İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ELECTROACTIVE INTERMEDIATES FOR THE SYNTHESIS OF CONDUCTING BLOCK AND GRAFT COPOLYMERS

Ph.D. Thesis by

Faruk YILMAZ

Department: Polymer Science and Technology

Programme: Polymer Science and Technology

MAY 2004

İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ELECTROACTIVE INTERMEDIATES FOR THE SYNTHESIS OF CONDUCTING BLOCK AND GRAFT COPOLYMERS

Ph.D. Thesis by
Faruk YILMAZ
(515002100)

Date of submission: 22 January 2004
Date of defence examination: 14 May 2004

Supervisor (Chairman): Prof. Dr. Yusuf YAĞCI
Members of the Examining Committee: Prof. Dr. Gürkan HIZAL (I.T.U.)
Prof. Dr. Sezai SARAÇ (I.T.U.)
Prof. Dr. Atilla GÜNGÖR (M.U.)
Assoc. Prof. Dr. Yusuf MENCELOĞLU (S.U.)

MAY 2004

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

İLETKEN BLOK VE AŞI KOPOLİMERLERİN SENTEZİNDE KULLANILAN ELEKTROAKTİF ARA MADDELER

DOKTORA TEZİ
Faruk YILMAZ
(515002100)

Tezin Enstitüye Verildiği Tarih: 22 Ocak 2004
Tezin Savunulduğu Tarih: 14 Mayıs 2004

Tez Danışmanı : Prof. Dr. Yusuf YAĞCI

Diğer Jüri Üyeleri: Prof. Dr. Gürkan HIZAL (İ.T.Ü.)

Prof. Dr. Sezai SARAÇ (İ.T.Ü.)

Prof. Dr. Atilla GÜNGÖR (M.Ü.)

Doç. Dr. Yusuf MENCELOĞLU (S.Ü.)

MAYIS 2004

Özlem, İsmail Hakkı, Tevfik Burak, anne-baba ve kardeşlerime...

ACKNOWLEDGEMENTS

I would like to express my gratitude to my thesis supervisor Prof. Yusuf Yağcı for his kind guidance, valuable comments, suggestions, support, offering valuable help in all possible ways and helpful criticism throughout this research.

My thanks also to Prof. Levent Toppare, Prof. Koichi Ito, Assoc. Prof. Yeşim Hepuzer, Dr. Ioan Cianga and Dr. Luminita Cianga. They assisted me in many ways, including performing experiments, literature searches and showing good humor.

In addition, I would like to thank my Laboratory colleagues Ali Ekrem Müftüoğlu, Ergün Gonca, Ramazan Öztürk, Mustafa Değirmenci, Atilla Taşdelen, Seda Yurteri, Fatmanur Kasapoğlu, Canan Dursun, Nihan Yönet, Ali Çirpan, and Yusuf Güner for their moral support and confidence.

Finally, during all stages involved in the preparation of this thesis I have sought the forbearance of my wife and son for my neglect. I have been given not only this but also her full support, patience, understanding and good humor as well. Therefore I'm grateful to them. I also acknowledge my father and mother for their encouragement and support throughout my education.

January 2004 Faruk YILMAZ

TABLE of CONTENTS

LIST of ABBREVIATIONS

CRP : Controlled Radical Polymerization
ATRP : Atom Transfer Radical Polymerization
NMP : Nitroxide Mediated Polymerization
SFRP : Stable Free Radical Polymerization
RAFT : Reversible Addition-Fragmentation Chain Transfer Polymerization
ROP : Ring-Opening Polymerization
FRP : Free Radical Polymerization
PI : Photoinitiator
S : Sensitizer
I : Initiator
CTA : Chain Transfer Agent
PPI : Polymeric Photoinitiator
MWD : Molecular Weight Distribution
PDI : Poly Dispersity Index
CP : Conductive Polymers
CTC : Charge Transfer Complex
GPC : Gel Permeation Chromatography
IR : Infrared Spectrophotometer
NMR : Nuclear Magnetic Resonance Spectroscopy
UV : Ultra Violet
DSC : Differential Scanning Calorimetry
TGA : Thermal Gravimetry Analysis
SEM : Scanning Electron Microscopy
CV : Cyclic Voltammetry
MO : Molecular Orbital
CCE : Constant Current Density
WE : Working Electrode
RE : Reference Electrode
M : Monomer
St : Styrene
MMA : Methyl Methacrylate
MTM : 3-Methylthienyl Methacrylate
ε-CL : Epsilon Caprolactone
PSt : Polystyrene
PMMA : Poly(methyl Methacrylate)
PCL : Poly(ε-Caprolactone)
COI : Coinitiator
bpy : Bipyridine
PPy : Polypyrrole
PTh : Polythiophene

PEO	: Poly (ethyelene oxide)
MBThi	: N-(4-(3-thienyl methylene)-oxycarbonylphenyl) maleimide (MBThi)
TOET	: 2-[(3-thienylcarbonyl) oxy] ethyl 3-thiophene carboxylate
TOPT	: 2, 3-bis [(3-thienylcarbonyl) oxy] propyl 3-thiophene carboxylate
TOTPT	: 3-[(3-thienylcarbonyl) oxy]-2, 2-bis {[(3-thienylcarbonyl) oxy]} propyl 3-thiophene carboxylate
MBA	: Maleimidobenzoic acid
TM	: Thiophene methanol
TCA	: Thiophene carboxylic acid
EG	: Ethylene glycol
G	: Glycerol
PE	: Pentaeritritol
DPE	: 1, 1-dipheylethene
VBCI	: *p*-vinylbenzyl chloride
AIBN	: α,α’-Azobisisobutyronitrile
DMPA	: ω, ω–Dimethoxy-ω-phenylacetophenone
TEMPO	: 2,2,6,6-tetramethylpiperidine-*N*-oxyl
TBAFB	: Tetrabutylammonium tetrafluoroborate
ACN	: Acetonitrile
PTSA	: *p*-toluene sulfonic acid
PEOVB	: Poly (ethylene oxide) Macromonomer with *p*-vinylbenzyl chloride end group
PSt-*alt*-MBThi	: Alternating Copolymers of Styrene with N-(4-(3-thienyl methylene)-oxycarbonylphenyl) maleimide (MBThi)
PMTM-*r*-PEOVB	: Random Copolymers of 3-Methylthienyl methacrylate with PEOVB
PMMA-*b*-PMTM	: Block Copolymers of Methylmethacrylate and 3-Methylthienyl methacrylate
PMBThi/PPy	: Conducting Block Copolymers of PMBThi with Pyrrole
PMBThi/Th	: Conducting Block Copolymers of PMBThi with Thiophene

LIST of TABLES

LIST of FIGURES

LIST of SYMBOLS

$\Phi_{R\cdot}$: Quantum Yield of Radical Formation
λ : Wavelength
$h\upsilon$: Radiation
$R^{\cdot}$: Radical
I : Initiator
COI : Coinitiator
M : Monomer
C^{+} : Cation
$C^{+\cdot}$: Radical Cation
C^{-} : Anion
S : Sensitizers
E_{pc} : Catodic potential
E_{pa} : Anodic potential
M_n : The Number Average Molecular Weight
M_w : The Weight Average Molecular Weight
M_w/M_n : The Molecular Weight Distribution
k_{act} : Rate constant of activation step of the initiation in radical polymerization
k_{deact} : Rate constant of deactivation step of the initiation in radical polymerization
k_p : Rate constant of propagation step
k_t : Rate constant of termination step
M_t^n : Transition metal

ELECTROACTIVE INTERMEDIATES FOR THE SYNTHESIS OF CONDUCTING BLOCK AND GRAFT COPOLYMERS

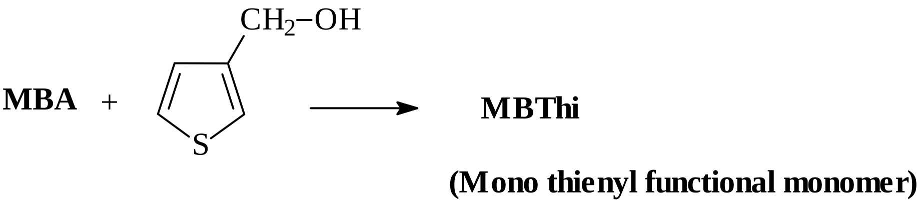
SUMMARY

Electrically conducting polymers have received growing interest because of their wide range applications in the areas such as rechargeable batteries, membranes, optical displays, and electro chromic devices. These materials are often termed as synthetic metals due to the fact that they combine chemical and mechanical properties of the polymers with the electronic properties of the metals and semicunductors. Polythiophene is one of the polymers among a general type of conducting polymers that include polyacetylenes, polypyrrole, polyanilines, polyphenylenes, polycarbazoles, polyquinolines, and polyphtalocyanines.

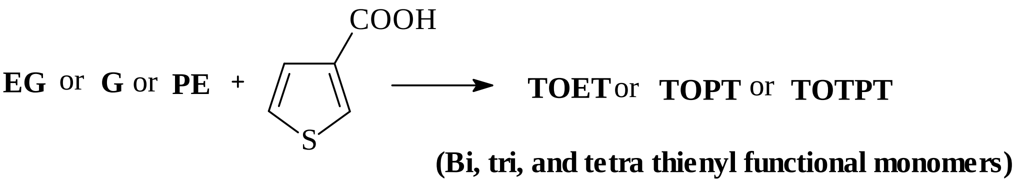
Macromonomers are usually referred to reactive oligomers or polymers in which a polymerizable functional group is incorporated to the chain end(s). Macromonomers can conveniently be copolymerized with conventional monomers to yield graft copolymers with well defined structures. Structure of the polymer chain of the macromonomer affects the properties of the graft copolymer while the end group controls the reactivity in polymerization. Macromonomers possessing one or two electroactive groups at the chain end(s) are usually prepared by using functional initators or by end capping the living growing chains.

In this research, reactive intermediates based on monomeric and polymeric structures with thiophene moieties were synthesized and possibility of their use in electropolymerization through thiophene groups was attempted.

For this purpose, mono, bi, tri, and tetra thienyl functional monomers namely, N-(4-(3-thienyl methylene)-oxycarbonylphenyl)maleimide (MBThi), 2-[(3-thienylcarbonyl) oxy] ethyl 3-thiophene carboxylate (TOET), 2, 3-bis [(3-thienylcarbonyl) oxy] propyl 3-thiophene carboxylate (TOPT), 3-[(3-thienylcarbonyl) oxy]-2, 2-bis {[(3-thienylcarbonyl) oxy]} propyl 3-thiophene carboxylate (TOTPT) were synthesized respectively by the esterification reaction of 4-maleimidobenzoic acid (MBA) with thiophene methanol (TM) and by the condensation reactions of thiophene carboxylic acid (TCA) with ethylene glycol (EG), glycerol (G), and pentaeritritol (PE) and characterized (reaction 1, 2).

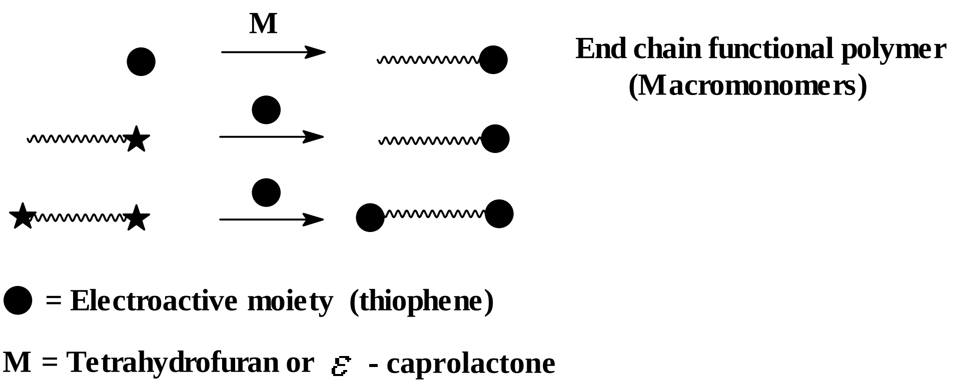


(1)



(2)

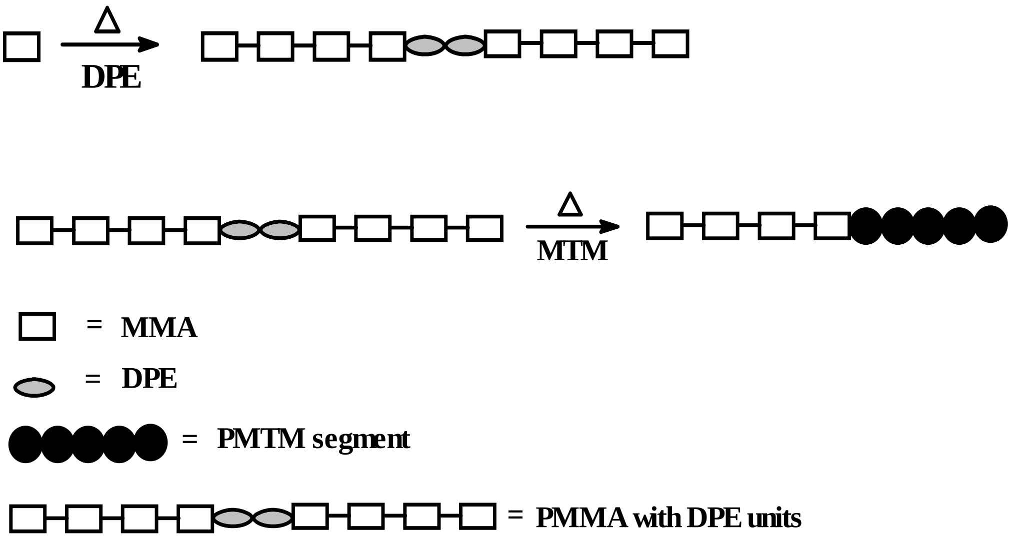
The present work also describes synthetic pathways to prepare thiophene functional macromonomers involving controlled/living polymerizations such as anionic and cationic ring opening polymerizations (ROP). The novel well-defined end(s) functional macromonomers of poly (ethylene oxide) (PEO), polytetrahydrofurane (PTHF) and poly (ε-caprolactone) (PCL) were prepared by controlled/living polymerization methods. The anionic living ROP of ethylene oxide (EO) at 40 ^{0}C initiated by 3-thiophene ethanol-potassium naphthalene salt system and terminated with methacryloyl chloride (MAC) yielded well-defined α-ω heterofunctional PEO macromonomers. Cationic living polymerization of tetrahydrofurane (THF) in bulk at 25 ^{0}C was performed using methyl triflate and trifilic anhydride as initiators. Living ends of PTHF were terminated with sodium thiophene methonate to prepare PTHF macromonomer with thiophene group at the termini. The ROP of ε-caprolactone (ε-CL) in bulk at 110 ^{o}C by means of 3-thiophene methanol in conjunction with the stannous-2-ethylhexanoate ($Sn(Oct)_2$) catalyst resulted in well-defined macromonomers of poly(ε-caprolactone) with the expected thiophene group. The GPC, IR, and ^{1}H-NMR spectroscopic studies revealed that low-polydispersity PEO, PTHF, and PCL macromonomers with desired electroactive functionality at the chain end (s) were obtained. The synthetic strategy followed for the preparation of the macromonomers is described in scheme 1.



(3)

Scheme 1. Schematic representation for preparation of macromonomers

Additionally, the preparation of block copolymers by using 1, 1-diphenylethene (DPE) as molecular weight regulator was reported. Previously, it was presented that if small amounts of DPE were added to the polymerization system, many radical polymerizations could be controlled. By heating a preformed polymer containing DPE units in the presence of a second monomer yielded block copolymers with numerous monomers. In the first step, homopolymers of methyl methacrylate (MMA) were prepared in the presence of DPE. Polydispersities of homopolymers are slightly below 1.5. In the second step, prepolymers containing DPE units were used as free radical generators. Upon heating the polymeric radicals formed and initiated the free radical polymerization of 3-methylthienyl methacrylate (MTM). The block copolymers of MMA with MTM were obtained. The GPC spectrum of block copolymers (PMMA-*b*-PMTM) clearly showed that the prepolymers were converted into block copolymers (reactions 4, 5).

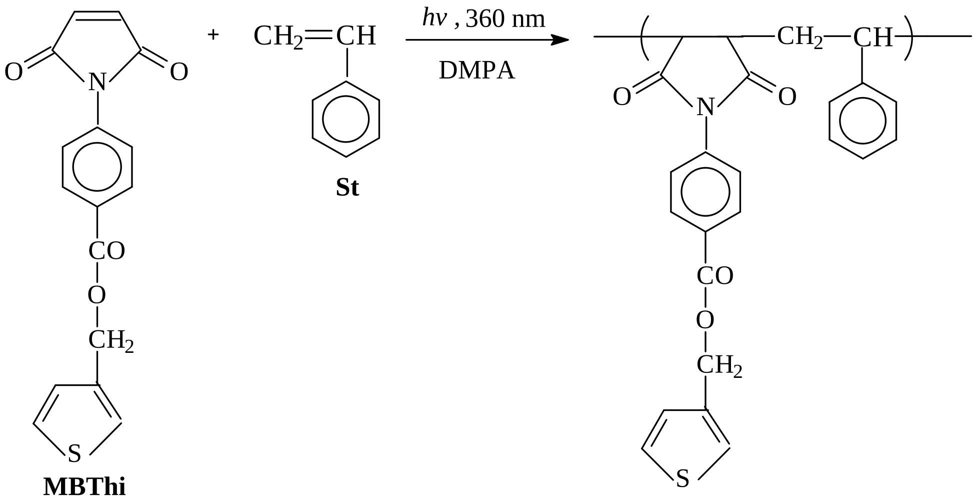


(4)

(5)

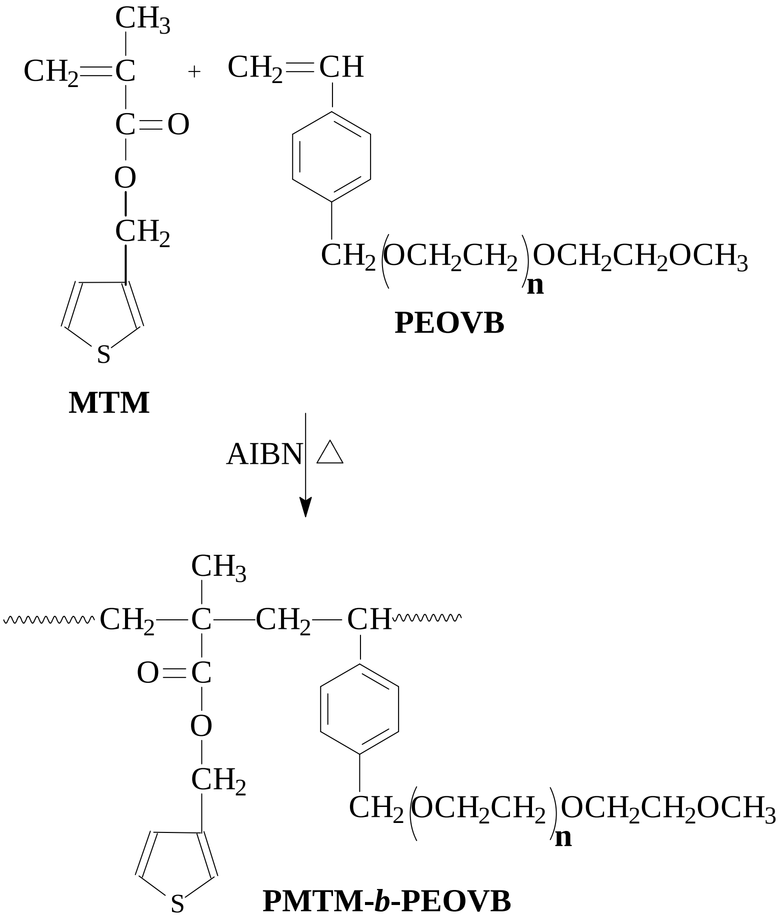
Scheme 2. Schematic representation for preparation of block copolymers via DPE method

In order to extend the use of various polymerization systems into macromolecular architecture of conducting graft copolymers, side chain thiophene functional alternating and random copolymers were prepared. Alternating copolymers of styrene (St) and N-(4-(3-thienyl methylene)-oxycarbonylphenyl) maleimide (MBThi), (PSt-*alt*-MBThi), were synthesized by photopolymerization (reaction 6). Successful alternating copolymerization has been confirmed by ^{1}H-NMR spectral measurement.



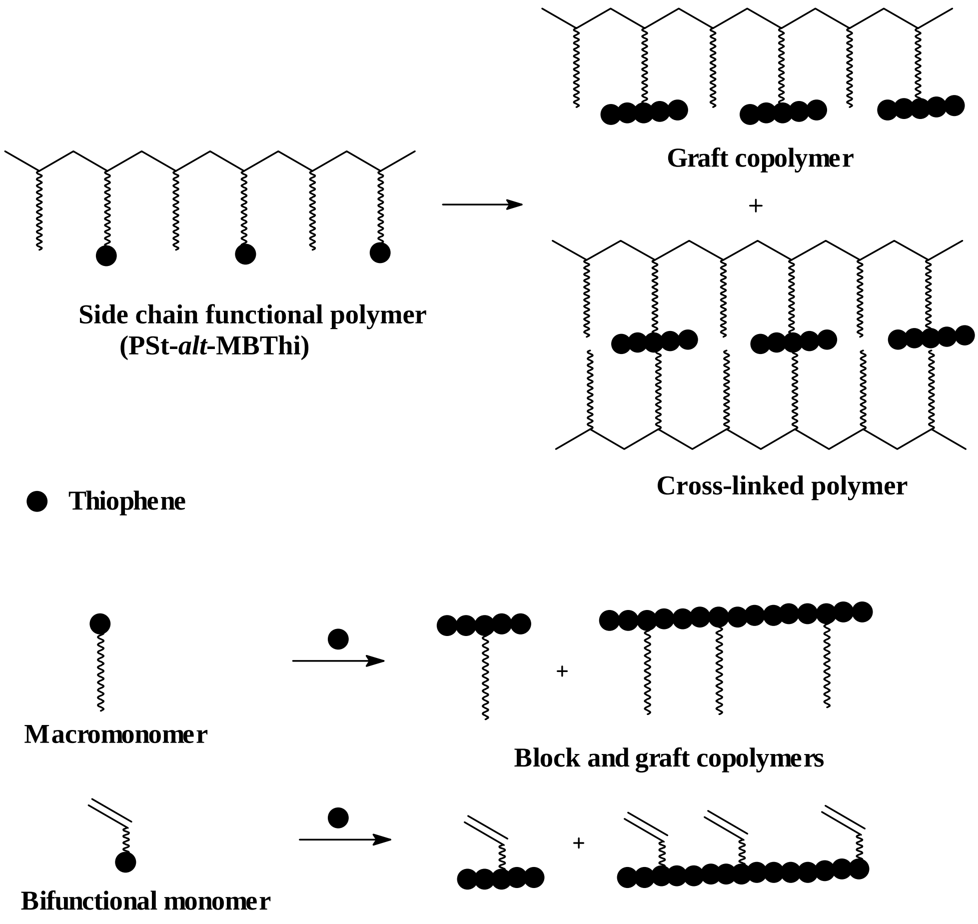
(6)

Random copolymers of MTM and *p*-vinyl benzyl terminated poly (ethylene oxide) macromonomer, (PMTM-*r*-PEOVB), were prepared by free radical polymerization with the use of AIBN as the initiator (reaction 7).



(7)

In the final part of the work, mono thienyl functional MBThi monomer was subsequently used in electropolymerization to yield conducting block and graft copolymers. As it is presented in scheme 3 after electrochemical and chemical polymerization in the presence of low molar mass monomers such pyrrole (Py) or thiophene (Th) structurally different products are obtained. While graft copolymers and crosslinked products are formed from the side-chain functional precursors, monomers (macromonomers) yield block and graft copolymers. Characterization of the resulting copolymers performed via cyclic voltammetry (CV), four-probe technique, FTIR, differential scanning calorimetry (DSC), thermal gravimetry analysis (TGA), and scanning electron microscopy (SEM) showed that electrically conducting copolymers of MBThi with Py and Th were obtained.



(8)

Scheme 3. Schematic representation for preparation of conducting blocks and graft copolymers

İLETKEN BLOK VE AŞI KOPOLİMERLERİN SENTEZİNDE KULLANILAN ELEKTROAKTİF ARA MADDELER

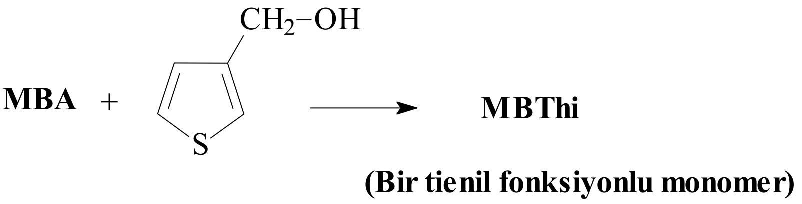
ÖZET

Şarz edilebilen piller, membranlar, optik göstergeler ve elektro kromik aletler gibi çok geniş bir alandaki uygulamalarından dolayı elektriği ileten polimerler gittikçe büyüyen bir araştırma konusu olmuştur. İletken polimerler, polimerlerin mekanik ve kimyasal özellikleri ile metal ve yarı metallerin elektronik özelliklerini kapsadığından sentetik metaller olarak da adlandırırlar. Politiyofen iletken polimerlerin önemli bir türüdür. Ayrıca, poliasetilen, polipirol, polianilin, polifenilen, polikarbazol, polikinolin ve polifitalosiyen iletken polimerlerden bazılarıdır.

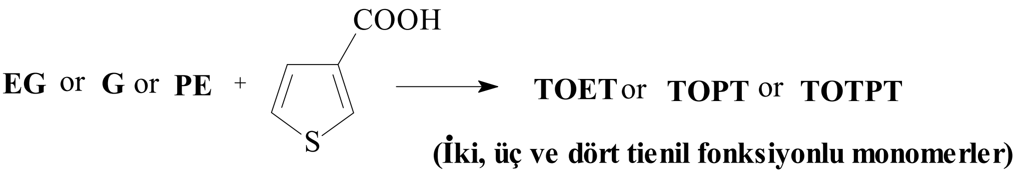
Makromonomer kavramı reaktif oligomer veya polimerler için kullanılır. Genellikle bir makromonomer, zincir ucunda veya uçlarında polimerizasyon reaksiyonlarının başlatılmasını sağlayan fonksiyonel grup içeren makromolekülü ifade etmektedir. Makromonomerler, klasik monomerlerle aşı kopolimer oluşturabilir. Makromonomerin polimer zincir yapısı aşı kopolimerin özelliklerini etkilerken, uç grup da polimerizasyonda reaktiviteyi kontrol eder. Zincir uçlarında bir veya iki elektroaktif grup içeren makromonomerler genellikle fonksiyonel başlatıcılarla veya yaşayan zincirlerin sonlandırılması ile hazırlanırlar.

Bu çalışmada, tiyofen grupu içeren monomerik ve polimerik reaktif ara maddelerin sentezi ve bu ara madddelerin tiofen grubu ile elektropolimerizasyonda kullanılabilme olasılığı incelenmiştir.

Bu amaçla, bir, iki, üç ve dört tienil fonksiyonuna sahip monomerler, N-(4-(3-tienil metilen)-oksikarbonilfenil)maleimid (MBThi), 2-[(3-tienilkarbonil) oksi] etil 3-tiyofen karboksilat (TOET), 2, 3-bis [(3-tienilkarbonil) oksi] propil 3-tiyofen karboksilat (TOPT), 3-[(3-tienilkarbonil) oksi]-2, 2-bis {[(3-tienilkarbonil) oksi]} propil 3-tiyofen karboksilat (TOTPT), sırasıyla 4-maleimidbenzoik asidin (MBA) tiyofen metanol (TM) ve tiyofen karboksilik asidin (TCA) etilen glikol (EG), gliserol (G) ve pentaeritritol (PE) kondesyasyon reaksiyonlari ile sentez edildi ve karakterizasyonu yapıldı (tepkime 1, 2).

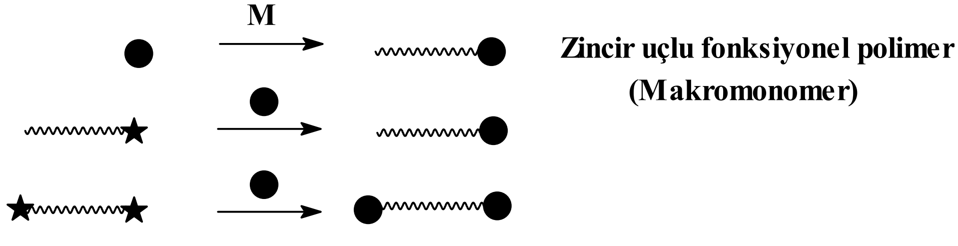


(1)



(2)

Ayrıca bu çalışmada, kontrollü/yaşayan polimerizasyon sistemi olan Anyonik ve Katyonik Halka Açılması polimerizasyonu (ROP) yöntemi ile zincir ucunda tiyofen fonksiyonel grubu içeren makromonomerlerin hazırlanışı incelenmiştir. Zincir uçlarında tiyofen grubu bulunan poli(etilen oksit) (PEO), politetrahidrofuran (PTHF) ve poli(ϵ-kaprolakton) (PCL) makromonomerler kontrollü/yaşayan polimerizasyon metodu ile hazırlandı. Etilen oksidin (EO) Anyonik Halka Açılması polimerizasyonu, 40 ^{0}C’ de 3-tiyofen etanol-potasyum naftalin tuz sistemi ile başlatıldı ve metakriloil klorür ile sonlandırılarak α-ω heterofonksiyonel PEO makromonomerler elde edildi. Tetrahidrofuranın (THF) katyonik yaşayan polimerizasyonu, 25 ^{0}C de ve çözücüsüz ortamda trifilik anhidrür ve metil triflat başlatıcıları kullanılarak gerçekleştirildi. Yaşayan PTHF zincirleri sodyum tiyofen metanoat tuzu ile sonlandırılarak uçlarında tiyofen grubu bulunan PTHF makromonomerleri sentezlendi. Є-kaprolakton’un Halka Açılması polimerizasyonu ise 3-tiyofen metanol başlatıcısı ve kalay oktoat, Sn(Oct)$_2$, katalizörü varlığında çözücüsüz ortamda, 110 ^{0}C’de gerçekleştirildi. Dar molekül ağırlığı dağılımına sahip ve elekroaktif grup içeren PEO, PTHF ve PCL polimerlerinin karekterizasyonu GPC, IR ve ^{1}H-NMR spektroskopik yöntemler ile yapıldı. Makromonomerlerin sentetik olarak hazırlanışı şekil 1’de gösterilmiştir.



