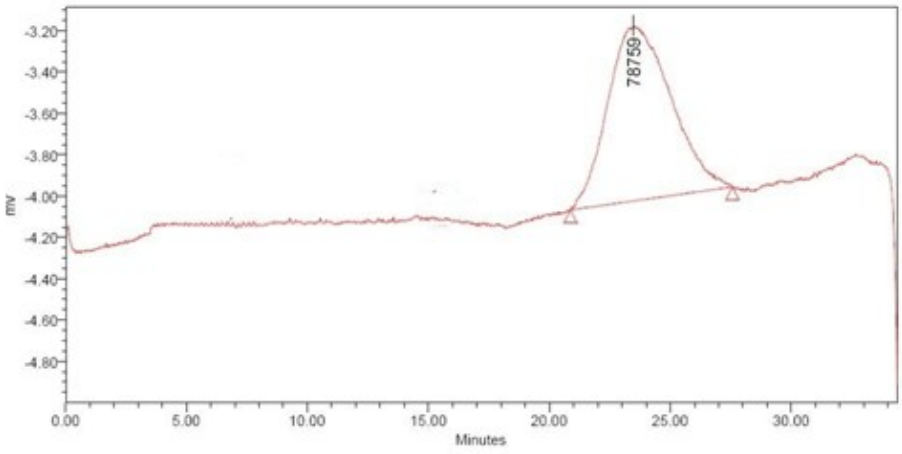


Figure 3.3. ^{1}H NMR spectrum of PMMA-AB-PMMA

Figure 3.3 is the ^{1}H NMR spectrum of polymer PMMA-AB-PMMA. The observed signals at δ 6.31–7.40 in the ^{1}H NMR spectrum of the polymer corresponds to the protons of the initiator revealing successful incorporation of mechanophore into the polymer chain. Slight shielding of aromatic protons in the polymer compared to that in initiator further confirmed covalent incorporation of mechanophore in the PMMA chain. Hence ^{1}H NMR gave direct evidence for the potential of bisfunctional initiator in initiating polymerization of MMA under modified SET-LRP conditions. Molecular weight of the polymer was calculated using ^{1}H NMR. The signal at δ 3.53 ppm in the ^{1}H NMR spectrum of the polymer was assigned to the methoxy protons in PMMA (6H, integral value, $I_{3.5}$ = 522.29). Based on the aromatic signal at 7.40 (4H, integral value, $I_{7.40}$ = 0.56) the molecular weight of PMMA-AB-PMMA sample calculated from the NMR spectrum

is 70 kDa. Protons signals at δ 0.78, 0.95, and 1.14 ppm can be ascribed to syndiotactic (integral value = 322.14), atactic (integral value = 166.26) and isotactic (integral value = 33.35) methyl groups, respectively. Based on these, tacticity of the mechanophore attached PMMA was calculated as 61.74% syndiotactic, 31.87% atactic and 6.39% isotactic which is in good agreement with the tacticity distribution for traditional radical polymerization of MMA.[10] This result indicates that the SET-LRP with **ABI** as the macroinitiator proceeded via a radical-mediated mechanism. GPC trace of the polymer PMMA-AB-PMMA is given in Figure 3.4.



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		57797	78383	78759	102720	128760		1.356178		

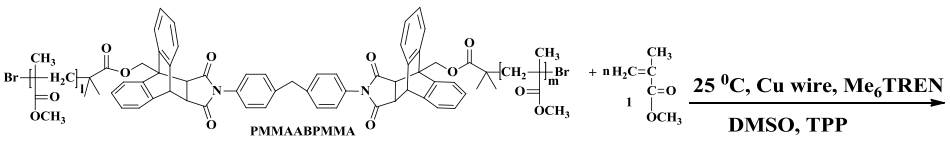
Figure 3.4. GPC trace of PMMA-AB-PMMA

Molecular weight obtained from GPC is 78 kDa which is in good agreement with the molecular weight estimated on the basis of NMR analysis. PDI obtained is 1.3 which suggests a narrow MWD. Good correlation between the number-average molecular weight of PMMA-AB-

PMMA obtained from NMR and GPC indicated that the polymerization featured controllable property.

3.2.1.1.1 Chain extension experiment polymerization from a Br terminated PMMA-AB-PMMA macroinitiator.

SET-LRP provides a novel methodology to produce polymer with good control over molecular weight with high chain end group fidelity. But it is very challenging to achieve high chain end group fidelity as it is associated with competing chain termination process. The loss of halide chain end is considered to be the main limiting factor. In order to assess chain end group retention, further investigation was carried out using chain extension reaction. Accordingly, the obtained macroinitiator PMMA-AB-PMMA [more rigorously represented as Br-(PMMA-AB-PMMA)-Br] was further reinitiated for chain extension reaction to obtain polymer having molecular weight around 108 kDa (Figure 3.5) confirming the living nature of PMMA-AB-PMMA. Procedure for chain extension reaction is explained in Scheme 3.3. However, the PDI after chain extension was much higher at 1.96.



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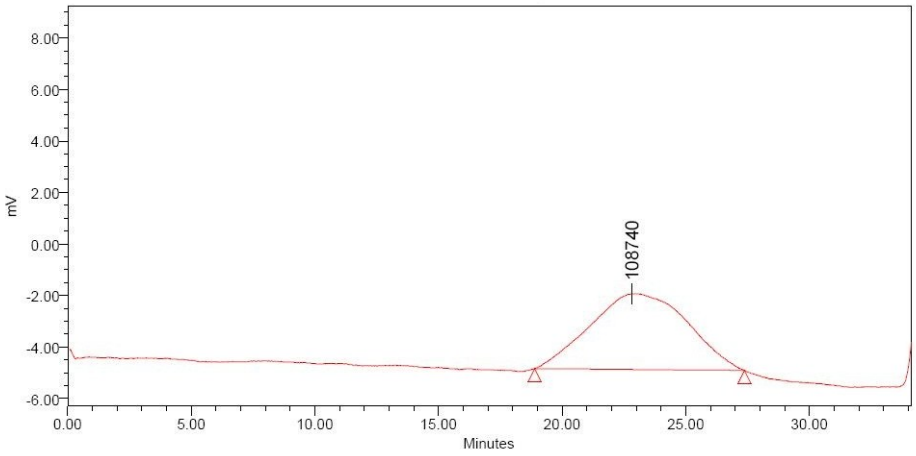
Scheme 3.3. Chain extension reaction of PMMA-AB-PMMA macro initiator



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		71330	140179	108740	279359	454299		1.965222		

Figure 3.5. GPC trace of PMMA-AB-PMMA after chain extension

3.2.1.1.2. Control experiments to rule out the possibility of competing self polymerization of MMA

To rule out the possibility of competing self polymerization of MMA to give PMMA along with PMMA-AB-PMMA, we performed a control experiment. Control experiment was carried out by eliminating initiator **AB1** while maintaining all other conditions applied above unchanged. In the absence of **AB1**, polymerization of MMA to PMMA was not observed. SET-LRP temperature maintained was below 25 ºC which ruled out the possibility of thermal initiation of MMA to get PMMA. These results clearly indicate the exclusive generation of PMMA-AB-PMMA without contamination from adventitious PMMA.

While chain extension itself is a wonderful achievement, the more exciting prospect of chain extension did not go unnoticed: it paves an unparalleled method for the synthesis of block copolymers (*vide infra*)!

3.2.1.1.3 Tolerance of SET-LRP towards air-Triphenylphosphine, an efficient reducing agent in SET-LRP

To further investigate the efficiency of TPP as reducing agent, SET-LRP was carried out in the presence of air but in the absence of triphenylphosphine. Here also SET-LRP failed to initiate polymerization of MMA.

3.2.1.1.4 Investigation of the potential application of triphenylphosphine to act as ligand in SET-LRP

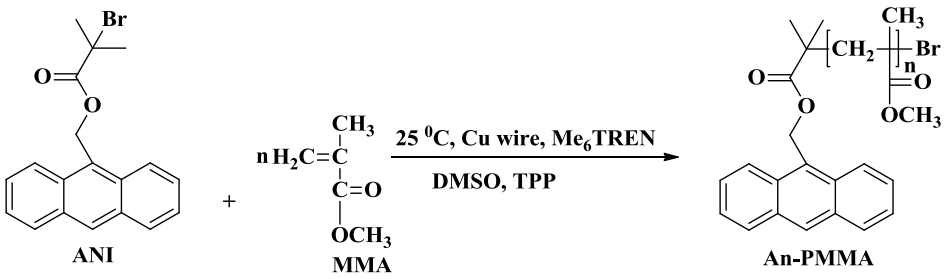
Triphenylphosphine-assisted successful polymerization in the presence of oxygen pushed us to investigate the compatibility of triphenylphosphine as a ligand in SET-LRP instead of the more expensive Me_6TREN. Unfortunately SET-LRP failed in the absence of Me_6TREN. Hence we conclude that triphenylphosphine is not a good stabilizing ligand in SET-LRP. Our major findings of SET-LRP under different conditions employed by us are tabulated in Table 3.1. Based on the data presented in Table 3.1, we conclude that the conditions highlighted red is best suited to generate the required polymer in high yields.

Table 3.1: SET LRP under different conditions

Monomer (MMA, mL)	Solvent (DMSO, mL)	Initiator (BMI, mg)	Ligand (Me_6TREN, mg)	TPP (mg)	Deoxygenation	Reaction time	Yield
1	0.5	40	0.86	0. 98	x	1 h	80 %
1	0.5	40	0.86	x	x	8 h	x
1	0.5	x	0.86	0.98	x	8 h	x
1	0.5	40	x	0.98	x	8 h	x

3.2.1.2 Synthesis of anthracene end capped PMMA (An-PMMA) in the presence of air using triphenylphosphine as reducing agent.

An-PMMA was synthesized in order to investigate the feasibility of Diels–Alder reaction at room temperature and also to investigate the feasibility of mechanically induced [4+2] Diels–Alder reaction. An-PMMA was synthesized using monofunctional initiator anthracen-9-ylmethyl 2-bromo-2-methylpropanoate (**ANI**) using the strategy given in Scheme 3.4. Purity of the synthesized polymer was determined by FT-IR, ^{1}H NMR, ^{13}C NMR and GPC techniques. An-PMMA exhibited good solubility in THF, chloroform, dichloromethane and toluene.



Scheme 3.4. Synthesis of anthracene end capped PMMA (An-PMMA)

UV-Vis and PL spectra of An-PMMA recorded in chloroform are shown in Figure 3.6. UV-Vis and PL spectra of chloroform solution of polymer showed identical peaks in shape and peak position as shown by initiator (Absorption peaks:- 334 nm, 351 nm, 368 nm, 388 nm, Emission peaks:- 394 nm, 417 nm, 441 nm). This indicated the presence of anthracene moiety in PMMA. Evidently, these characteristic bands in the absorption spectra originate from π–π* electronic transitions of anthracene chromophore.

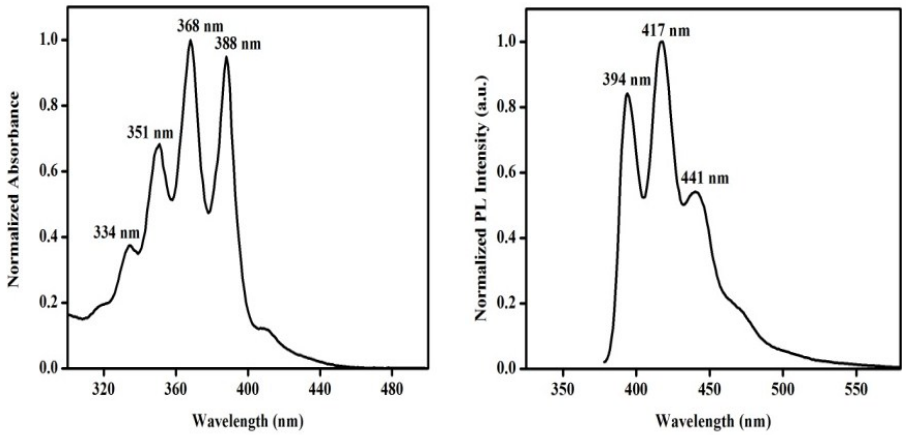


Figure 3.6. UV-Vis and PL spectra of An-PMMA in chloroform

^{1}H NMR spectra of initiator (**ANI**) and anthracene end capped PMMA (An-PMMA) are given in Figures 3.7 and 3.8 respectively. Peaks between δ 7.40 and 8.44 are assigned to aromatic protons in the initiator. The methylene hydrogens attached to anthracene yielded a singlet at δ 6.14. Presence of two methyl groups is evidenced by the singlet observed at δ 1.80. The observed signals at δ 7.40–8.44 in the ^{1}H NMR spectrum of the polymer corresponds to the protons of the initiator revealing successful incorporation of mechanophore into the polymer. Chemical incorporation of anthracene unit in PMMA is confirmed by the multiple splitting and shielding of proton signal in $–CH_2$- group attached to anthracene ring compared with the single peak of the same group in the initiator. The number-average molecular weight ($M_{n,\ NMR)}$ calculated by comparison of the integration values of the aromatic protons in mechanophore and the carbomethoxy protons of the MMA units was determined to be 13 kDa. The signals at δ 3.60 in the ^{1}H NMR spectrum of the polymer was assigned to the protons of carbomethoxy group in

PMMA (3H, integral value, $I_{3.6}$ = 402.17). Based on the aromatic signal at 8.52 (1H, integral value, $I_{8.52}$ = 1.00) the molecular weight of PMMA sample calculated from the NMR spectrum was 13 kDa. The chemical shifts at about δ 0.85, 1.02, and 1.41 ppm can be ascribed to syndiotactic (integral value = 262.13), atactic (integral value = 128.56) and isotactic (integral value = 26.21) methyl groups, respectively. Based on the integral values, tacticity of the anthracene end capped PMMA was calculated as 62.87% syndiotactic, 30.83% atactic and 6.28% isotactic which indicated a radical mechanism for polymerization.