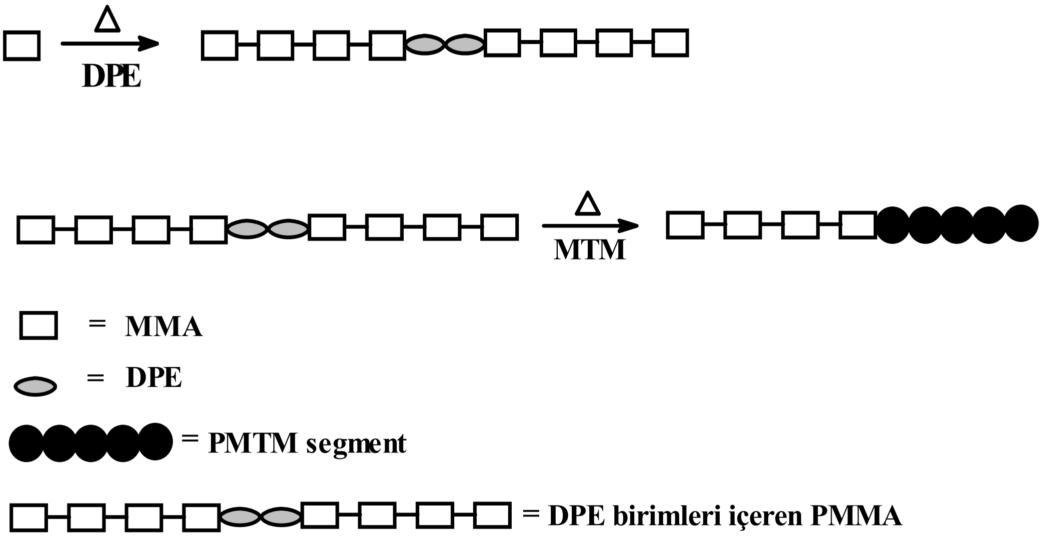
(3)

● = Elektroaktif grup (tiyofen)

M = Tedrahidrofuran veya ε-kaprolakton

Şekil 1. Makromonomerlerin hazırlanışının şematik olarak gösterimi

İlave olarak, molekül ağırlığı düzenleyici etkisi olan 1,1-difenil etilen (DPE) kullanılarak blok kopolimer hazırlanışı incelenmiştir. Çok az bir miktar DPE polimerizasyon sistemine ilave edildiğinde, bir çok radikal polimerizasyon sisteminin kontrol edilebilineceği önceden rapor edilmiştir. DPE birimleri bulunan önpolimer, ikinci bir monomer varlığında ısıtıldığında blok kopolimerlere dönüştüğü görülmüştür. İlk aşamada, DPE varlığında metil metakrilatın (MMA) homopolimerleri hazırlandı (tepkime 4). Hazırlanan homopolimerlerin molekül ağırlığı dağılımı 1.5'in biraz altında olduğu tesbit edildi. İkinci aşamada ise, DPE birimleri içeren önpolimer (PMMA) serbest radikal kaynağı olarak kullanıldı. Isıtma ile oluşan polimerik radikaller, 3-metiltienil metakrilat (MTM) monomerinin serbest radikal polimerizasyonunu başlattı ve böylece MMA ve MTM monomerlerinden oluşan blok kopolimerler elde edildi (tepkime 5). GPC ölçümleri ile önpolimerlerin (PMMA) blok kopolimerlere (PMMA-*b*-PMTM) dönüştüğü açıkça görüldü. Blok kopolimerlerin DPE metodu ile hazırlanışı şekil 2' de verilmiştir.

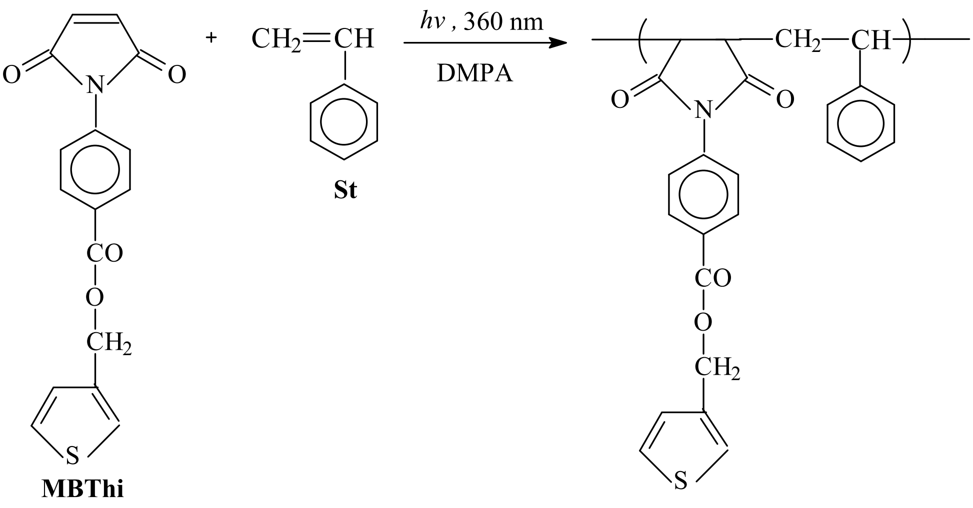


(4)

(5)

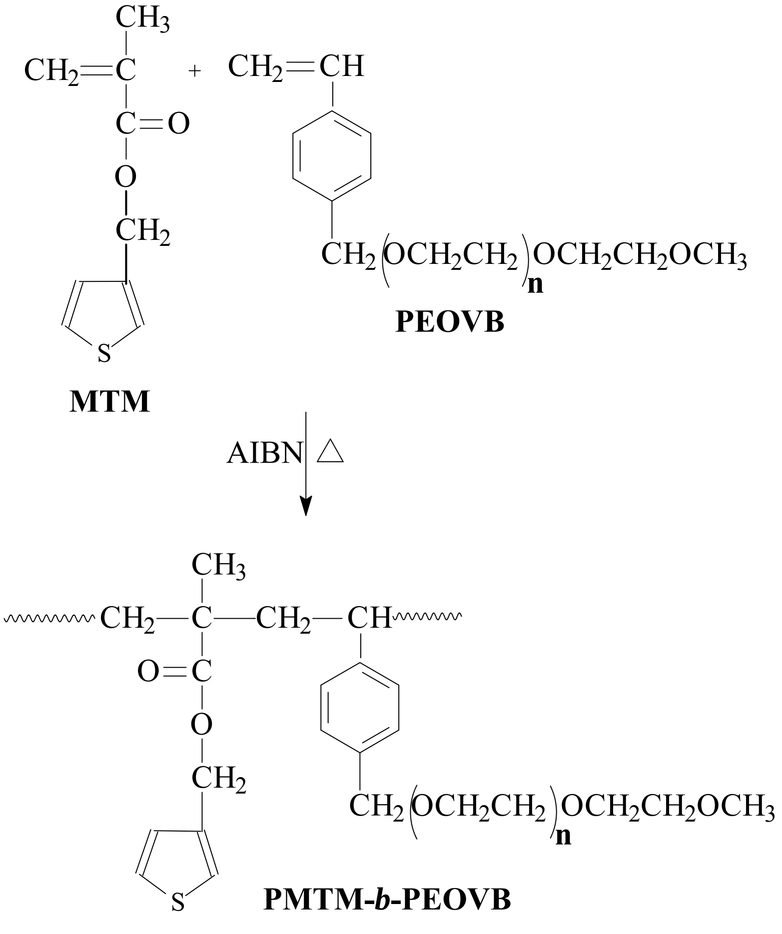
Şekil 2. Blok kopolimerlerin DPE metodu ile hazırlanışının şematik olarak gösterimi

İletken aşı kopolimerlerin makromoleküler mimarisinde kullanımını genişletmek için yan zincirde tiyofen grubu içeren alternatif ve rastgele kopolimerler hazırlandı. Sitiren (St) ve N-(4-(3-tienil metilen)-oksikarbonilfenil)maleimid (MBThi) monomerlerinden oluşan alternatif kopolimerler (PSt-*alt*-MBThi) fotopolimerizasyon yöntemi ile sentezlendi (tepkime 6). Başarılı alternatif kopolimerizasyon ^{1}H-NMR ölçümü ile doğrulandı.



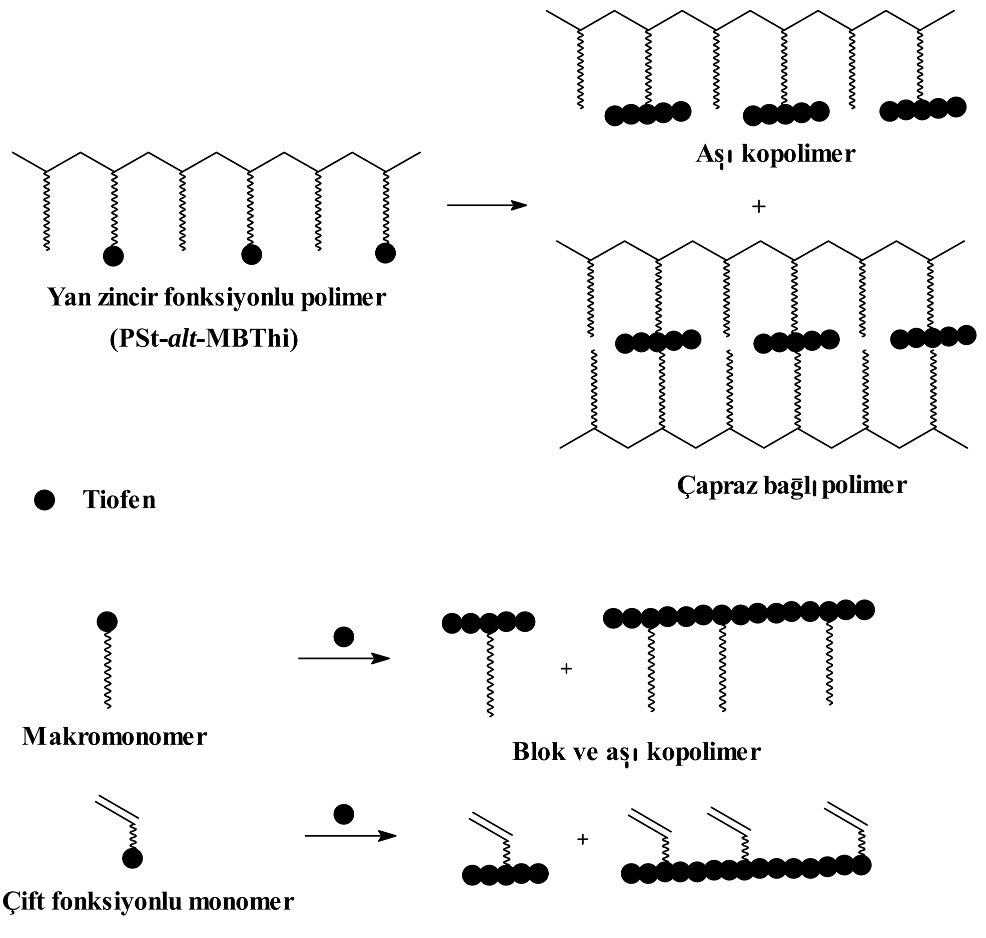
(6)

MTM monomeri ile *p*-vinil benzil sonlu poli(etilen oksit) (PEOVB) makromonomerlerinden oluşan rastgele kopolimerler (PMTM-*r*-PEOVB) ise AIBN başlatıcı varlığında serbest radikal polimerizasyonu yöntemi ile sentezlendi (tepkime 7).



(7)

Çalışmanın son kısmında, tek tienil fonksiyonlu MBThi monomeri elektropolimerizasyonda kullanılarak iletken blok kopolimerler hazırlandı. Şekil 3’ de görüldüğü gibi tiyofen (Th) ve pirol (Py) gibi hafif molar ağırlıklı monomer varlığında, elekrokimyasal ve kimyasal polimerizasyon yöntemleri ile farklı yapılı ürünler elde edilir. Aşı kopolimerler ve çapraz-bağlı ürünler yan-zincir fonksiyonlu polimerlerden meydana gelirken, monomerler (makromonomerler) blok veya aşı kopolimerler oluşumuna sebebiyet verirler. CV, FTIR, DSC, TGA ve SEM kullanılarak karakterize edilen kopolimerlerin iletken olduğu gözlendi.



(8)

Şekil 3. İletken blok ve aşı kopolimerlerin hazırlanışının şematik olarak gösterimi

1. INTRODUCTION

The properties of organic polymers and the electronic properties of semiconductors can be combined in conducting polymers. Recently, electrically conducting polymers such as polypyrrole and polythiophene have become an extremely rapidly growing field [1] due to their potential use in many applications such as light emiting diodes [2], batteries [3], electrochromic devices [4], sensors [5], electromagnetic shielding [6], and corrosion inhibition [7].

However, all unsubstituted organic conducting polymers are insoluble and infusible because of their rigid π-conjugated backbone and strong interactions. Imparting new chemical and phsyical properties to conducting polymers is achievable by the addition of an appropriate functional group to a conventioanal polymer. Many functional groups having chemical reactivity for polymerizations including cationic, anionic, radical and ring-opening polymerizations have been incorporated to polymer chains and their utilization in graft copolymerization have been studied in detail [8]. The most commonly faced problem in conducting polymers is the poor mechanical properties, which create processing problems. Various methods, such as introduction of alkyl groups into the main chain, synthesis of soluble precursors, and preparation of conducting polymer composites, blends, and coplymers, can be used to improve mechanical and physical properties [9-10].

Polymers with end-functional groups have attracted considerable attention as prepolymers (macromonomers) for synthesizing block and graft copolymers, star polymers, and polymer networks. Macromonomers are usually referred to reactive oligomers or polymers in which a polymerizable functional group is incorporated to the chain end(s). Macromonomers can be synthesized via various methods including anionic, cationic, radical polymerizations, and chemical modifications of polymer ends [8]. They can conveniently be copolymerized with conventional monomers to yield graft copolymers with well defined structures. Structure of the polymer chain of the macromonomer affects the properties of the graft copolymer while the end group controls the reactivity in polymerization. Mechanical and physical properties of conducting polymers can also be improved by the macromonomer technique. In this technique, polymers containing precursors of the conducting polymer (e.g., pyrrole and thiophene group(s)), can be subjected to electropolymerization to yield block and graft copolymers.

Macromonomers containing pyrrole moiety were prepared in a living manner which allowed a better control of the molecular weights, polydispersities, and end functionalities. For example, living cationic polymerization of tetrahydrofuran terminated with potassium salt of pyrrole [11-13]. Mono- and bi-functional macromonomers, depending on the functionality of the initiator used in the cationic step, obtained were not electroactive themselves but readily transformed into block copolymers upon electropolymerization via single- and two-step procedures. As in the case of polypyrrole, thiophene moiety must be incorporated to polymer chains to obtain conducting block and graft copolymers based on polythiophene. Macromonomers and side-chain thiophene functionalized polymers hitherto prepared via various polymerization techniques [14-21].

Conducting polymers can be synthesized by either chemical methods or electrochemical polymerization methods. Electropolymerization technique allows the preparation of conducting polymers directly on the electrode surface with a controlled film thickness. However, it suffers from the poor mechanical and physical properties, and also interfacial adhesion of the conducting polymer to the electrode. The latter problem can be overcomed by two step processes based on the chemisorption of the preformed conducting polymer or its precursor and chemical grafting of electroactive acrylate type monomer and subsequent electrografting through pyrrole and thiophene groups incorporated [22-27].

Polythiophenes (PThs) have received a great deal of attention due to their electrical properties, environmental stability in doped and undoped states, non-linear optical properties, and highly reversible redox switching [28]. Thiophene possesses a rich synthetic flexibility, allowing for the use of several polymerization methods and the incorporation of various side chain functionalities. Thus, it is of no great surprise that PThs have become the most widely studied of all conjugated polyheterocycles [29]. The polymerization of thiophene, to yield intractable polythiophene, was first carried out in a controlled manner in the early 1980s [30-33]. Even in such an unyielding form, this polymer displayed many promising optical and electronic properties. Unfortunately, its lack of processibility precluded further exploration of these attractive attributes. However, incorporation of substituents onto 3-position of polythiophenes has been shown to afford polymers with attractive properties such as solubility with melt processability, good electrical conductivity, and optical tunability.

This study describes the preparation of novel **a)** monomers with thienyl functional groups **b)** macromonomers (PEO, PTHF, and PCL) possessing mono and bifunctional electroactive groups via controlled/living polymerization methods namely, ROP, **c)** side-chain thiophene functionalized polymers. The study also reports the possibility of their use in electropolymerization through thiophene groups.

2. THEORETICAL PART

2.1 Free Radical Polymerization (FRP)

The study of polymer science begins with understanding the methods in which these materials are synthesized. Polymer synthesis is a complex procedure and can take place in a variety of ways. Addition polymerization describes the method where monomers are added one by one to an active site on the growing chain. The most common type of addition polymerization is free radical polymerization (FRP) which involves the reaction of carbon-carbon double bonds with an unpaired electron on a species that is called a radical. A free radical is simply a molecule with an unpaired electron. FRP is used to make polymers from vinyl monomers, that is, from small molecules containing carbon-carbon double bonds. Polymers made by free radical polymerization include polystyrene, poly (methyl methacrylate), poly (vinyl acetate) and branched polyethylene.

FRP gains much attention in the field of industrial polymer synthesis due to its simplicity, compatibility and convenience. Polymers prepared by free-radical means are used in the manufacture of numerous products, such as fabrics, surface coatings and paints, plastics, packaging, spectacle and contact lenses and surgical devices. It has distinct advantages over other polymerization methods, such as tolerance to trace impurities, less stringent conditions, and also to be able to polymerize a wide range of monomers.

2.1.1 Initiators

Substances, which generate radicals when heated or irradiated or by any other means may initiate free radical polymerization under certain conditions. The free radical initiators can be classified into three basic groups as thermal, redox and photoinitiators. More commonly, the initiators are azo-compounds, peroxides or benzoin derivatives.

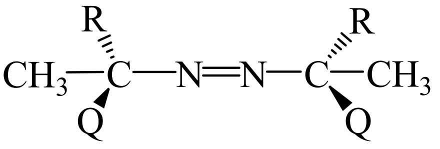
2.1.1.1 Thermal Initiators (Intramolecular Bond Cleavage)

Azo Initiators

There are two general classes of azo–compounds namely, the dialkyldiazenes and the dialkyl hyponitries (2.1)

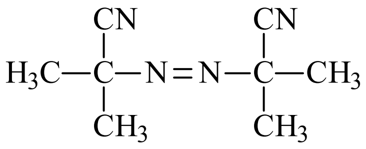
$$\underset{\text{dialkydiazenes}}{R{-}N{=}N{-}R'} \qquad \underset{\text{dialkyl hyponitries}}{R{-}O{-}N{=}N{-}O{-}R'} \qquad (2.1)$$

Most of the compounds are represented by the formula where R is an alkyl and Q is a simple carboxylic acid residue or a derivative (nitrile, ester) (2.2).



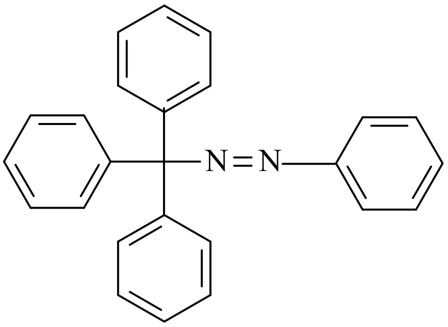
(2.2)

2, 2'–azobis (2-methylpropanenitrile) (better known as azobis (isobutyronitrile) or AIBN) is the most widely used initiator. Also, triphenylmethyl azobenzene is one of the unsymmetrical dialkyldizenes (2.3).



$$H_3C{-}\overset{\overset{CN}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}N{=}N{-}\overset{\overset{CN}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}CH_3$$

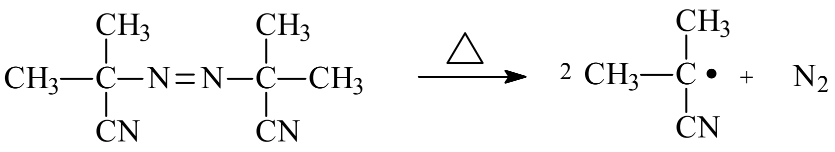
AIBN



triphenylmethyl azobenzene

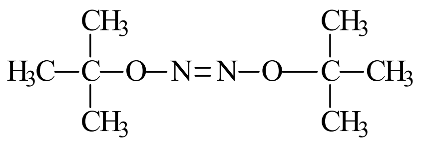
(2.3)

Thermal decomposition of AIBN and its analogues is generally considered to produce cyanoisopropyl radicals (or analogues) according to the following reaction (2.4).



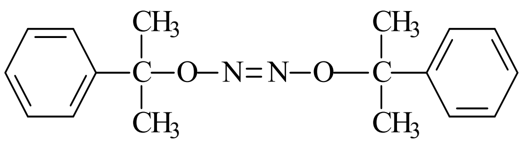
$$CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}{-}N{=}N{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}{-}CH_3 \xrightarrow{\triangle} 2\ CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CN}{|}}{C}}\bullet + N_2 \qquad (2.4)$$

The hyponitrites, derivatives of hyponitrous acid (HO–N=N–OH), are low temperature sources of alkoxy or acyloxy radicals. Di–t–butyl and dicumyl hyponitrites have proved convenient sources of t–butoxy and cumyloxy radicals respectively in the laboratory (2.5).



$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-O-N=N-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

di-t-butyl- hyponitrite

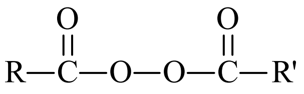


dicumyl hyponitrite

(2.5)

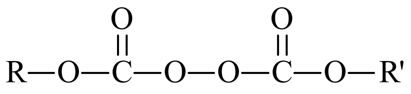
Peroxy Compounds

Many types of peroxides (R – O – O – R) are known. Those in common use as initiators include: diacyl peroxides, peroxydicarbonates, peresters, dislkyl peroxides, hydroperoxides, and inorganicperoxides (e.g. persulfate) (2.6) [34-39].



$$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R'$$

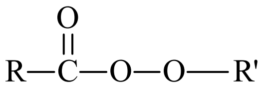
diacyl peroxides



$$R-O-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-O-R'$$

peroxydicarbonates

(2.6)



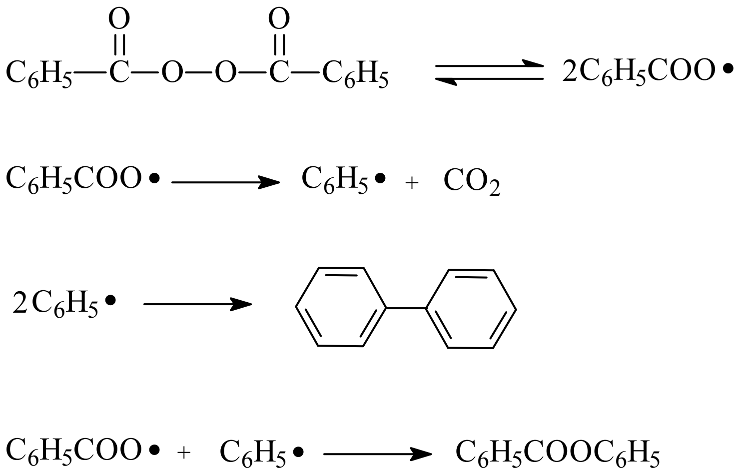
$$R-\overset{O}{\overset{\|}{C}}-O-O-R'$$

peresters

$R-O-O-R'$

dislkyl peroxides

Benzoyl peroxide is a well-established initiator of polymerization. As with other peroxides, the primary step in the thermal decomposition is scission of the $-O-O-$ bond to give two acyloxy radicals. A number of secondary processes may follow; in addition to reacting with monomer, benzoyloxy radicals may recombine or undergo β-scission to phenyl radicals and carbon dioxide. Further, recombination reactions giving biphenyl and phenyl benzoate may then occur (2.7).



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 \rightleftharpoons 2C_6H_5COO\bullet$$

$$C_6H_5COO\bullet \longrightarrow C_6H_5\bullet + CO_2$$

$$2C_6H_5\bullet \longrightarrow$$

$$C_6H_5COO\bullet + C_6H_5\bullet \longrightarrow C_6H_5COOC_6H_5$$

(2.7)

2.1.1.2 Redox Initiators

Radicals produced by many oxidation-reduction reactions can be used to initiate polymerization. This type of initiation is referred as *redox initiation, redox catalysis,* or *redox activation.* A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular redox system, including initiation at moderate temperatures of 0-50 ^{0}C and even lower. This allows a greater freedom of choice of the polymerization temperature that is possible with the thermal homolysis of initiators [40].

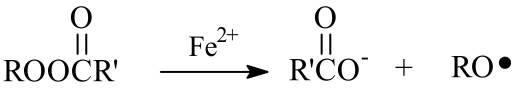
Peroxides in the presence of a reducing agent are a common source of radicals, for example, the reaction of hydrogen peroxide with ferrous ion (2.8)

$$H_2O_2 + Fe^{2+} \longrightarrow HO^- + HO\bullet + Fe^{3+} \qquad (2.8)$$

Ferrous ion also induces the decomposition of a variety of other compounds including various types of organic peroxides (2.9).

$$\mathrm{ROOR} \xrightarrow{Fe^{2+}} \mathrm{RO^-} + \mathrm{RO\bullet}$$

$$\mathrm{ROOH} \xrightarrow{Fe^{2+}} \mathrm{HO^-} + \mathrm{RO\bullet} \qquad (2.9)$$



$$\mathrm{ROO\overset{\overset{O}{||}}{C}R'} \xrightarrow{Fe^{2+}} \mathrm{R'\overset{\overset{O}{||}}{C}O^-} + \mathrm{RO\bullet}$$

Also, Cr^{2+}, V^{2+}, Ti^{3+}, Co^{2+}, and Cu^+ can substitute ferrous ion in many instances.

The combination of a variety of inorganic reductants and inorganic oxidants initiates radical polymerization (2.10), for example,

$$\mathrm{SO_3^-{-}O{-}O{-}SO_3^-} + \mathrm{Fe_2^+} \longrightarrow \mathrm{Fe^{3+}} + \mathrm{SO_4^{2-}} + \mathrm{SO_4^-\bullet} \qquad (2.10)$$

$$\mathrm{SO_3^-{-}O{-}O{-}SO_3^-} + \mathrm{S_2O_3^{2-}} \longrightarrow \mathrm{SO_4^{2-}} + \mathrm{SO_4^-\bullet} + \mathrm{S_2O_3^-\bullet}$$

Other redox systems include reductants such as HSO_3^-, SO_3^{2-}, $S_2O_3^{2-}$, and $S_2O_5^{2-}$ in combination with oxidants such as Ag^+, Cu^{2+}, Fe^{3+}, ClO_3^-, and H_2O_2.

Organic-inorganic redox pairs initiate polymerization, usually but not always by oxidation of the organic component, for example, the oxidation of an alcohol by Ce^{4+} or by V^{5+}, Cr^{6+}, Mn^{3+} (2.11).

$$\mathrm{RCH_2OH} + \mathrm{Ce^{4+}} \longrightarrow \mathrm{Ce^{3+}} + \mathrm{H^+} + \mathrm{R\overset{\bullet}{C}HOH} \qquad (2.11)$$

There are some initiator systems in which the monomer itself acts as one component of the redox pair. Examples are thiosulfate plus acrylamide or methacrylic acid and N,N-dimethylaniline plus methyl methacrylate.

2.1.1.3 Photoinitiators

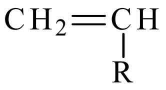
Photoinitiators for FRP fall into two classes: those which on irradiation undergo intramolecular bond cleavage with radical generation and those which form radicals when photoexcited species abstract hydrogen atoms from H-donors. Detailed information will be given in part 2.2.1.

2.1.2 Monomers Fitted for Free Radical Polymerization

Commonly monosubstituted or unsymmetrically (1,1-) disubstituted ethylenes, $CH_2=CHX$ or $CH_2=CXY$ work in free-radical polymerization whereas symmetrically disubstituted (1,2-) ethylenes don’t homopolymerize readily as a rule (2.12).

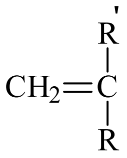
$CH_2{=}CH_2$

Unsubstituted (ethylene)
Works fine.



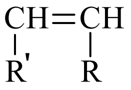
$CH_2{=}\underset{\underset{\displaystyle R}{|}}{C}H$

Monosubstituted
Works fine.



$CH_2{=}\overset{\overset{\displaystyle R'}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}$

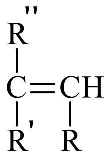
1,1-Disubstituted
Usually works.



$\underset{\underset{\displaystyle R'}{|}}{C}H{=}\underset{\underset{\displaystyle R}{|}}{C}H$

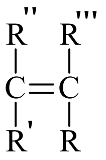
1,2-Disubstituted
Seldom works.

(2.12)



$\overset{\overset{\displaystyle R''}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}{=}\underset{\underset{\displaystyle R}{|}}{C}H$

Trisubstituted
Almost never works.

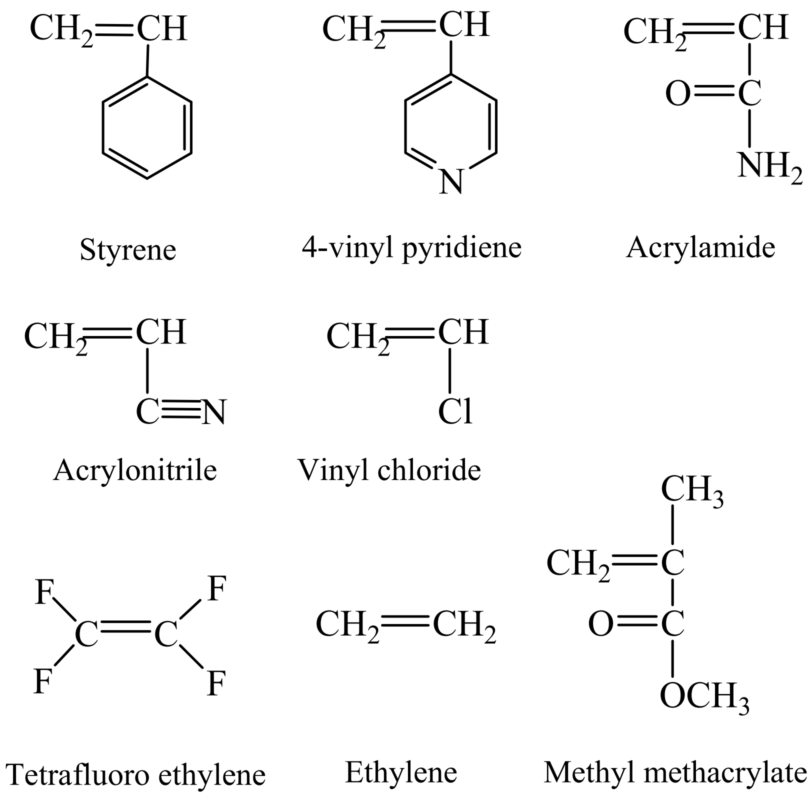


$\overset{\overset{\displaystyle R''}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}{=}\overset{\overset{\displaystyle R'''}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}$

Tetrasubstituted
Almost never works.

The only exceptions to the unreactivity of tri- and tetra-substituted vinyl monomers are those with fluorine, like tetrafluoroethylene ($CF_2{=}CF_2$). The main cause of this reactivity pattern is the steric size of the substituents.

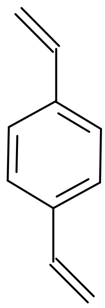
Most of vinylic, acrylic and diene monomers (2.13) can undergo free radical polymerization.



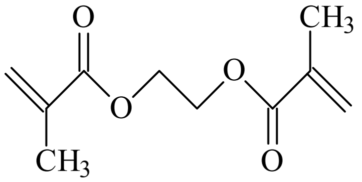
(2.13)

There are many monomers that have been developed containing more than one polymerizable vinyl group such as *p*-divinyl benzene, ethylene glycol dimethacrylate, N,N′-methylenebisacrylamide, and pentaerythritol tetraacrylate (2.14). When these groups are relatively far apart on the molecule, they react independently. Either one or both double bonds may participate in polymerization; when both react, cross-linked structures are generated and the polymer will be a thermoset, and cannot be dissolved or melted.

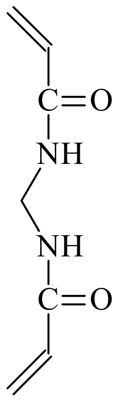
.



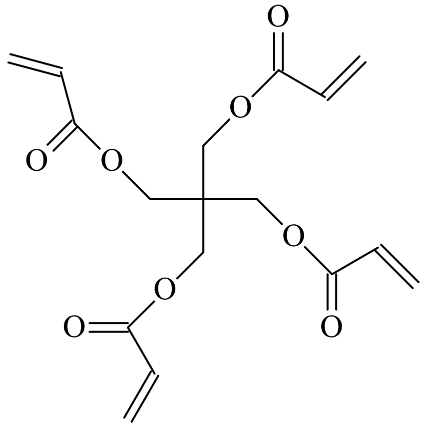
Divinylbenzene



Ethylene glycol dimethacrylate



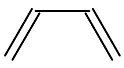
N,N'**-methylenebisacrylamide**



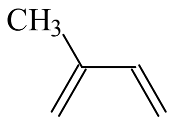
Pentaerythritol tetraacrylate

(2.14)

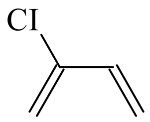
In contrast to the crosslinking monomers above, when the vinyl groups are adjacent and conjugated to each other (a "1,3-dienes"), more complicated possibilities ensue. For example, the polymerization can occur through only one of the two double bonds, leaving the other one pendant. This is known as 1,2-propagation. In the second possibility, both double bonds get involved. The repeat unit winds up with a double bond within the backbone. This mechanism is known as 1,4-propagation. Examples of dienes containing conjugated double bonds are butadiene, isoprene, and chloroprene (2.15). These important monomers may react by 1,2 or 3,4 addition, or by 1,4 addition. In the former two cases polymerization gives chains with pendant vinyl groups, whereas 1,4 addition leads to unsaturation within polymer chains. Note that the double bond within the backbone can be cis or trans. Natural rubber is mostly poly(cis-1,4-isoprene).