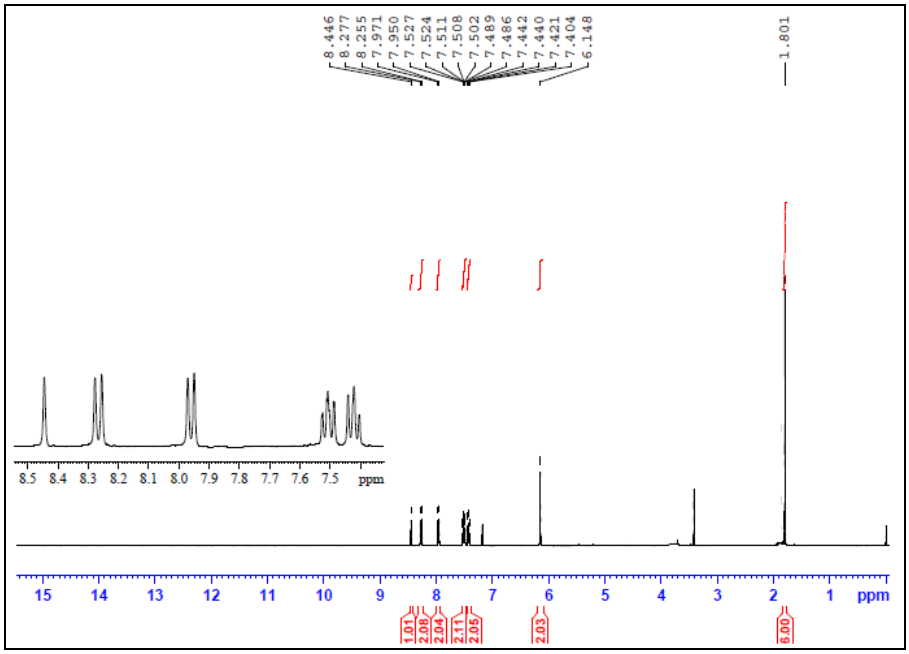


Figure 3.7. ^{1}H NMR spectrum of ANI

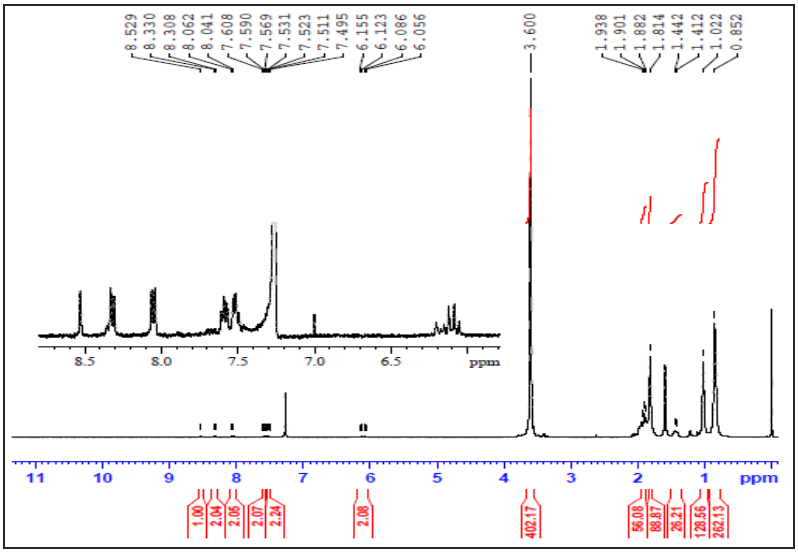
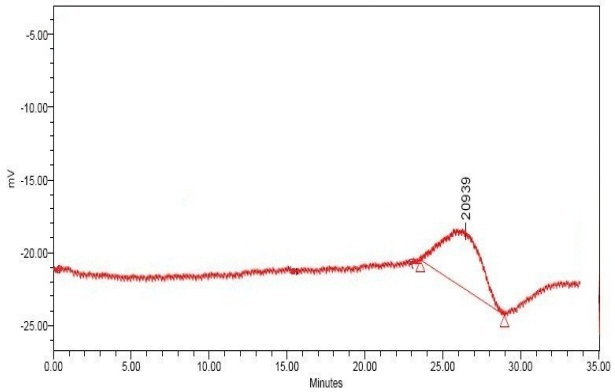


Figure 3.8. ^{1}H NMR spectrum of An-PMMA

GPC trace of An-PMMA is given in Figure 3.9. Molecular weight of the polymer calculated from GPC analysis ($M_{n,GPC}$) is 20 kDa and PDI is 1.2 which indicated a narrow molecular weight distribution indicating controlled polymerization.



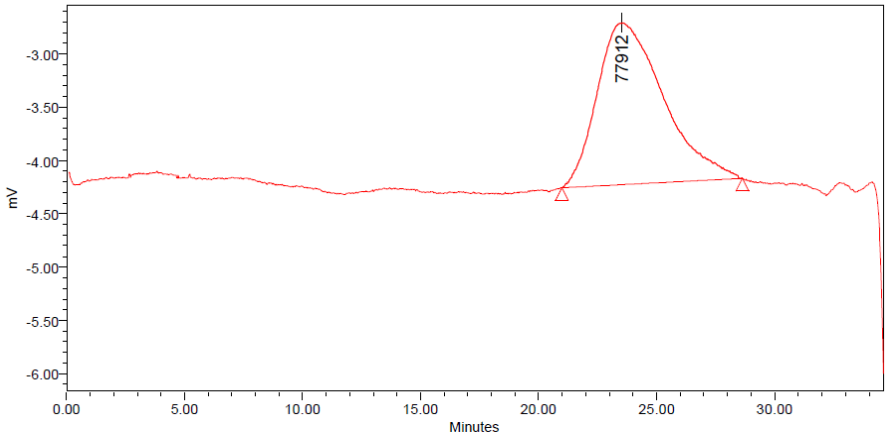
GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		20917	25944	20939	32034	38354		1.240337		

Figure 3.9. GPC trace of An-PMMA

3.2.1.2.1 Chain extension of Br terminated An-PMMA macroinitiator

An-PMMA was successfully chain extended using it as a macroinitiator for the polymerization of MMA under the modified SET-LRP conditions perfected by us. After chain extension, molecular weight of the polymer was determined by GPC (Figure 3.10). Substantially increased molecular weight of 77 kDa for chain-extended material confirmed living character of An-PMMA polymer.



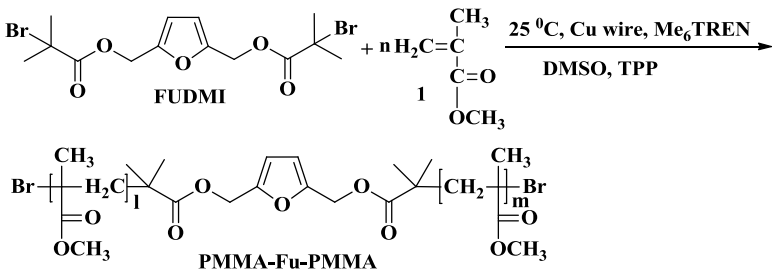
GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		48445	71260	77912	95637	119591		1.470928		

Figure 3.10. GPC trace of An-PMMA after chain extension reaction

3.2.1.3 Synthesis of furan centered PMMA (PMMA-Fu-PMMA) in the presence of air using triphenylphosphine as reducing agent

Furan centered PMMA was synthesized using bisfunctional initiator furan-2,5-diylbis(methylene) bis(2-bromo-2-methylpropanoate) (**FUDMI**) using the strategy given in Scheme 3.5.



Scheme 3.5. Synthesis of furan centered PMMA

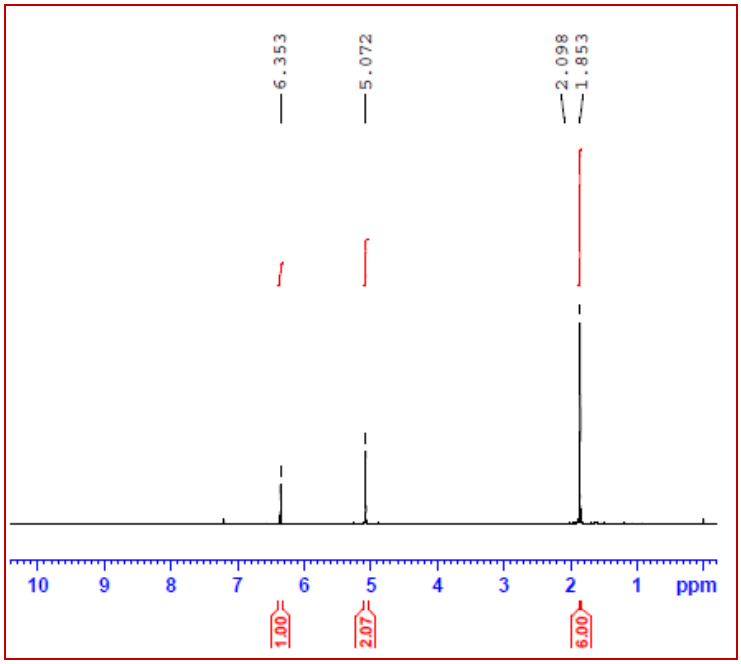


Figure 3.11. ^{1}H NMR spectrum of initiator FUDMI

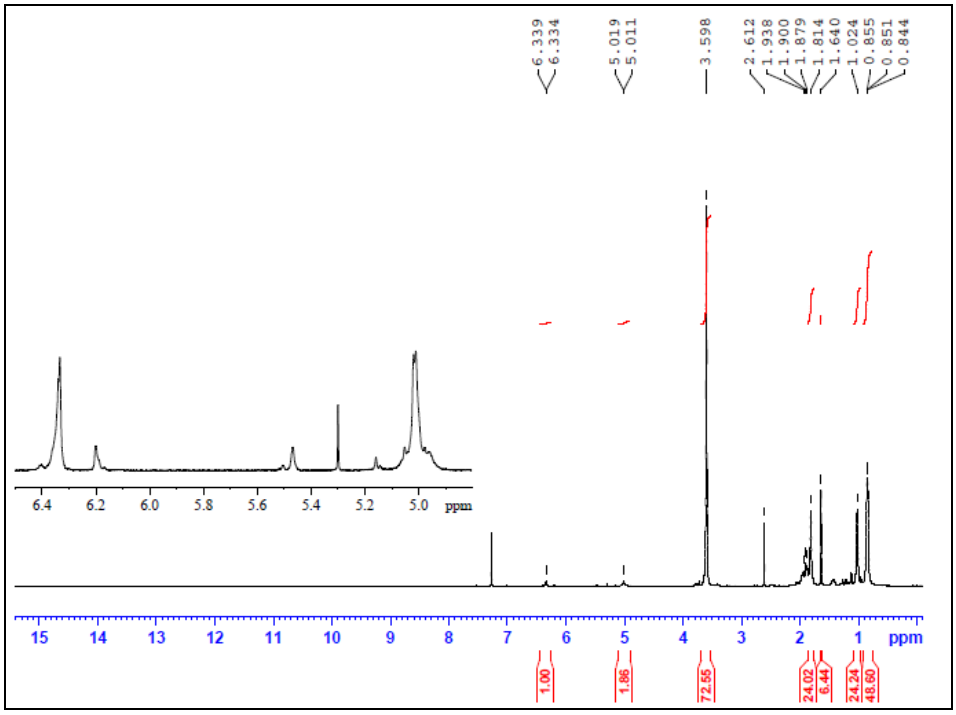


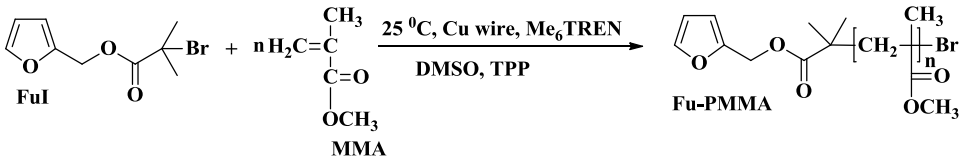
Figure 3.12. ^{1}H NMR spectrum of PMMA-Fu-PMMA

^{1}H NMR spectra of initiator **FUDMI** and polymer **PMMA-Fu-PMMA** are given in Figures 3.11 and 3.12 respectively. The observed signals at δ 6.34 in the ^{1}H NMR spectrum of the polymer corresponds to the aromatic protons of the furan ring of initiator revealing the successful incorporation of mechanophore into the polymer. Slight shielding of methylene protons in the polymer compared to that of the initiator further confirmed covalent incorporation of mechanophore in the PMMA chain. The signals at δ 3.59 in the ^{1}H NMR spectrum of the polymer was assigned to the protons of carbomethoxy group in PMMA (6H, integral value, $I_{3.5}$ = 72.55). Based on the aromatic signal at δ 6.33(2H, integral value, $I_{6.33}$ = 1.00) the molecular weight of PMMA sample calculated

from NMR data was ~2.4 kDa. The chemical shifts at about δ 0.84, 1.02, and 1.64 ppm can be ascribed to syndiotactic (integral value = 48.60), atactic (integral value = 24.24), and isotactic (integral value = 6.44) methyl groups, respectively. Based on these, tacticity of the mechanophore attached PMMA was calculated as 61.30% syndiotactic, 30.57% atactic and 8.12% isotactic which is in good agreement with the tacticity distribution for traditional radical polymerizations.[10] This result indicates that the SET-LRP with **FUDMI** as the macroinitiator proceeded via a radical-mediated mechanism.

3.2.1.4 Synthesis of furan end capped PMMA (Fu-PMMA)

Furan end capped PMMA was synthesized using monofunctional initiator furan-2-ylmethyl 2-bromo-2-methylpropanoate (**FuI**) using the strategy given Scheme 3.6.



Scheme 3.6. Synthesis of furan end capped PMMA (Fu-PMMA)

Figures 3.13 and 3.14 are the ^{1}H NMR spectra of initiator **FuI** and polymer **Fu-PMMA** respectively. The observed signals at δ 6.35–7.49 in the ^{1}H NMR spectrum of the polymer corresponds to the aromatic protons of the furan ring of initiator revealing successful incorporation of mechanophore into the polymer. As with previous cases, slight shielding of methylene protons in the polymer compared to that in the initiator further confirmed covalent incorporation of mechanophore in the PMMA chain. The signals at

δ 3.61 in the ^{1}H NMR spectrum of the polymer was assigned to carbomethoxy protons in PMMA (3H, integral value, $I_{3.6}$ = 1352.21). Based on the aromatic signal at δ 7.48 (1H, integral value, $I_{7.48}$ = 1.01) the molecular weight of Fu-PMMA sample calculated from the NMR spectrum was ~45 kDa. The chemical shifts at about δ 0.85, 1.02, and 1.41 ppm can be ascribed to syndiotactic (integral value = 852.68), atactic (integral value = 429.47), and isotactic (integral value = 71.78) methyl groups, respectively. Based on these, tacticity of the mechanophore attached PMMA was calculated as 62.97% syndiotactic, 31.72% atactic and 5.3% isotactic which is in good agreement with the tacticity distribution for traditional radical polymerizations.[10] This result indicates that the SET-LRP with **Fu1** as the macroinitiator proceeded via a radical-mediated mechanism.

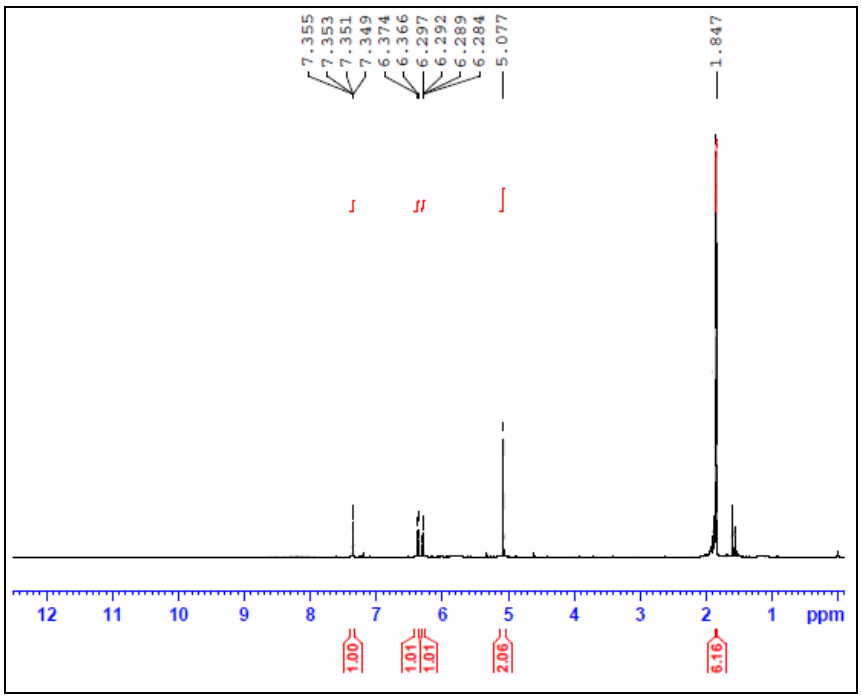


Figure 3.13. ^{1}H NMR spectrum of FuI

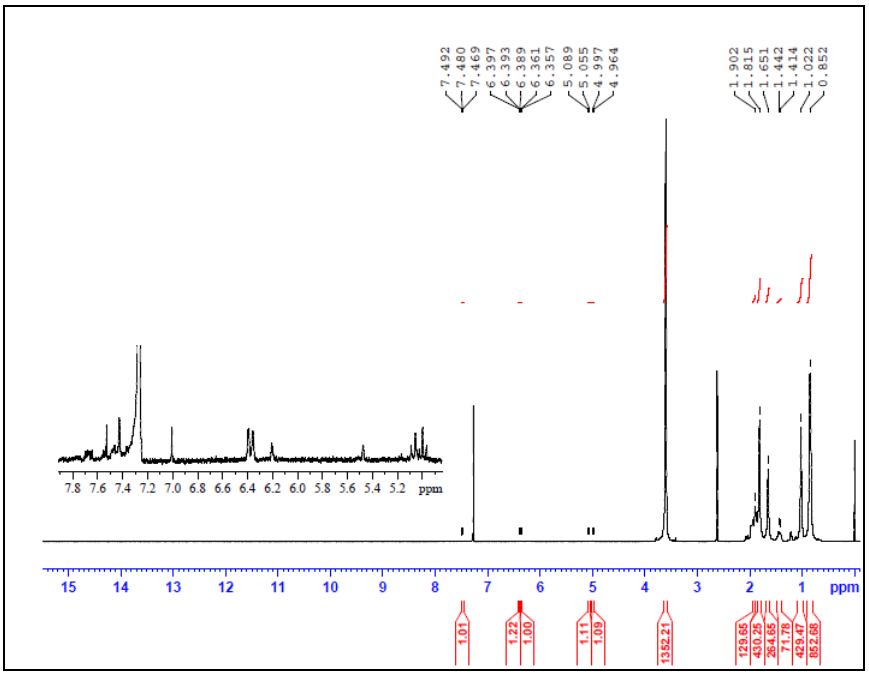
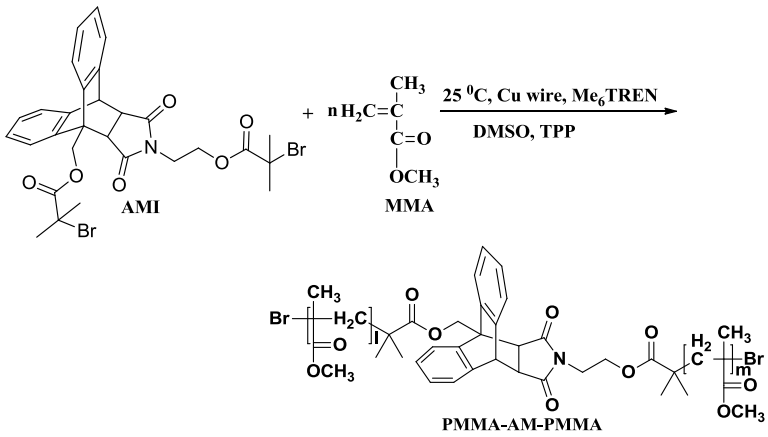


Figure 3.14. ^{1}H NMR spectrum of Fu-PMMA (400 MHz, $CDCl_3$)

3.2.1.3 Synthesis of anthracene-maleimide cycloadduct based mechanophore centered PMMA (PMMA-AM-PMMA)

Ethanoanthracene based L-shaped difunctional initiator ((9,10)-13-(2-((2-bromo-2-methylpropanoyl)oxy)ethyl)-12,14-dioxo-10,11,12,13,14,15-hexahydro-9*H*-9,10-[3,4]epipyrroloanthracen-9-yl)methyl 2-bromo-2-methylpropanoate (**AMI**) successfully initiated the polymerization of MMA via modified SET-LRP to give anthracene-maleimide cycloadduct centered PMMA. Synthetic route of PMMA-AM-PMMA is given in Scheme 3.7.



Scheme 3.7 Synthesis of anthracene-maleimide cycloadduct based mechanophore centered PMMA (PMMA-AM-PMMA)

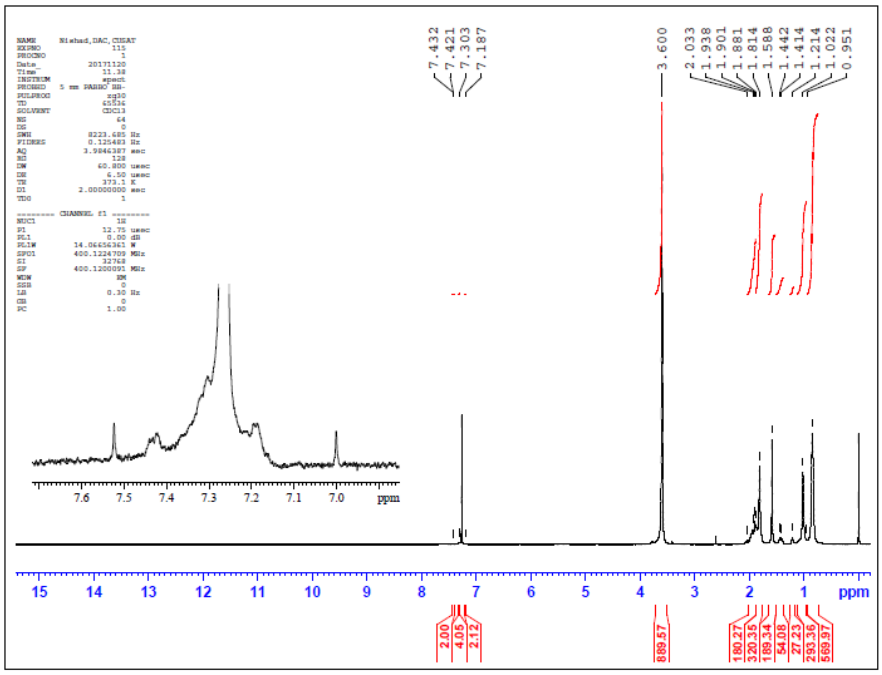


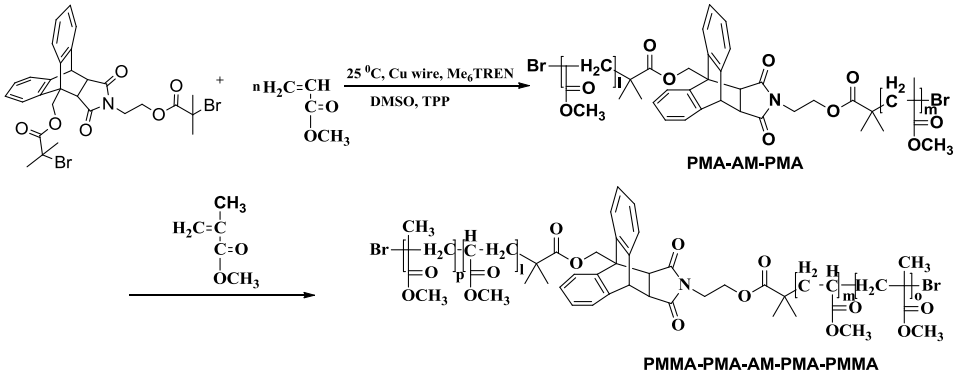
Figure 3.15. ^{1}H NMR spectrum of PMMA-AM-PMMA

^{1}H NMR spectrum of PMMA-AM-PMMA is given in Figure 3.15. Incorporation of mechanophore was confirmed by the presence of peaks

in the δ 7.43-7.18 region. Due to poor solubility of the material, good quality NMR spectrum could not be recorded. This impeded our attempts to estimate molecular mass of this polymer.

3.2.1.4 Synthesis of anthracene maleimide mechanophore centered methacrylate-methyl methacrylate block copolymer (PMMA-PMA-AM-PMA-PMMA)

In an attempt to exploit the potential of strategy for the generation of block copolymers, we attempted the synthesis of methacrylate-methyl methacrylate block copolymer by the iterative addition of methyl acrylate (MA) and methyl methacrylate (MMA) (Scheme 3.8). Initially generated bis Br-terminated PMA-AM-PMA polymer acts as a macroinitator to polymerize MMA by successful chain extension to give highly ordered block copolymer PMMA-PMA-AM-PMA-PMMA. Successful incorporation of both PMA and PMMA blocks was confirmed by the presence of two peaks at δ 3.66 and 3.60 ppm attributable to carbomethoxy protons in PMA and PMMA blocks in the ^{1}H NMR spectrum of the resultant block copolymer (Figure 3.16).



Scheme 3.8. Synthesis of anthracene-maleimide mechanophore centered methyl acrylate-methyl methacrylate block copolymer (PMMA-PMA-AM-PMA-PMMA)

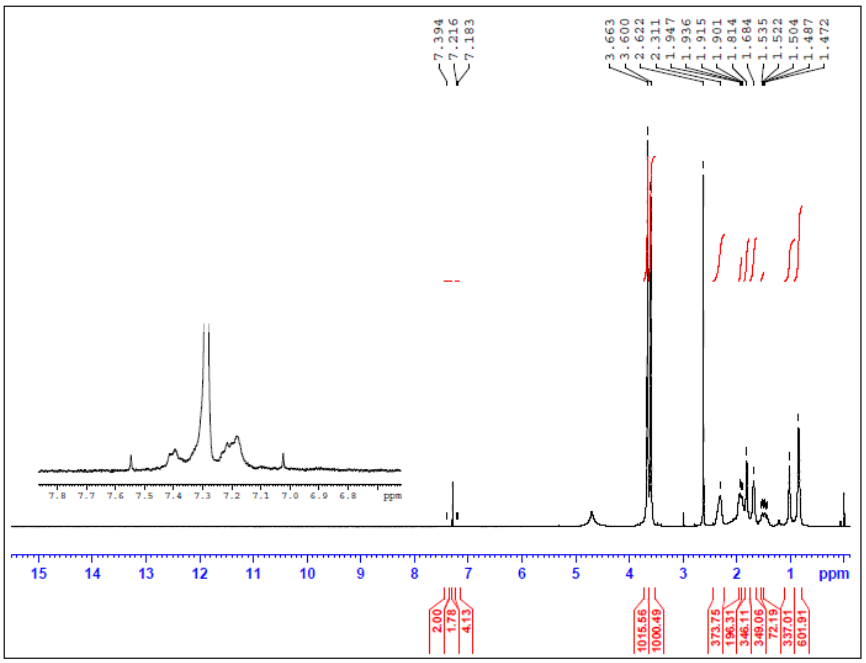
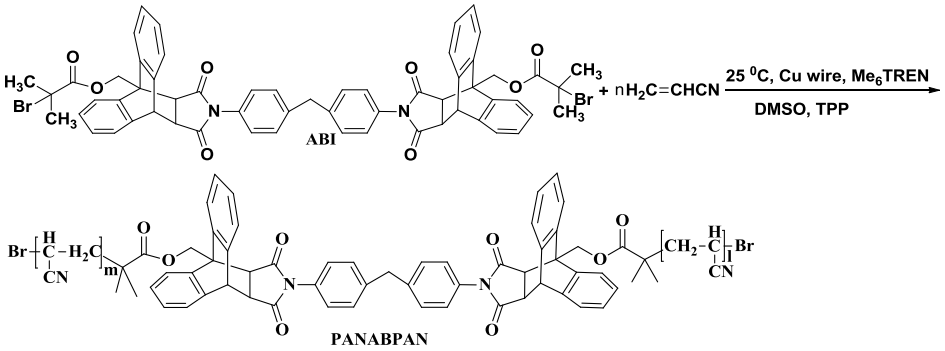


Figure 3.16. ^{1}H NMR spectrum of PMMA-PMA-AM-PMA-PMMA)

3.2.1.3 Synthesis of anthrcene-bismaleimide mechanophore centered polyacrylonitrile (PAN-AB-PAN)

Efficacy of anthracene bismaleimide initiator to initiate polymerization of non activated monomers such as acrylonitrile was investigated by the successful synthesis of mechanophore incorporated polyacrylonitrile (PAN). PAN-AB-PAN with centrally located mechanophore was synthesized using bisfunctional initiator (**ABI**) capable of initiating bidirectional SET-LRP. The protocol used for the synthesis is given in Scheme 3.9.



Scheme 3.9. Synthetic route to PAN-AB-PAN

Successful generation of mechanophore incorporated PAN is evident from ^{1}H NMR spectrum of the sample (Figure 3.17).

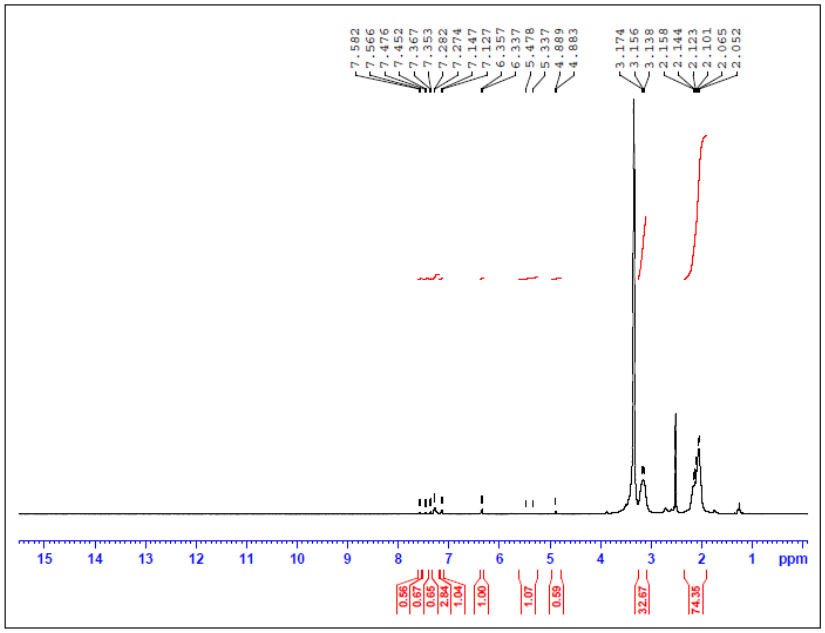


Figure 3.17. ^{1}H NMR spectrum of PAN-AB-PAN

The number average molecular weights calculated by comparison of the integration values of methylene signals in bismalemide and PAN is

around 3 kDa. Results obtained in this preliminary investigation reveal the efficacy of **ABI** initiator to polymerize acrylonitrile and there by underscoring its potential to polymerize several other monomers.

3.3 Conclusions

We demonstrated the feasibility of synthesized mechanophore initiators mentioned in the previous chapter to act as SET-LRP initiators by synthesizing diene, dienophile as well as mechanophore attached PMMA by our modified SET-LRP in the presence of air. We verified that SET-LRP could be achieved without rigorous deoxygenation in the presence triphenylphosphine as reducing agent within a short period with good control over molecular weight and polydispersity. Our method eliminated stringent deoxygenation procedures such as *freeze pump thaw* cycle and the polymerization was carried out in less than 1 hour without the need of Schlenk lines. Number average molecular weight calculated from ^{1}H NMR spectroscopy agreed well with that obtained from GPC analysis which is an indication of good control over molecular weight. Remarkably, living character of synthesized polymer via modified SET-LRP was substantiated further by *in situ* chain extension and block copolymerization via iterative monomer addition in one-pot. Our modified method afforded simple and facile route to synthesize polymer under relatively less demanding reaction conditions due to its tolerance towards air and moisture. Structures and structure types of synthesized diene and mechanophore incorporated polymers using our modified SET-LRP are given below.