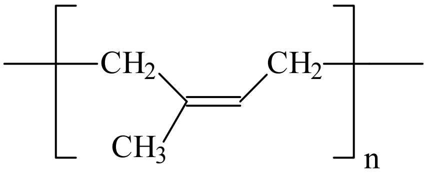
Butadiene



Isoprene



Chloroprene

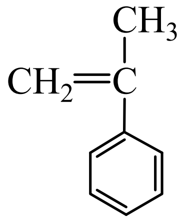


Natural Rubber

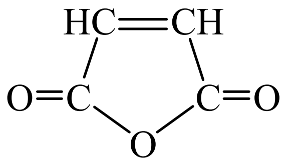
Poly(*cis*-1, 4-isoprene)

(2.15)

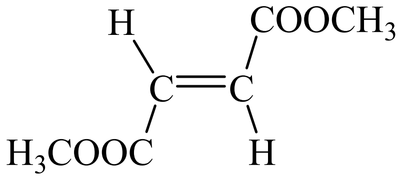
Some potential monomers do not form polymers under usual free radical polymerization conditions. Such as α-methyl styrene is involved in polymerization-depolymerization equilibrium above a ceiling temperature. Maleic anhydride and dimetyl fumarate (2.16) are symmetrically substituted ethylenes therefore; they can not be polymerized by free radical polymerization.



α-methyl styrene



maleic anhydride



dimetyl fumarate

(2.16)

2.1.3 Mechanism of Free Radical Polymerization

A typical free-radical polymerization possesses four elementary steps: initiation, propagation, termination and chain transfer [41, 42]. These steps are *completely independent.* They are separate chemical reactions with different mechanisms, kinetics, and thermodynamics.

In *initiation,* a free radical R• derived from an initiator, the "primary radical", adds to a monomer molecule to form an active center (2.17).

Initiation

$$\mathbf{I} \longrightarrow \mathbf{2R\bullet} \qquad (2.17)$$

$$\mathbf{R\bullet} + \mathbf{M} \longrightarrow \mathbf{M_1\bullet} \text{ (Growing chain)}$$

Propagation or growth reaction is just the repetitive addition of a radical to the vinyl group of the monomer, each time reproducing the reactive species at the growing chain end (2.18). Usually, it occurs in head-to-tail fashion, because the free radical formed is more stable. However, as with initiation, alternatives are possible and head-to-head, tail-to-head, and tail-to-tail modes occur, usually to minor extents.

Propagation

$$\mathbf{M_1\bullet} + \mathbf{M} \longrightarrow \mathbf{M_2\bullet} \qquad (2.18)$$

$$\mathbf{M_n\bullet} + \mathbf{M} \longrightarrow \mathbf{M_{n+1}^{\bullet}}$$

In *termination* of free radical polymerization, secondary reactions stop propagation by the destruction of propagating radicals. The two most common termination reactions are radical combination and disproportionation (2.19).

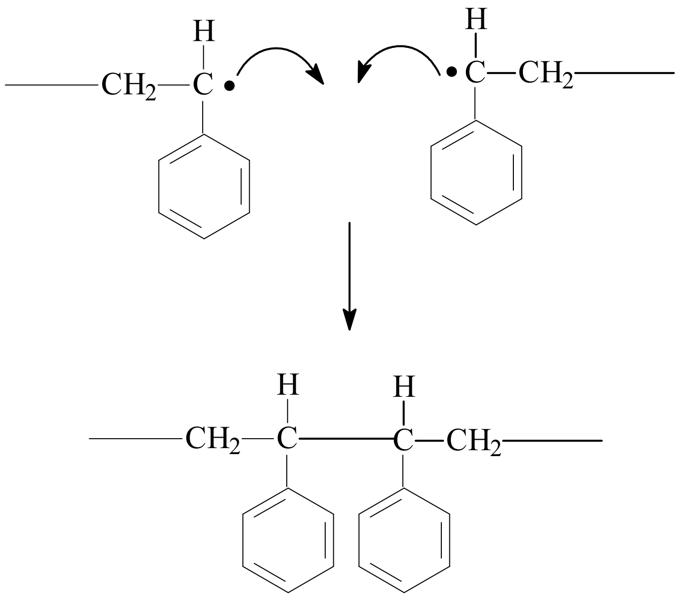
Termination

$$\mathbf{M_m^{\bullet}} + \mathbf{M_n^{\bullet}} \longrightarrow \mathbf{M_{m+n}} \text{ (Termination by combination)}$$

$$(2.19)$$

$$\mathbf{M_m^{\bullet}} + \mathbf{M_n\bullet} \longrightarrow \mathbf{M_m} + \mathbf{M_n} \text{ (Termination by disproportionation)}$$

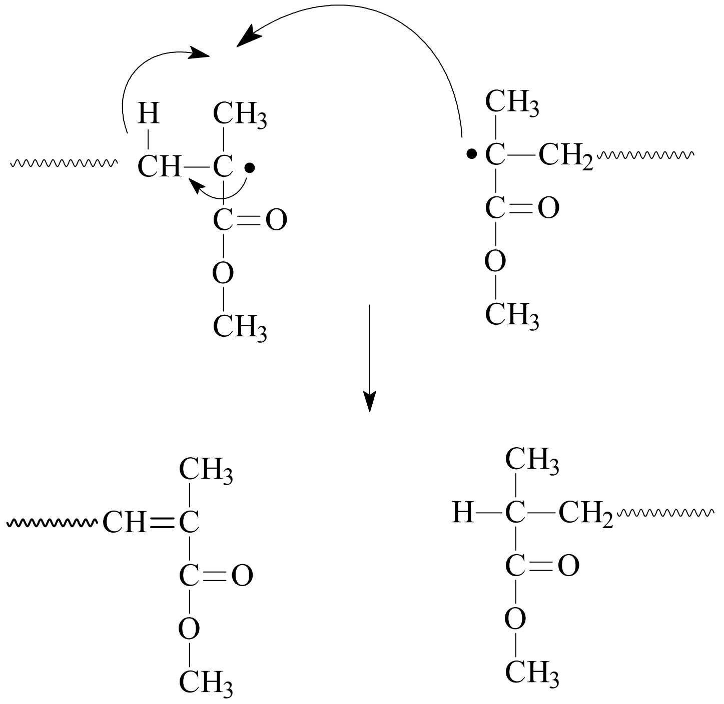
In termination by combination, two polymeric radicals couple and form a new polymer chain with higher molecular weight.



(2.20)

Creates one head to head link. Doubles MW

As for disproportionation, one chain reacts with the penultimate (second-to-last) carbon on the backbone by abstracting a hydrogen atom. In other words, the free radical removes a hydrogen atom with one of the two electrons in its former bond to produce a new (single) bond. Thus, the first chain is deactivated. The second chain is left with the other electron formerly part of the bond to the hydrogen (now removed), and its original propagating radical. These two electrons combine with the single bond to the last carbon atom on the chain to form a double bond. This double bond is rather crowded in most cases compared to the monomer, so it is essentially unreactive to radicals subsequently. In this way, the second chain is terminated as well. Because only a hydrogen atom is exchanged, the MW of the two chains is hardly affected by disproportionation. Each chain winds up with one original initiator fragment. The relative proportion of termination by the two mechanisms varies from monomer to monomer, and is also dependent on the solvent and temperature. For example, some polymers like polystyrene (2.20) terminate nearly exclusively by combination, while others such as PMMA (2.21) mostly by disproportionation, and still others by some of both mechanisms.



(2.21)

Two cahins are terminated, but they have different end groups.
No negligible change to MW

There is another type of termination, known as chain transfer, which stops one chain (2.22) and possibly starts another (2.23). Chain transfer is a kind of termination reaction. It differs from the "normal" termination reactions in that the growing chain radical reacts with chemical species that has an even number of electrons (that is, not another free radical, as is the case for normal termination). Atom (often hydrogen) abstraction from saturated molecules is a well-known reaction of free radicals and, as would be expected, is important in free-radical polymerization. It leads to the chain-transfer process, which brings about the cessation of growth of a propagating radical and at the same time produces a new small radical which may propagate. A great variety of species can participate in chain transfer, act as transfer agents. Chain transfer, therefore, occurs widely; it commonly involves reaction of growing chains with monomer or solvent or other additive and is well established for polymers and some initiators. Atoms other than hydrogen, notably halogens (except fluorine), may be transferred.

Chain transfer to monomer (M) or Solvent (S)

$$\mathbf{M_n\bullet + M'' \longrightarrow M_n + M''\bullet} \qquad (2.22)$$

$$\mathbf{M_n\bullet + M_n\bullet \longrightarrow M_n + S\bullet}$$

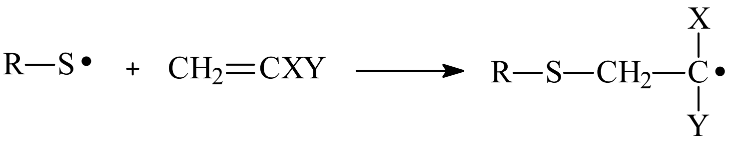
Reinitiation by transfer agent

$$\mathbf{M''\bullet + M \longrightarrow M''{-}M\bullet} \qquad (2.23)$$

$$\mathbf{S\bullet + M \longrightarrow S + M\bullet}$$

There are many forms of chain transfer in vinyl free radical polymerization. They can be transfer to polymer, transfer to monomer, transfer to initiator, and transfer to solvent or impurities. In some circumstances, it is helpful to add deliberately a chain transfer agent (CTA). This is a compound with a weak bond, capable of terminating a growing chain. Various compounds can act as chain transfer agents, but the most common ones are structures with an S-H bond, known as mercaptans or thiols (2.24). Mercaptans have the unfortunate property that the smell is really bad. For example, a trace of mercaptan is added to natural gas to give it odor.

$$R_n^\bullet + R{-}SH \longrightarrow R_n{-}H + R{-}S\bullet$$

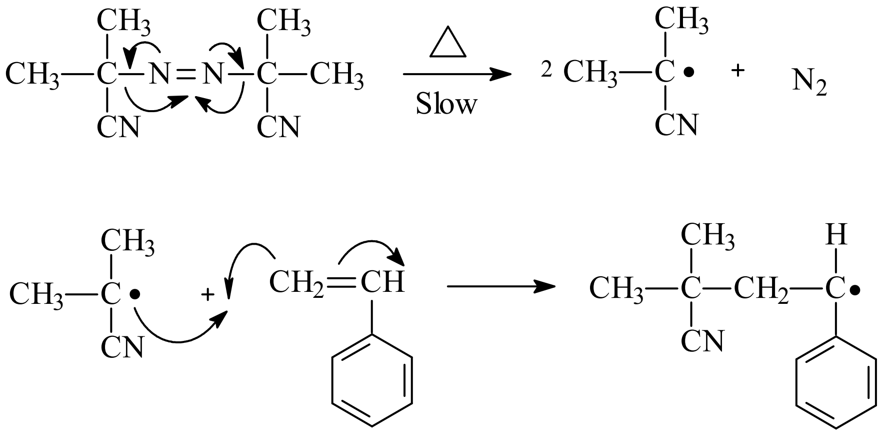


$$R{-}S\bullet + CH_2{=}CXY \longrightarrow R{-}S{-}CH_2{-}\overset{\displaystyle X}{\underset{\displaystyle Y}{C}}\bullet \qquad (2.24)$$

At the other extreme, the new free radical produced by chain transfer can be so unreative that it does not start any new chains. In this circumstance, the chain transfer agent is better described as an inhibitor, that is, a substance that stops polymerization by reacting with free radicals. Hindered phenols are among the most commonly used inhibitors. Most commercial monomers are packaged with traces of inhibitor to prevent premature polymerization during shipping and storage. The inhibitor can be removed by distillation, extraction, or chromatography. Alternatively, one can simply use extra initiator to overwhelm the inhibitor. Molecular oxygen (O_2) is a particularly strong inhibitor of almost any vinyl free radical polymerization reaction. Therefore, the reaction mixtures are thoroughly purged with inert gas such as nitrogen. Paradoxically, oxygen can also indirectly be an initiator of free radical polymerization, because it can react with some monomers or impurities to generate peroxides that are thermal initiators.

A complete example of free radical polymerization styrene initiated with AIBN:

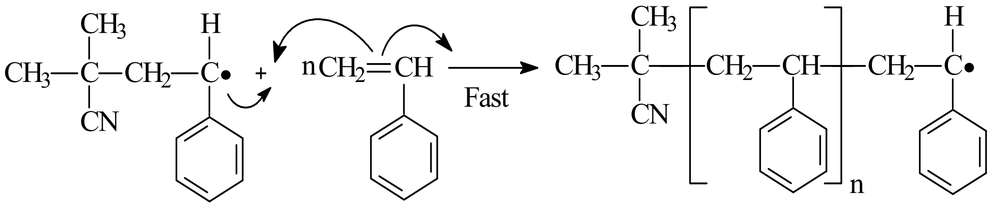
Initiation



(2.25)

Initiator breaks down smoothly to generate a low, steady-state concentration of radicals (2.25).

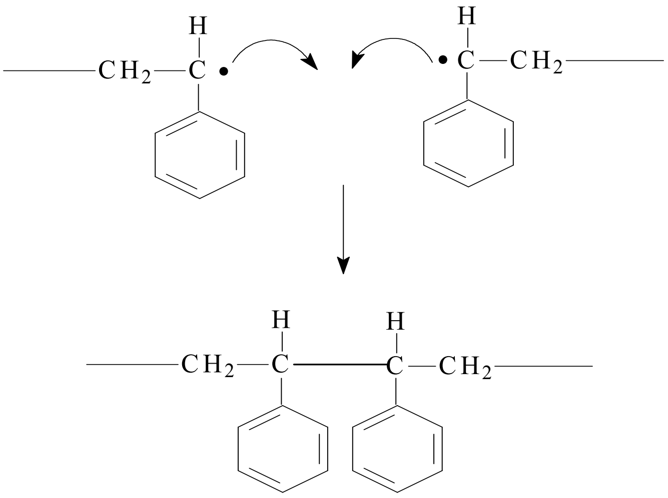
Propagation



(2.26)

Monomer adds quickly to the small number of growing chains present at any given time (2.26).

Termination by coupling



(2.27)

Termination is a *bimolecular* process, and occurs when two growing chain ends find each other (2.27).

All chain polymerizations have the steps of initiation, propagation, and termination. These three steps are completely independent, each occurring with different kinetics and chemical mechanism. One can visualize these processes by the "factory" model (Figure 2.1) [43].

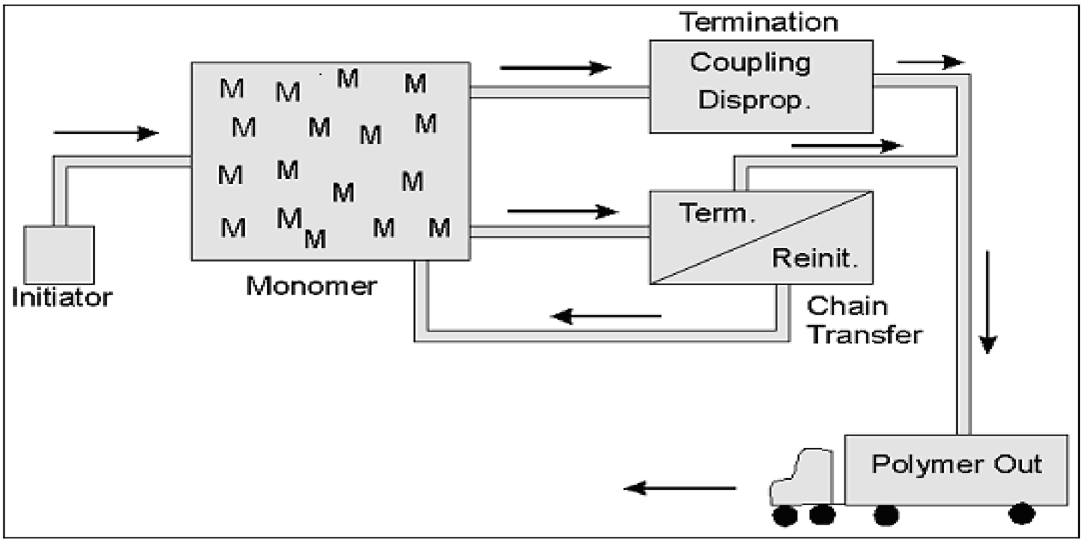


Figure 2.1. Factory model of free radical polymerization

2.2 Photoinitiated Polymerization

Radical photopolymerization of vinyl monomers played an important role in the early development of polymerization. One of the first procedures for polymerizing vinyl monomers was the exposure of monomer to sunlight. Blyth and Hoffman [44] reported on the polymerization of styrene by sunlight more than 150 years ago. If polymerization is initiated by means of light and both the initiating species and growing chain ends are radicals, it is called *radical* photopolymerization. In the more general sense, photoinitiated polymerization means the increase of molecular weight caused by light and includes the photocrosslinking of preexisting macromolecules. Although vinyl polymerization can be initiated by ionic species as well as by free radicals, almost all examples of photoinitiated polymerization are of a free radical character.

It has to be pointed out that the *absorption* of incident light by one or several components of the polymerization mixture is the crucial prerequisite in the initiation step. If a photosensitive compound absorbs the photon energy directly it undergoes a homolytic bond rupture forming radicals, which may initiate the polymerization. However, the photon energy is absorbed by a compound that itself is not prone to radical formation in some cases. These so called sensitizers transfer their electronic excitation energy to reactive constituents of the polymerization mixture, which finally generate radicals. The radicals generated react with intact vinyl monomer starting a chain polymerization. Under favorable conditions, a single free radical can initiate the polymerization of a thousand molecules. The spatial distribution of initiating species may be arranged in any desired manner.

Comparing the thermally initiated polymerizations, photopolymerization can be carried out at room temperature. This is a basic advantage for both classical polymerization of monofunctional monomers and modern curing applications. Also photopolymerization of monofunctional monomers takes place without side reactions such as chain transfer whereas the probability of chain transfer is high which brings about a high amount of branched macromolecules in thermal polymerization. Therefore, photopolymerization can be used successfully to obtain low-energy stereospecific polymeric species, namely of syndiotactic configuration. Another important use refers to monomers with low ceiling temperature. They can only be polymerized at moderate temperatures, otherwise depolymerization dominates over polymerization. By means of photopolymerization these monomers are often easily polymerizable. Furthermore, biochemical applications, such as immobilization of enzymes by polymerization, also usually need low temperatures.

Light induced free radical polymerization has enormous commercial use. Techniques related to curing of coatings on wood, metal and paper, adhesives, printing inks and photoresists are based on photoinitiated radical vinyl polymerization.

Photocurable formulations are mostly free of additional organic solvents; the monomer, which serves as reactive diluent, is converted to solid, environmentally safe resin without any air pollution. UV curing is often a very fast process, taking place as pointed out above without heating. If the polymerization mixture absorbs solar light and the efficiency of radical formation is high, photocuring can be performed with no light source but sun light. These features make photopolymerization an ecologically friendly and economical technology that has high potential for further development.

2.2.1 Photoinitiated Free Radical Polymerization

Photoinitiated free radical polymerization has four distinct steps:

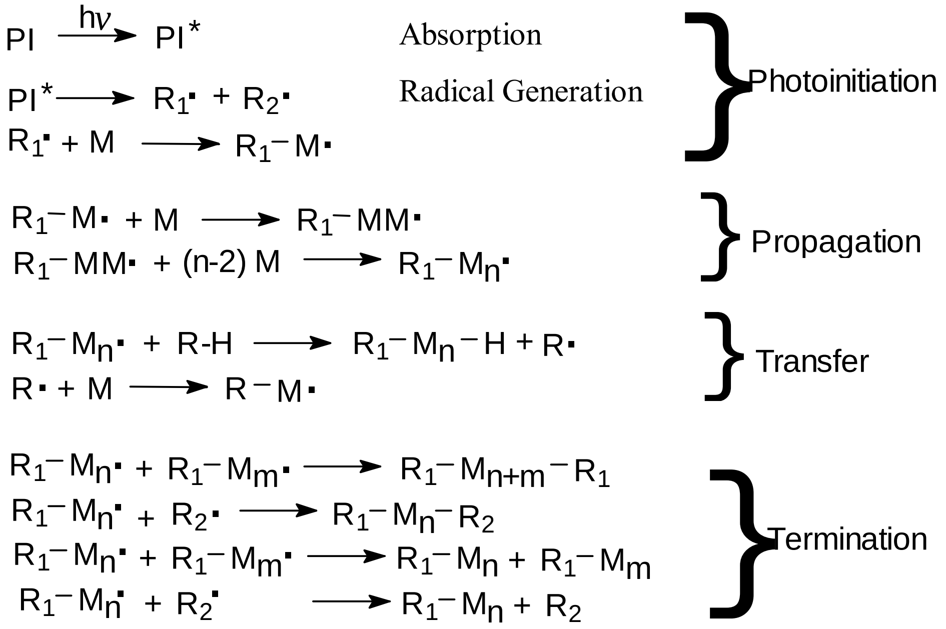
***Photoinitiation*:** It is based on absorption of light by a photosensitive compound or transfer of electronic excitation energy from a light absorbing sensitizer to the photosensitive compound. Homolytic bond rupture results in the formation of a radical that reacts with one monomer unit. This step is the only difference between photopolymerization and thermal radical polymerization.

***Propagation*:** It is repetitive addition of monomer units to the chain radical producing the polymer backbone.

***Chain transfer*:** It is termination of growing chains via hydrogen abstraction from various species like solvent and accompanying production of a new radical capable of initiating another chain reaction.

***Termination*:** Polymeric radicals are used up by coupling or disproportionation reactions.

Four steps of photopolymerization are summarized in reactions 2.28.



(2.28)

It should be pointed out that the role of light in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating radicals. The reaction of these radicals with monomer, propagation, transfer and termination are purely thermal processes and they are not affected by light.

2.2.1.1 Absorption of Light

When the light is absorbed by a molecule, its electrons are excited, what lessens the stability of a bond and can, under favorable circumstances, lead to its dissociation. Functional groups that have high absorbency, like phenyl rings or carbonyl groups, are referred to as chromophoric groups. Naturally, photoinduced bond dissociations do often take place in the proximity of the light absorbing chromophoric groups. In some examples, however, electronic excitation energy may be transferred intramolecularly to fairly distant, but easily cleavable bonds to cause their rupture.

If the monomer possesses chromophoric groups and is sensitive towards light (i.e., it undergoes photoinduced chemical reactions with high quantum yields) one can carry out photopolymerizations by just irradiating the monomer. In many cases, however, monomers are not efficiently decomposed into radicals upon irradiation. Furthermore, monomers are often transparent to light at $\lambda>320$ nm, where commercial lamps emit.

In these cases, photoinitiators are used. These compounds absorb light and bring about the generation of initiating radicals.

2.2.1.2 Radical Generation

2.2.1.2a Radical Generation by Monomer Irradiation

Some monomers can generate radical species via absorption of light. Studies carried out on various vinyl compounds show that a monomer biradical is formed (2.29).

$$\mathrm{M} \xrightarrow{h\nu} \boxed{\cdot\mathrm{M}\cdot} \qquad (2.29)$$

These species can react with intact monomer molecules and thus leading to growing chains. Readily commercially available monomers which undergo polymerization and copolymerization through UV irradiation to some extent are listed in Table 2.1

Table 2.1.

Photosensitive Monomers
Allyl methacrylate
Barium acrylate
Cinnamyl methacrylate
Diallyl phthatlate
Diallyl isophtalate
Diallyl terephthalate
2-Ethylhexyl acrylate
2-Hydroxyethyl methacrylate
2-Hydroxypropyl acrylate
N,N’-Methylenebisacrylamide
Methyl methacrylate
Pentaerythritol tetramethacrylate
Styrene
Tetraethylene glycol dimethacrylate
Tetrafluoroethylene
N-Vinylcarbazole
Vinyl cinnamate
Vinyl 2-fuorate
Vinyl 2-furylacrylate

On the other hand, radical generation via irradiation of vinyl monomer does not play a role due to regarding technical applications such as very low efficiency of radical formation and usually unsatisfactory absorption characteristics.

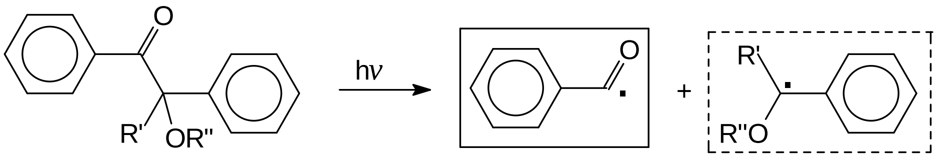
2.2.1.2b Radical Generation by Initiators

The function of initiators in the photoinduced polymerization applications is usually to generate radicals. Efficient photoinitiators find everyday usage. They are generally divided into two classes based on process by which initiating radicals are formed [45].

1. Type I Photoinitiators: Initiators undergo a homolytic bond cleavage upon absorption of light**.** From the point of view of chemical kinetics, the fragmentation that leads to the formation of radicals is a unimolecular reaction (2.30). Although type I photoinitiators are highly reactive UV photoinitiators, they are less frequently used in visible light curing systems.

$$\underset{\text{photoinitiator}}{\mathrm{PI}} \xrightarrow{h\nu} \underset{\text{excited photoinintiator}}{\mathrm{PI}^*} \xrightarrow{\text{Unimolecular reaction}} \underset{\text{free radicals}}{\mathrm{R}_1^\bullet + \mathrm{R}_2^\bullet} \qquad (2.30)$$

The number of initiating radicals formed upon absorption of one photon is termed as quantum yield of radical formation ($\phi_{R\cdot}$) Theoretically, cleavage type photoinitiators should have a Φ_{R}. value of two since two radicals are formed by the photochemical reaction. However, Φ_{R}. values are much lower because of various deactivation routes of the photoexcited initiator other than radical generation. These routes include physical deactivation such as fluorescence or non-radiative decay and energy transfer from the exited state to other, ground state molecules, a process referred to as quenching. The reactivity of photogenerated radicals with polymerizable monomers is also to be taken into consideration. In most initiating systems, only one in two radicals formed adds to monomer thus initiating polymerization. The other radical usually undergoes either combination or disproportionation. Regarding the energy necessary, it has to be said that the excitation energy of the photoinitiator has to be higher than the dissociation energy of the bond to be ruptured. The bond dissociation energy, on the other hand, has to be high enough in order to ensure long term storage stability. The majority of Type I photoinitiators are aromatic carbonyl compounds with appropriate substituents, which spontaneously undergo *α-cleavage* generating free radicals (2.31). The benzoyl radical formed by the reaction depicted is very reactive towards the unsaturations of vinyl monomers [46].



R' = H, Alkyl, subst. Alkyl
R'' = H, Alkyl, subst. Alkyl

(2.31)

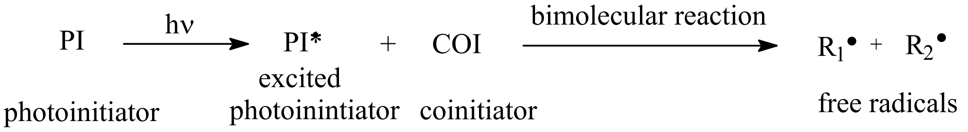
The α-cleavage often referred to as Norrish Type I reaction [47] of carbonyl compounds starts from the initiator's triplet state, which is populated via intersystem crossing. Notably, the excited triplet states are usually relatively short lived that prevents excited molecules to undergo side reactions with constituents of the polymerization mixture. While triplet quenching by oxygen can, in most cases, be neglected due to the short lifetime of the triplet states, quenching by monomer sometimes plays a role. However, this refers exclusively to monomers with low triplet energies, like, e.g., styrene ($E_T = 259$ kJ mol^{-1} [48]).

If the absorption characteristics of a cleavable compound are not meeting the requirements, i.e., the compound absorbs at too low wavelengths, the use of sensitizers (S) with matching absorption spectra is recommendable. Sensitizers absorb the incident light and are excited to their triplet state (2.32). The triplet excitation energy is subsequently transferred to the photoinitiator which forms initiating radicals (2.33). This process has to be exothermic, i.e., the sensitizer's triplet energy has to be higher than the triplet energy level of the initiator. Through energy transfer, the initiator is excited and undergoes the same reactions of radical formation as if it were excited by direct absorption of light. The sensitizer molecules return to their ground state upon energy transfer; they are therefore not consumed in the process of initiation.

$$\mathrm{S} \xrightarrow{h\nu} {}^{3}\mathrm{S}^{*} \qquad (2.32)$$

$$^{3}\mathrm{S}^{*} + \mathrm{PI} \longrightarrow \mathrm{S} + {}^{3}\mathrm{PI}^{*} \qquad (2.33)$$

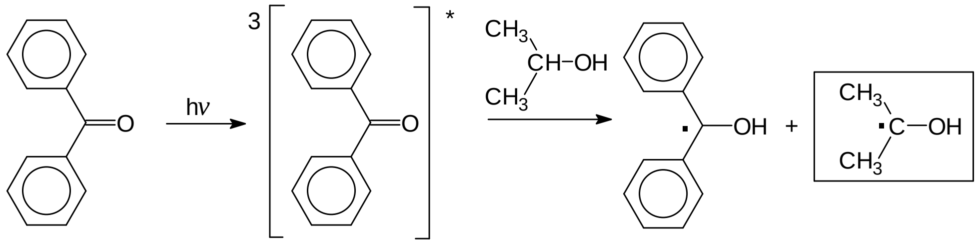
2. Type II Photoinitiator or **PI_2-type initiator:** They are the photoinitiators in the excited state interacting with a second molecule (a coinitiator) to generate radicals in a bimolecular reaction (2.34). Type II photoinitiators are versatile initiators for UV curing system and visible light photoinitiators belong almost exclusively to this class of photoinitiators.



$$\underset{\text{photoinitiator}}{\mathrm{PI}} \xrightarrow{h\nu} \underset{\substack{\text{excited}\\ \text{photoinintiator}}}{\mathrm{PI}^*} + \underset{\text{coinitiator}}{\mathrm{COI}} \xrightarrow{\text{bimolecular reaction}} \underset{\text{free radicals}}{R_1^\bullet + R_2^\bullet} \tag{2.34}$$

The excited states of certain compounds do not undergo Type I reactions because their excitation energy is not high enough for fragmentation, i.e., their excitation energy is lower than the bond dissociation energy. The excited molecule can, however, react with another constituent of the polymerization mixture, the so-called coinitiator (COI), to produce initiating radicals. There are two distinct pathways of radical generation by Type II initiating systems, namely *hydrogen abstraction, photoinduced electron transfer reaction and subsequent fragmentation.*

Hydrogen abstraction takes place from a suitable hydrogen donor. Photoinitiators of this group are generally aromatic ketones and include benzophenone, benzil, quinones, Michler's ketone, and thioxanthanes. When photoexcited these compounds do not dissociate but enter into bimolecular abstraction reactions with hydrogen donors such as alcohols, ethers, tertiary amines, and so on. As a typical example, the photoreduction of benzophenone by isopropanol is depicted (2.35). Bimolecular hydrogen abstraction is limited to diaryl ketones [47]. From the point of view of thermodynamics, hydrogen abstraction is to be expected if the diaryl ketone's triplet energy is higher than the bond dissociation energy of the hydrogen atom to be abstracted.



(2.35)

In electron transfer reactions, the photoexcited molecule, termed as sensitizer for the convenience, can act either as electron donor or electron acceptor according to the nature of the sensitizer and coinitiator (2.36). Fragmentation yields radical anions and radical cations (2.37), which are often not directly acting as initiating species themselves but undergo further reactions (2.38), by which initiating free radicals are produced.

$$S \xrightarrow{h\nu} S^* \tag{2.36}$$

$$S^* + A \longrightarrow S^{+\bullet} + A^{-\bullet} \dashrightarrow \text{further reactions} \tag{2.37}$$

$$S^* + D \longrightarrow S^{-\bullet} + D^{+\bullet} \dashrightarrow \text{further reactions} \tag{2.38}$$

Electron transfer is often observed for aromatic ketone/amine pairs and always with dye/coinitiator systems.

2.3 Controlled Radical Polymerization (CRP)

The synthesis of well-defined polymers has long been of great interest in polymer chemistry. A main topic in modern polymer synthesis is the controllability of polymer composition, molecular weight and molecular weight distribution by means of polymerization process. Until recently polymerizations with a high degree of structure control were only possible by means of relatively complex methods, such as anionic, cationic or group transfer polymerization. But these methods have the disadvantage that the high structure control is balanced by a limited choice of monomers and high sensitivity of the reaction impurities. Besides living ionic systems, controlled radical polymerization became an established method to obtain specific polymer architectures, such as star or block copolymers.

As free Radical polymerization (FRP) can be used for many vinyl monomers under mild reaction conditions, requiring the absence of oxygen but tolerant to water, and large temperature ranges (-20 to 200 ^{o}C) it is a very important commercial process for preparing high molecular weight polymers. Also a large number of monomers can be easily copolymerized to yield copolymers with properties dependent via FRP. On the other hand, the poor control of macromolecular structures including degrees of polymerization, polydispersities, end functionalities, chain architectures and compositions is the disadvantage of FRP. Various processes have been developed to control FRP during the last decade and thus polymers with low polydispersities, new architectures, compositions, functionalities and molecular composites were synthesized. Figure 2.2 gives the products of CRP.

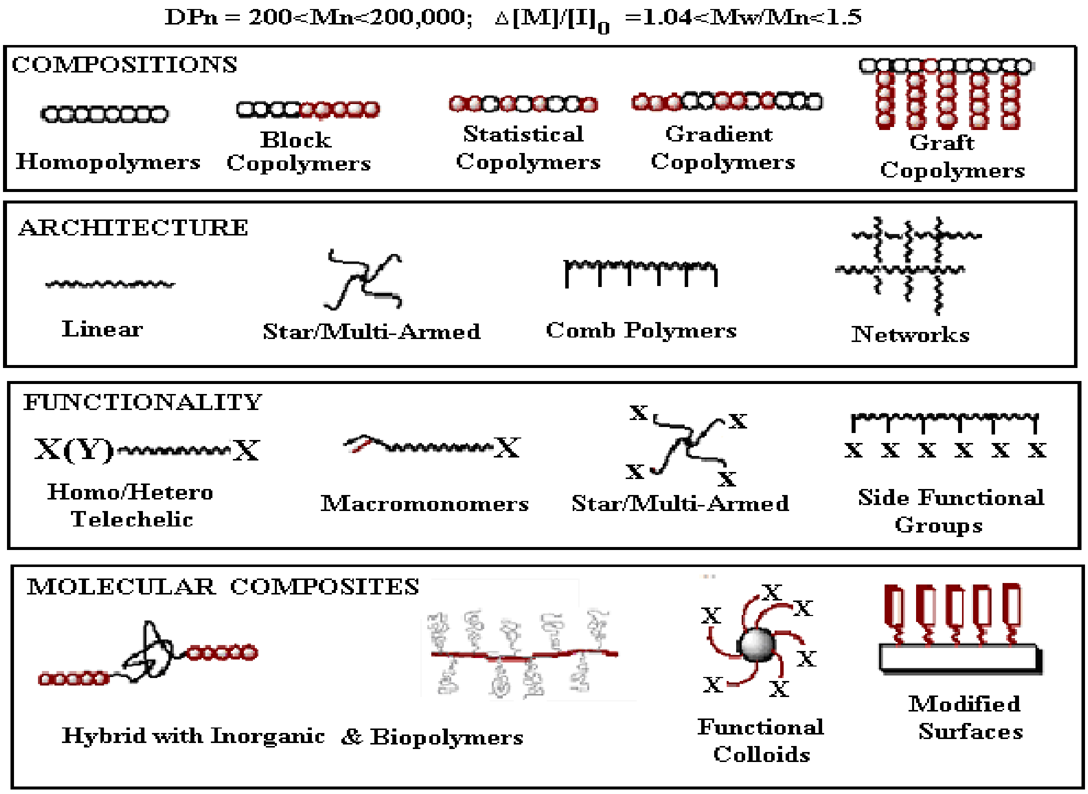


Figure 2.2. Products obtained via controlled radical polymerization

There are two necessary conditions leading to control for FRP. First, the equilibrium between dormant and active (free radical) species must lie strongly to the side of the dormant species to assure that the overall concentration of propagating radicals will remain very low and that the rate of irreversible termination will be negligible relative to the apparent rate of polymerization. Second, the rate of exchange between dormant and active species must be faster than the rate of propagation to assure that all polymer chains have equal probability of adding monomer. If these conditions are met, then conventional radical polymerization is converted to a controlled/living radical polymerization yielding polymers with a wide range of molecular weights and narrow molecular weight distributions (MWDs) is possible [49].

Basic difference between conventional radical (i.e., azobis (isobutyronitrile) - or peroxide-initiated processes) and controlled radical polymerizations lies in the lifetime of the propagating radicals during the course of the reaction. In conventional radical processes, radicals generated by decomposition of the initiator undergo propagation and bimolecular termination reactions take place within a second. However, in a CRP, the lifetime of a growing radical can be extended to several hours, enabling the preparation of polymers with predefined molar masses, low polydispersity, controlled compositions, and functionality for the equilibrium. This difference is showed in Figure 2.3 [50, 51].

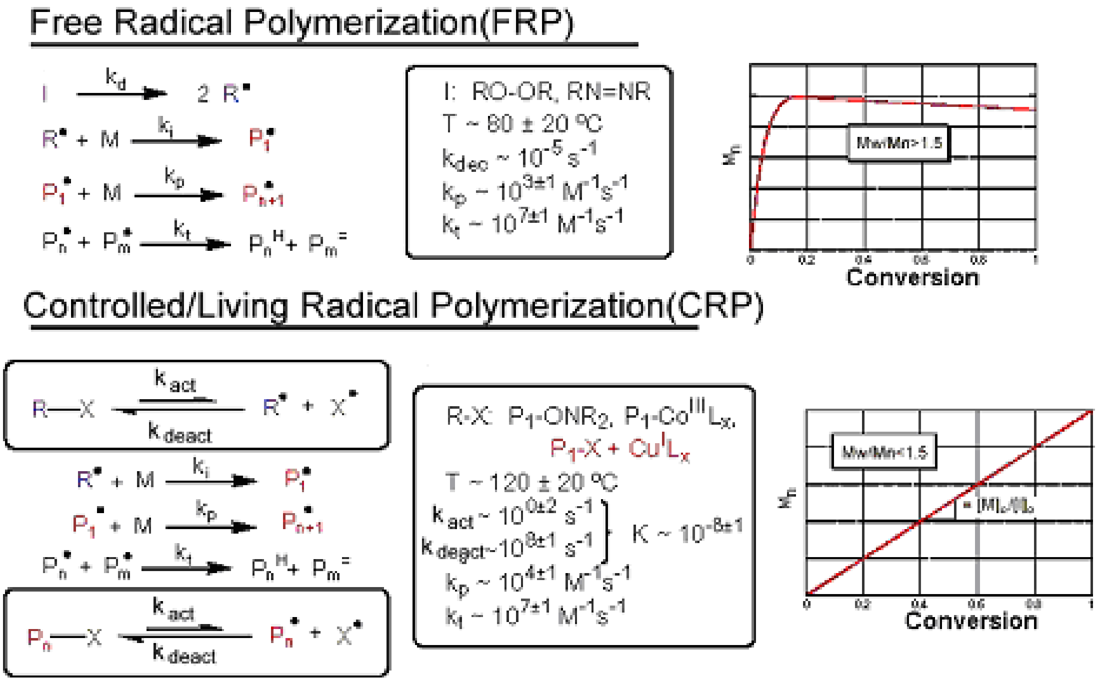


Figure 2.3. Comparison between FRP and CRP

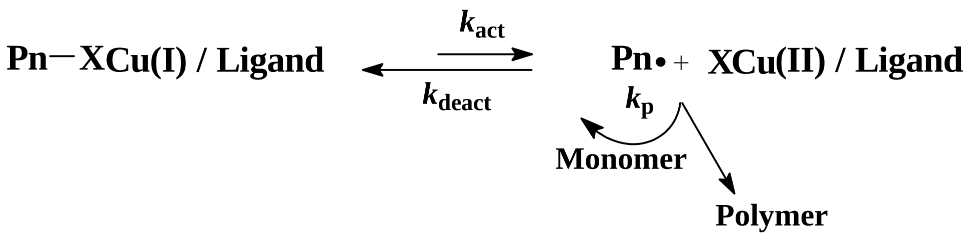
The mechanism invoked in CRP processes to extend the lifetime of growing radicals utilizes a dynamic equilibration between dormant and active sites with rapid exchange between the two states. Unlike conventional radical processes, CRP requires the use of persistent radical (deactivator) species, or highly active transfer agents to react with propagating radicals. These persistent radicals/transfer agents react with radicals (deactivation or transfer reactions with rate constant, k_{deact}) to form the dormant species. Conversely, propagating radicals are generated from the dormant species by an activation reaction (with rate constant, k_{act}) [52].

Currently, several methods appeared to enable controlled radical copolymerization. These methods include: stable free-radical polymerization (SFRP), best represented by polymerization mediated with TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) [53], metal-catalyzed atom transfer radical polymerization (ATRP) [54], reversible addition–fragmentation chain transfer (RAFT) [55] and Diphenylethene method

(DPE) [56]. Using these polymerization methods, the molecular weight of the polymers linearly increases with conversion and the polydispersities are well below 1.5.

2.3.1 Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is one of the most convenient methods to synthesize well–defined low molecular weight polymers. It is a radical polymerization with reversible deactivation by atom transfer and based on the reversible transfer of halogen atoms between dormant alkyl halides and transition metal catalysts by redox chemistry (2.39).



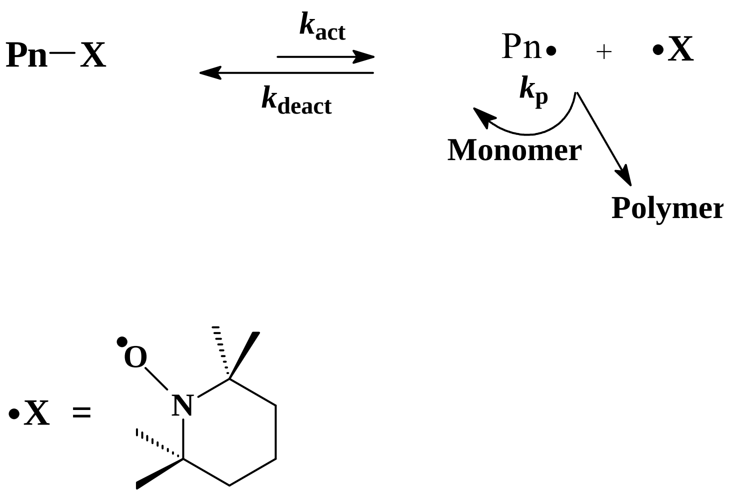
(2.39)

This method utilizes a reversible halogen atom abstraction step, in which a lower oxidation state metal (Mt^n complex by a ligand LGN) reacts with an alkyl halide (Pn-X) to generate a radical ($P_n^{\cdot}$) and a higher oxidation state metal complex ($XMt^{n+1}LGN$, k_{act}). This radical then adds monomer to generate the polymer chain (k_p). The higher oxidation state metal can then deactivate the growing radical to generate a dormant chain and the lower oxidation state metal complex (k_{deact}) [57, 58].

ATRP system consists of an initiator, a catalyst, ligand(s), and monomer. Alkyl halide with an activating group at the α-position is utilized as an initiator and its main function is to quantitatively generate growing polymer chains. Generally, initiator that is homologous to the structure of dormant polymer end group is the best initiator for that particular monomer. Transition metal compounds complexes (Ru, Cu, Fe, Ni, and other transition metal complexes) with suitable ligands like bipyridyls, aryl phosphines, aliphatic amines are used to catalyze ATRP. It has been used successfully with styrene, (methyl) acrylates, acrylates and also applied to other monomers like acrylonitrile and 4-vinyl pyridine. As atom transfer equilibrium depends upon the combination of halide initiator and metal catalyst, the reaction conditions of each monomer are different. Concentrations and the structures of all compounds in ATRP affect the polymerization rate and the properties of the resulting polymer. Therefore, choice of initiator, metal, ligands, deactivator, temperature, reaction time and solvent depend on each particular ATRP [50]. On the other hand, ATRP has a few limitations. The attractive flexible initiation with RX/transition metal catalysts is often overcompensated by the difficulties of catalyst removal from the polymer. Therefore, its industrial application is unlikely as long the toxic and colored catalysts can not be removed from the polymers properly. In addition, ATRP cannot be used for polymerization of more reactive monomers like olefins, ethylene, vinyl acetate, and vinyl alcohol due to the limitations of present-generation catalysts.

2.3.2 Stable Free Radical Polymerization (SFRP)

SFRP is controlled free radical polymerization method with reversible termination by coupling with a persistent radical, namely (e.g. nitroxide) (2.40). Currently, the best example in this class is alkoxyamine-initiated or nitroxide-mediated polymerization first described by Rizzardo et al. [59], and later developed by Georges [60] and Hawker [61]. The stable nitroxide radicals such as 2, 2, 6, 6 – tetramethyl – 1 – piperidinyloxy (TEMPO) are known to act as strong polymerization inhibitors.



(2.40)

As have been shown in 2.20, the key reactions are the alternating activation–deactivation process, in which the polymer-nitroxide adduct P_n-X (dormant species) is reversibly activated by thermal homolysis into the polymer radical ($P_n^{\cdot}$) and the stable nitroxyl ($X^{\cdot}$). This dramatically lowered the concentration of active chain species in the polymerization system and, coupled with the inability of the nitroxide radicals to initiate new chains lead to a controlled polymerization [62]. All the chains propagate at nearly equal rate through these activation–deactivation cycles and thus, the chain length and its distribution are controlled. The resulting alkoxyamine is stable at temperatures below whereas homolitic cleavage takes place in the C-O bond at temperatures higher than 100°C resulting in the propagation again. SFRP have been shown to be efficient for the controlled polymerization of styrene and substituted styrenes.

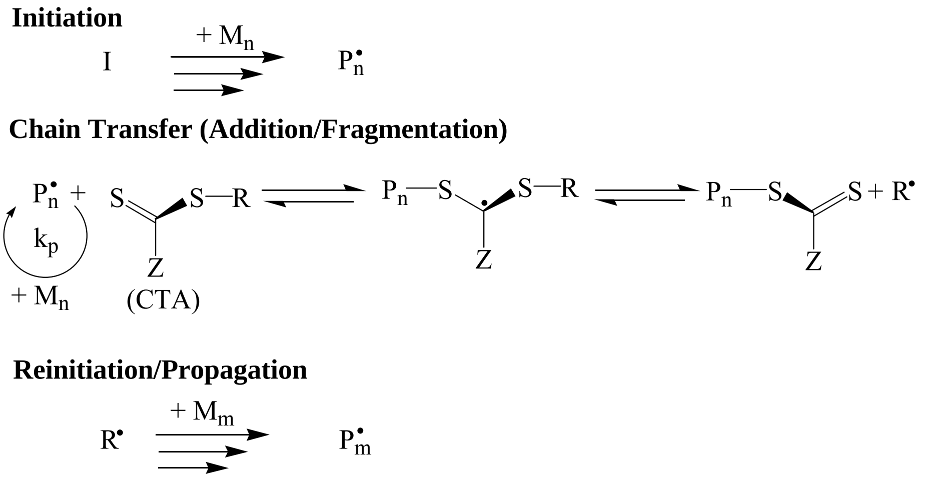
Although TEMPO-mediated polymerization is one of the simplest methods of controlled free radical polymerization (CRP), it shows some disadvantages. Polymerization is carried out at high temperature (>120°C) because it is inherenly slow. Also many monomers will not polymerize because of the stability of the dormant alkoxyamine that forms. Furthermore, TEMPO is expensive and thermolabile.

Recent studies in SFRP are related to the synthesis and evaluation of new nitroxide radicals, chain end functionalization, and the exploration of the synthesis of block, random, star, and graft copolymers. A review has recently been published which covers these topics in detail [53].

2.3.3 Reversible Addition–Fragmentation Chain Transfer Polymerization (RAFT)

RAFT is free-radical polymerization with reversible chain transfer for achieving living character [55]. The initiation of RAFT system consists of a standard free-radical initiator and a suitable thiocarbonylthio compound. The latter acts as highly efficient reversible addition–fragmentation chain transfer agent (CTA agent) and also provides the polymerization with living characteristics.

As CTA is transferred between the active and the trapped chain, it is called trapping agent. These trapped chain, usually called dormant chains, are unable to propagate but also unable to terminate. Because, chain termination is bimolecular reaction. The termination rate is second order with respect to the radical concentration $[M_m\cdot]$, while chain propagation is first order to the radical concentration $[M_m\cdot]$ and proportional to the monomer concentration [M]. So we can see the termination rate is far less than propagation rate. Therefore, the probability of termination is largely reduced with respect to that of chain growth. So this leads to a negligible amount of terminated chains at the end of process. This is why RAFT has a living character. However, since terminations are definitely present, so this polymerization is also referred to as living radical polymerization. The resultant polymer has a controlled molecular weight and narrow molecular weight distribution [63, 64].



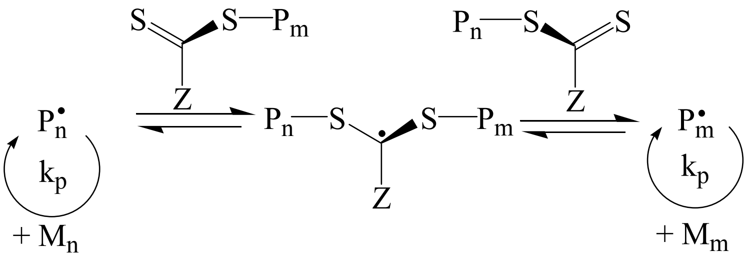
(2.41a)

(2.41b)

(2.41c)

RAFT involves a reversible chain transfer in which a dithioester acts as a chain transfer agent (CTA). The CTA reacts with either the primary radical or a propagating chain, forming a new CTA and eliminating R·, which then re-initiates polymerization. The dithioester transferred between the active and dormant chains maintain the living character of the polymerization. As seen from 2.41a, b, c, the basic difference between normal free radical polymerization and RAFT is the presence of a special kind of chain transfer agent (CTA), which leads to addition-fragmentation, re-initiation/propagation and chain equilibrium between chain radical and a new CTA. As the addition-fragmentation chain transfer process is reversible, the process is called reversible addition-fragmentation chain transfer polymerization (RAFT) (2.42a, b).

Chain Equilibration

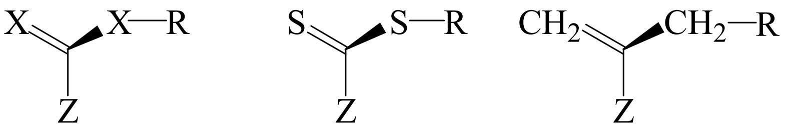


(2.42a)

Termination

$$P_n^{\bullet} + P_m^{\bullet} \longrightarrow \text{Dead Polymer} \qquad (2.42b)$$

Since RAFT process is actually a kind of degenerative chain transfer reaction, that is, activation and deactivation occur at the same time or an active site migrates from one chain to another. Therefore, successful RAFT polymerization depends on selection of highly efficient CTA (2.43a). The polymerization is carried out in the presence of thiocarbonylthio of general structure (2.43b) and results in the formation of end-functionalized polymers. Z should activate the C=S double bonds [55, 65]. So the rate of addition and fragmentation must be fast relative to the rate of propagation. This leads to rapid consumption of the RAFT agent and fast equilibrium of the dormant and active chain. On the other hand, the leaving group R must be easily to leave and be able to re-initiate polymerization for the chain reaction to proceed. Generally, R should be a good homolytic leaving group when compared to polymer chain. Macromonomers (2.43c), where X is CH_2, can also function as RAFT agents [66-69].



(a) (b) (c)

(2.43)

The incredible range of polymerizable monomers can be used in RAFT under a broad range of experimental conditions. As long as the monomer can undergo radical polymerization, the process will most likely be compatible with RAFT. However, there are many major drawbacks that arise when using this process. The diversity is achieved only by using selected dithioesters for specific monomers. Some problems of RAFT are related to the dithioesters themselves. They are not commercially available and resulting polymers are sometimes colored. Furthermore, dithioesters and their reaction products can give rise to unpleasant odor and toxicity.

2.3.4 1, 1-Diphenylethene Method (DPE)

As the name implies, this method involves the use of 1, 1-diphenylethene (DPE) as an additive in the classical free radical polymerization. Addition of DPE enables the control of free radical polymerization [56]. In a typical synthesis of the first block, the monomer, initiator and 1-diphenylethene are heated at 60°C to 110 °C for 2 to 12 hours. A second monomer is then added, and the mixtures are heated at 60°C to 110 °C for a further for 6 to 12 hours. Depending on the choice of monomer, this gives hydrophobic, amphiphilic or water-soluble block copolymers in a one-pot synthesis. DPE method is surprisingly flexible with respect to the choice of monomers and solvent. The method works with all common monomers, which are capable of free radical homopolymerization or copolymerization, even N-vinyl compounds and vinyl acetate. The polymerization can be carried out in organic solvents, in water or without a solvent. The reaction conditions are the usual ones for conventional free radical polymerization, which is very beneficial for industrial implementation of DPE method. DPE is commercially available, odorless, colorless and known without toxicity. It is known as a non polymerizable styrene derivative, [70] which was useful only as molecular weight regulator [71]. The radical polymerization of many common monomers in the presence of DPE shows the characteristics of a controlled polymerization and, therefore, this strategy opens a wide new field in polymer chemistry.

2.3.4.1 Homopolymerization

Some characteristics of DPE method are different from free radical polymerization. Figure 2.4 (left) indicates the time-conversion graph of bulk polymerization of styrene at 80 °C. The DPE-free polymerization was performed with AIBN as an initiator in the same amount as in the polymerization in presence of DPE. A retarding effect on the conversion is observed by adding a small amount of DPE in comparison to the free radical polymerization. Figure 2.4 (right) shows the molecular weight and the poly dispersity index (PDI) versus conversion of the bulk polymerization of styrene with and without DPE. The DPE controlled polymerization shows slightly increasing molecular weight with conversion after a short period of uncontrolled polymerization. During this period polymers with a relatively high molecular weight are formed. The DPE-free radical polymerization shows the expected behaviors [72].

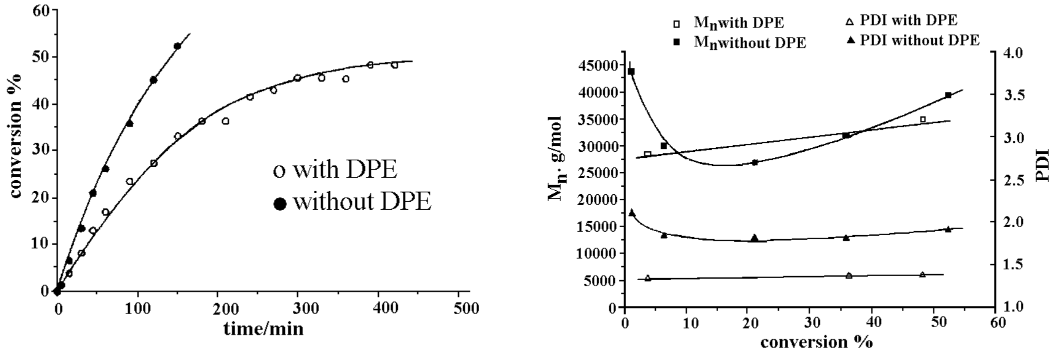


Figure 2.4. Time-conversion plot (left), molecular weight and PDI versus conversion plot (right), polymerization of styrene in the presence of DPE and without DPE

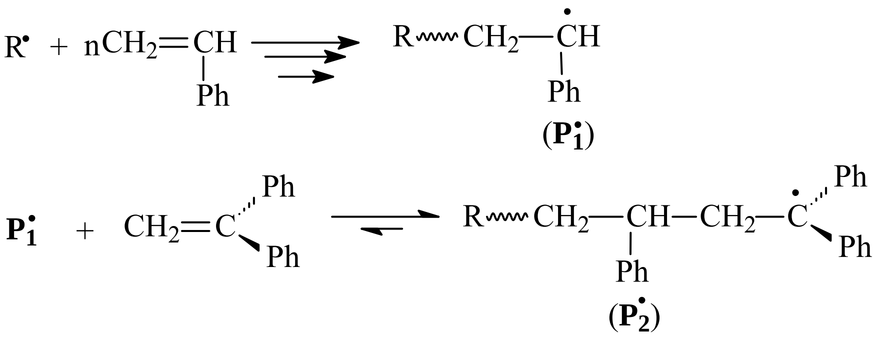
The PDI of the polymers which were synthesized in the presence of DPE are significant lower than in the free radical polymerization. This indicates a protection of the growing chain ends against termination by mutual deactivation. All these observations indicate that DPE gives a certain control over the polymerization.

2.3.4.2 Block Copolymerization

Homopolymers containing DPE units can initiate the polymerization of second monomer over certain temperature. The yield of block copolymers depends on the type of monomers used.

Initiation

$$\mathrm{AIBN} \longrightarrow 2R^{\bullet} + N_2$$



$$R^{\bullet} + n\,CH_2{=}\underset{Ph}{CH} \rightleftharpoons R\text{~~~}CH_2{-}\underset{Ph}{\overset{\bullet}{C}H} \quad (P_1^{\bullet})$$

(2.44a)

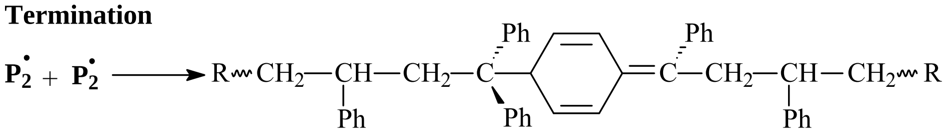
(2.44b)

$$P_1^{\bullet} + CH_2{=}C(Ph)_2 \rightleftharpoons R\text{~~~}CH_2{-}\underset{Ph}{CH}{-}CH_2{-}\overset{\bullet}{C}(Ph)_2 \quad (P_2^{\bullet})$$

(2.44c)

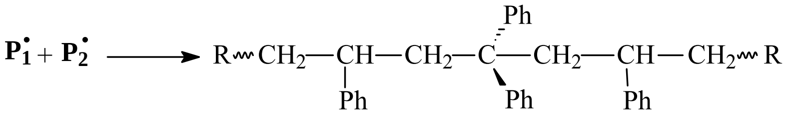
Reactions 2.44 show how homopolymerization occurs. In the first step an active chain end $P_1^\cdot$ is formed. Then $P_1^\cdot$ reacts with a DPE molecule under formation of a stable diphenylmethyl radical $P_2^\cdot$ (2.44c). This radical is a kind of a dormant species which can avoid transfer reactions.

Termination



(2.45a)

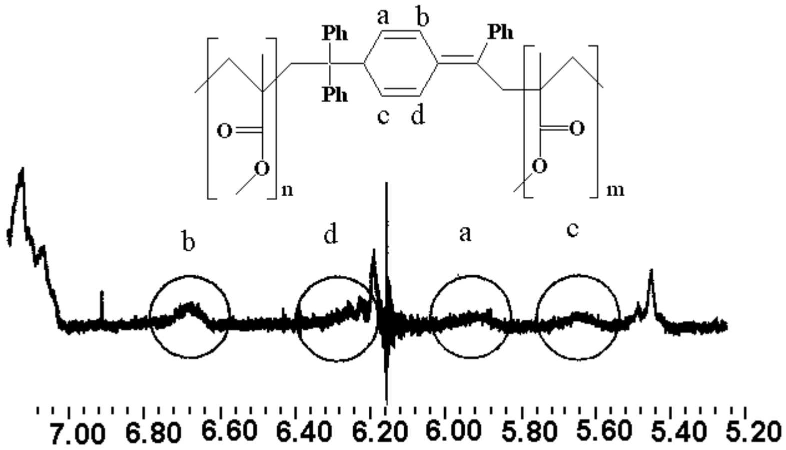
P_2P_2



$$P_1^\bullet + P_2^\bullet \longrightarrow R\sim CH_2-\underset{Ph}{CH}-CH_2-\overset{Ph}{\underset{Ph}{C}}-CH_2-\underset{Ph}{CH}-CH_2\sim R \quad (2.45b)$$

P_2P_1

Coupling of two P_2 radicals (2.45b) occurs through tetraphenylethane unit, which are thermolabile, as have been shown by different authors [73-75]. The tetraphenylethane unit in the polymer chains will be a chinone like structure as have been shown for hindered tetraphenylethanes [76]. In the ^{1}H-NMR spectrum of DPE containing PMMA characteristic signals of the chinone protons are visible (Figure 2.5).

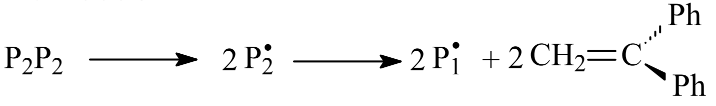


.

Figure 2.5. ^{1}H-NMR spectrum of PMMA containing DPE units (Mn=4450 g/mol)

If the homopolymers containing DPE units along the chain are heated in the presence of a second monomer, they split into two P_2 radicals. P_2 radicals formed also split into P_1 and free DPE. Thus, the polymerization of second monomer (M_m) can be initiated by polymeric P_1 radicals to yield block copolymers (2.46a, b).

Reinitiation



$$P_2P_2 \longrightarrow 2\,P_2^{\bullet} \longrightarrow 2\,P_1^{\bullet} + 2\,CH_2{=}C(Ph)_2 \qquad (2.46a)$$

$$P_1^{\bullet} + mM \longrightarrow \text{Block Copolymer} \qquad (2.46b)$$

Although the polydispersities of polymers are not as narrow as those synthesized with ATRP, SFRP, or RAFT, this system might be suitable even for industrial application because of its versatility and simplicity combined with mild conditions and short reaction times [77].

2.4 Ring-Opening Polymerization

Polycondensation of hydroxycarboxylic acids or the ring-opening polymerization (ROP) of cyclic esters are two different approaches for preparation of polylactones and polylactides. Although the former is less expensive than the latter, it is difficult to obtain high molecular weight polymers, to achieve specific end groups, and to prepare well-defined copolyesters via polycondensation of hydroxycarboxylic acids. ROP is also employed in the polymerization of cyclic ethers.

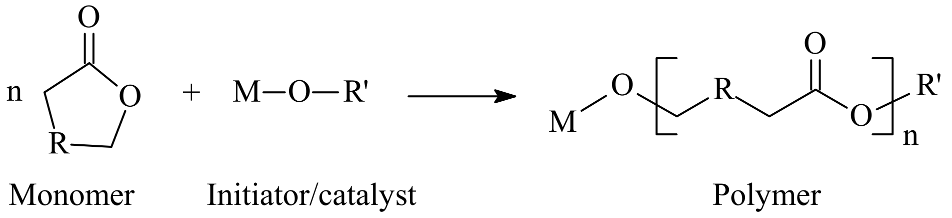
There are several reasons for studying the polymerization of cyclic esters. First, to exploit the potential of synthetic polymer chemistry to prepare a variety of polymers with control of the major variables affecting polymer properties. Experimental conditions have to be optimized in order to find the best polymerization system for a desired technological or industrial process. Factors such as economy, toxicology, and technical apparatus development are important. A second reason for studying ROP is to enable various advanced macromolecules, including homopolymers with well-defined structures or end groups, to be prepared, as well as copolymers with different architectures, e.g., block, graft, or star copolymers. The physical, mechanical, and degradation properties of these various macromolecules are studied to determine the structure/property relationship. The third reason for studying these kinds of systems is that they are valuable models for the examination of the kinetics [78] mechanisms [79] of elementary reactions in polymerization.

Aliphatic polyesters used in biomedical and pharmaceutical applications are an attractive class of polymer. One reason behind the growing interest in this type of degradable polymer is that their chemical and physical properties can be varied over a wide range via copolymerization and macromolecular architecture techniques. The synthesis of novel polymer structures through ring-opening polymerization has been studied for a number of years. The development of macromolecules with strictly defined structures and properties, aimed at biomedical applications, leads to complex and advanced architecture and a diversification of the hydrolysable polymers.

Degradable materials with new mechanical properties and modified degradation profiles have been produced and characterized. The increasing demands of a larger number of biomedical applications have resulted in an increasing interest in producing macromolecules through controlled polymerization.