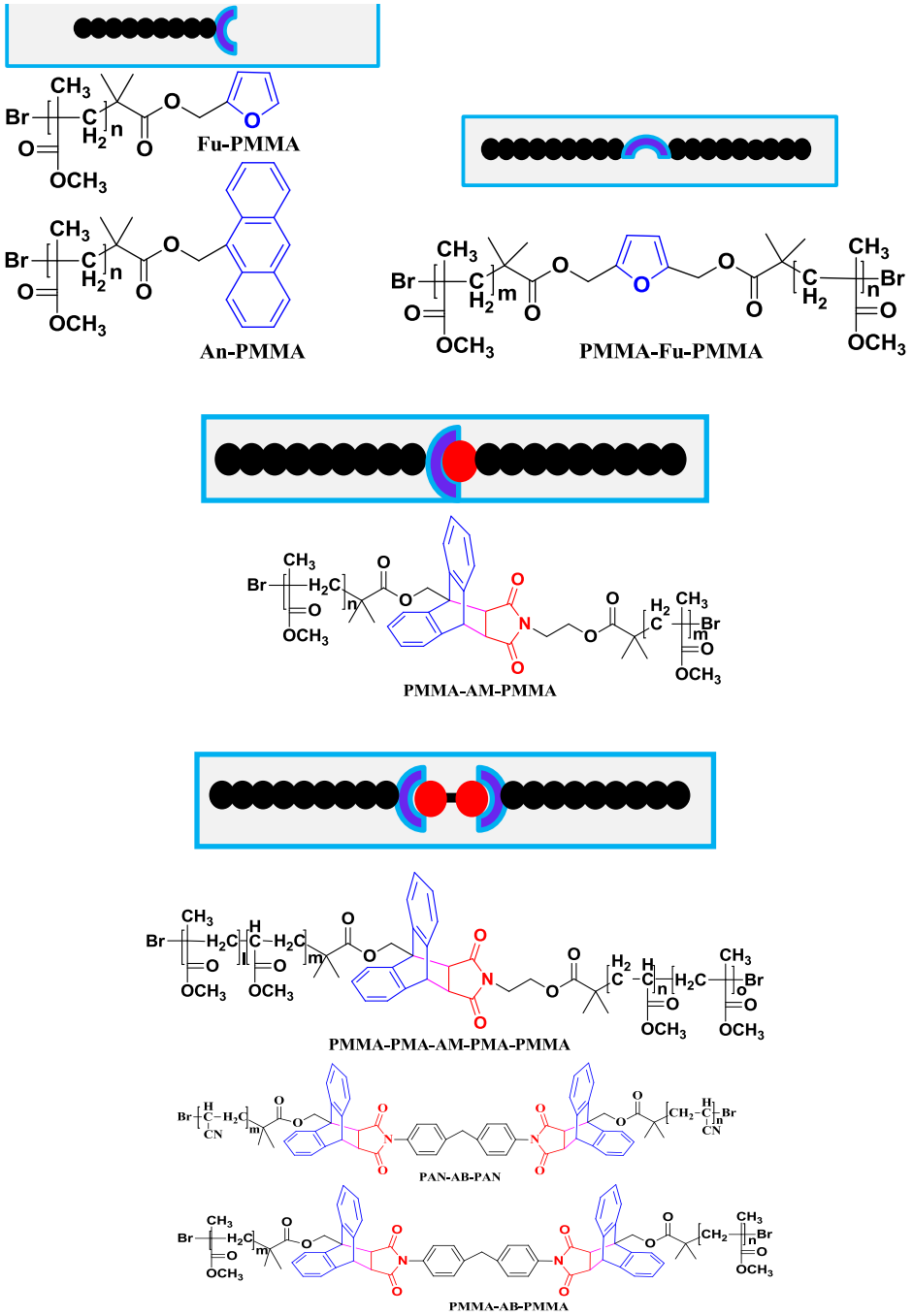


Figure 3.18 Structures and structure types of synthesized diene and mechanophore incorporated polymers

3.4 Experimental Section

3.4.1 Materials

Unless otherwise stated, all commercially available materials were purchased from either Spectrochem or Sigma Aldrich and were used as received without further purification. Solvents were dried and purified by following known protocols. Methyl methacrylate (99%) was filtered through basic alumina (activated, basic, 50-200 nm) to remove inhibitor and then washed twice with an aqueous solution of sodium hydroxide (5%) followed by washing with distilled water, until the solution was neutralized, then dried with anhydrous magnesium sulfate overnight, and then distilled under reduced pressure. The distillate was stored at -18 °C before use.

3.4.2 Methods

Infrared spectra were recorded on *Jasco 4100* FT-IR spectrometers. Absorption spectra were recorded using Evolution 201 UV-Vis spectrophotometer. Emission spectra were recorded using Shimadzu-RF-5301PC spectroflurophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz *Bruker AvanceIII* FT-NMR spectrometer using deuterated chloroform or deuterated dimethyl sulphoxide as solvent with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) were reported in parts per million (ppm) downfield of TMS. Multiplicities were designated as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Gel permeation chromatography (GPC) was carried out with Waters 1515 Isocratic HPLC pump, Waters (2414) Refractive Index Detector and a series of 4 Waters HR Styragel columns. GPC was calibrated using monodisperse

polystyrene standards. Eluent used was toluene at a flow rate of 1mL/minute and the injection volume was 40 μL.

3.4.3 Experimental

3.4.3.1 Synthesis of tris[2-dimethylamino)ethyl]amine

Me_6TREN was synthesized by a known procedure.[11]

3.4.3.2 General procedure for polymerization

Cu wire (15 cm of gauge 20 wire wrapped around a Teflon coated stir bar) and the solvent DMSO (0.5 mL) were stirred in a Schlenk tube in the presence of triphenylphosphine (0.98 mg, 0.003 mmol) for 10 minutes. Me_6TREN (0.86 mg, 0.003 mmol), initiator (0.01 mmol) and MMA (1 mL, 9.3 mmol) were added and kept under stirring for 30 minutes. After 30 minutes, polymerization mixture was dissolved in DCM and passed over basic alumina to remove any copper present in the product followed by precipitation in cold methanol. The white product was then dried under vacuum.

3.4.3.2.1 Chain extension experiment:- polymerization from a Br terminated PMMA macroinitiator

Chain extension of PMMA-AB-PMMA was carried out using the same polymer as macroinitiator. Procedure was identical to that described earlier except that initiator was replaced by the obtained PMMA-AB-PMMA.

3.4.3.2.2 Generation of block copolymer:

PMMA-PMA-AB-PMA-PMMA block copolymer was synthesized by the iterative addition of MA and MMA to the reaction mixture

containing Cu(0) wire Me_6TREN, TPP. The rest of the procedure of synthesis is same as given in **2.4.3.2.**

3.4.3.2.3 Control experiments to rule out the possibility of self polymerization of MMA

Cu wire (15 cm of gauge 20 wire wrapped around the Teflon coated stir bar) and the solvent DMSO (0.5 mL) were stirred in a Schlenk tube in the presence of triphenylphosphine (0.98 mg, 0.003 mmol) for 10 minutes. Me_6TREN (0.86 mg, 0.003 mmol) and MMA (1 mL, 9.3 mmol) were added and kept for stirring for 30 minutes. After 30 minutes, polymerization mixture was poured in to cold methanol and analyzed by GPC.

3.4.3.2.4 Tolerance of SET-LRP towards air-Triphenyl phosphine an efficient reducing agent in SET-LRP

Efficacy of triphenylphosphine to act as oxygen scavenger in SET-LRP was analyzed by carrying out polymerization using triphenylphosphine in the presence and absence of air. The procedure of synthesis is same as given in **2.4.3.2.**

3.4.3.2.5 Investigation of potential of triphenylphosphine to act as ligand in SET-LRP

Cu wire (15 cm of gauge 20 wire wrapped around the Teflon coated stir bar) and the solvent DMSO (0.5 mL) were stirred in a Schlenk tube in the presence of triphenylphosphine (0.98 mg, 0.003 mmol) for 10 minutes. Initiator (40 mg, 0.03 mmol) and MMA (1 mL, 9.3 mmol) were added and kept for stirring for 30 minutes. After 30 minutes, polymerization mixture was poured in to cold methanol. No polymer formation was observed under these conditions.

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Chapter 4

Mechanochemical Activation Studies

Contents

Conspectus: *Our findings on mechanoresponsive healable PMMAs having anthracene-bismaleimide adduct derived mechanophore at the centre are reported in this chapter. Mechanochemical response of mechanophore centered PMMAs in solution was investigated using utrasonication force. Irradiating toluene solution of the polymers with ultrasound resulted in formal cycloreversion of the DA adduct derived mechanophore as determined by UV-Vis and PL spectroscopic techniques. Studies on the effect of molecular weight on mechanochemical activation unveiled molecular weight dependence of mechanochemical activity. Furthermore, we have examined the feasibility of mechanically induced Diels–Alder reaction by synthesizing DA adduct using ultrasonication force. Investigation on self-healing ability revealed that our polymer is capable of healing at room temperature without any external stimulus.*

4.1 Introduction

Chemical reactions are induced by heat,[1,2] light,[3-5] electric potential[6-8] etc. Polymer which respond to chemical, thermal, photochemical and electrical stimulus have been widely explored. However, in stark contrast to above, mechanoresponsive polymers are scantly investigated. In polymer mechanochemistry[9] macroscopic forces are directed preferentially to a weak bond in the mechanophore. The chemical reactions associated with the macroscopic forces are directed to elicit productive pooling of energy to program intrinsic physical responses in material properties such as self-sensing of damage,[10-15] restoration of material property after damage[16-19] etc. Polymer mechanochemistry launch most prevalent strategy to impart stress probing through mechanoresponsive polymers. Despite these noteworthy achievements, the design and synthesis of new mechanophores having the intrinsic ability of stress-sensing, self-healing and stress induced strengthening[20] characteristics that expand upon the obtainable repertoire is a foremost concern here. The mechanical responsive behavior of many reported mechanophores is based on scissile activation leading to chain rupture. One of the main limitations of using scissile mechanophore for mechanoresponsive application is the non-reusability as scission cause permanent failure or irreversible change in properties of materials. Our attempt is to develop a polymer which can perform the mechanoresponsive function with minimal change in the mechanical and material properties. An exciting possibility would be the use of DA[21-24] click/rDA unclik chemistry in mechanophore synthesis. To materialize this idea, we have synthesized DA adduct derived mechanophore

incorporated polymers. Here we chose to investigate the mechanochemical ring-opening reaction of anthracene-bismaleimide adduct derived mechanophore for demonstrating stress responsive behavior as well as optical probing of mechanical stress. The aforementioned mechanophore is a scissile one. In the DA adduct mechanophore, initially the scissile activation events occur to give warning signals about stress or damage by regenerating active DA participants. DA participants generated under stress opens up possibility for constructive bond formation via DA click reaction to outpace destructive bond scission in materials under stress.

Mechanochemical activation using ultrasound irradiation predates the first studies to establish the responsiveness of new mechanoresponsive motifs.[25] Here also ultrasound irradiation of polymer solutions is used to monitor mechanochemical activation of mechanophores. The methodology called sonochemistry is particularly convenient and efficient since this method requires only small sample quantity and also it has proven to have good reproducibility and high strain rate. Ultrasound induced mechanochemical activation is influenced by many experimental factors, including temperature,[26] solvent,[27] and sonication intensity,[28] etc., So proper precautions were taken to keep these factors constant, details of which are presented in Chapter 1.

4.2 Results and Discussion

4.2.1 Mechanochemical activation studies to investigate stress responsive behavior of anthracene-bismaleimide adduct derived mechanophore linked PMMA

Anthracene-bismaleimide adduct derived mechanophore linked PMMA (PMMA-AB-PMMA) was used to investigate the ultrasound-induced electrocyclic ring opening. Position 9 of anthracene was taken as the attachment point of PMMA since this system is known to transmit force efficiently to the weak bond. Our choice for bismaleimide is dictated by the two active sites per mechanophore unit which provide potential to act as cross linker in polymerization reactions. Mechanochemical activation was studied by giving force in the form of ultrasound radiation using ultrasonicator. Toluene was chosen as the solvent for making polymer solutions due to good solubility of all of the polymers in this solvent. All the factors which influence mechanochemical activation were kept under strict control as amplitude 35%, pulse sequence 7s on and 3s off and temperature between 10 to 15 ºC. Mechanochemical activation was monitored using UV-Vis and PL spectroscopy, since regeneration of anthracene via *retro* Diels–Alder reaction is accompanied by the emergence of a strong absorption and emission. Upon subjecting dilute solution of polymers to ultrasound irradiation, the mechanophore underwent a *retro* Diels–Alder reaction and concomitant development UV−Vis absorption and emission of anthracene chromophore.

With increase in time an increase in the UV-Vis absorbance of the solution was observed. The structure of the mechanophore incorporated PMMA-AB-PMMA type polymer used for the study is given in Figure

4.1 and proposed mechanism of stress-sensing and self-healing is given in Scheme 4.1.

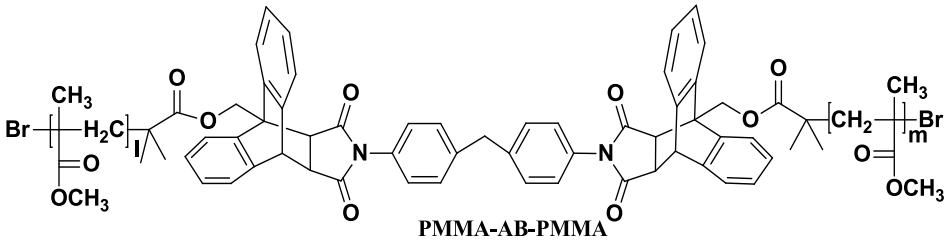
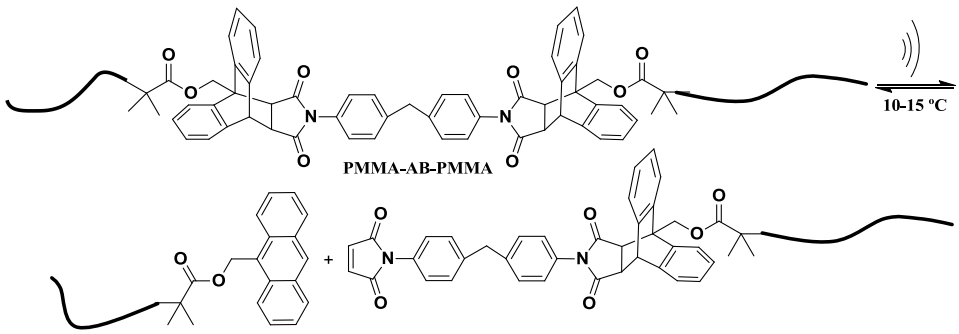


Figure 4.1. Anthracene-bismaleimide adduct derived mechanophore incorporated PMMA.



Scheme 4.1. Proposed mechanism for stress-sensing

Observed mechanochemical activity of the systems under investigation is due to the cleavage of polymer at the mechanophore site *via* mechanically induced *retro* Diels–Alder reaction. Mechanochemical activity results in chain scission leading to two complimentary polymer chains. One of these is anthracene (diene) terminated while the second one is maleimide (dienophile) terminated. In principle, the two complimentary chains can recombine through a Diels–Alder (click) reaction to regenerate

the parent polymer resulting in retention of polymer characteristics even after subjecting to a potentially damaging external stimulus. Thus, external stress is effectively mitigated and the polymer undergoes self-healing by constructive pooling of the external stimulus. Our attempt to monitor mechanochemical activation began with the synthesis of two PMMA-AB-PMMA type polymers having molecular weight 40 kDa and 70 kDa. Under ultrasound irradiation, significant mechanochemical activation was observed in the case of polymer having molecular weight 70 kDa. Absorption and emission spectra of this material recorded after sonication for different periods are given in Figures 4.2 and 4.3 respectively. Progressive development of anthracene absorption and emission with respect to sonication time is clearly visible in these figures. On the other hand, ultrasonic irradiation of PMMA-AB-PMMA type polymer having molecular weight 40 kDa under identical conditions resulted in substantially less or no chain cleavage as evidenced by lack of development anthracene absorption as a function of sonication time (Figure 4.4). As evident from absorption and emission profiles of polymers before and after sonication given in the Figures 4.2, 4.3 and 4.4, both absorption and fluorescence intensity attributable to anthracene component continued to increase with increase in sonication time in the case of polymer having high molecular weight whereas absorption spectrum remained unchanged in the case of lower molecular weight material. Driving force behind the observed *retro* Diels–Alder reaction may be either thermal or mechanochemical. If thermal activation is behind the observed *retro* Diels–Alder reaction, irrespective of molecular mass, any species containing anthracene-bismalemide cycloadduct

components should behave identically. But we observed molecular weight dependence for the advent of *retro* Diels–Alder reaction. Observed molecular weight dependence of *retro* DA reaction confirms that the activation was induced by mechanical force and not by thermal energy. It appears that mechanical energy is pooled to induce a chemical reaction having the lowest activation energy which, in the present case, appears to be the *retro* Diels–Alder reaction. However, to cross the activation barrier, sufficient number of chemical bonds is available to absorb and then pool energy sufficient enough to cross the activation threshold. In other words, polymers having sufficiently high molecular mass will have the required number of bonds to absorb required amount of energy to induce bond scission through a *retro* Diels–Alder pathway.

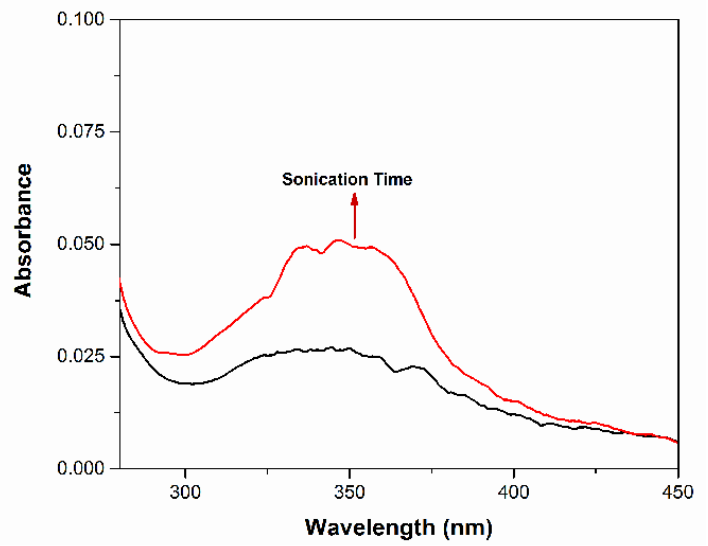


Figure 4.2. UV-Vis spectra of PMMA-AB-PMMA having molecular weight 70 kDa sonicated for different time duration

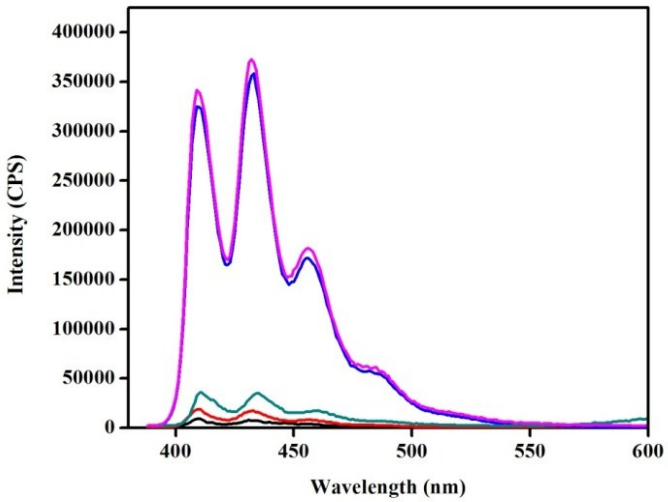


Figure 4.3. PL spectra of PMMA-AB-PMMA having molecular weight 70 kDa sonicated for different time duration

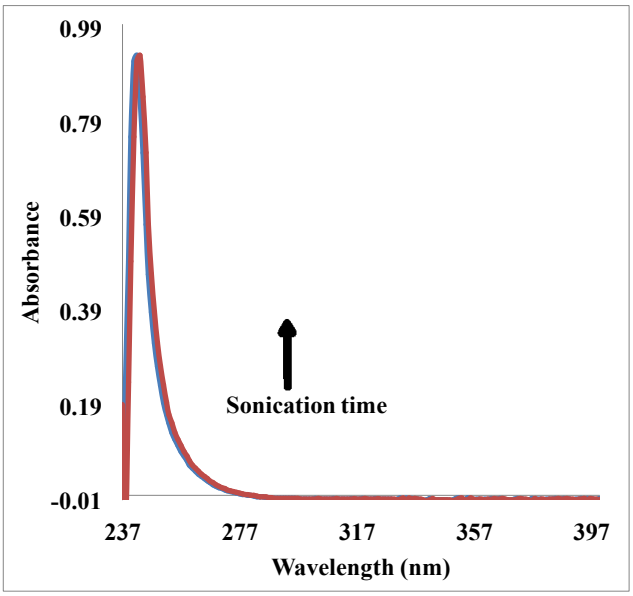


Figure 4.4. UV-Vis spectra of PMMA-AB-PMMA having molecular weight 40 kDa sonicated for different time duration

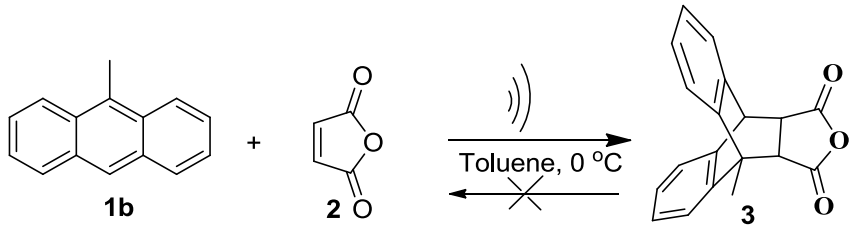
GPC and NMR techniques were also used to examine the mechanochemical activation. Both these techniques gave no evidence for mechanochemical activation and consequent *retro* Diels–Alder unclick reaction: both molecular mass and ^{1}H NMR spectra of the samples remained unchanged before and after subjecting to mechanochemcial activation. These results are in contradiction with those obtained from UV-Vis absorption and emission data. So, we examined the emission data for ultrasonicated samples of polymer having 70 kDa molecular mass more closely. We observed that the fluorescence intensity continued to increase with increase in sonication time but up to a certain level after which it remained unchanged. Similarly increase in absorbance also flattened out after sonication for 5 hour. These observations are compatible with a dynamic equilibrium where *retro* Diels–Alder reaction leading to polymer scission and Diels–Alder reaction leading to chain recombination proceed at equal rates. In other words, active chain ends generated upon sonication might be susceptible to DA reaction under stress. Hence anticipating that the aforementioned behavior is due to competing Diels–Alder and *retro* Diels–Alder reactions under the influence of an identical external stimulus, viability of mechanically induced DA reaction was explored. Typically, activation barrier for Diels-Alder reaction is lower than that for *retro* Diels–Alder reaction. So, under controlled conditions, dienes and dienophiles react together to give the expected [4+2] cycloadduct without serious competition from [4+2] cycloreversion. In contrast to this general trend, we observed that sonication of polymer solution resulted in competitive *retro* Diels–Alder and Diels–Alder reactions. Based on our investigations using polymers of

different molecular mass (*vide supra*), we surmise that energy pooling enables higher polymers to cross the activation barrier for *retro* Diels–Alder reaction. It was also revealed that there is little possibility for *retro* DA reaction in low molecular weight materials. Thus, our observations on polymers of different molecular mass further corroborate the assumption that it is possible to decouple both DA and *retro* DA reaction during sonication. In lower molecular weight materials, insufficient energy pooling will make *retro* Diels–Alder reaction unviable while Diels–Alder reaction is free to operate if sonication provides enough energy to cross the threshold for DA reaction to occur. Since it is necessary to eliminate competition from *retro* DA reaction, it is advisable to keep molecular mass of diene and dienophile components to the bare minimum. To this end, we designed control experiments using simple but significant (to our studies) dienes and dienophiles with a view to demonstrate mechanically induced Diels–Alder reactions.

4.2.2 Model Reactions to analyze the feasibility of mechanically induced DA reactions

Chemical reactions are driven by chemical, electrical, mechanical and thermal activation. Here we carried out Diels–Alder reaction *via* ultrasonication**.** Dienes selected were anthracene (**1a**), 9-methylanthracene (**1b**) and anthracene-9-carboxaldehyde (**4**) and dienophiles were maleic anhydride (**2**), bismaleimide (**5**) and trismaleimide (**7**).

Scheme of mechanochemical synthesis of Diels-Alder adduct **3** is given in Scheme 4.2.



Scheme 4.2. Scheme for mechanochemical synthesis of (9,10)-9-methyl-9,10, 11,15-tetrahydro-9,10-[3,4]furanoanthracene-12,14-dione (3)

DA adduct **3** was synthesized mechanochemically by sonicating toluene solution of maleic anhydride and 9-methyl anthracene for 7 h. After 7 h, toluene was evaporated and the product was purified by column chromatography to give **3** in 90% yield.

IR spectrum of **3** showed strong carbonyl absorptions at 1831 and 1773 cm^{-1} which are characteristics of anhydride carbonyl groups. In the ^{1}H NMR spectrum (Figure 4.5), aromatic protons appeared as multiplet from δ 7.40 to 7.18. The doublet from δ 4.80 to 4.79 is assigned to bridgehead proton. The hydrogen in the 11 position appeared as quartet from δ 3.59 to 3.56. The hydrogen in the 15 position appeared as doublet from δ 3.16 to 3.13. The methyl group appeared as a singlet at δ 2.28. In the ^{13}C NMR spectrum the peaks at δ 170.4 and 169.4 are attributed to carbonyl carbons. The twelve peaks at δ 143.5, 141.2, 140.5, 138.2, 127.6, 127.4, 126.97, 126.92, 125.1, 124.0, 122.4 and 122.1 are due to aromatic carbons. Methyl carbon appeared at δ 15.0. Carbons at 9, 10, 11and 15 positions appeared at δ 51.8, 49.4, 45.3 and 44.9 respectively. The proposed structure was further supported by GC-MS which showed $[M^{+}]$ ion peak at 290.36.

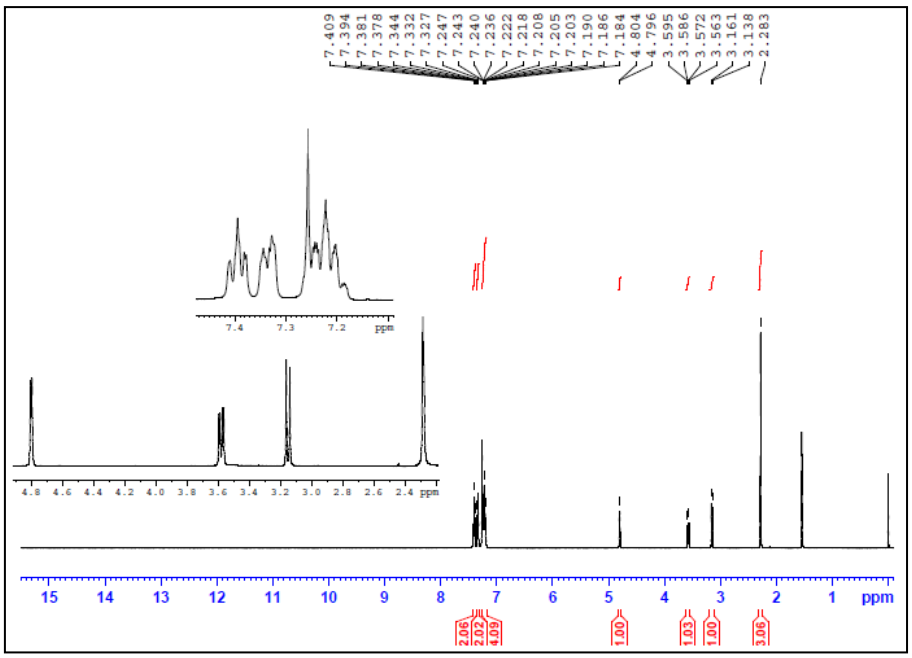
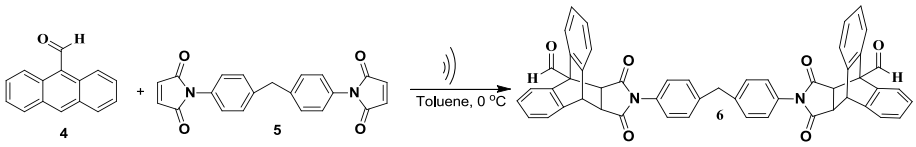


Figure 4.5. ^{1}H NMR spectrum of 3

In order to establish the generality of ultrasonication induced DA reaction, we examined the reaction between a more electron deficient anthracene such as **4** with bismalemide **5**. Scheme for mechanochemical synthesis of DA adduct **6** through the reaction between **4** and **5** is given in Scheme 4.3. DA adduct **6** was synthesized mechanochemically by sonicating toluene solution of 1,1'-(methylenebis(4,1-phenylene))bis(1*H*-pyrrole-2,5-dione) (**5**) and 9-anthraldehyde **(4)** for 7 h. After 7 h, toluene was evaporated and the product was purified by column chromatography to give **6** in 80% yield. This is a highly satisfying result since it established high efficiency for sonication induced Diels–Alder reaction on a relatively less reactive anthracene derivative.