2.4.1 Ring-Opening Polymerization of Cyclic Esters and Ethers

Polylactones and polylactides of high molecular weight are exclusively produced by the ROP of the corresponding cyclic monomers. Polyester is formed when cyclic esters are reacted with a catalyst or initiator. In a similar way, polyethers are synthesized via the ROP of the corresponding cyclic ethers as well. Reaction 2.47 depicts the reaction pathways for the ROP of cyclic ester.

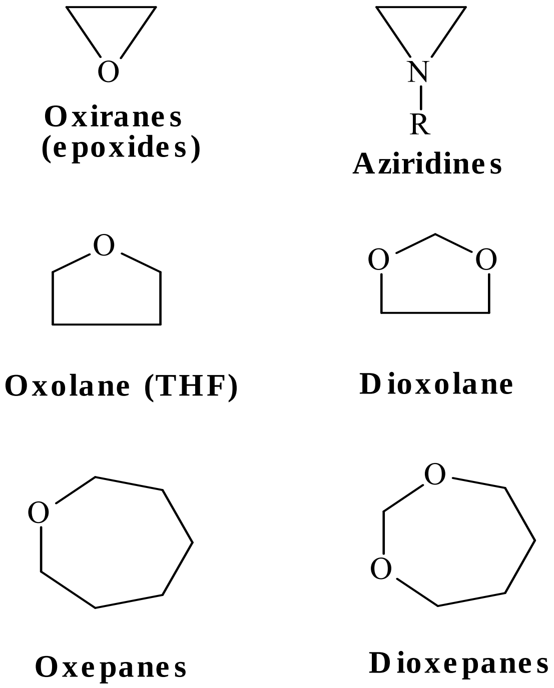


(2.47)

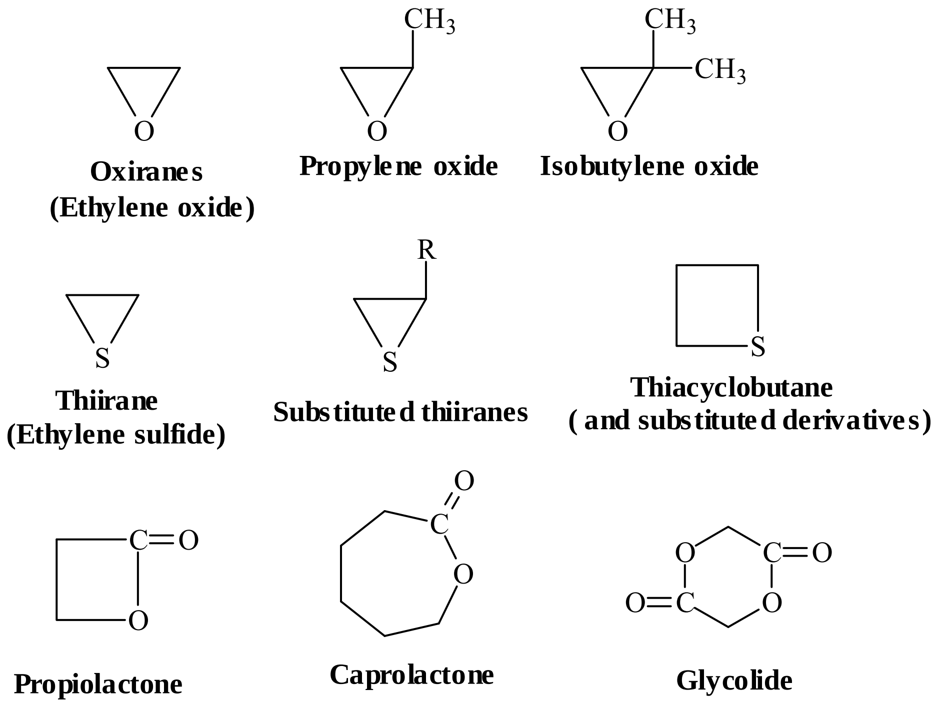
R= $(CH_2)_{0-3}$, M= Metal

Each macromolecule formed generally contains one chain end terminated with a functional group originating from the termination reaction and one terminus end capped with a functional group originating from the initiator. By altering the catalyst or initiator and the termination reaction, the nature of the functional groups can be varied to fit the application of the polymer. The types of initiator and end group play important roles in determining both the thermal stability and hydrolytic stability of the resulting polyester [80]. Functional groups accessible to post-polymerization reactions can also be introduced into the polymer structure in this way.

The ring-opening reaction can be performed either as a bulk polymerization, or in solution, emulsion, or dispersion. A catalyst or initiator is necessary to start the polymerization. Under rather mild conditions, high-molecular weight aliphatic polyesters of low polydispersity can be prepared in short periods of time. Problems associated with condensation polymerization, such as the need for exact stoichiometry, high reaction temperatures, and the removal of low molecular weight by-products (e.g., water) are excluded in ROP. Heterocycles monomers which can be polymerized cationically and anionically are given in 2.48 and 2.49 respectively.



(2.48)



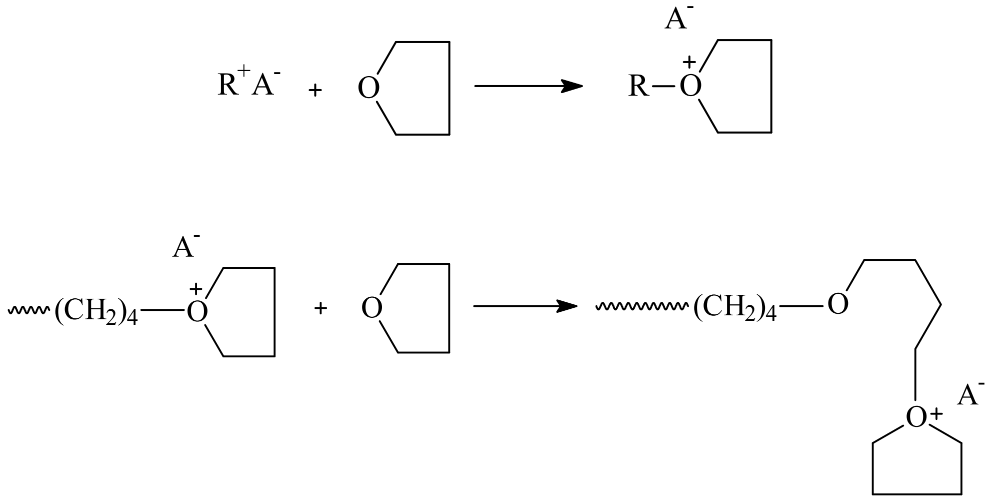
(2.49)

Depending on the initiator the polymerization proceeds according to three different major reaction mechanisms [81], *viz.*, cationic, anionic, or "coordination-insertion" mechanisms [82-84]. In addition, radical, zwitterionic [85], or active hydrogen [81] initiation is possible, although such techniques are not used to any great extent. Here cationic, anionic, and the "coordination-insertion" mechanism are described briefly.

2.4.1.1 Cationic Ring-Opening Polymerization

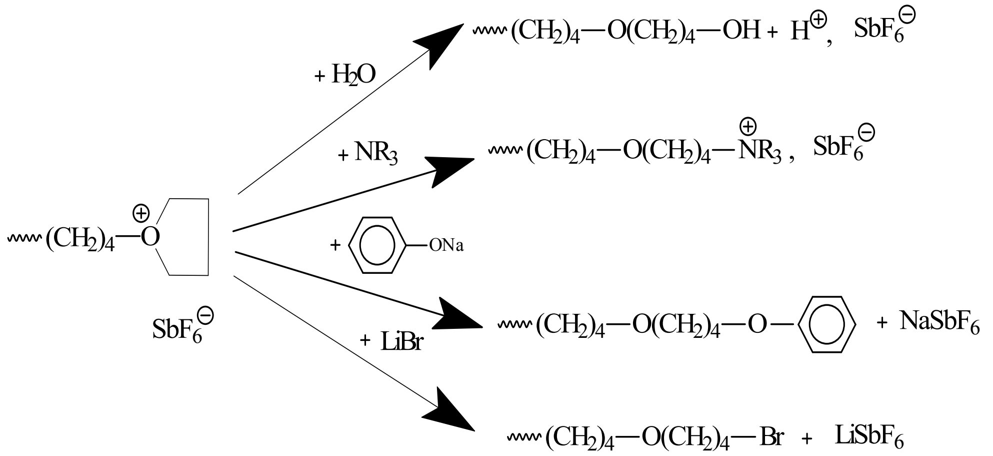
Within the context of polyaddition, cationic polymerization refers to chain growth reactions promoted by active species possessing electrophilic character: carbenium, carbonium, oxonium, sulfonium, ammonium and phosphonium ions, but also molecular chain carriers, ie, mostly esters, which are sufficiently polarized to induce propagation. In these systems, the intrinsic structure and reactivity of the active species are maintained throughout the growth of a polymer molecule. Typical examples of such polyadditions are the cationic polymerizations of alkenyl monomers through the opening of the C=C double bond and of saturated heterocyclic monomers through ring-opening. The two systems differ in that the active species in the polymerization of alkenes are carbenium ions, whereas onium ions are the active species in the polymerization of heterocycles [86].

The ring opening polymerization of several heterocycles proceeds by cationic initiation via oxonium sites that are formed upon alkylation (or protonation) of the monomer. The mechanism of chain growth involves nucleophilic attack of the oxygen of an incoming monomer onto carbon atom in α-position with respect to the oxonium site, whereby the cycle opens and the active site is reformed on the attacking unit (2.50).



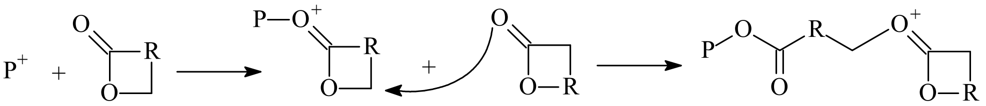
(2.50)

Living polymerization allows the preparation of various well-defined polymers with functional groups. It is known that tetrahydrofuran can be polymerized without chain transfer and termination reactions under closely controlled conditions. Methyl trifluoromethanate sulfonate (methyl triflate) and trifluoromethanate sulfonic anhydride (triflic anhydride) have been described as initiators which lead to mono and bifunctional living polytetrahydrofurans respectively [87, 88]. The oxonium group of the living chain can react with nucleophiles and thus gives rise to a variety of functional groups (reaction 2.51) [89-91].



(2.51)

Among the cyclic esters, 4-, 6-, and 7- membered rings form polyesters when reacted with cationic catalysts [81]. The cationic ROP involves the formation of a positively charged species which is subsequently attacked by a monomer (reaction 2.52). The attack results in a ring-opening of the positively charged species through an S_N^2-type process.



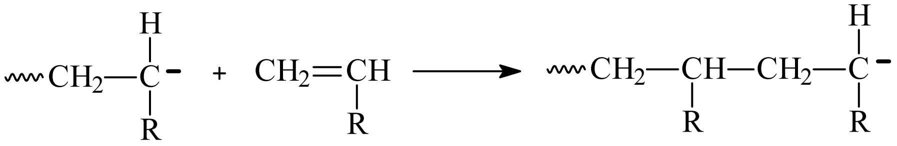
(2.52)

P= Polymer

The cationic polymerization is difficult to control and often only low-molecular weight polymers are formed. When the bulk and solution polymerization of 1,5-dioxepan-2-one (DXO) with cationic initiators were studied, the highest molecular weight achieved was about 10,000. More detailed reviews on cationic ROP have been published by Penczek and coworkers [92, 93].

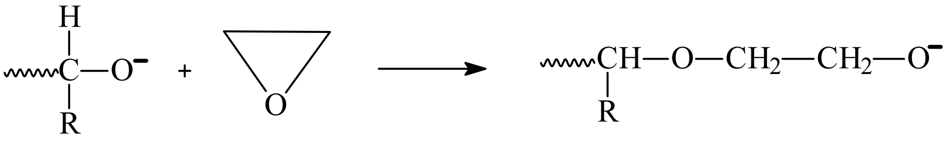
2.4.1.2 Anionic Ring-Opening Polymerization

Anionic polymerizations proceed via metal organic sites: Carbanions (or oxanions) with their metallic counter ions to provide for electrical neutrality. Such processes have been studied extensively over the past decades. Carbanions are nucleophiles, and monomers bearing an electro attractive substituent are therefore best fitted for anionic polymerization. The basic principle of the anionic growth reaction (propagation) is the nucleophilic attack of a carbanion onto a monomer, whereby a new carbanionic site is formed at the chain end (2.53).



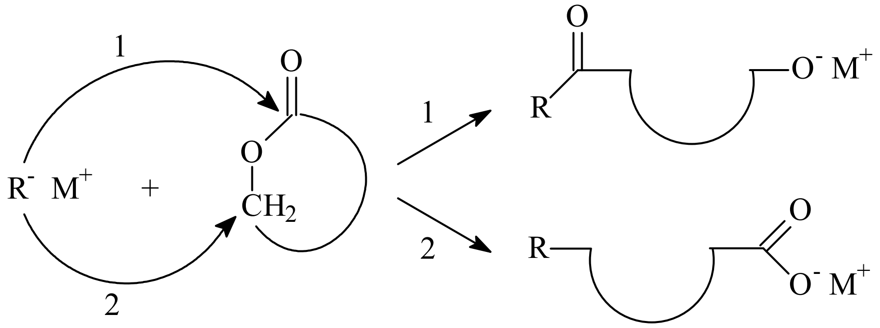
$$\sim CH_2-\overset{H}{\underset{R}{C}}{}^{-} + CH_2=\underset{R}{CH} \longrightarrow \sim CH_2-\underset{R}{CH}-CH_2-\overset{H}{\underset{R}{C}}{}^{-} \qquad (2.53)$$

The same is true for the ROP of cyclic monomers containing some function sensitive to nucleophiles (2.54), such as oxirane, thiiranes, lactones, etc.



(2.54)

Anionic ROP of cyclic ester monomers takes place by the nucleophilic attack of a negatively charged initiator on the carbonyl carbon or on the carbon atom adjacent to the acyl oxygen, resulting in linear polyester. Reaction 2.55 shows the reaction pathway for the ROP of a cyclic ester by anionic initiation, ring-opening of monomer by 1) acyl-oxygen bond cleavage and 2) alkyl-oxygen bond cleavage [94]. The propagating species is negatively charged and is counter-balanced with a positive ion. Depending on the nature of the ionic propagating chain end and the solvent, the reacting complex varies from completely ionic to almost covalent.

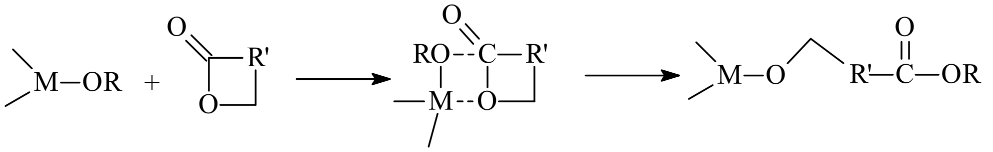


(2.55)

One of the best controlled methods leading to high molecular weight polymers is anionic polymerization carried out in a polar solvent. The Jedlinski group developed living anionic ROP methods for 4- and 5-membered ring lactones and has reported well-defined polymers and copolymers of high molecular weight [95]. The anionic ring-opening of four-membered rings (b -lactones) occurs through alkyl-oxygen or acyl-oxygen cleavage giving a carboxylate or alkoxide. Larger lactones, such as ε-caprolactone (ε-CL) or lactide, react only by an attack of the anion on the carbonyl carbon atom with acyl-oxygen scission and the formation of an alkoxide as the growing species. A problem associated with the anionic ROP is the extensive back-biting, and in some cases only polyesters of low molecular weight are achieved.

2.4.1.3 Coordination-Insertion Ring-Opening Polymerization

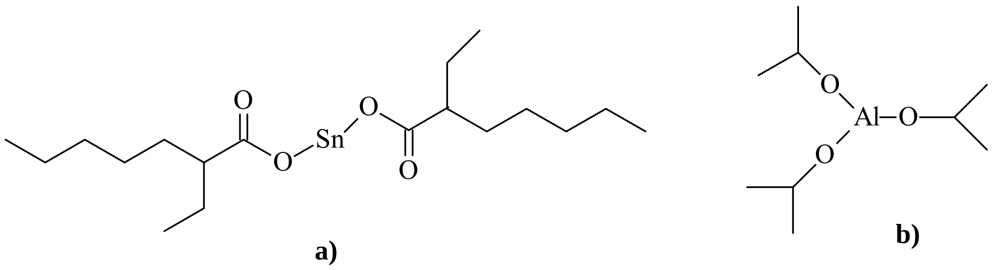
The pseudo-anionic ROP is often referred to as coordination-insertion ROP, since the propagation is thought to proceed by coordination of the monomer to the active species, followed by insertion of the monomer into the metal-oxygen bond by rearrangement of the electrons [82, 83]. Reaction 2.56 shows a schematic presentation of the proposed reaction pathway for the ROP of a cyclic ester by the coordination-insertion mechanism. The growing chain remains attached to the metal through an alkoxide bond during the propagation. The reaction is terminated by hydrolysis forming a hydroxy end group. With functional alkoxy-substituted initiators, macromers with end groups active in post-polymerization reactions are produced.

 (2.56)

The coordination-insertion type of polymerization has been thoroughly investigated since it may yield well-defined polyesters through living polymerization [83]. When two monomers of similar reactivity are used, block copolymers can be formed by sequential addition to the “living” system.

The synthesis of novel initiators and the ROP of existing or new monomers and macromonomers substituted with functional groups provide a very interesting and promising strategy for producing structurally advanced macromolecules.

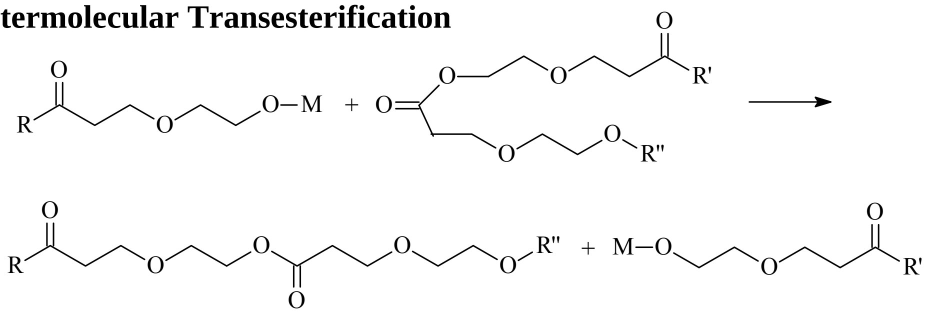
A large variety of organometallic compounds, e.g., metal alkoxides and metal carboxylates, has been studied as initiators or catalysts in order to achieve effective polymer synthesis [96]. Many reactions catalyzed by metal complexes are highly specific and, by careful selection of metal and ligands, reactions can be generated to form a desired polymer structure. The covalent metal alkoxides with free *p* or *d* orbitals react as coordination initiators and not as anionic or cationic initiators. Formulas in 2.57 show some of the most frequently used initiators and catalysts in ROP of lactones. **a)** Stannous octoate and **b)** aluminum isopropoxide



a) **b)** (2.57)

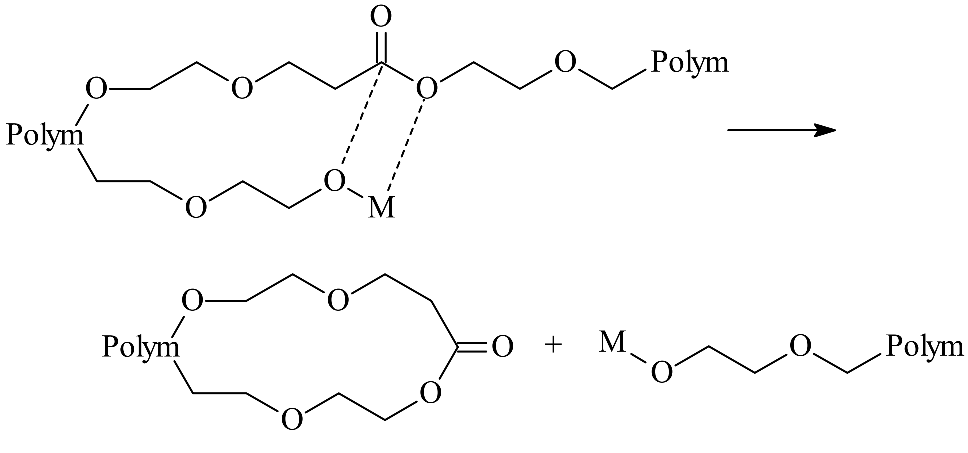
It is well known from the ROP of lactones and lactides that the catalyst or initiator causes transesterification reactions at elevated temperatures [97] or at long reaction times (reactions 2.58 and 2.59) [98].

Intermolecular Transesterification



(2.58)

Intramolecular Transesterification (back-biting)



(2.59)

Intermolecular transesterification reactions modify the sequences of copolylactones and prevent the formation of block co-polymers. Intramolecular transesterification reactions, i.e., back-biting, cause degradation of the polymer chain and the formation of cyclic oligomers. Both types of transesterification reaction broaden the molecular weight distribution (MWD).

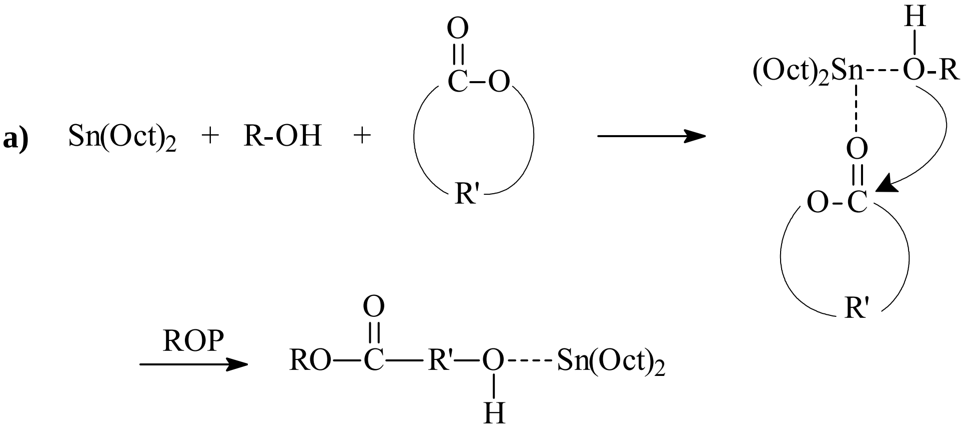
As displayed in the proposed scheme, each intramolecular transesterification randomly breaks the polymer chain. In this way, an attack on the polymer chain leads to a free residual polymer and a new randomized, modified polymer. Consequently, an original copolymer with a block-like structure would be converted to a randomized copolymer after undergoing *n* transesterifications.

Parameters that influence the number of transesterifications are temperature, reaction time, and type and concentration of catalyst or initiator [99]. Depending on the metal used, the initiator is more or less active towards side-reactions such as transesterification reactions [99]. The relative reactivity of different metal alkoxide initiators towards chains already formed has been reported to be:
$Bu_2Sn(OR)_2 > Bu_3SnOR > Ti(OR)_4 > Zn(OR)_2 > Al(OR)_3$ [99].

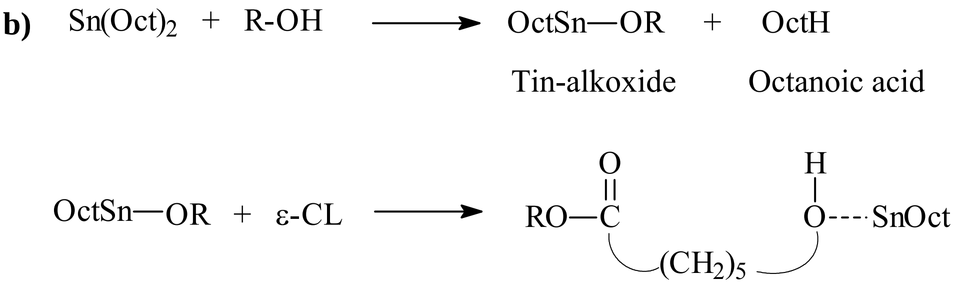
Tin(II) 2-Ethylhexanoate

Tin(II) 2-ethylhexanoate, commonly referred to as stannous octoate [$Sn(Oct)_2$], is a frequently used catalyst in the ROP of lactones and lactides [100]. $Sn(Oct)_2$ has been approved as a food additive by the American Food and Drug Administration (FDA). The mechanism of polymerization has been widely discussed. Despite several proposals [101] over a long period of time, it is not until now that the ROP mechanism is about to be elucidated [102, 103]. The $Sn(Oct)_2$ is not thought to be the actual initiator since the molecular weight does not depend on the monomer-to-$Sn(Oct)_2$ molar ratio. The most promising mechanism is a "coordination-insertion" mechanism where a hydroxy functional group is thought to coordinate to $Sn(Oct)_2$, forming the initiating tin alkoxide complex.

Investigations of the coordination-insertion mechanism have resulted in two slightly different reaction pathways. Kricheldorf and coworkers have proposed a mechanism [103] where the co-initiating alcohol functionality and the monomer are both coordinated to the $Sn(Oct)_2$ complex during propagation. Penczek and coworkers have presented a mechanism [102] where the $Sn(Oct)_2$ complex is converted into a tin alkoxide before complexing and ring-opening of the monomer. Direct observation of this tin-alkoxide complex has been reported by using MALDI-TOF spectroscopy for both lactide [102] and ε-CL polymerization. Reactions 2.60 and 2.61 show the two different proposals. The main ROP mechanism proposals with $Sn(Oct)_2$ as catalyst, **a)** complexation of a monomer and alcohol prior to ROP and **b)** formation of a tin-alkoxide before ROP of ϵ-CL.



(2.60)



(2.61)

The $Sn(Oct)_2$ catalyst is a strong transesterification agent, and the resulting copolymers normally have a randomized microstructure [98]. An increase in reaction temperature or reaction time increases the amount of transesterification reactions.

The ROP of lactide with $Sn(Oct)_2$ is fairly slow and it is desirable for economic and commercial reasons to increase the rate of polymerization. The addition of an equimolar amount of triphenylphosphine increases the rate and, as an additional advantage, this compound delays the occurrence of the undesirable back-biting reactions.

b) Aluminum Tri-Isopropoxide

ROP initiated with aluminum tri-isopropoxide has been extensively investigated by several research groups since it yields well-defined polymers through living polymerization [104]. A living polymerization is a chain polymerization which proceeds in the absence of the kinetic steps of termination or chain transfer [104].

Polymerization with aluminum tri-isopropoxide is assumed to proceed through a “coordination-insertion” mechanism, which consists of monomer complexation to the active species and insertion by rearrangement of the covalent bonds. The mechanism leads to cleavage of the acyl-oxygen bond of the monomer and of the metal-oxygen bond of the propagating species. The propagation is characterized by the almost total absence of side-reactions such as transesterification reactions, at least until complete monomer conversion has occurred. The initiator is active at low temperatures (reaction temperatures of 0 –25 °C are often reported) and the initiator is preferentially used in solution polymerization.

c) Tin(IV) Alkoxides

Monotin alkoxides, tin dialkoxides and cyclic tin alkoxides have been utilized as initiators in the ROP of cyclic esters. The tin alkoxides are known to form cyclic species during synthesis and the dibutyltin alkoxides are known to exist as monomers and dimers. The cyclic tin alkoxides were originally studied because of their resistance towards hydrolysis. The tin alkoxides have been reported to be effective transesterification catalysts initiating polymerization at moderate temperatures [105].

The tributyl derivatives have been thoroughly studied since they are easily synthesized by nucleophilic substitution of commercial tributyltin chloride, they are easy to handle due to their moisture resistance, and they are relatively soluble in lactones.

The polymerization of lactones with tin alkoxides is thought to follow the “coordination-insertion” mechanism. The ring-opening of the monomer proceeds through acyl-oxygen cleavage with retention of the configuration. Tin(IV) complexes have been used to produce predominantly syndiotactic poly(b-hydroxybutyrate), macrocyclic poly(b-hydroxybutyrate), poly(ε-CL), and polylactide [105]. The cyclic tin alkoxides have the additional advantage of offering a convenient synthetic pathway for the synthesis of macromers, triblock, and multiblock copolymers.

d) Tin(II) Alkoxides

Recently, tin(II) butoxide was used in the polymerization of L,L-lactide [106].The initiation is fast and quantitative and no transesterification or back-biting reactions are observed. The reaction proceeds with acyl-oxygen bond scission with retention of the configuration, and can be used both in bulk and solution (THF, 20–80 ^{o}C) polymerization. It is possible to control the molecular weight in the range of 10^3 to 10^6 with a MWD of 1.15 –1.85. The polymerization is very fast, k p = 5 x10^{-1} mol^{-1} L s^{-1} , with only the rare earth alkoxides being faster.

e) Lanthanide Alkoxides

ROP of lactones and lactides using lanthanide alkoxide-based initiators is a relatively recent discovery. The first example of lactones polymerization by lanthanide alkoxide complexes was reported in a DuPont patent written by McLain and Drysdale in 1991 [107]. In general, the activity of these catalysts is much higher than that determined for aluminum alkoxides, especially in lactide polymerization. Polymers of relatively high molecular weight and narrow MWD are formed. The negative side-reactions such as macrocycle formation, transesterification, and racemization are absent.

Yttrium isopropoxide and yttrium 3-oxapentoxide initiators were the first lanthanide alkoxides described in the literature for the ROP of ε-CL [108]. The discovery of lanthanide-based initiator systems allowed the block copolymerization of ε-CL with compounds such as ethylene, tetrahydrofuran [109], L-LA, trimethylene carbonate, and methyl methacrylate. This type of initiator has also been used to prepare poly(b - butyrolactone)s.

2.5 Conducting Polymers (CP)

Conductive polymers have been the subjects of study for many decades as possible synthetic metals following the first report of electrical conductivity in a conjugated polymer (polyacetylene) in 1977 [110]. Many of these polymers, especially those with a conjugated π -bond system, often yield higher conductivity once having undergone the doping process. Conducting polymers are materials constituted by polymeric molecules with high conductivity. In this sense, the category includes inorganics (e.g. polysulfonitrle), organometalic (e.g. phtalocyanines) and organic (e.g. polythiophene) polymers. In a more narrow definition, the term applies to organic polymers in which the monomeric units are covalently linked. For these materials the fundamental prerequisite for conduction is the existence of extended polyconjuction. They all contain $\pi-$ conjugated systems, single and double bonds alternating along the polymers chain. A basic research goal in this field is to understand the relationship between the chemical structure of the repeating unit of the polymer and its electrical properties.

2.5.1 Historical Background

Polyacetylene is the simplest conjugated polymer and has been studied extensively since the initial reports of high conductivity in doped complexes in 1977 [110, 111]. Owing to its structural and electronic simplicity, polyacetylene serves as a model for developing both the electronic and physical properties of electronically conducting polymers with unique properties in both its reduced semi-conducting and highly doped conducting forms. Polyacetylene is highly crystalline, which has allowed direct structural analysis of both the doped and undoped forms [112-116].

Polythiophenes (PThs) have a special place among the conductive polymers due to its electrical properties, environmental stability in doped and undoped states, non-linear optical properties, and highly reversible redox switching [28]. As thiophene has a rich synthetic flexibility, allowing for the use of several polymerization methods and the incorporation of various side chain functionalities, PThs have become the most widely studied of all conjugated polyheterocycles [29]. In order to yield intractable polythiophene, the polymerization of thiophene was first carried out in a controlled manner in the early 1980s [30-33]. Even in such an unyielding form, this polymer displayed many promising optical and electronic properties. Unfortunately, its lack of processibility precluded further exploration of these attractive attributes.

Pyrrole (Py) is a five-membered heterocycle like thiophene. It has distinctly different behavior and a far greater tendency to polymerize oxidatively due to the presence of nitrogen in the ring. The first report of the synthesis of polypyrrole (PPy) related to its electrically conductive nature was published in 1968 [117]. It was synthesized through electrochemical polymerization and carried out in 0.1 N sulfuric acid to yield a black film. The improvements resulted from in-depth solvent and electrolyte studies have made the electrochemical synthesis of PPy the most widely employed method since then [118-120]. The properties of electrosynthesized PPy are quite sensitive to the electrochemical environment in which it is obtained. The conductivity, film morphology, and overall performance of synthesized PPy depend on the electrolytes employed in its electropolymerization. [121-123]. Furthermore, the water solubility of pyrrole allows aqueous electrochemistry [124], which is of prime importance for biological applications [125].