Scheme 4.3. Mechanochemical synthesis of bis DA adduct 6

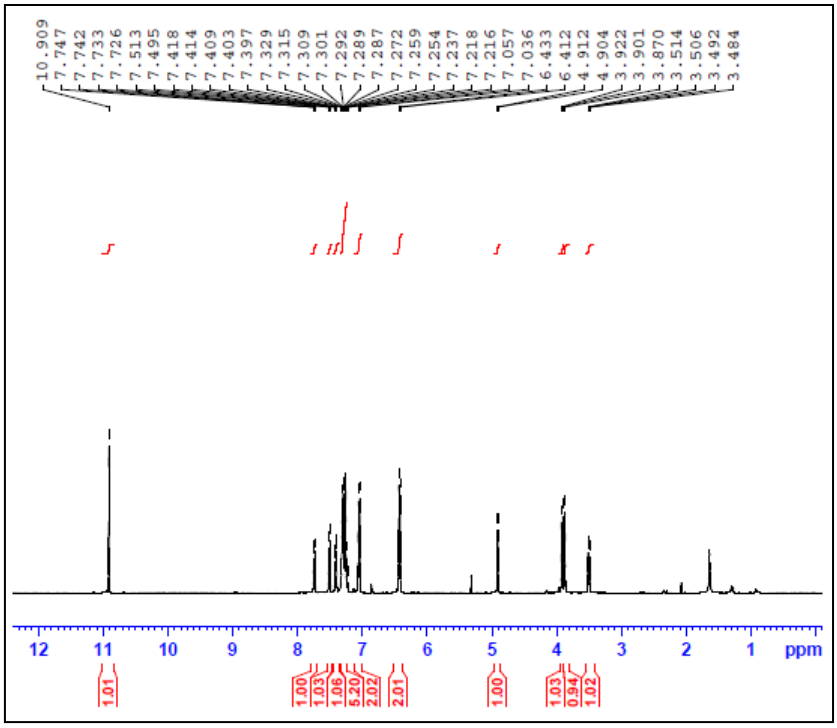
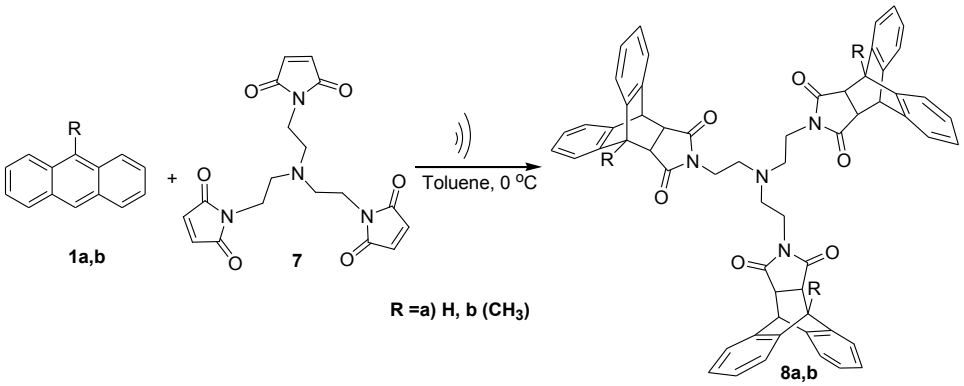


Figure 4.6. ^{1}H NMR spectrum of 6

IR spectrum of **6** showed strong carbonyl absorptions at 1777 and 1714 cm^{-1} which are due to imide and aldehyde groups respectively. Characteristic CH stretching bands of aldehyde group appears at 2842 and 2737 cm^{-1}. In the ^{1}H NMR spectrum of **6** (Figure 4.6), aldehyde proton appears as a singlet at δ 10.90. Aromatic protons appear as multiplet from δ 7.74 to 7.03. The doublet from δ 4.91 to 4.90 is

assigned to bridgehead proton. In the ^{13}C NMR spectrum of **6**, the peaks at δ 199.7 and two peaks at δ 175.4 and δ 174.9 are attributed to carbonyl carbons of aldehyde and imide groups respectively. The peaks at δ 141.0, 138.9, 138.3, 136.6, 129.6, 129.2, 127.67, 127.6, 127.4, 126.8, 126.3, 125.5, 124.8, 123.7 and 123.0 are assigned to aromatic carbons. The proposed structure was further supported by FAB mass spectrum which showed peaks at 794.24 [M+24], 793.27 [M+23] and 788.22 [M+18].

Mechanochemical synthesis of a tris DA adduct **8a,b** is given in Scheme 4.4. DA adduct **8** was synthesized mechanochemically by sonicating toluene solution **1a,b** and **7** for 7 h. After 7 h, toluene was evaporated and the product was purified by column chromatography. Under these conditions, **8a,b** were generated in 80% yield testifying high efficiency of sonication to induce DA reaction.



Scheme 4.4. Mechanochemical synthesis of tris DA adduct 8

IR spectrum of **8b** showed strong carbonyl absorptions at 1767 cm^{-1} and 1694 cm^{-1} which were assigned to imide carbonyls. In the ^{1}H NMR

spectrum (Figure 4.7), aromatic protons appeared as a multiplet from δ 7.33 to 7.05. The doublet from δ 4.66 to 4.65 is assigned to bridgehead proton. The methyl group appears as a singlet at δ 2.19. In the ^{13}C NMR spectrum the peaks at δ 175.3 and δ 174.7 are attributed to carbonyl carbons of amide groups. The peaks at δ 143.5, 140.8, 140.1, 137.7, 125.9, 125.7, 125.4, 124.0, 122.7, 121.2 and 121.0 are attributable to aromatic carbon. The proposed structure was further supported by FAB mass spectrum which showed [M+1] peak at 963.49 and [M+2] peak at 964.47.

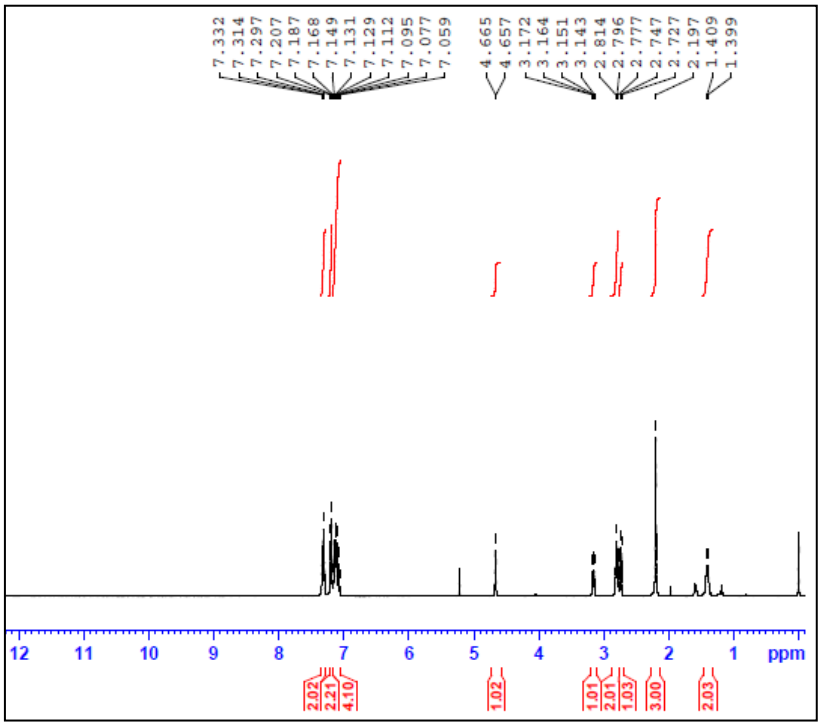
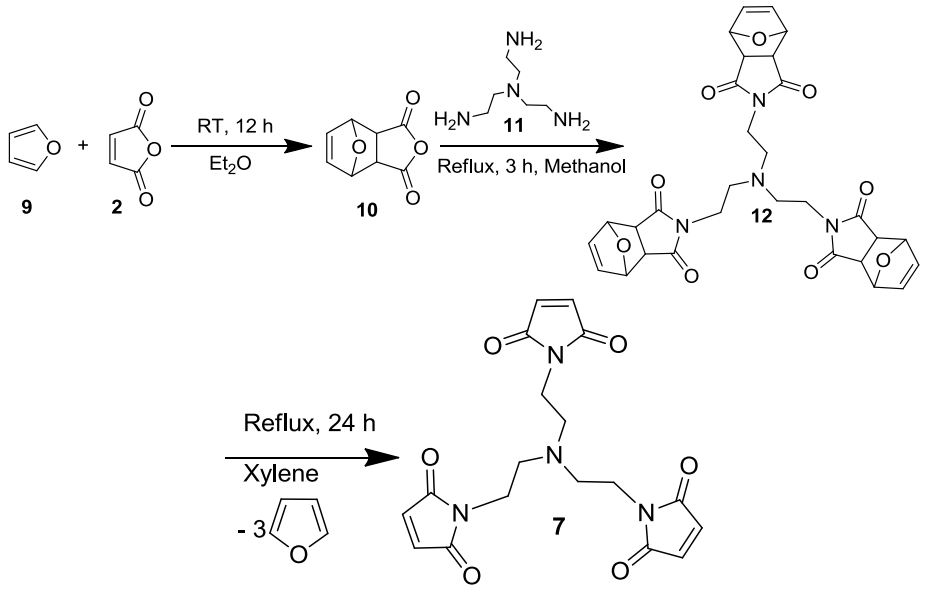


Figure 4.7. ^{1}H NMR spectrum of 8b

Trismaleimide **7** needed for the above reaction was synthesized by the protocol given in Scheme 4.5. Though unintentional, Scheme 4.5

subtly reveals differential energy requirement for DA and rDA reactions to proceed gainfully.



Scheme 4.5. Synthesis of 7

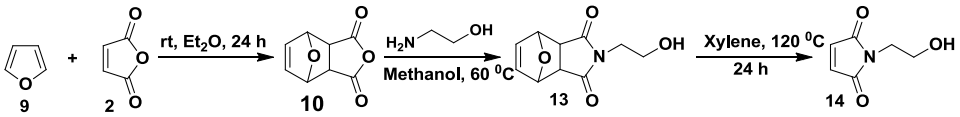
In order to examine the possibility of competing *retro* Diels–Alder reaction, we subjected adduct **3** to sonication for 7h (Scheme 4.2). Analysis of the reaction mixture yielded unchanged **3** in near-quantitative amounts. This experiment indicated that *retro* Diels–Alder reaction is not competitive under conditions employed for generation of **3** given above.

4.2.3 Mendability analysis

Room temperature healing behavior of PMMA-AB-PMMA was investigated using a model reaction between anthracene end capped PMMA (An-PMMA) and 1-(2-hydroxyethyl)-1*H*-pyrrole-2,5-dione (**14**) as a tool to analyze the potential of DA click chemistry in inducing room temperature healing without any external intervention. This

experiment was designed on the assumption that PMMA-AB-PMMA will undergo stress induced cleavage through a *retro* Diels–Alder reaction to give two polymer strands end-capped with anthracene and bismaleimide components. In principle, these to strands can recombine through a Diels–Alder reaction to regenerate the original polymer. Recombination can take place under mechanochemical or thermal activation. If recombination can occur at room temperature, self-healing of the polymer under ambient conditions will emerge as an attractive feature for PMMA-AB-PMMA. In order to demonstrate this exciting possibility, a film was made with chloroform solution of anthracene end capped PMMA (An-PMMA) and 1-(2-hydroxyethyl)-1*H*-pyrrole-2,5-dione (**14**). The film was then kept for 24 h under ambient conditions to test self-healing. UV-Vis and ^{1}H NMR spectra were recorded before and after self-healing study.

The scheme of synthesis of 1-(2-hydroxyethyl)-1*H*-pyrrole-2,5-dione (**14**) is given in Scheme 4.6.[30]



Scheme 4.6. Scheme of synthesis of 1-(2-hydroxyethyl)-1*H*-pyrrole-2,5-dione

^{1}H NMR spectrum of 1-(2-hydroxyethyl)-1*H*-pyrrole-2,5-dione (**14**) is given in Figure 4.8. Singlet at δ 6.74 was assigned to olefinic protons. The methylene protons appeared as a multiplet between δ 3.79-3.71 while the -OH proton appeared as a broad singlet at δ 2.29 ppm.

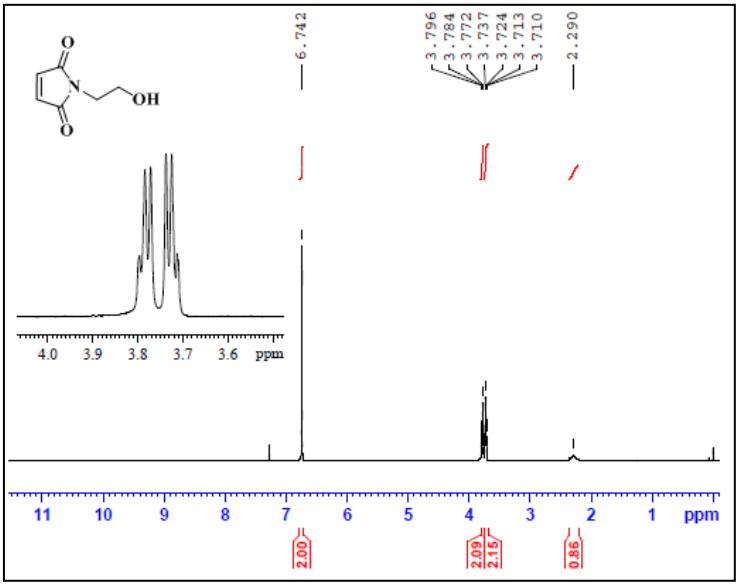


Figure 4.8. ^{1}H NMR spectrum of 14

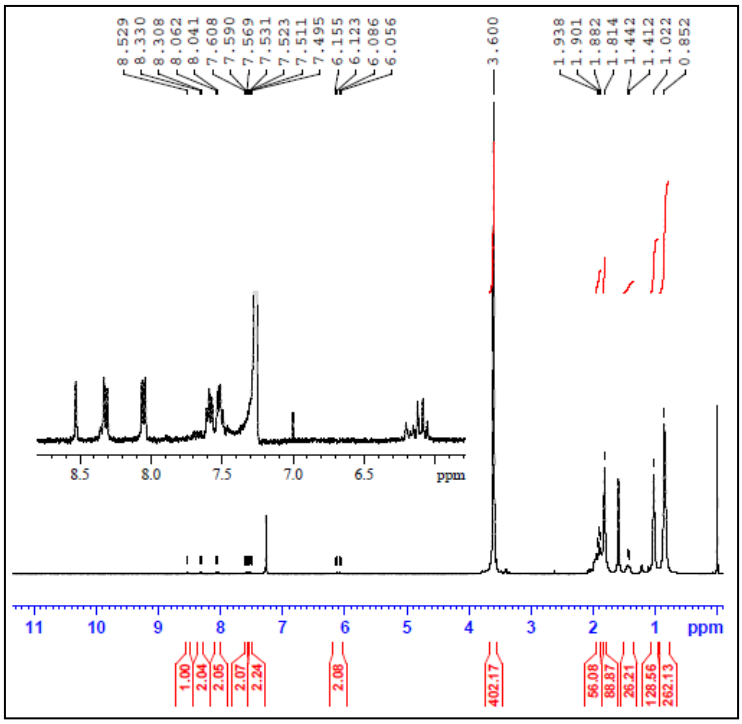
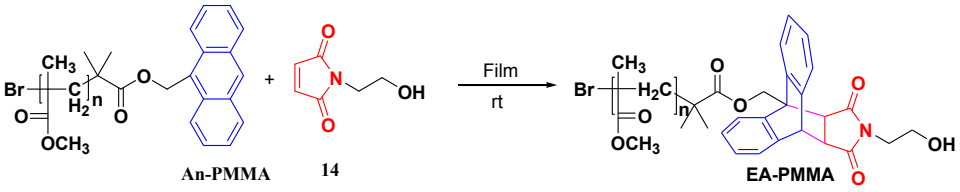


Figure 4.9. ^{1}H NMR spectrum of An-PMMA

^{1}H NMR spectrum of **An-PMMA** is given in Figure 4.9. Peaks between δ 8.52 and 7.49 were assigned to aromatic protons of anthracene unit. The methylene hydrogen attached to anthracene yielded a doublet of doublet between δ 6.05-6.15. The methoxy protons of PMMA component appeared at δ 3.60.

The proposed mechanism of healing is given in Scheme 4.7 which is based on room temperature Diels–Alder click reaction.



Scheme 4.7. Proposed mechanism of self healing

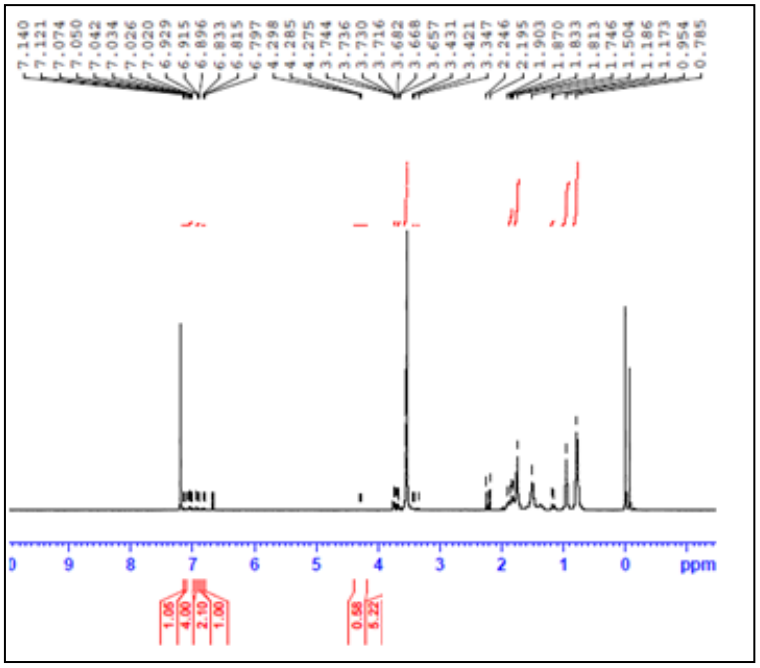


Figure 4.10. ^{1}H NMR spectrum of self-healed polymer EA-PMMA

Drastic changes in peak positions of aromatic protons, complete disappearance of maleimide proton at δ 6.74 and appearance of new peaks in the range δ 3.34-3.43 (imide protons) and δ 4.27-4.29 (bridgehead hydrogen) are attributed to the ethanoanthracene cycloadduct structure which also indicate near-quantitative Diels–Alder reaction at room temperature and hence autonomous healing. Interestingly, prolonged sonication of EA-PMMA failed to induce *retro* Diels–Alder reaction as evidenced by lack of anthracene absorption and emission of sonicated samples. This is not an unexpected result since end groups are inert towards mechanochemical activation.[29]

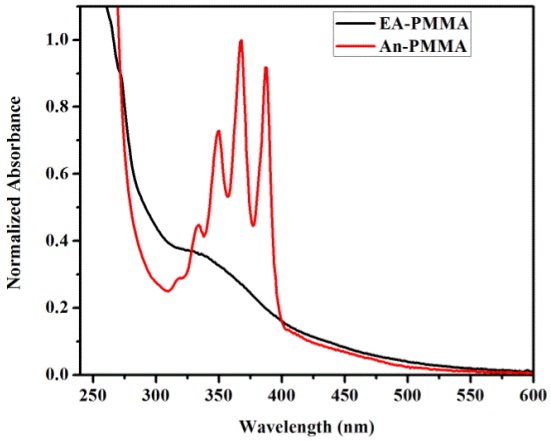
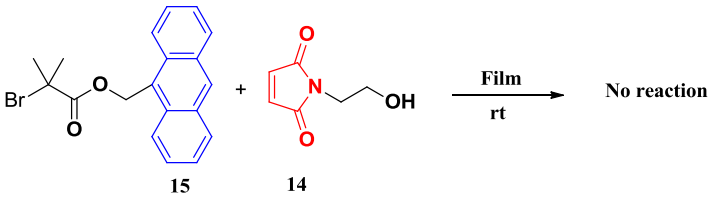


Figure 4.11. UV-Vis spectra showing self healing at room temperature

The mending ability was also monitored via UV-Vis as well as PL spectroscopy. The anthracene absorbance of polymer is found to disappear after 24 h indicating the room temperature reaction between anthracene and maleimide (Figure 4.11).

In continuation, we examined the room temperature reaction between anthracen-9-ylmethyl 2-bromo-2-methylpropanoate (**15**) and 1-

(2-hydroxyethyl)-1*H*-pyrrole-2,5-dione (**14**) under conditions analogous to those indicated in Scheme 4.7. Under these conditions, **14** and **15** remained unchanged indicating that room temperature Diels-Alder reaction is not possible for simple compounds while efficient cycloaddition is feasible when the diene component is part of a polymer chain.



Scheme 4.8. Attempted reaction between 15 and 14

4.3 Conclusions

Mechanically induced *retro* Diels–Alder reaction was observed during the sonication of toluene solution of anthracene-bismaleimide DA adduct derived mechanophore attached polymer. Mechanochemical activation studies with polymer having different molecular weight established molecular weight dependence of mechanochemical activation. In contrast to PMMA-AB-PMMA having molecular weight 70 kDa, the sonicated PMMA-AB-PMMA solution having molecular weight 40 kDa didn't exhibit absorption and fluorescence which dispel the possibility of thermally induced *retro* [4+2] DA reactions. Model reactions were carried out to investigate the feasibility of [4+2] DA reactions. The results propose the use of DA reactions for stress induced bond formation and hence for stress induced strengthening of materials. Interestingly the studies show that mechanophore is found to have a unique combination of optical sensing of damage, stress induced bond formation and room

temperature healing without any external intervention. In summary, incorporating anthracene-bismaleimide adduct mechanophore enabled us to create damage sensing polymers coupled with self-healing ability without any external intervention. This study promises to open way to the design of a wide range of smart materials having properties such as stress-sensing, as well as autonomous room temperature healing coupled stress induced strengthening.

In addition, taking an anthracene derivative as prototypical example, we have demonstrated that Diels–Alder reaction though not feasible at room temperature for a diene, turns feasible when it is part of a polymer chain.

4.4 Experimental

4.4.1 Materials

Unless otherwise stated, all commercially available materials were purchased from either Spectrochem or Sigma Aldrich and were used as received without further purification. Solvents were dried and purified by following known protocols. Unless otherwise mentioned, all sonication experiments were performed at 10-15 ºC with a pulse sequence of 7s on 3s off, 30% amplitude.

4.4.2 Methods

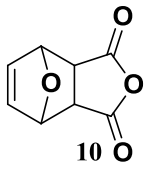
Melting points were determined on a *Neolab* melting point apparatus and are uncorrected. Infrared spectra were recorded on *Jasco 4100* and *ABB Bomem (MB Series)* FT-IR spectrometers. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz *Bruker AvanceIII* FT-NMR

spectrometer using deuterated chloroform or deuterated dimethyl sulphoxide as solvent with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) were reported in parts per million (ppm) downfield of TMS. Multiplicities were designated as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Elemental analysis was performed using *Elementar Systeme (Vario EL III)*. Molecular mass was determined by electron impact (EI) method using GC-MS (*Agilent GC-7890A, Mass-5975C*) and fast atom bombardment (FAB) using *JMS 600 JEOL* mass spectrometer.

4.4.3 Synthesis of 1-(2-hydroxyethyl)-1*H*-pyrrole-2,5-dione[30] (14)

4.4.3.1 Synthesis of Protected Maleic Anhydride – 3,6-Epoxy-1,2,3,6-tetrahydrophthalic Anhydride[30] (10)

The synthesis was carried out following a modified literature procedure. In a 50 mL round-bottom flask maleic anhydride (**2**, 1.00 g, 10 mmol) and furan (**9**, 0.69 g, 10 mmol) were dissolved in 10 mL of diethyl ether. The mixture was stirred for 24 h at room temperature after which the white precipitate formed was collected by filtration and washed thrice with cold diethyl ether and dried under vacuum. The filtrate was reduced to 5 mL and cooled to 4 °C overnight to isolate a second crop of the product. Crystals formed were collected by filtration and washed with diethyl ether. Finally, the crystals were dried under vacuum.

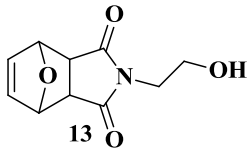


10

White solid; Yield: 90%; IR (KBr): 3143, 3099, 1857, 1780 cm^{-1}.

4.4.3.2 Synthesis of 2-(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-epoxyisoindole-1,3(2*H*)-dione[30](13)

In a 50 mL round-bottom flask fitted with a condenser and dropping funnel, 3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (**10**, 1.00 g, 6 mmol) in 5 mL methanol was added. To the stirred solution of **10** ethanolamine (0.55 g, 6 mmol) in 5 mL methanol was added dropwise. After the addition, the solution was heated at 60 ºC for 6 h during which the solution turned light brown in color. Then the solution was concentrated to get brown oil.

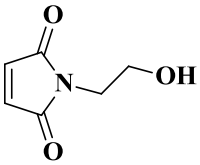


13

White solid; Yield: 88%; IR (KBr): 3143, 3099, 1857, 1780 cm^{-1}.

4.4.3.3. Synthesis f 1-(2-hydroxyethyl)-1*H*-pyrrole-2,5-dione (14)

In a 50 mL round-bottom flask fitted with a condenser containing **13** (1.01 g, 4.7 mmol), 10 mL of xylene was added. The mixture was refluxed for 24 hours and after that hot filtered. The filtrate was then kept in a refrigerator and the crystals formed were filtered out and used after repeated recrystallization in methanol.



14

White solid; Yield: 88%; IR (KBr): 3451,1780 cm^{-1}.

4.4.4 Synthesis of 1,1',1''-(nitrilotris(ethane-2,1-diyl))tris(1H-pyrrole-2,5-dione)[30] (7)

4.4.4.1 Synthesis of 2,2',2''-(nitrilotris(ethane-2,1-diyl))tris(3a,4,7,7a-tetrahydro-1*H*-4,7-epoxyisoindole-1,3(2*H*)-dione)[30] (12)

In a 50 mL round-bottom flask fitted with a condenser and dropping funnel, 3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (**10**, 0.99 g, 6 mmol) in 5 mL methanol was added. To the stirred solution of **10**, tris(2-aminoethyl)amine (**11**, 0.29 g, 2 mmol) in 5 mL methanol was added dropwise. After the addition, the solution was heated at 60 ºC for 6 h during which the solution turned light brown in color. Solvent was evaporated under reduced pressure and the product was purified by column chromatography. Yield: 88%; IR (KBr): 1857, 1780 cm^{-1}.

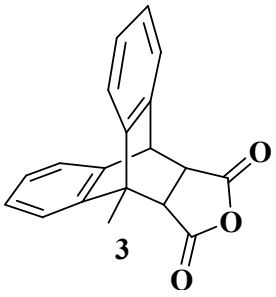
4.4.4.2 Synthesis of 1,1',1''-(nitrilotris(ethane-2,1-diyl))tris(1*H*-pyrrole-2,5-dione)[30] (7)

In a 50 mL round-bottom flask fitted with a condenser containing compound **12**, (1.00 g, 1.6 mmol), 10 mL of xylene was added. The mixture was refluxed for 24 hours after that hot filtered. The filtrate was then kept in a fridge and the crystals formed were filtered out and used after repeated recrystallization in methanol. Yield: 88%; IR (KBr): 1857, 1784 cm^{-1}

4.4.5 Mechanochemical synthesis of (9,10)-9-methyl-9,10,11,15-tetrahydro-9,10-[3,4]furanoanthracene-12,14-dione (3)

Mixture of maleic anhydride (**2**, 0.05 g, 0.50 mmol) and 9-methylanthracene (compound no. 0.03 g, 0.50 mmol) in toluene solution was ultrasonicated for 7 h. After 7 h, solvent was removed and the compound was purified by column chromatography.

Spectral and analytical data of compound (3)



3

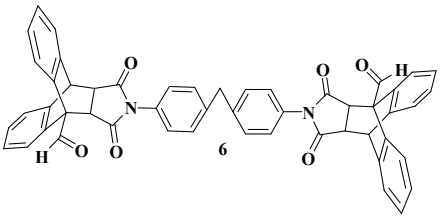
White crystalline solid; Yield: 90%; IR (KBr): 1831, 1773 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.40 (m, 8H), 4.79-4.80 (d, *J* =3.2 Hz, 1H), 3.56-3.59 (dd, *J* = 9.2, 3.6 Hz, 1H), 3.13-3.16 (d, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 169.4, 143.5, 141.2, 140.5, 138.2,127.6, 127.4, 126.97, 126.92, 125.1, 124.0, 122.4, 122.1, 51.8, 49.4, 45.3, 44.9, 15.0; MS: *m/z* 290 (M^+), Elemental analysis calculated for $C_{19}H_{14}O_3$: C: 78.61, H: 4.86; Found C: 78.58, H: 4.82.

4.4.6. Mechanochemical synthesis of 13-(4-(4-((9,10)-9-formyl-12,14-dioxo-11,12,14,15-tetrahydro-9*H*-9,10-[3,4]epipyrroloanthracen-13(10*H*)-yl)benzyl)phenyl)-12,14-dioxo-10,11,12,13,14,15-hexahydro-9*H*-9,10-[3,4]epipyrroloanthracene-9-carbaldehyde (6)

Mixture of 9-anthraldehyde (**4**, 0.05 g, 0.24 mmol) and 1,1'-(methylenebis(4,1-phenylene))bis(1*H*-pyrrole-2,5-dione) (5, 0.04 g,

0.02 mmol) in toluene was ultrasonicated for 7 h. After 7 h the solvent was removed and the compound was purified by column chromatography.

Spectral and analytical data of compound 6



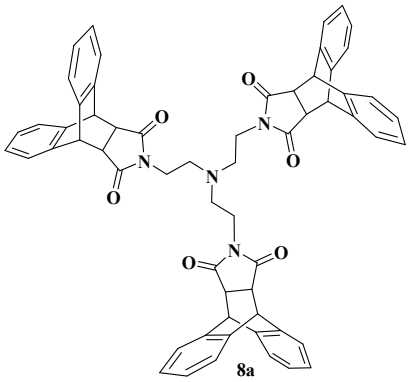
6

White crystalline solid; Yield: 83%; mp: 208 ºC; IR (KBr): 3060, 2959, 2842, 2737, 1777, 1714, 1509 ,1459 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.74-7.72 (1H, dd), 7.49 - 7.51 (1H, *J* = 7.2 Hz, d), 7.39-7.41 (1H, m), 7.21-7.32 (5H, m), 7.03 -7.05 (2H, *J* = 8.4 Hz, d), 6.41-6.43(2H, *J* = 8.4 Hz, d), 4.90-4.91(1H, *J* = 8.4 Hz, d), 3.90-3.92 (1H, *J* = 8.4 Hz, d), 3.87 (1H, s), 3.48-3.51 (1H, *J* = 8.8 Hz, 3.2 Hz, dd); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 175.4, 174.9, 141.0, 138.9, 138.3, 136.6, 129.6, 129.2, 127.67, 127.63, 127.4, 126.8, 126.3, 125.5, 124.8, 123.7, 123.0, 57.9, 48.0, 47.4, 46.2, 40.9; MS: *m/z* 794.24 [M+24], 793.27 [M+23], 788.22 [M+18],; Elemental analysis calculated for $C_{51}H_{34}N_2O_6$: C: 79.47, H: 4.45, N: 3.63; Found C: 79.45, H: 4.40, N: 3.61.

4.4.7 Mechanochemical synthesis of anthracene trismaleimide adduct (8a)

Mixture of anthracene (**1a**, 0.05 g, 0.28 mmol) and 1,1',1''-(nitrilotris(ethane-2,1-diyl))tris(1*H*-pyrrole-2,5-dione) (**7,** 0.03 g, 0.09 mmol) in toluene solution was ultrasonicated for 7 h. After sonication, solvent was removed under reduced pressure and the compound was purified by column chromatography.

Spectral analytical data for 8a.