Polyaniline (PANI) is perhaps the oldest of the conducting polymers. References dating back to 1862 can be found describing a material known as “aniline black” [126]. A few reports surfaced on PANI in the 1960s [127-130], most notably a study investigating the effects of acids on PANIs conductivity [131], but it was not until the 1980s that its electrically conducting properties became fully appreciated [132]. Owing to its low cost and remarkable stability under a variety of conditions, PANI has become an extremely well-studied conducting polymer, (CP). This has resulted in PANI being the conjugated polymer of choice for many technological applications and led to its development as a commercial product [133-134].

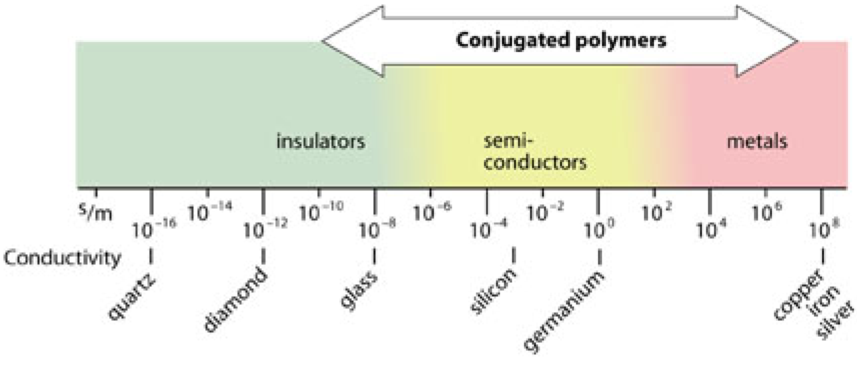
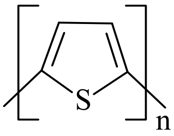
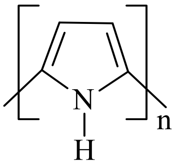


Figure 2.6. Conductivity range (s/cm)

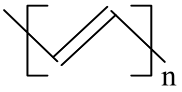
When polyacetylene [$(CH)_n$] produced by Shirikawa’s method exposed to oxidizing agents, its electrical conductivity increased 12 order of magnitude. Since that discovery, a vast array of other CPs has been synthesized. The most common of conductive polymers are shown in (2.62).



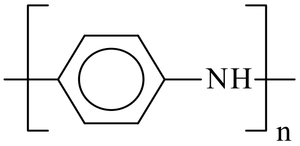
Polythiophene (PTh)



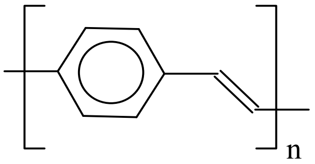
Polypyrrole (PPy)



Polyacetylene (PA)

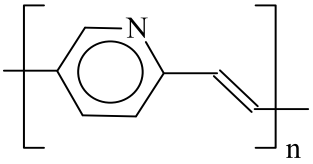


Polyaniline (PAn)

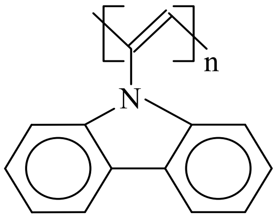


Poly(p-phenylenevinylene) (PPV)

(2.62)



Poly(2-vinylpyridine) (P2VP)



Poly(N-vinylcarbazole) (PVCZ)

2.5.2 Band Theory

All of the conducting polymers share one common structural feature, namely a rigid nature brought about by the sp^2 carbon-based backbone except polyaniline. The utilization of the conjugated construction affords polymer chains possessing extended π-systems, and it is this feature alone that separates CPs from their other polymeric counterparts. Using this generic, lowest energy (fully bonding) molecular orbital (MO) representation as shown by the π-system model, the picture of primary concern that is generated by these networks consists of a number of π and π^* levels (Figure 2.7). However, unlike the discreet orbitals that are associated with conjugated organic molecules, the energy of the polymers' MOs are so close in energy that they are indistinguishable. In fact, for long chains orbital separation is so small that band formation occurs as illustrated by the MO diagram (Figure 2.8).

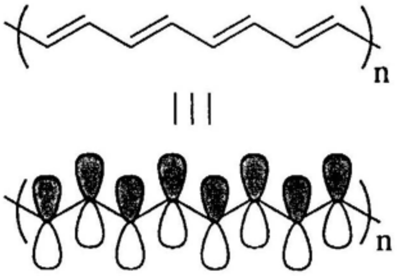


Figure 2.7. The π-system model

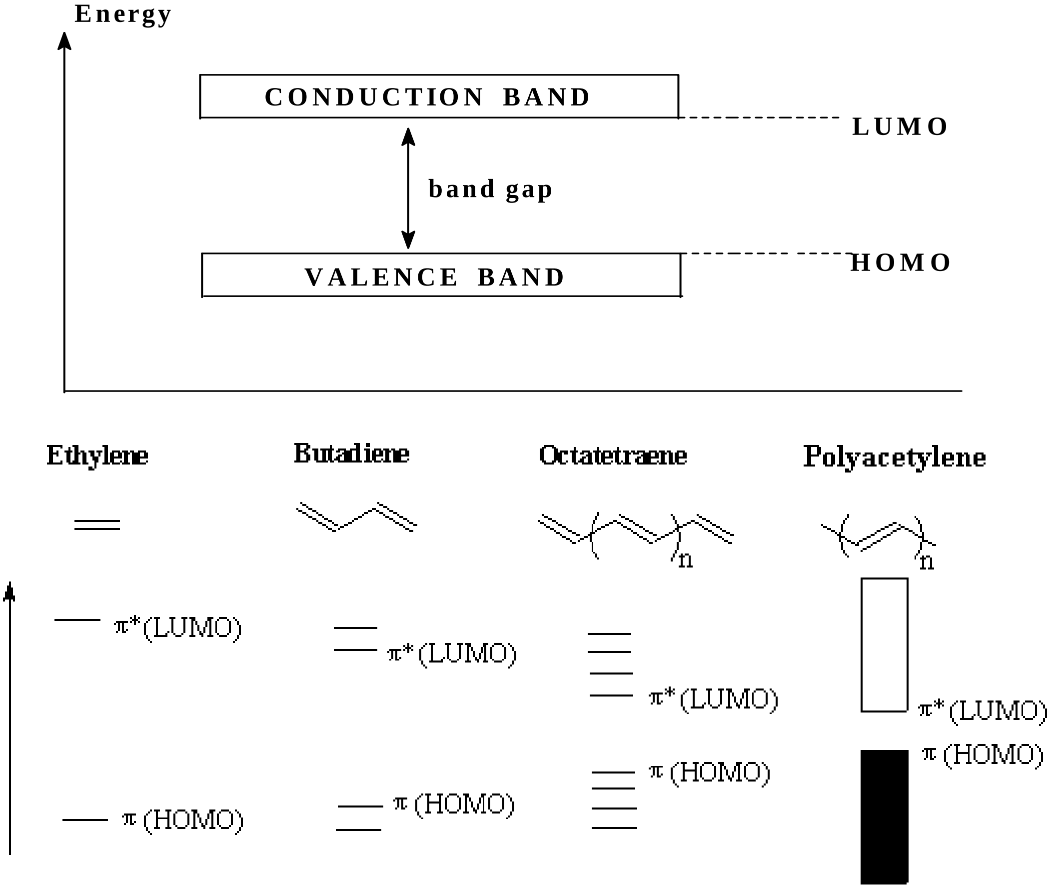


Figure 2.8. Molecular orbital (MO) diagram

The electrical properties of any material are based on the material's electronic structure. The presumption that CPs form bands through extensive molecular orbital overlap leads to the assumption that their electronic properties can be explained by band theory. With such an approach, the bands and their electronic population are the chief determinants of whether or not a material is conductive. As has been shown in Figure 2.9, materials are classified into three groups in terms of conductivity as being metals, semiconductors, or insulators. Metals are materials that possess partiallyfilled bands, and this characteristic is the key factor leading to the conductive nature of this class of materials. Semiconductors, on the other hand, have filled (valence bands) and unfilled (conduction bands) bands that are separated by a range of forbidden energies (known as the 'band gap'). The conduction band can be populated, at the expense of the valance band, by exciting electrons (thermally and/or photochemically) across this band gap. Insulators possess a band structure similar to semiconductors except here the band gap is much larger and inaccessible under the environmental conditions employed.

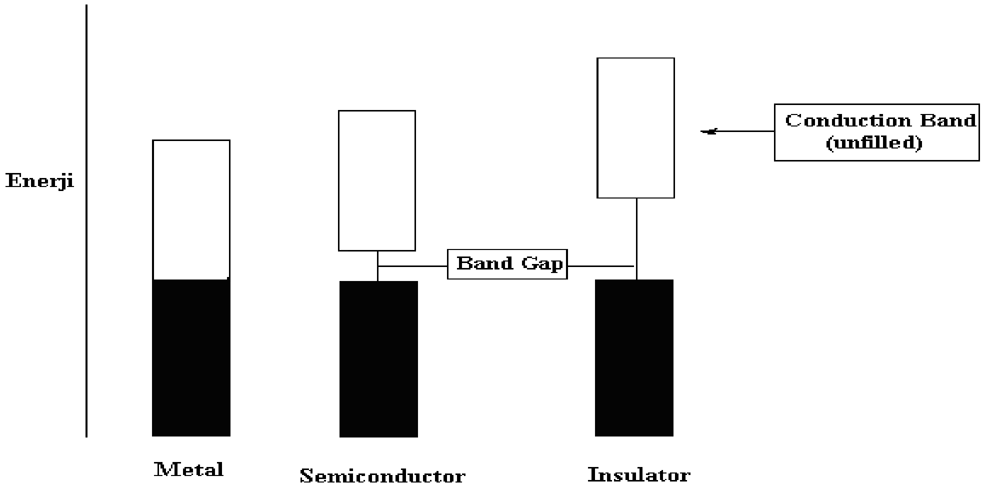


Figure 2.9. Energy level diagrams for three types of solids in terms of conductivity

CPs in their neutral state are insulators or, at best, weak semiconductors. Hence, there is enough of an energy separation between the conduction and valence bands that thermal energy alone is insufficient to excite electrons across the band gap. To explain the conductive properties of these polymers, several concepts from band theory and solid state physics have been adopted. For electrical conductivity to occur, an electron must have a vacant place (a hole) to move to and occupy. When bands are completely filled or empty, conduction can not occur. Metals are highly conductive because they possess unfilled bands. Semiconductors possess an energy gap small enough that thermal excitation of electrons from the valance to the conduction bands is sufficient for conductivity; however, the band gap in insulators is too large for thermal excitation of an electron across the band gap.

2.5.3 Doping and Electrical Conductivity

How can conjugated polymers conduct electricity? When an electron is removed from the top of the valence band of a conjugated polymer, such as polyacetylene or pyrrole, a vacancy (hose or radical cation) is formed that does not delocalize completely, as would be expected from classical band theory. Only partial delocalization occurs, extending over several monomeric units causing them to deform structurally. The diffuse nature of the extended π-system readily allows electron removal from, or injection, into the polymer. The term 'doping' has been borrowed from semiconductor physics with 'p-doping' and 'n-doping' being used to describe polymer oxidation and reduction, respectively. Doping in regards to semiconductors is quite different, as it is a very distinct process carried out at low levels 1% as compared to CP doping (usually 20-40%). However, the manner by which doping transforms a neutral CP into a conductor remained a mystery for many years. EPR (Electron Paramagnetic Resonance) studies have shown that both the neutral and heavily doped CPs possess no net spin, interpreted as no unpaired electrons, while moderately doped materials were discovered to be paramagnetic in nature. Conductivity experiments showed that it was the 'spin-less' heavily doped form that is the most conductive for a given CP. Such behaviour marks an sudden departure from simple band theory, which centres around spin-containing charge carriers.

Polyacetylene turns out to be a special case when considering its neutral and doped forms. Comparison of the two neutral forms, shown in Figure 2.10, reveals them to be structurally identical, and thus, their ground states are degenerate in energy. Two successive oxidations on one chain could yield radical cations that, upon radical coupling, become non-associated charges termed positive 'solitons'.

In contrast to polyacetylene, the other CPs shown in 2.61 have non-degenerate ground states (i.e. they do not possess two equivalent resonance forms), and thus, do not show evidence of soliton formation. In this instance, the oxidation of the CP is believed in the destabilization (raising of the energy) of the orbital from which the electron is removed. This orbital's energy is increased and can be found in the energy region of the band gap as shown in Figure 2.11. Initially, if only one electron per level is removed a radical cation is formed and is known as a 'polaron' (Figure 2.11b). Further oxidation removes this unpaired electron yielding a dicationic species termed a ‘bipolaron’(Figure 2.11c). High dopant concentrations create a bipolaron-‘rich’ material and eventually lead to band formation of bipolaron levels. Such a theoretical treatment, thereby, explains the appearance, and subsequent disappearance, of the EPR signal of a CP with increased doping as the neutral polymer transitions to the polaronic form and subsequently to the spinless bipolaronic state.

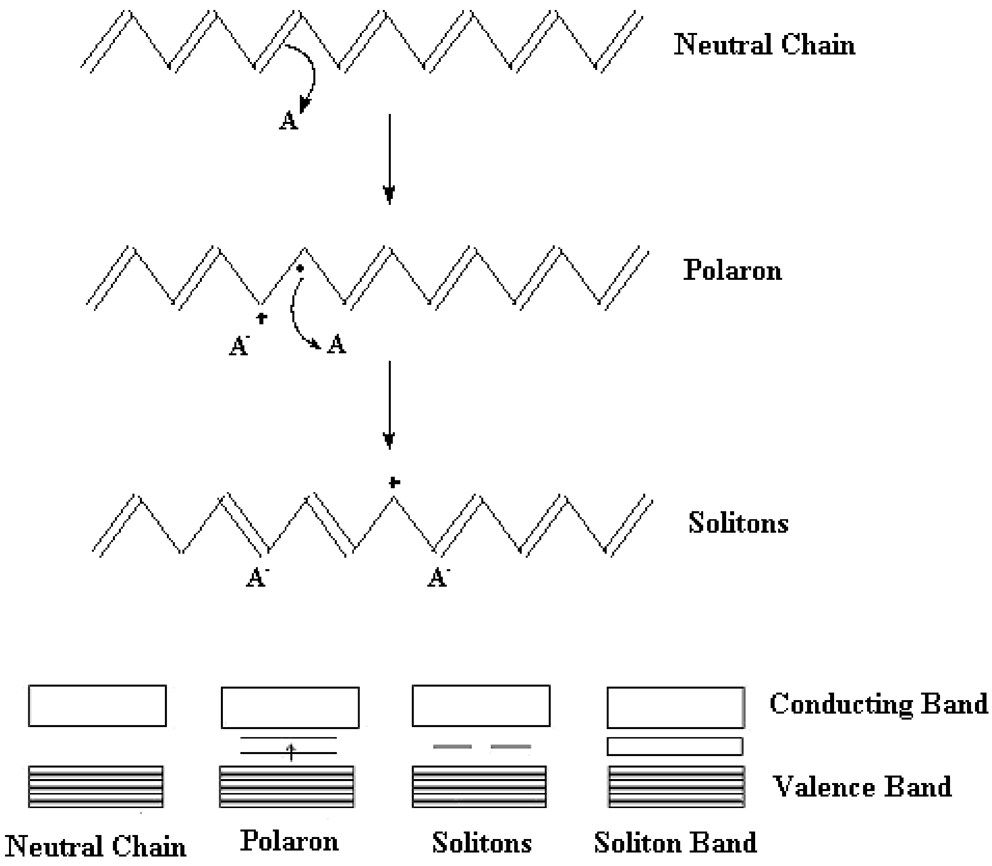


Figure 2.10. Neutral and doped forms of polyacetylene

Contrary to polyacetylene’s independent charges, the bipolaron unit remains intact and the entire entity propagates along the polymer chain. This behavior of polythiophene is given in 2.63a as the example. In the case of unsubstituted polythiophene, the bipolaronic unit is believed to spread over six to eight rings. This ‘bipolaron length’ is by no means an absolute number as different polymer backbone and substituent types yield various lengths [135]. Also, the polaron and bipolaron unit of polypyrrole are showed in 2.63b.

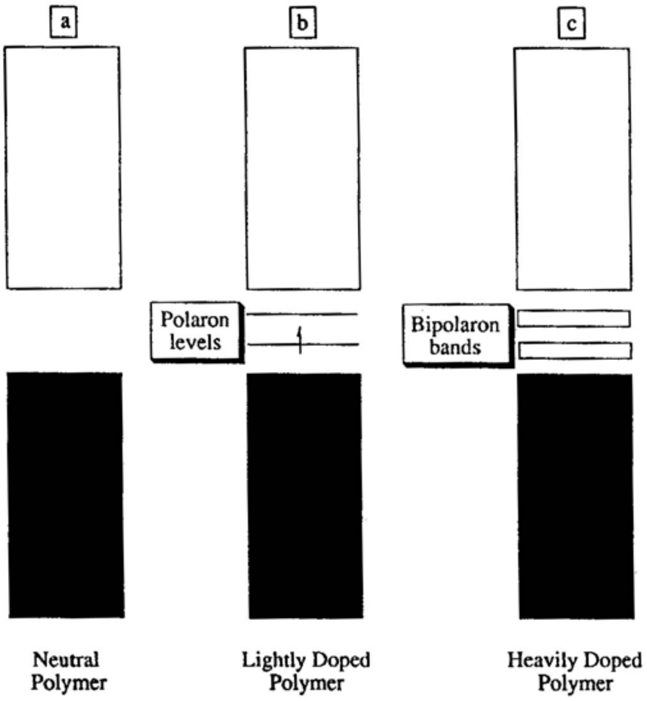
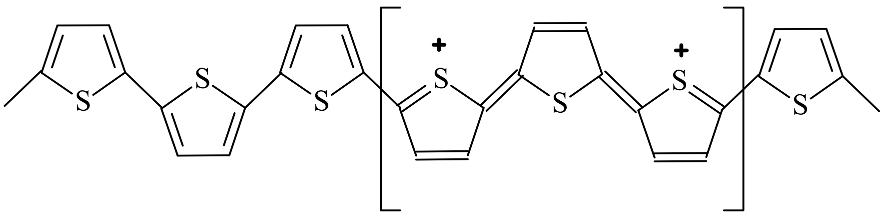
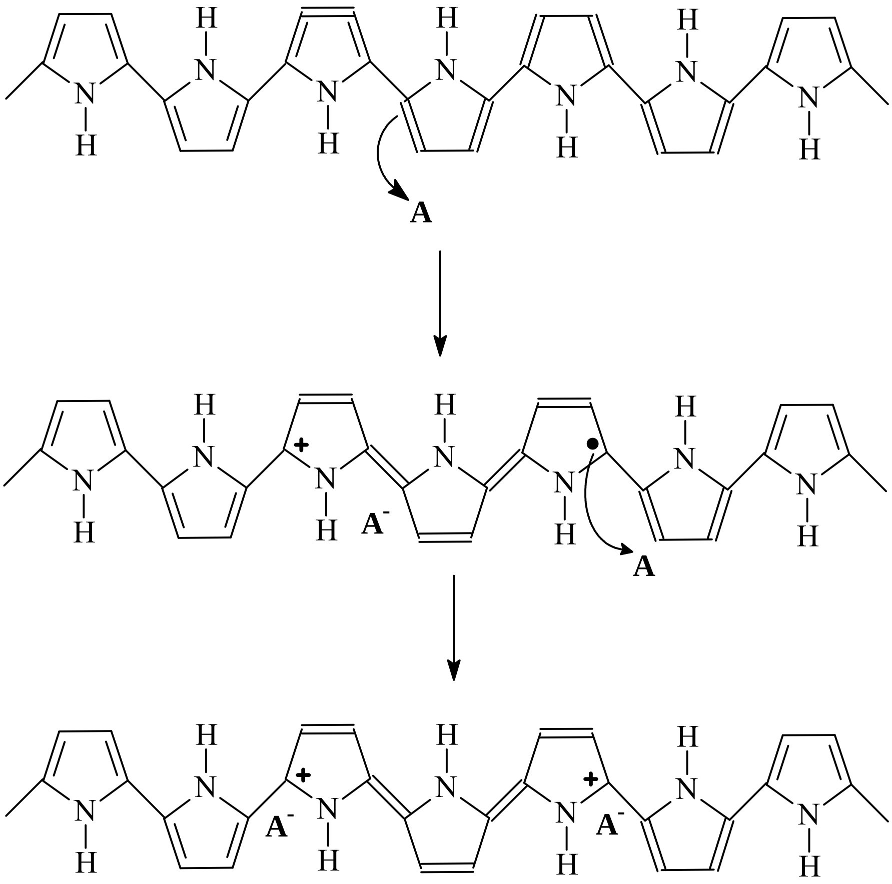


Figure 2.11. Band Structures of **a)** neutral polymer **b)** lightly doped polymer **c)** heavily doped polymer



(2.63a)



(2.63b)

2.6 Synthesis of Conducting Polymers

Conducting polymers can be prepared either chemically or electrochemically [136]. The latter is generally preferred because it provides a better control of film thickness and morpholgy, and cleaner polymers when compared to chemical oxidation. The chemical oxidation method usually leads to fine powders, while electrochemical synthesis provides free-standing films on electrode.

Generally, poly(heterocycles)s are synthesized via chemical methods with the route of oxidative coupling and condensation of the monomeric precursors. Oxidative coupling is based on the oxidation of monomer under Friedel-Crafts conditions whereas condensation relies on coupling of dihalogen aromatics by reducing agent. On the other hand, the electrochemical routes to poly(heterocycle)s are anodic and oxidative coupling, which parallel the chemical oxidative coupling and condensation reactions (2.64).

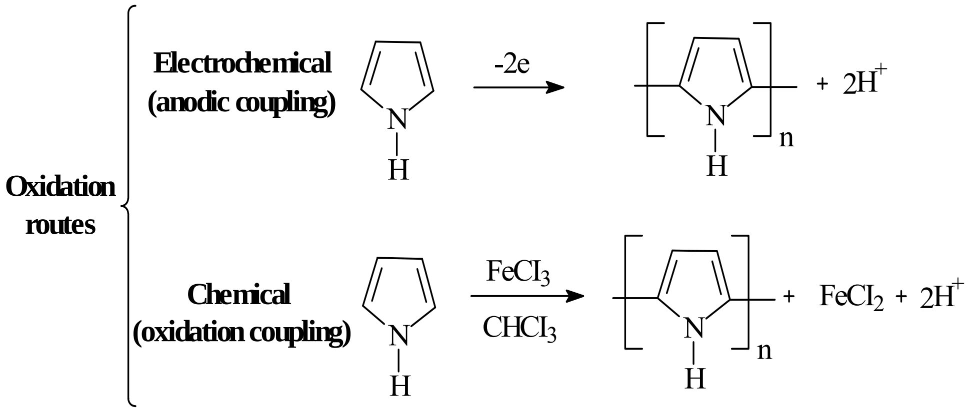
Anodic coupling consists of the oxidation of the monomer to a polymer with proton elimination whereas cathodic coupling is based on the reduction of the suitable dihalogen-substituted monomer to a polymer with halogenide release.

Anodic coupling is preferred because:

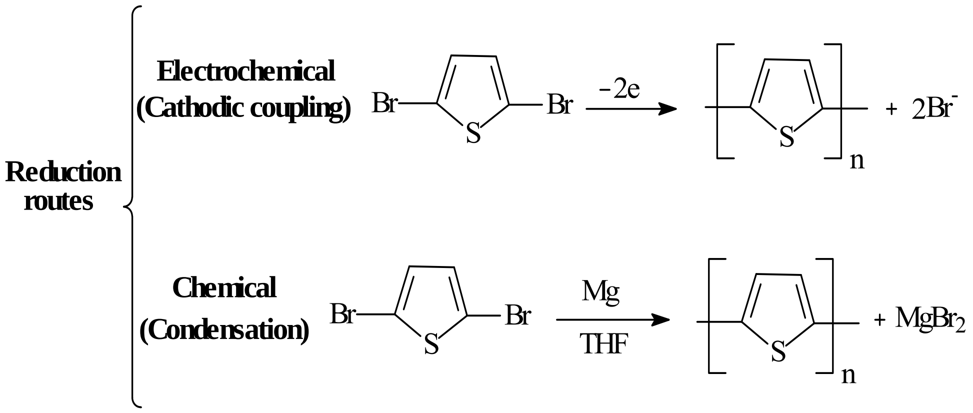
(1) It uses the modified monomer,

(2) The formed polymer, being more oxidized (doped), is produced in the conductive state and therefore, allows the continuous deposition of the material up to considerable thicknesses.

The anodic coupling method is used for the most investigated polymers such as polypyrrole and polythiophene. On the other hand, cathodic coupling is employed when the anodic one is precluded by the non-oxidizability of the monomer, the occurrence of demolitive oxidation in the course of coupling and when the requirement of definite positions of coupling are not guaranteed by highly selective spin densities in radical cation.



(2.64)



Electrosynthesis conditions involve many experimental variables such as solvent, monomer concentration, electroyte type, temperature, electrode material, and applied electrical conditions.

The solvent must be of sufficiently high dielectric constant to ensure the ionic conductivity of the electrolytic medium, i.e., to dissolve and dissociate the supporting electrolyte. It must also possess a potential window open at the potential required to oxidize or reduce the monomer. The degree of nucleophilicities of solvent and electrolyte is very important because polymerization reaction is sensitive to the nucleophilicity of the environment in the region of the electrode surface owing to the presence of radical cation.

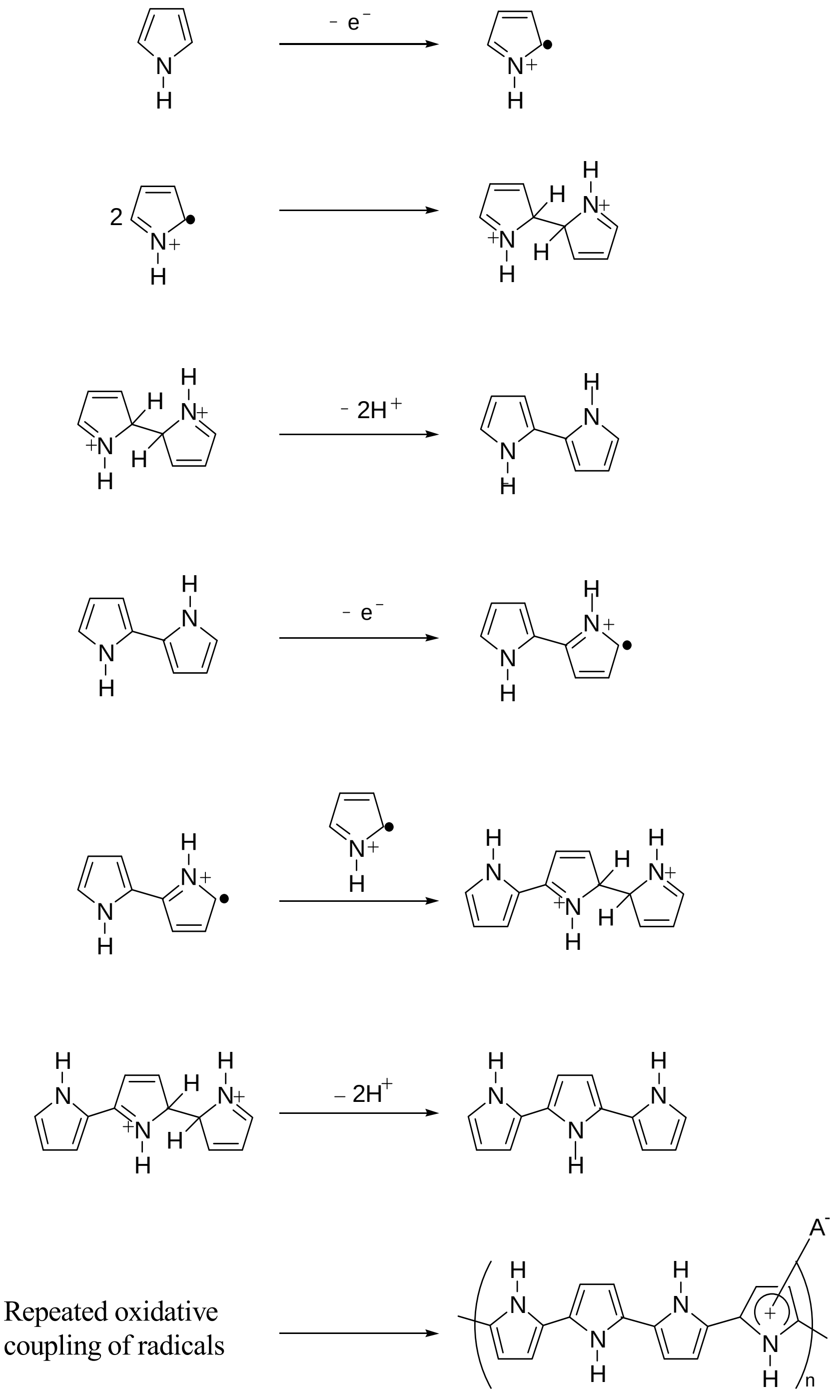
The monomer concentration is generally high (0.1M or more) to avoid competitive reactions of the radical cations or of the oxidized polymer with nucleophiles in the medium. But this parameter mostly depends on the oxidation potential of the monomer. As the monomer is more easily oxidized the competition of parasitic reactions decreases so that even milimolar concentration may be used for efficient electropolymerization.

The type of supporting electrolyte and the particuarly the anion in the case of anodic coupling, is most important. Anion part of the electrolyte must be “innocent” type such as perchlorate, tetrafluoroborate or hexafluorophosphate.

Working electrode material should be so selected that it does not oxidize concurrently with the monomer. To enable this condition, anodes are made from inert conducting materials such as platinium, gold, glassy carbon, and tin or indium-tin oxide (ITO) [137].

2.6.1 Mechanism of Electrochemical Synthesis

In an electrochemical polymerization of heterocycles, the mechanism proposed by anodic coupling [138] is analogous to the already known coupling of aromatic compounds [139, 140]. In the first step oxidation, radical cation of the monomer is formed. The second involves the coupling of two radical cations to produce a dihydrodimer dication which leads to a dimer after loss of two protons and rearomatization (2.65). Due to the applied potential, the dimer, which is more easily oxidized than the monomer, occurs in its cation radical form and undergoes a further coupling with a monomeric radical. Subsequent electrochemical and chemical steps proceed until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the electrode surface. Coupling is generally a second order reaction between radical cations followed by fast proton release as shown for pyrroles (2.65). The coupling rate decreases as the oligomer length is increased and the activation energy increases linearly with the inverse of the oligomer length [141].



(2.65)

2.6.2 Electrochemical Techniques

The electrochemical techniques generally employed in the electrochemical synthesis of conducting polymers are potentiostatic or galvanostatic electrolysis. They have advantages over chemical oxidative polymerization.

Polymerization carried out via electrochemical techniques is simple, selective, and reproducible. Reactions are done at room temperature. Thickness of the films can be controlled and it is also possible to produce homogenous polymers. Films are directly formed at the electrode surface. Moreover, graft and block copolymers can be easily obtained.

2.6.2.1 Constant-Current Electrolysis (Galvanostatic)

Constant-current, or controlled-current, electrolysis (CCE) is very simple and carried out in a cell containing two electrodes. In this method, current is kept constant throughout the electrolysis and potential is allowed to vary. In a typical experiment, a direct current of fixed magnitude between the anode and cathod is passed for the necessary time. This may be done by using current sources either with a variable voltage in series with the cell (as resistor) or a fixed voltage source and a variable resistor. Although CCE is simple in application, it has some disadvantages. The major disadvantage of constant-current electrolysis is the lack of selectivity. As the potential is a variable parameter, all possible redox processes may take place. Also, the involvement of species present in the system in addition to the monomer is inevitable. Therefore, complications may arise in initiation and propagation steps.

2.6.2.2 Constant-Potential Electrolysis

Three-electrode system is employed in constant potential electrolysis. The potential of the working electrode (WE) with respect to that of a reference electrode (RE) is adjusted to a desired value and kept constant by a potentiostat while current is allowed to vary. The voltage between the working and the reference electrodes may be called the polymerization potential. Creation of undesired species is prevented by keeping the potential constant and thus the initiation becomes selective, that is, through the monomer itself.