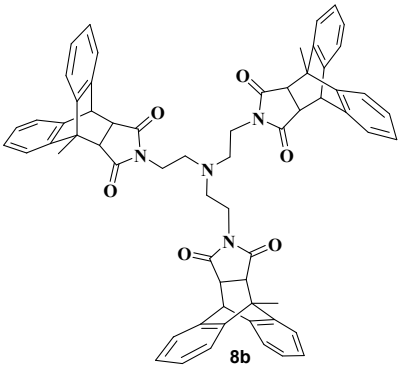
White crystalline solid; Yield: 81%; mp: 248 ºC; IR (KBr): 1771, 1698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06-7.31 (m, 8H), 4.68 (s, 2H), 3.12 (s, 2H), 2.75-2.79 (t, J = 7.4, 1H), 1.46-1.42 (t, J = 7.2Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 140.5, 137.6, 126.0, 125.6, 124.0, 123.2, 48.9, 45.7, 44.5, 35.0; MS: *m/z* 920.36 (M^+); Elemental analysis calculated for $C_{60}H_{48}N_4O_6$: C: 78.24, H: 5.25, N: 6.08; Found C: 78.20, H: 5.20, N: 6.02.

4.4.8 Mechanochemical synthesis of 9-methylanthracene trismaleimide adduct (8b)

Mixture of 9-methylanthracene (**1b**, 0.05 g 0.26 mmol) and 1,1',1''-(nitrilotris(ethane-2,1-diyl))tris(1*H*-pyrrole-2,5-dione) (7, 0.03 g, 0.08 mmol)

in toluene solution was ultrasonicated for 7 h. After sonication the solvent was removed and the compound was purified by column chromatography.

Spectral and analytical data of compound 8b



8b

White crystalline solid; Yield: 82%; mp 192 ºC; IR (KBr): 1767, 1694, 1461 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29-7.33 (t, *J* = 7 Hz, 2H), 7.05-7.20 (m, 6H), 4.65-4.66 (d, *J* =3.2 Hz, 1H), 3.14-3.17 (dd, *J* = 8.4, 3.2 Hz, 1H), 2.77-2.81 (t, *J* = 7.4, 1H), 2.72-2.74 (d, *J* = 8Hz, 1H), 2.19 (s, 3H); 1.39-1.40 (2H, *J* = 4 Hz, d); ^{13}C NMR (100 MHz, $CDCl_3$): 175.3, 174.7, 143.5, 140.8, 140.1, 137.7, 125.9, 125.7, 125.4, 124.0, 122.7, 121.2, 121.0, 49.4, 48.8, 47.3, 44.5, 44.0, 34.8, 14.2; MS: *m/z* 962.40 (M^+), 963.49 (M+1), 764.47 (M+2); Elemental analysis calculated for $C_{63}H_{54}N4O_6$: C: 78.56, H: 5.65, N: 5.82; Found C: 78.50, H: 5.60, N: 5.82.

4.4.9 Sonication of (9,10)-9-methyl-9,10,11,15-tetrahydro-9,10-[3,4] furanoanthracene-12,14-dione (3)

A solution of **3** in toluene (0.1g. 0.3mmol in 5 mL) was ultrasonicated for 7 h. Work up of the reaction mixture yielded unchanged **3** in near quantitative amounts.

4.4.10 Synthesis of anthracene end capped PMMA -An-PMMA

PMMA-An-PMMA was synthesized by a modified SET-LRP method developed by us the procedure of which is given in Chapter 3.

4.4.11 Room temperature reaction between An-PMMA and 14

Solvent cast film of a mixture of An-PMMA and **14** was kept for 24 h under ambient conditions to test self-healing. UV-Vis and ^{1}H NMR spectra recorded before and after self-healing study indicated near-quantitative Diels–Alder between An-PMMA and **14**.

4.4.12 Attempted room temperature reaction between anthracen-9-ylmethyl 2-bromo-2-methylpropanoate (15) and 1-(2-hydroxyethyl)-1*H*-pyrrole-2,5-dione (14)

Solvent cast film of a mixture of **15** and **14** was kept for 24 h under ambient conditions. TLC analysis at the end of 24 h gave no indication for the formation of any new products. Both 15 and 14 remained completely unchanged indicating total failure of room temperature rDiels-Alder reaction between these two reaction partners.

4.4.13 General procedure for sonication experiment

For each experiment, mechanophore-containing polymer (5 mg) was weighed and dissolved in 7 mL of toluene. Temperature of polymer solution was kept between 10 and 15 ºC. Polymer solution was sonicated for 7 h with pulse sequence of 7 s on and 3 s off.

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Chapter 5

Summary and Conclusions

Mechanochemistry deals with chemical reaction driven by mechanical force. Polymer mechanochemistry has progressed to the level where energy from mechanical force can be used for constructive purposes such as stress-sensing, stress induced strengthening, stress induced cross linking, self-healing etc., which may have otherwise resulted in destructive processes via bond breaking, leading to material degradation. This mechanical to chemical energy transition is brought about by functional moieties called mechanophores, which are attached to polymer scaffolds. To this end considerable amount of research has been focused on the design and synthesis of new mechanophores as well as on the detailed understanding of transduction of mechanical force at the molecular level. The work presented in this dissertation has two overarching objectives. First one is to synthesize novel mechanophores and the second one is the investigation of the potential of synthesized mechanophores in the context of stress-sensing, self-healing and stress induced strengthening. In the thesis entitled "Synthesis of Mechanoresponsive Healable Polymers through Diels–Alder Unclick/Click Chemistry via Single Electron Transfer-Living

Radical Polymerization", we report the synthesis of a few mechanophores tailored to exhibit stress-sensing, self-healing and stress induced strengthening characteristics. In order to bring together all these properties in a single moiety we have chosen Diels–Alder Click/Unclick chemistry in the mechanophore synthesis. Though mechanical as well as thermal reversibility of Diels–Alder reaction have been investigated, there are only a few reports on using these systems in stress-sensing, self-healing and stress induced strengthening applications. Anthracene and furan as dienes and maleimide and maleic anhydride as dienophiles were used for the mechanophore synthesis via Diels–Alder reaction. Detailed synthesis of mechanophore with structural elucidation by FT-IR, ^{1}H NMR, ^{13}C NMR, GC-MS and LC-MS are outlined in Chapter 2. Out of the eleven mechanophores synthesized, seven are novel compounds. In continuation, mechanophore initiators were synthesized by functionalizing with α-bromo ester groups. Initiators synthesized include diene, dienophile as well as mechanophore functionalized moieties. Unfortunately during purification by column chromatography some of the initiators decomposed over silica and/or alumina surface and hence we had to resort to repeated recrystallization for their purification. We have synthesized seven initiators that could initiate SET-LRP. Out of these three are novel compounds. Detailed protocol for initiator synthesis as well as structural confirmation by FT-IR, ^{1}H NMR, ^{13}C NMR, GC-MS and LC-MS are included in Chapter 2.

Mechanophore centered polymers were synthesized using modified SET-LRP. Conventional SET-LRP lacked the important attribute of oxygen tolerance. We have demonstrated a simple, efficient and

economical approach for SET-LRP in which tiresome deoxygenation procedures were eliminated by the use of triphenylphosphine and the thesis entails the first description of SET-LRP using triphenylphosphine. Compatibility of our modified SET-LRP towards polymerization of methyl acrylate (MA), methyl methacrylate (MMA) and acrylonitrile (AN) was investigated by synthesizing corresponding polymers using each of the aforementioned mechanophores, dienes and dienophiles derived initiators. Tolerance of our modified SET-LRP method towards oxygen was confirmed by the characterization of 7 polymers including, 3 novel ones, by ^{1}H NMR, ^{13}C NMR, GPC, UV-Vis and PL techniques. We observed that polymerization profiles under modified conditions complied with those of the classical SET-LRP process. All the polymerizations were completed in less than 1 hour and the polymers were featured with good control over MW, low poly dispersity indices and narrow molecular weight distribution. Control experiment was carried out to rule out the possibility of formation of PMMA along with mechanophore centered PMMA by carrying out polymerization with all reagents except initiator. In the absence of initiators, polymer formation was not observed.

The use of triphenylphosphine as an additive eliminated stringent reaction conditions and made SET-LRP a powerful, reliable and robust tool for the synthesis of new polymeric materials with novel structures under ambient conditions. Mechanism of SET-LRP suggests that addition of small amounts of reducing agent triphenylphosphine to the reaction mixture reduces Cu_2O generated by the oxidation of Cu(0) wire with air, regenerating Cu(0) and allowing for the synthesis of polymers with predictable molecular weight and perfect retention of chain end functionality.

Living nature of the modified SET-LRP method was further highlighted by successfully demonstrating exciting possibilities such as chain extension and generation of diblock polymers using the polymer synthesized by us. Chapter 3 highlights advantages of our modified method of SET-LRP.

Anthracene-bismaleimide Diels-Alder adduct derived mechanophore centered polymer was used to study the mechanochemical activation using ultrasonication and hence the mechanoresponsive behavior. We showed that the anthracene-bismaleimide DA adduct structural motif underwent *retro* Diels–Alder reaction under the influence of mechanical stress to generate free anthracene and bismaleimide terminated chains, which can thus function as a stress sensor.

Effect of molecular weight on the mechanochemical activation was studied with mechanophore centered PMMA having high and low molecular weights. Higher mechanochemical activity was exhibited by polymer sample having higher molecular mass demonstrating that molecular weight of the polymer is a key descriptor of mechanochemical activation.

Potential of Diels–Alder reaction for self-healing at room temperature without any external intervention was demonstrated using anthracene end capped PMMA and 1-(2-hydroxyethyl)-1*H*-pyrrole-2,5-dione. Diels–Alder reaction between anthracene end capped PMMA and 1-(2-hydroxyethyl)-1*H*-pyrrole-2,5-dione cycloaddition reaction in the solid state was fast enough for completion within 12 h at room temperature without leaving any

anthracene residue as evident from both UV-Vis and PL spectroscopy. This observation substantiated the click character as well as potential of DA reaction for room temperature healing without any external intervention. We also considered the possibility of using energy from the stress for Diels–Alder click reaction *i.e.*, demonstration of mechanically induced Diels–Alder reaction which can permit mechanically induced reforming property. In order to analyze the same, model DA reactions were carried out by sonicating chloroform solutions of simple dienes and dienophiles. Results of the experiment inveterate the formation of DA adduct under sonication and hence the viability of mechanically induced DA reaction without competition from *retro* Diels–Alder reaction. Based on this model experiment, we propose the utility DA reaction for stress induced strengthening or stress induced cross linking applications. Unlike simple molecules, polymers having sufficiently high molecular mass underwent both DA (click) and *retro* DA (unclick) reactions under ultrasonication. Thus, our polymer combines stress-sensing (*retro* DA unclick reaction under sonication) with self-healing (DA click reaction under sonication or spontaneous) without any external stimuli at room temperature as well as potential stress induced strengthening characteristics.

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Chapter 6

Future Outlook

Our work has mainly been based on mechanochemical activation studies using sonication where force was applied to polymer chains in a dilute solution via ultrasonication. For commercial applications such as crack sensing, detailed understanding of factors affecting solid state mechanochemical activation, as opposed to solution state is needed. Solid state mechanophore based polymers and their mechanochemical responses have not been thoroughly studied. With this idea in mind we synthesized the following cross linkers with a view to covalently attach these into various polymer matrices and to study the mechanochemical activation in solid state. Structure of newly synthesized mechanophore cross linkers are given in the Figure 6.1. Efficiency of these compounds to act as cross linkers were examined by the successful synthesis of PMMA cross linked copolymers using these cross linkers. Investigations on the mechanoresponsive and self-healing ability of these polymers are currently underway.

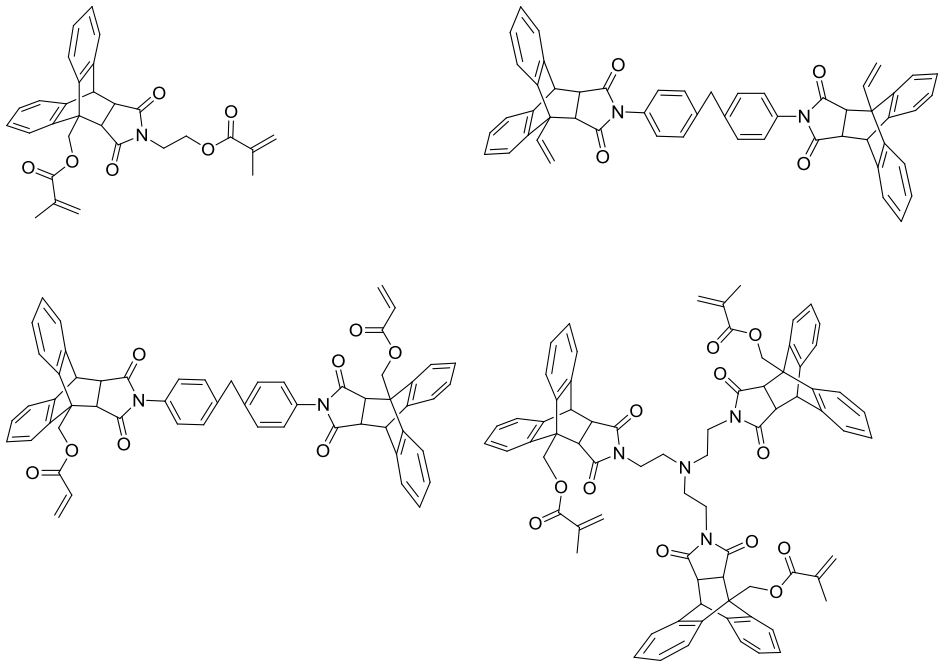

Figure 6.1. Mechanophore cross linkers

We found that mechanical force can induce both DA (click) and retro DA (unclick) reactions so that DA unclick/click chemistry can bring about both stress sensing, self-healing and stress induced strengthening characteristics. A domino sequence of stress induced retro Diels–Alder unclick and Diels–Alder click reactions will ensure both stress sensing as well as stress induced strengthening of polymers decorated with suitable mechanophore components. Hence we are also interested in synthesizing a polymer in which cross-linking through stress induced Diels–Alder reaction between *in situ* generated diene and pre-attached dienophile components is feasible as shown in the Figure 6.2. Beauty of our system is that both unclick and click reactions are feasible under identical

stimulus in a single polymer, and both these processes are observable by following switching on/switching off of anthracene fluorescence.

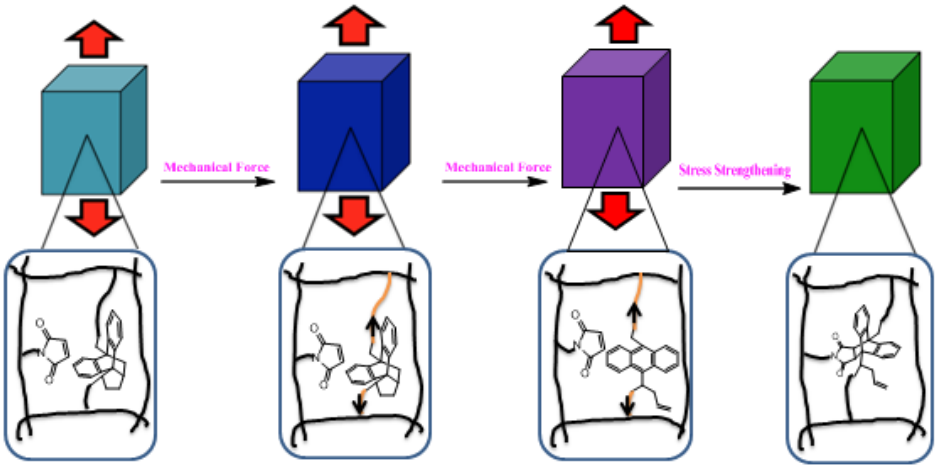

Figure 6.2. Gaining strength under stress using intramolecular Diels–Alder adduct based mechanophore attached polymer.

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