2.6.2.3 Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is used to find out the electrochemical behavior of electroactive species. In this technique the potential is linearly scanned up to a value suitable for polymer formation and then reversed to its initial value. The voltage applied to the working electrode as a cyclic triangular wave (Figure 2.12) and then current response is plotted as a function of applied potential by a recorder (Figure 2.13). The shape of the cyclic voltammogram of a material is highly dependent on relative rates of electron transfer, mass transport, and any chemical reactions at the electrode. The formation of conducting polymer can be clearly followed by cyclic voltammetry. As the polymer coated on the electrode is conductive, this causes the increase of electrode surface area, peak height continously increases with repetitive scannings. Shortly, the cyclic voltammogram of a material provides to understand its electroactivity, redox potential, mechanism of the electrochemical reaction.

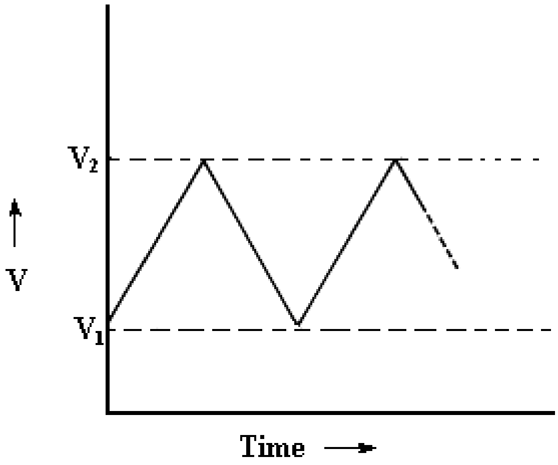


Figure 2.12. Triangular wave function

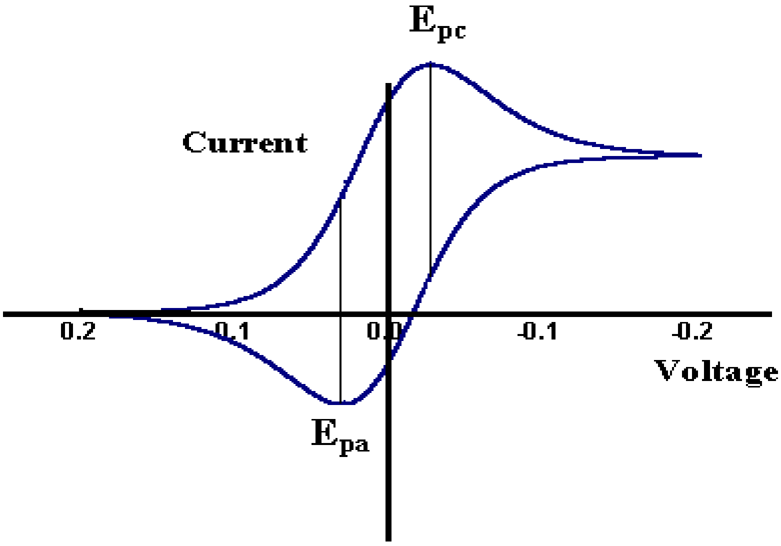


Figure 2.13. Cyclic voltammogram of reversible process

2.6.3 Oxidative Chemical Polymerization

Oxidative chemical polymerization is very simple method to prepare conducting polymers [142]. In this method, a stoichiometric amount of oxidizing reagent is used to form polymer that is in its doped or conducting form. $FeCl_3$ is generally employed as a chemical oxidant in the polymerization of the heterocyclic monomers [143,144]. Reduction of the synthesized monomer to the neutral state is achieved by addition of a strong base such as ammonium hydroxide or hydrazine. Benzene can also undergo oxidative polymerization with $AlCl_3$/ $CuCl_2$ to yield poly (p-phenylene) [28a].

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Methyl Methacrylate (MMA) (Aldrich)

It was washed with 5% aq. NaOH solution, dried over $CaCl_2$ and vacuum distilled from CaH_2 prior to use.

Epsilon Caprolactone (ε-CL)

It was vacuum distilled over calcium hydride just before use.

Tetrahydrofuran (THF)

THF (Merck) was dried over KOH, distilled over sodium wire, and finally distilled over sodium/benzophenone ketyl prior to use.

Ethylene Oxide

It was purified by repeated trap-to-trap distillations over calcium hydride and finally distilled over sodium mirror.

Styrene (Fluka)

Styrene were purified by the usual methods and distilled in vacuo over CaH_2.

Pyrrole (Py) (Aldrich) and Thiophene (Th) (Aldrich)

It was distilled before use.

3.1.2 Solvents

Dichloromethane (CH_2Cl_2) (Lab-scan)

Methylene chloride was used as solvent for dissolving bulky polymer formations, It was first washed with conc. H_2SO_4 until the acid layer remained colourless, then washed with water, aq. %5 NaOH and then water again. It was pre-dried with $CaCl_2$ and distilled from CaH_2 kept over activated molecular sieve (type 4 A^0).

Chloform (Lab-scan)

It was dried by diphosphorous pentaoxide and distilled over calcium hydride.

n- Hexane (Aldrich)

It was used without further purification.

Tetrahydrofuran (THF) (J.T. Baker)

It was used as eluent for chromatography as received (HPLC grade).

Methanol (Technical)

It was used for the precipitation of polymers without further purification.

3.1.3 Initiators and Other Chemicals

Triflic anhydride (Merk)

It was distilled under vacuum and kept over nitrogen.

Methyl triflate (Fluka)

It was distilled under vacuum and kept over nitrogen.

α,α'-Azobisisobutyronitrile (AIBN) (Fluka)

It was used as an initiator for free radical polymerization and recrystallized from methanol.

ω,ω–Dimethoxy-ω-phenylacetophenone (DMPA) (Ega-Chemia)

It was used as a photoinitiator without further purification.

Maleic anhydride (aldrich)

It was sublimed before use.

Diphenyl Ethylene (Merck)

It was distilled before use.

Thionyl chloride (Fluka)

It was distilled just before use.

Methacryloyl chloride (MAC) (Fluka

It was distilled over calcium hydride.

Acryloyl Chloride (Fluka)

It was distilled over calcium hydride.

The following chemicals were used as received from the indicated suppliers.

Ethlene Glycol (Merck), Glycerol (Merck), Pentaeritritol (Merck), Acetic anhydride (Merck), *p*-amino benzoic acid (Fluka), Hydroquinone (Fluka), Calcium Hydride (Merck), NaH (Merck), Thiophene methanol (Merck),

Thiphene ethanol (Aldrich), Thiphene carboxcylic acid (Aldrich), $FeCI_3$ (Aldrich), $MgSO_4$ (Aldrich).
And the other chemicals were used as received.

3.2 Equipments

3.2.1. Photoreactor

A merry-go-round type photoreactor equipped with 16 Philips 8W / O6 lamps emitting light nominally at 350 nm was used.

3.2.2 Infrared Spectrophotometer (IR)

IR spectra were recorded on a Shimadzu IR-470 infrared spectrophotometer.

3.2.3 Elemental Analysis

Elemental analysis measurements were performed by a CHNS-932 (LECO) instrument

3.2.4 Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR analyses were recorded on a Bruker 250 MHz NMR Spectrometer.

3.2.5 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) analyses were performed on Agilent 1100 instrument with a set up consisting of an Agilent 1100 RI dedector equipped with three Waters ultrastyragel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min. Molecular weights were calculated by using monodisperse polystyrene standards. For molecular weight of polymers of ε-caprolactone the following conversion formula was used [145]. $M_{\mathrm{PCL}} = 0.259 M_{\mathrm{PSt}}^{1.073}$

3.2.6 Potentiostat and Galvanostat

Films were electrochemically polymerized by potentiostatic methods by using Wenking Model POS 73 and ST 88 potentiostats. The function of potentiostat is to maintain the potential of the working electrode (WE) at an adjusted level with respect to a fixed reference electrode (RE). The potential difference between the WE and RE is equal to input potential that can be controlled externally. The current driven by the potentiostat (between WE and RE) can be determined by measuring the voltage drop across a small resistance R connected to the counter electrode in series.

In a three electrode potentiostatic system, the major current passes only through the counter electrode (CE) and WE. The current amplifier supplies current to the cell (between the WE and CE), regardless of the solution resistance. By this way the purpose of maintaining potential control between the two electrodes has been accomplished. Films were electrochemically polymerized by galvanostatic method by using NEL PS 2000 galvanostat.

3.2.7 Electrolysis Cell

Electrochemical polymerization was carried out in a H-shaped cell which can hold 50 mL solution. Working and the counter electrodes were platinum foils with area of 1.5 cm^2. This cell is a three-compartment one which is divided into two compartments as the catholyte and anolyte with a medium porosity sintered glass disc of 2.0 cm in diameter. Reference electrode was inserted to the working side of the cell and a Ag/Ag^+ (10^{-2} M) was utilized as the reference electrode. The cell has gas inlets to pass the N_2 gas through the solution.

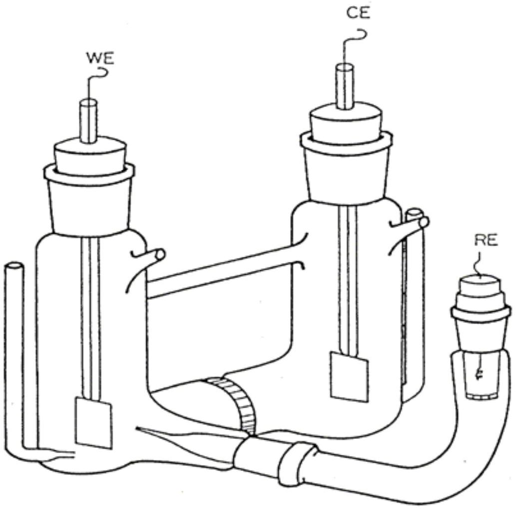


Figure 3.1. H-shaped electrolysis cell

3.2.8 Cyclic Voltammetry (CV)

Cyclic voltammetry system is a convenient way of obtaining the oxidation-reduction peak potentials of the substrates such as monomers and to analyze the electroactivity of polymers. The cell consists of a platinum bead working electrode of 1 cm wire in length, a platinum spiral counter electrode (3 cm coil), and a Ag/Ag^+ reference electrode. The volume of the cell was about 15 mL. CV experiments were carried out by a Bank Wenking POS 2 potentiostat/galvanostat. XY recorder was used to obtain the voltammograms.

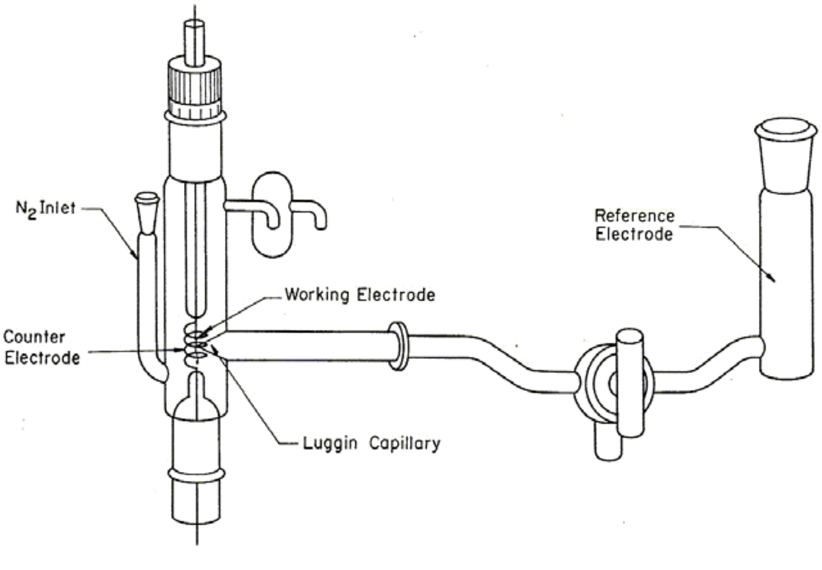


Figure 3.2. Cyclic voltammetry cell

3.2.9 Differential Scanning Calorimetry (DSC)

A Du Pont modular thermal analyzer system in conjunction with 910 differential scanning calorimeter was used to perform thermal analysis. A constant heating rate of 10 ˚C/min was using during DSC experiments.

3.2.10 Thermal Gravimetry Analysis (TGA)

A Du Pont modular thermal analyzer system in conjunction with 951 thermal gravimetric analyzer was used to perform thermal analysis. TGA experiments were performed under a dry nitrogen purge.

3.2.11 Four Probe Conductivity Measurements

Conductivity measurements can be performed by four probe and two probes techniques. The former is preferred, because it eliminates the error caused by contact resistance, whereas the latter does not. Two probe technique is usually used, prior to four technique, to see if the material is conductive or not.

In four probe technique, four equally spaced osmium tips were placed onto a head. The head was lowered to the sample until the four probes touch the sample. A constant source was used to pass a steady current through the outermost probes and voltage drop across the inner two was measured (Figure 3.3.).

Conductivity was given by the equation:

$$\sigma = \ln 2 / (\pi d \times i/V) \qquad \text{(Eq:3.1)}$$

where σ is the conductivity, i as the current applied through the outer probes, V voltage drop measured across the inner probes and d is the sample thickness.

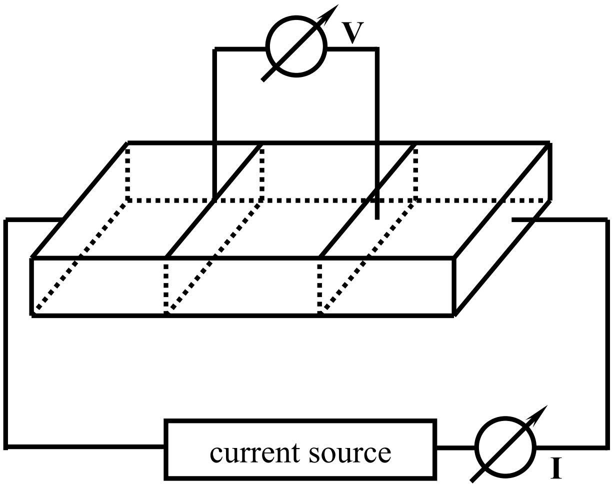


Figure 3.3. Schematic diagram of four probe technique

3.2.12 Scanning Electron Microscopy (SEM)

SEM is a surface analytical technique which is employed to study the morphology of conducting polymer film surfaces and provides valuable information on the structure of the monomer, the nature of dopant and the thickness of the film. SEM of copolymer films was performed using a JEOL model JSM-6400 scanning electron misroscope at 20 kV with varying levels of magnification.

3.3 Preparation Methods

3.3.1 Synthesis of Monomers Containing Thiophene Moiety (s)

3.3.1.1 Synthesis of Mono Thienyl Functional Monomer

3.3.1.1.1 Synthesis of 4-Maleimidobenzoic Acid (MBA)

MBA was synthesized by the condensation reaction of maleic anhydride with *p*-amino benzoic acid followed by cyclodehydration using acetic anhydride and sodium acetate according to literature procedure [146]. Yield: 79 %; mp: 232 ^{0}C (Literature [147] mp: 244 ^{0}C).

IR (cm^{-1}): 3460-3200 (COOH), 3105 (C=C), 2300 (COOH), 1720 (CO-N-CO), 1610 (C=C), 1400 (CH), 1217 (-C-O), 820 (phenyl), 720 (cis CH=CH).

3.3.1.1.2 Synthesis of 4-Maleimido Benzoic Acid Chloride (MBACI)

This intermediate was synthesized in 73% yield according to the literature procedure [146]. mp: 157-158 ^{0}C (literature [146] mp: 168-169 ^{0}C).

IR (cm^{-1}): 1770 (COCI), 1715 (CO-N-CO), 1600 [(C=C), 1370 (CH)], 700 (cis CH=CH).

3.3.1.1.3 Synthesis of N-(4-(3-thienyl methylene)-oxycarbonylphenyl)maleimide (MBThi)

To a mixture of 2.40 g (1.98 mL, 21 mmol) 3-thiophene methanol and 2.02 g (2.77 mL, 20 mmol) dry triethyl amine (TEA) in a two necked round bottom flask equipped with a reflux condenser and a dropping funnel, 4.71 g (20 mmol) of MBACI dissolved in 100 mL of dry chloroform was added dropwise with stirring. The reaction was then kept at reflux for 3 days with continuous stirring. Upon the completion of the reaction, the reaction mixture was washed with 1 % HCI solution and distilled water and dried over $CaCI_2$. After removal of solvent evaporation, the residue was extracted with methanol to remove unreacted thiophene methanol and MBA. Then residue was purified by reprecipitation three times from THF solution to hexane and a brownish solid product was obtained. After filtration, it was dried in vacuum oven. Yield: 55 %; mp: 85 ^{0}C.

IR (cm^{-1}): 3100 (C=C); 2900 ($-CH_2$); 1770, 1710, 1380, 1142, 699 (imide ring); 1710, 1270, 1210 (ester); 3110, 769 ($C-H_\alpha$ of thiophene ring); 3020, 856 ($C-H_\beta$ of thiophene ring)

Anal. Calcd. for $C_{16}H_{11}NO_4S$: C, 61.28 %; H, 3.51 %; N, 4.47 %; S, 10.21 %. Found: C, 61.33 %; H, 3.55 %; N, 4.56 %; S, 10.15 %.

^{1}H-NMR (δ, ppm from TMS in DMSO-d_6): 8.11-8.07 (d, 2H, Ar-H, ortho to ester group); 7.69 (s, 1H, Ar-H, ortho to imide group); 7.59-7.55 (m, 2H, 2- and 4-position in thiophene ring); 7.52 (s, 1H, Ar-H, ortho to imide group); 7.26-7.22 (bs, 3H, CH=CH and 5-position in thiophene ring); 5.36 (s, 2H, CH_2).

3.3.1.2 Synthesis of 2-[(3-thienylcarbonyl) oxy] ethyl 3-thiophene carboxylate (TOET)

A mixture of 3-thiophenecarboxylic acid (0.700 g, 5.4 mmol) and thionyl chloride (0.765 g, 6.5 mmol) was placed in 25 mL round bottom flask carrying a drying tube and refluxed gently at 100 ^{0}C for 30 min. A water aspirator vacuum to the top of the condenser was applied to remove any thionyl chloride, and ethylene glycol (2.5 mmol) was added to the mixture. The reaction was allowed to stand on the bath for 15 min. and then cooled, diluted with 50 mL ether, and transferred to a separatory funnel. The mixture was washed with water and twice with $NaHCO_3$ solution, and dried over $MgSO_4$. The solvent was removed over rotatory evaporator. A yellowish-oily product was obtained with 54% yield. The resultant product was further purified via column chromatography, and white crystals were obtained.

IR (KBr) (cm^{-1} IR (KBr) (cm^{-1}): 3150 cm^{-1} (aromatic C-H), 2950-2900 cm^{-1} (aliphatic C-H), 1725 cm^{-1} (C=0 stretching), 1260-1000 cm^{-1} (C-O-C symmetric and asymmetric stretching), 845 cm^{-1} (β -hydrogen of thiophene), 760 cm^{-1} (α -hydrogen of thiophene).

Anal. Calcd. for $C_{12}H_{10}O_4S_2$: C, 51.10 %; H, 3.55 %; S, 22.71 %. Found: C, 51.15 %; H, 3.60 %; S, 22.53 %.

^{1}H-NMR in $CDCl_3$ (δ ppm) : δ: 8.2 (m, 2, thiophene), 7.5 (m, 2, thiophene), 7.2 (m, 2, thiophene) and 4.2 ppm (t, 4, methylene) .

3.3.1.3 Synthesis of 2, 3-bis [(3-thienylcarbonyl) oxy] propyl 3-thiophene carboxylate (TOPT)

A mixture of 3-thiophenecarboxylic acid (0.7000 g, 5.4 mmol) and thionyl chloride (0.765 g, 6.5 mmol) was placed in 25 mL round bottom flask carrying a drying tube and refluxed gently at 100^{0}C for 30 min. A water aspirator vacuum to the top of the condenser was applied to remove any thionyl chloride, and glycerol (1.7 mmol) was added to the mixture. The reaction was allowed to stand on the bath for 15 min. more and then cooled, diluted with 50 mL ether and transferred to a separatory funnel. The mixture was washed with water and twice with $NaHCO_3$ solution and dried over $MgSO_4$. The solvent was removed over rotatory evaporator. A yellowish-oily product was obtained. The resultant product was further purified via column chromatography, and white crystals were obtained with 47% yield.

IR (KBr) (cm^{-1}): 3100 cm^{-1} (aromatic C-H), 2950-2850 cm^{-1} (aliphatic C-H), 1725 cm^{-1} (C=0 stretching), 1260-1000 cm^{-1} (C-O-C symmetric and asymmetric stretching), 845 cm^{-1} (β -hydrogen of thiophene), 750 cm^{-1} (α -hydrogen of thiophene).

^{1}H-NMR (δ, ppm) data for TOPT: 8.2 (m, 3H, thiophene), 7.5 (m, 3H, thiophene), 7.2 (m, 3H, thiophene), 4.6-4.3 (m-d, 4H, methylene), 5.6-5.2 ppm (quintet, 1H, methylene).

3.3.1.4 Synthesis of 3-[(3-thienylcarbonyl) oxy]-2, 2-bis {[(3-thienylcarbonyl) oxy]} propyl 3-thiophene carboxylate (TOTPT)

A mixture of 3-thiophenecarboxylic acid (0.833 g, 6.5 mmol) and thionyl chloride (0.942 g, 8.0 mmol) was placed in 25 mL round bottom flask carrying a drying tube and refluxed gently at 100 ^{0}C for 30 min. A water aspirator vacuum to the top of the condenser was applied to remove any thionyl chloride and then pentaerythritol (1.6 mmol) was added to the mixture. The reaction was allowed to stand on the bath for 15 min. more and then cooled. The product was collected by suction filtration and washed with water to remove unreacted pentaerythritol. The resultant product was further purified via column chromatography and white-fine crystals were obtained with 53% yield.

IR (KBr) (cm^{-1}): 3160 cm^{-1} (aromatic C-H), 2900-2850 cm^{-1} (aliphatic C-H), 1675 cm^{-1} (C=0 stretching), 1270-1000 cm^{-1} (C-O-C symmetric and asymmetric stretching), 845 cm^{-1} (β -hydrogen of thiophene), 740 cm^{-1} (α -hydrogen of thiophene).

^{1}H-NMR in $CDCl_3$ (δ ppm): δ: 8.2 (m, 4H, thiophene), 7.5 (m, 8H, thiophene), and 4.8 ppm (s, 8H, methylene).

3.3.2 Synthesis of Macromonomers Possessing Thiophene Moiety(s)

PEO macromonomers and their corresponding starting materials were kindly synthesized in Toyohashi University of Technology.

3.3.2.1 Synthesis of α-ω-Heterofunctional Polyethylene Oxide (PEO) Macromonomers

PEO macromonomers possessing thiophene moiety at one end and methacrylate group at the other end were prepared by a conventional high vacuum line technigue. 13.5 mmol of 3-Thiphene ethanol, 6 mmol of potassium naphthalene in THF, 295 mmol of EO and THF, each in an ampoule with a breakable seal, were fitted into a flask, baked under vacuum and sealed off from the vacuum line. 3-Thiphene ethanol and THF were introduced into the cleanly dried flask and then reacted with potassium naphthalene in THF. The dark green colour due to potassium naphthalene almost immediately disappeared. Then, EO, chilled by dry ice/isopropanol, was introduced to the flask and polymerized at 40 ^{0}C over 3 nights. Then the flask was fitted into a vacuum line with the ampoules containing 50 mmol of MAC and 15 mmol of triethylamine (TEA). After evacuation, the system was sealed off and the contents were mixed to terminate the poymerization by breaking the breakable seals. The reaction took place immediately to a cloudy appearence indicating formation of KCI and Et_3NHCI. The mixture was poured into a large amount of acetone (700 mL) to precipitate the salts, which were filtered off. The filtrate was concentrated by a rotary evaporator under a reduced pressure to about 70 mL and poured into a large amount of hexane (700 mL). The precipitated macromonomer was collected by filtration and freeze-dried from hexane. The yield was almost quantitative.

3.3.2.2 Synthesis of Poly(ε-Caprolactone) Macromonomers

Certain amounts of monomer (ε-caprolactone), stannous octoate and thiophene methanol were added under nitrogen in previously flamed and nitrogen- purged schlenk tubes equipped with magnetic stirrer. The ε-CL polymerizations were carried out in bulk at 110 ^{o}C. After a given time the mixtures were diluted with CH_2Cl_2 and poured into ten-fold excess of cold methanol. The polymers were collected after filtration and drying at room temperature in a vacuum for three days.

3.3.2.3 Synthesis of Thiophene Terminated Polytetrahydrofuran (PTHF) Macromonomers

3.3.2.3.1 Synthesis of Monofunctional PTHF Macromonomers

3.3.2.3.1.1 Synthesis of Thiophene Methonate

A solution of thiophene methanol (1.52 g, 13 mmol) in dry THF (30 mL) was added to a solution of NaH (0.50 g-60% in oil, 12.3 mmol) in dry THF (20 mL) at room temperature under nitrogen atmosphere. The resulting solution was stirred at room temperature for two hours. After removal of THF by rotary evaporation, it was dried in vacuum oven. An orange solid product was obtained.

Polymerization flask equipped with nitrogen inlet and a magnetic stirrer was flushed with dry nitrogen. Then 10 ml of freshly distilled THF was introduced with a syringe. The polymerization was started at room temperature by injecting methyl triflate (0.097 mL, 8.9×10^{-4} mol) as the initiator. After 30 minutes, an aliquot was taken out from reaction vessel and terminated by methanol. The rest was terminated with excess sodium thiophene methonate (8.9×10^{-3} mol), and the solution was stirred for additional one night. Polymerization mixture was precipitated in methanol and cooled. The precipitated polymer was filtered off and dried in vacuum.

3.3.2.3.2 Synthesis of Bifunctional PTHF Macromonomers

Polymerization flask equipped with nitrogen inlet and magnetic stirrer was flushed with dry nitrogen. Then, 10 mL of freshly distilled THF was introduced with syringe. The polymerization was started at room temperature by injecting triflic anhydride (0.074 mL, 4.45×10^{-4} mol) as the initiator. After 30 minutes, a small portion of sample was removed for GPC characterization with a syringe and poured into methanol. The remaining part of the reaction mixture was terminated by adding excess sodium thiophene methonate (4.45×10^{-3} mol) and stirred for one night. Polymerization mixture was precipitated in methanol and cooled. The precipitated polymer was filtered off and dried in vacuum.

3.3.3 Synthesis of Polymers of Side-Chain Thiophene Monomers

3.3.3.1 Block Copolymers

3.3.3.1.1 Synthesis of Prepolymer (PMMA) with Thermolabile Groups

Methyl methacrylate (MMA) (3 mL, 2.81 mmol) and 1, 1-diphenylethene (DPE) (0.014 mL, 0.08 mmol) were added into a glass tube and degassed by three freeze-pump-thraw cycles. After transferring α,α'-azobis(isobutyronitrile) (AIBN) (0.013 g, 0.08 mmol), the tube was sealed under vacuum and polymerization was performed in bulk at 80 °C. The mixture was poured into methanol; and the precipitated polymer was filtered off and dried in a vacuum oven.

3.3.3.1.2 Synthesis of Block Copolymers of Methylmethacrylate (MMA) and 3-Methylthienyl Methacrylate (MTM)

To a solution of 0.1 g of poly(methyl methacrylate) in 2 mL of dimethylformamide (DMF), 0.5 mL (0.54 g, 2.96 mmol) of 3-methylthienyl methacrylate (MTM) synthesized according to literature procedure [148] was added, sealed under vacuum and placed in an oil bath at 80 °C for 3 hours. The block copolymer was precipitated in methanol, filtered off and dried in vacuo.

3.3.3.2 Random Copolymers

3.3.3.2.1 Synthesis of PEO Macromonomer with p- Vinylbenzyl End-Functional Group (PEOVB)

PEO macromonomers possessing *p*-vinylbenzyl end-group was prepared by a conventional high vacuum line technique. 2-Methoxyethanol (13.5 mmol), 6 mmol of potassium naphthalene in THF, 295 mmol of EO and THF, each in an ampoule with a breakable seal, were fitted into a flask, baked under vacuum and sealed off from the vacuum line. 2-Methoxyethanol and THF were introduced into the cleanly dried flask and then reacted with potassium naphthalene in THF. The dark green colour due to potassium naphthalene almost immediately disappeared. Then, EO, chilled by dry ice/isopropanol, was introduced to the flask and polymerized at 40 ^{0}C over 3 nights. Then the flask was fitted into a vacuum line with the ampoules containing 50 mmol of *p*-vinylbenzyl chloride (VBCI) and 15 mmol of triethylamine (TEA). After evacuation, the system was sealed off and the contents were mixed to terminate the poymerization by breaking the breakable seals. The reaction took place immediately and the solution became turbid indicating formation of KCI and Et_3NHCI. The mixture was poured into a large amount of acetone (700 mL) to precipitate the salts, which were filtered off. The filtrate was concentrated by a rotary evaporator under a reduced pressure to about 70 mL and poured into a large amount of hexane (700 mL). The precipitated macromonomer was collected by filtration and freeze-dried from hexane. The yield was almost quantitative.

3.3.3.2.2 Synthesis of Random Copolymers of 3- Methylthienyl methacrylate (MTM) and PEOVB

Random copolymers of 3-methylthienyl methacrylate and PEOVB were prepared as follows: 0.2 g of PEOVB was dissolved in 1 mL DMF. To this solution, 0.10 g ($5.5x10^{-4}$ mol) of 3-methylthienyl methacrylate (MTM) was added. After transferring AIBN, the tube was degassed by three freeze-pump-thraw cycles and sealed under vacuum. Polymerization was performed at 80 °C for 3 hours. After the reaction time, the mixture was poured into n-hexane. The precipitated polymer was filtered off and dried in a vacuum oven.

3.3.3.3 Alternating Copolymers

3.3.3.3.1 Synthesis of Alternating Copolymers of N-(4-(3-thienyl methylene)-oxycarbonylphenyl) maleimide (MBThi) and Styrene (St)

Copolymer of maleimide momomer (MBThi) with St was synthesized as follows: The monomer MBThi was solved in dry dichloromethane, and the solution was introduced into a Pyrex polymerization tube. For copolymerization the appropriate amount of St was also added to the tube. After degassing the solution with the purified N_2 gas, the tupe was sealed and placed in a merry-go-round-type photoreactor equipped with 16 Philips 8W/06 lamps emitting light nominally at λ = 350 nm. The reactions were carried out at 25 ^{0}C for 3 days. Then the polymer was precipitated in methanol. The obtained polymer was filtered, washed with acetone to remove the unreacted maleimide monomer, and dried under vacuum. The product was purified by reprecipitation from dichloromethane solution in methanol.

3.3.4 Synthesis of Conducting Copolymers

3.3.4.1 Electropolymerization of N-(4-(3-thienyl methylene)-oxycarbonylphenyl)maleimide (MBThi)

3.3.4.1.1 Galvanostatic Polymerization of MBThi

The homopolymerization of the monomer was achieved by constant current electrolysis in a single compartment cell consisting of platinum working and counter electrodes. The galvanostatic polymerization was carried out in dichloro methane (DM) (20 mL)-tetrabutylammonium tetrafluoroborate (TBAFB) (0.1 M) solvent-electrolyte system with 50 mg monomer at 0 ^{0}C by appliying 20 mA for 30 min. The polymer (PMBThi) was obtained as a freestanding film on the electrode surface.

3.3.4.1.2 Synthesis of Copolymers of MBThi with Thiophene by Constant Potential Electrolysis

A wenking POS 73 potentiostat was used to synthesize the copolymer of monomer in a single electrolysis cell consisting of platinum working and counter electrodes and a silver wire reference electrode. The cell contains 0.05 M of TBAFB, 0.02 M thiophene and 20 mg monomer in acetonitrile (ACN). The electrolysis was carried out at 2.0 V for 30 min.

3.3.4.1.3 Synthesis of Conducting Block Copolymers of PMBThi with Pyrrole (Py) and Thiophene (Th) [PMBThi/PPy1, PMBThi/PPy2, PMBThi/PTh]

The synthesis of conducting block copolymers of PMBThi was accomplished in ACN-TBAFB and water-*p*-toluene sulfonic acid (PTSA) solvent electrolyte couples in an H shaped electrolysis cell via constant potential electrolysis technique by using PMBThi coated electrode as the working electrode. For the synthesis of PMBThi/PPy1 and PMBThi/PPy2 conducting block copolymers, two different solvent–electrolyte couples were used , water-PTSA and ACN-TBAFB respectively. The electrolyses were carried out in the presence of 0.02 M pyrrole, 0.05 M TBAFB or PTSA, in ACN or water respectively, at 1.1 V for 60 min. For the sythesis of PMBThi/PTh electrolyses were performed in the presence of 0.02 M thiophene, 0.05 M TBAFB in ACN at 2.0 V for 45 min. Finally, the copolymer films were taken from the electrode surface and washed with both DM in order to remove unreacted Py or Th.

3.3.4.1.4 Cyclic Voltammetry (CV) of MBThi

The redox behavior of monomer was examined by using a CV system that contains a potentiostat (Wenking POS 2), and X-Y recorder and CV cell. Platinum wires were used as the counter and working electrodes, and Ag wire was used as the reference electrode. CV studies were carried out in the presence of pyrrole and Th in ACN-TBAFB solvent–electrolyte couple under nitrogen atmosphere at room temperature.

4. RESULTS and DISCUSSION

4.1 Synthesis of Electroactive Monomers

The objective of this part was to synthesize monomers with thienyl group so as to produce conductive polymers.

4.1.1 Maleimide-Based Mono Functional Electroactive Monomer

Mono functional monomer (**MBThi**) was prepared by the esterification reaction of 4-Maleimidobenzoic Acid (**MBA**) with thiophene methanol (**TM**). The 4-Maleimidobenzoic acid, a very versatile reagent, was often used in the last decade to obtain different N-phenyl maleimide-type monomers [146, 147, 149, 150, and 151] or bismaleimides [151, 152]. We used the same reagent for the synthesis of the MBThi (reaction 4.1). The Structure of the monomer MBThi confirmed by IR (See the IR spectrum of MBThi in part 4.4 as Figure 4.19) and ^{1}H NMR (Figure 4.1) spectrocopies.

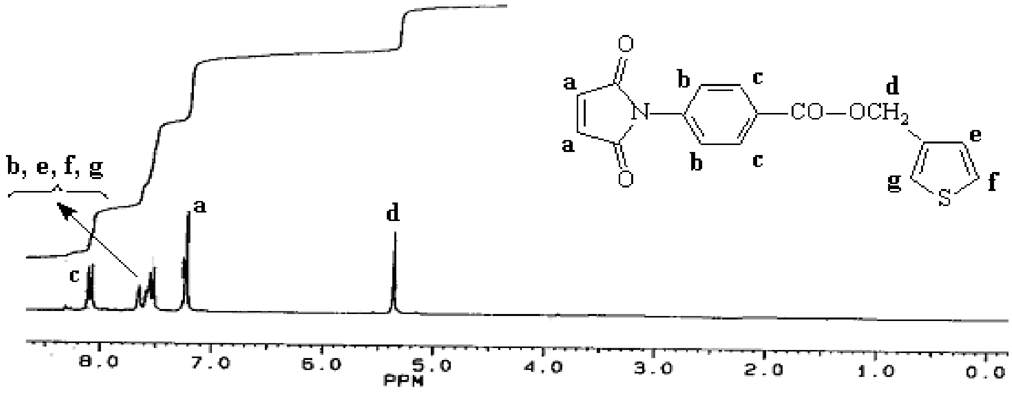
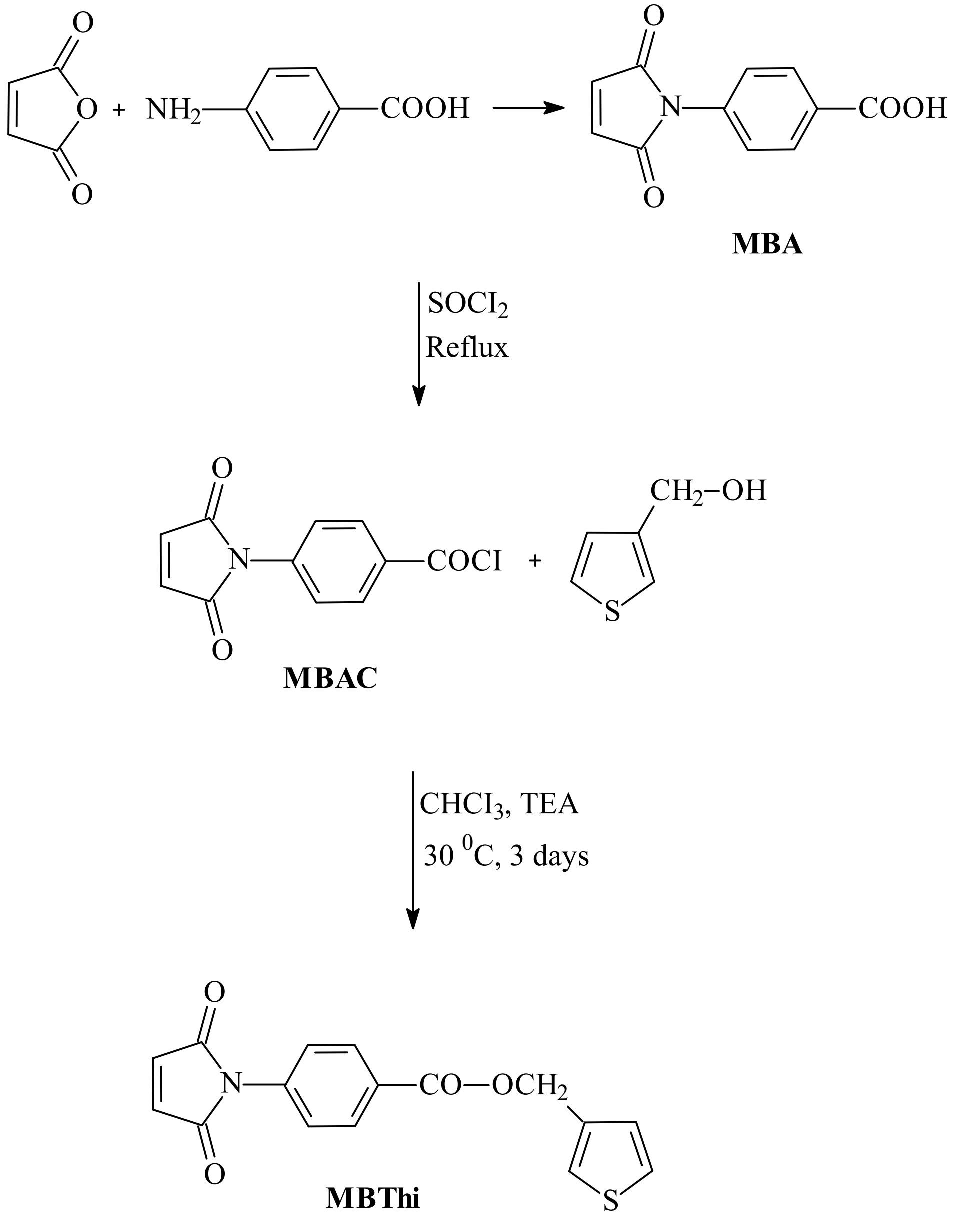


Figure 4.1. ^{1}H-NMR spectrum of **MBThi**



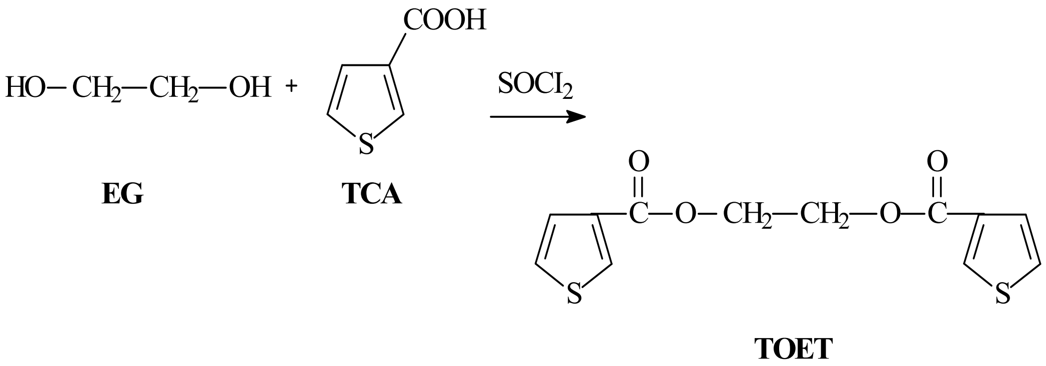
(4.1)

(Mono thienyl functional monomer)

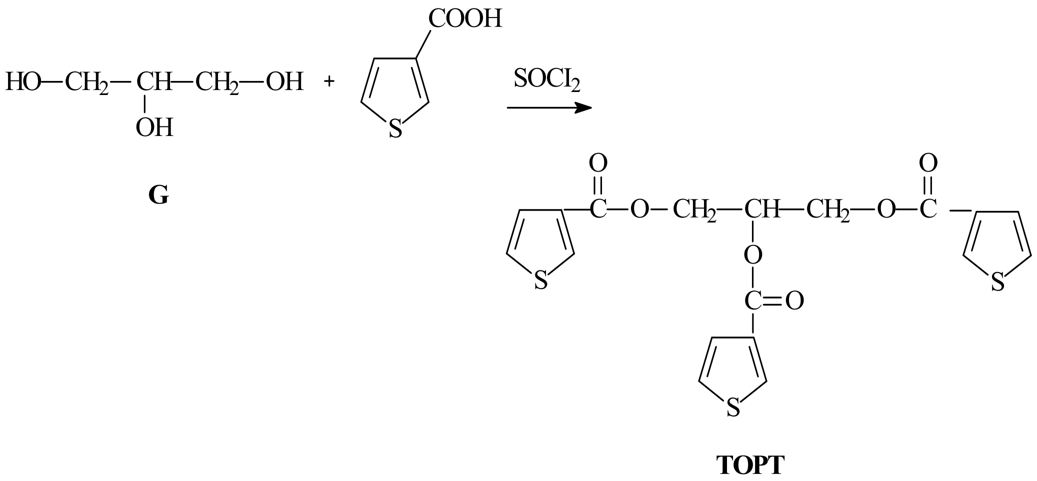
4.1.2 Ester Type Multi-Functional Electroactive Monomers

The condensation reactions of thiophene carboxylic acid (TCA) with the coresponding poly alcohols were utilized to prepare di, tri, and tetra thienyl functional monomers, namely (**TOET**), (**TOPT**) and (**TOTPT**), respectively. In the first step, the acid chloride of TCA was prepared by the treatment of TCA with thionyl chloride ($SOCI_2$). Then it was reacted with ethylene glycol (EG), glycerol (G), and pentaeritritol (PE). The reactions 4.2, 4.3 and 4.4 indicate the synthetic route of the monomers.

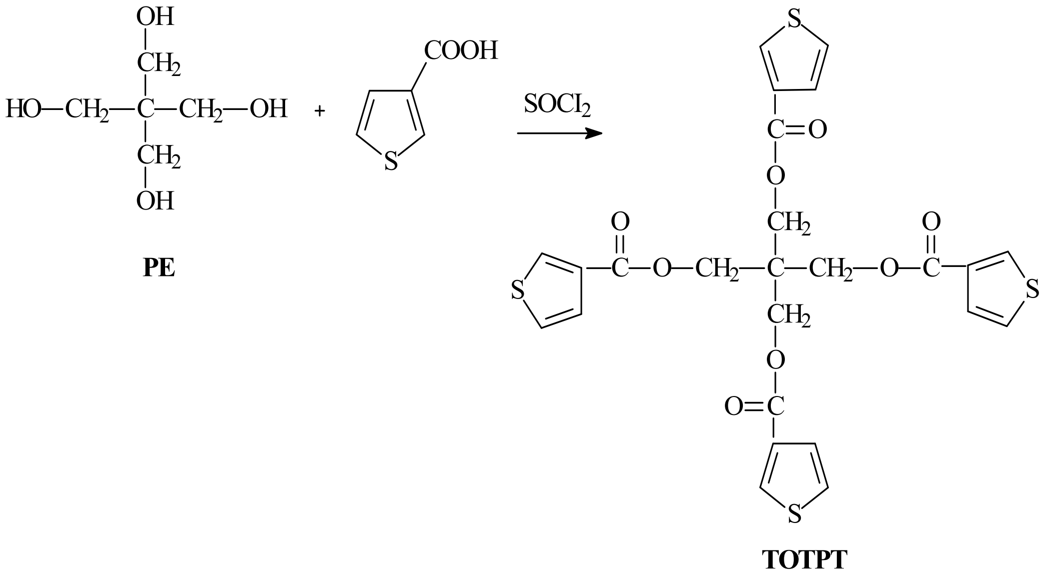
The structures of the new electroactive monomers were confirmed by spectroscopic investigations. The IR spectra of the monomers contain the peaks assigned to the carbonyl, aromatic, and α, β-hydrogen of thiophene groups (Figure 4.2). The ^1H-NMR (Figure 4.3, 4.4, and 4.5) also show the expected peaks confirming the structure of the monomers. The peaks appearing in the range of 8.5-7.2 ppm are attributed to the protons of thiophene ring.



(4.2)



(4.3)



(4.4)

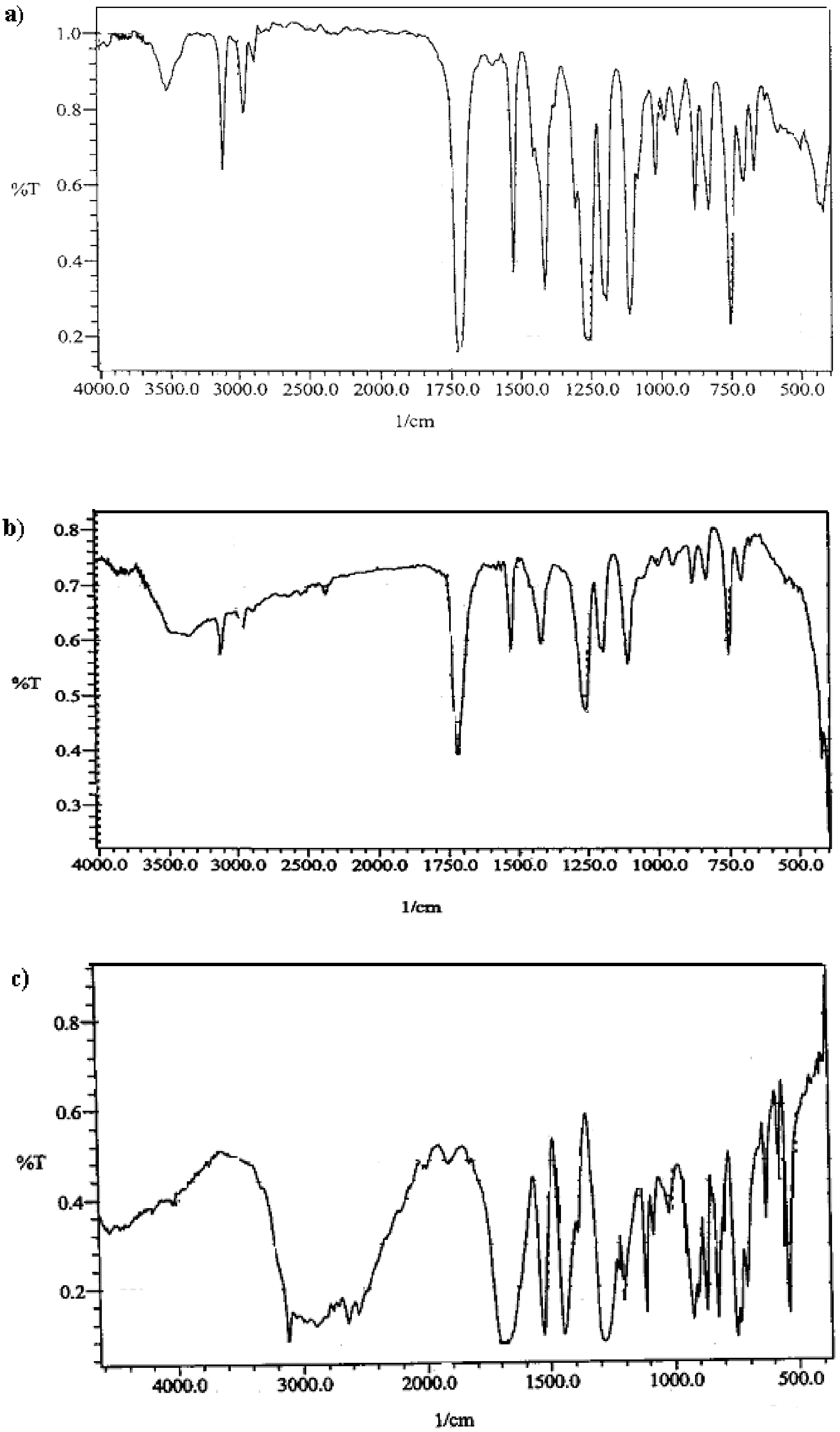


Figure 4.2. IR Spectrum of **a) TOET, b) TOPT** and **c) TOTPT**

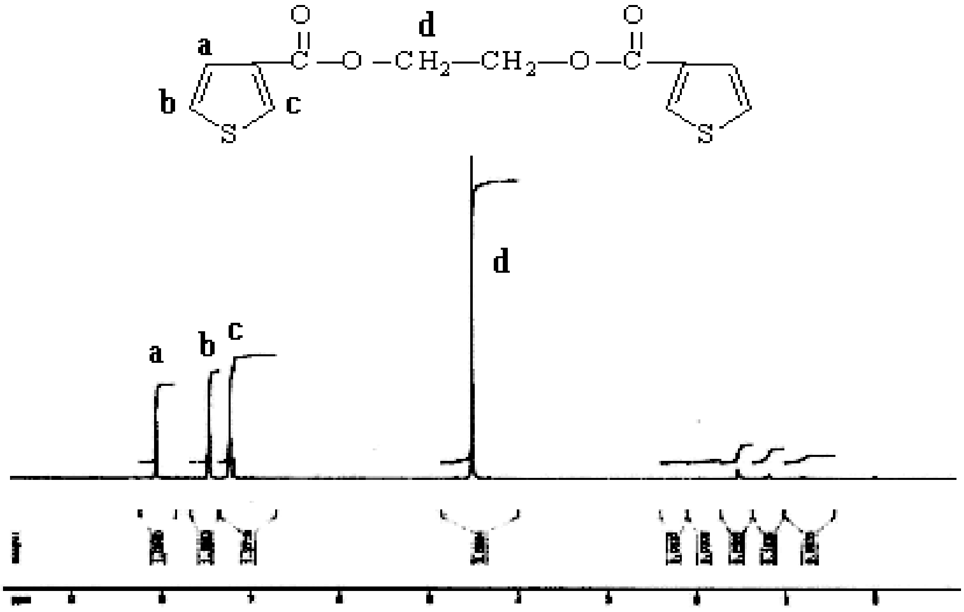


Figure 4.3. ^{1}H-NMR spectrum of **TOET**

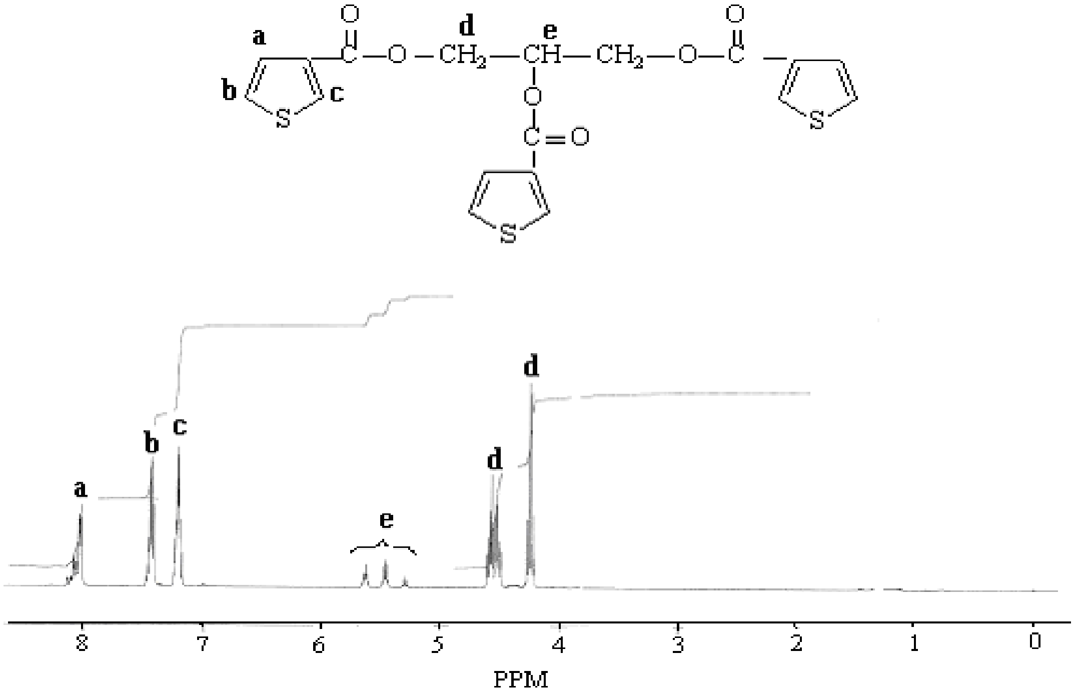


Figure 4.4. ^{1}H-NMR spectrum of **TOPT**

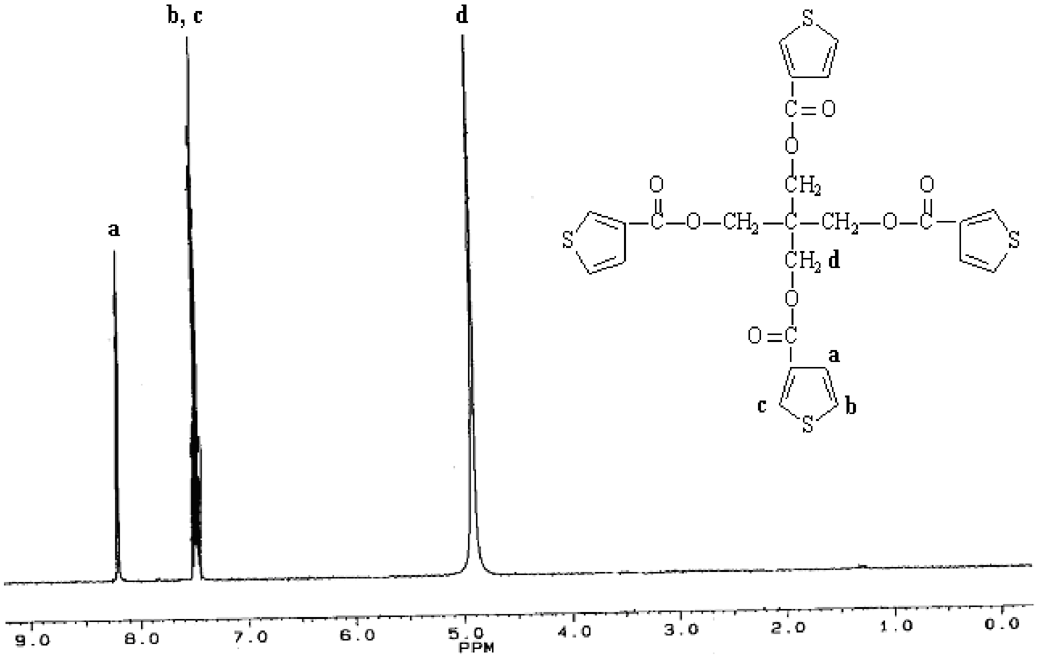


Figure 4.5. ^{1}H-NMR spectrum of **TOTPT**

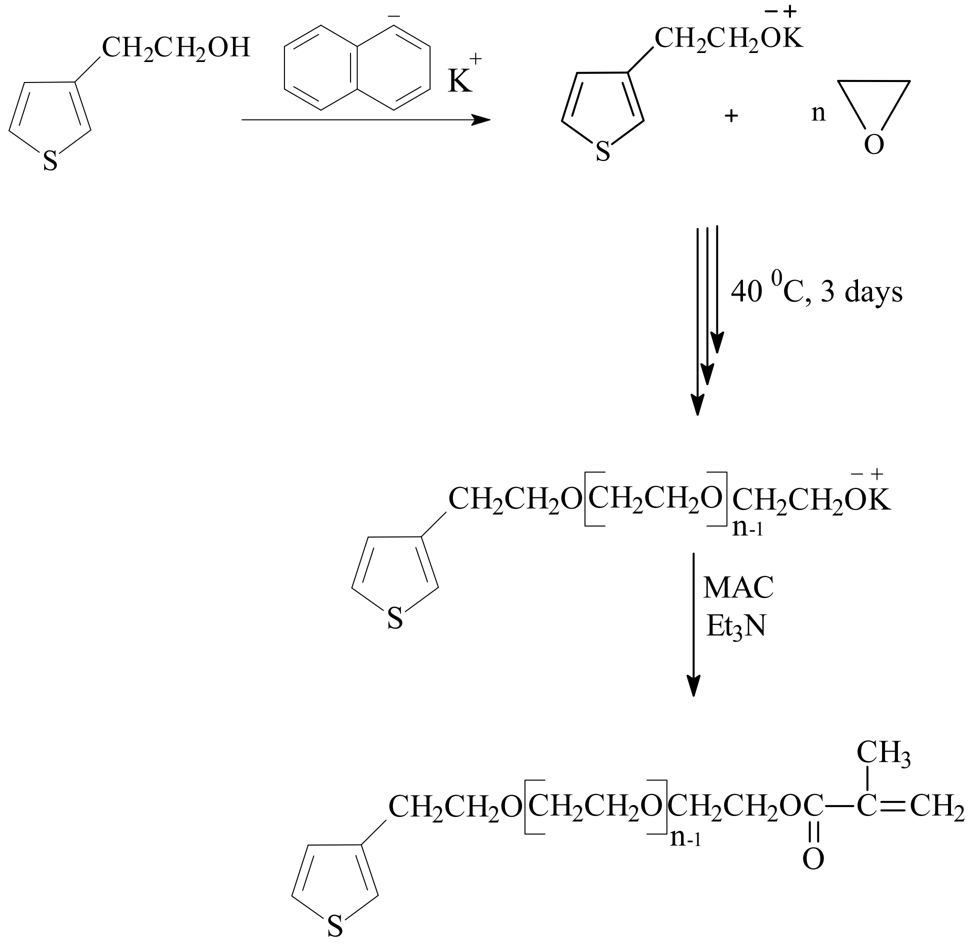
4.2 Synthesis of End-Functional Macromonomers

4.2.1 α-ω-Heterofunctional Polyethylene oxide (PEO) Macromonomers

A general method have been recently developed for synthesis of hetero-functional or hetero-telechelic PEO macromonomers by using a functional alcohol for initiating polymerization of EO followed by terminating with the other functionality. For example, *p*-vinylphenylalkyl- and hydroxy-ended PEO macromonomers, $CH_2=CHC_6H_4(CH_2)_mO[CH_2CH_2O]_n$-H, and dimethylamino- and methacryloyl-ended PEO macromonomer, $(CH_3)_2N$-$[CH_2CH_2O]_n$-$COC(CH_3)=CH_2$, have been prepared [153, 154].

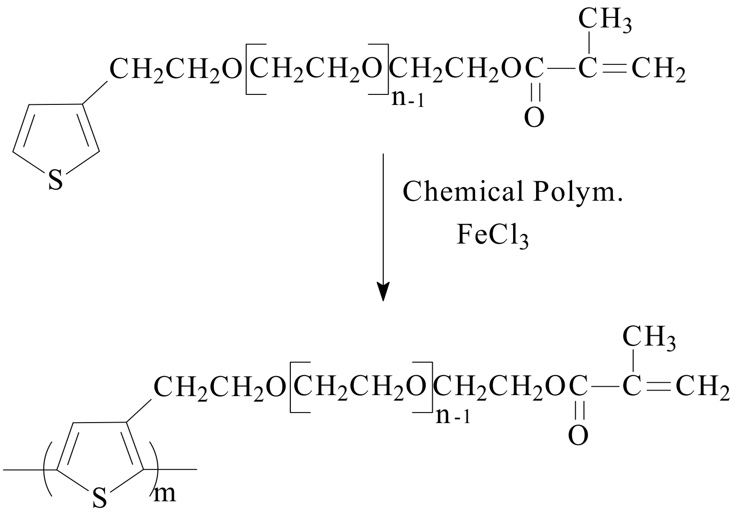
Poly(ethylene oxide) is used as the basic building block for many types of linear, branched or cross-linked solid polymer electrolytes [155, 156]. In order to improve the mechanical properties of these kind of polymers, different poly(*p*-phenylene)s carrying oligo(ethylene oxide) side chains were synthesized [157-160]. Some poly(*p*-phenylene vinylene)s with oligo(ethylene oxide)s side groups have been reported for light-emitting electrochemical cells (LECs) applications [161]. Also, polyfluorenes functionalized with PEO-like segments were synthesized as materials for light-emitting diodes (LEDs) [162-164]. This study aims at describing the synthesis of PEO having methacrylate and 3-thiophene ethyl end-groups and its application for radical and chemical polymerizations.

The anionic living polymerization of EO initiated by 3-thiophene ethanol- potassium naphthalene salt system was terminated with methacryloyl chloride (MAC). The reaction path is represented in reaction 4.5. The structure of macromonomer was confirmed by ^{1}H-NMR measurements and GPC analyses. The molecular weight of the macromonomer calculated from ^{1}H-NMR spectrum is consistent with the molecular weight obtained from GPC spectrum (Table 4.1). The molecular weight of PEO macromonomer which is taken into account for further calculations, was calculated by comparing the integral peak area of the protons of thiophene ring to that of ethylene oxide. The ^{1}H-NMR spectrum of PEO macromonomer terminated by methacryloyl chloride exhibits signals in the range of 7.31-6.92 corresponding to –CH protons of thiophene rings, 6.08-5.53 corresponding to vinyl protons, 4.27-4.23 ($COOC\mathbf{H}_2$), 3.65-3.30 ($C\mathbf{H}_2O$), 2.90-2.85(Thi-$C\mathbf{H}_2$) and 1.92 ppm ($C\mathbf{H}_3$) (Figure 4.6a).



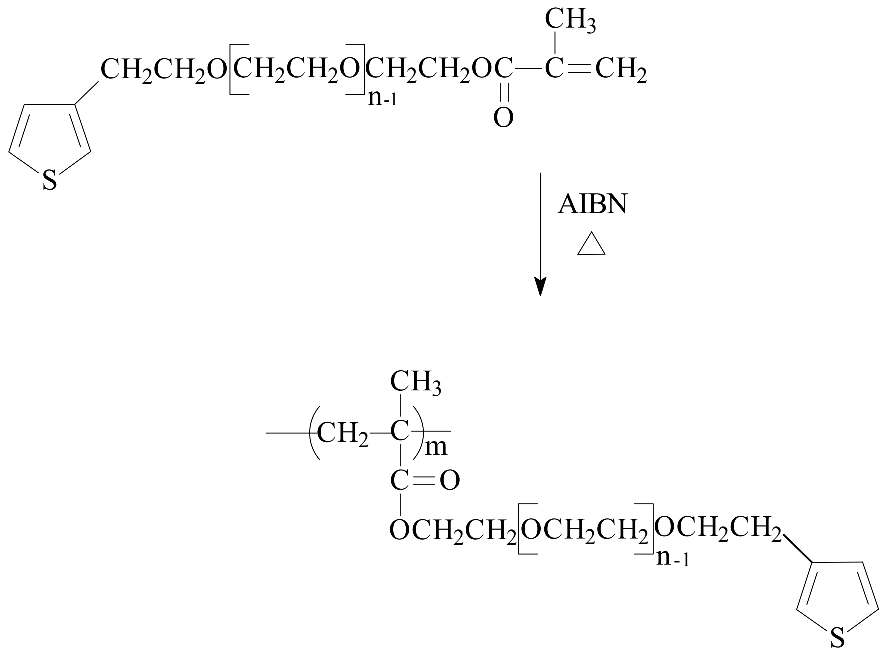
(4.5)

The obtained macromonomer has two polymerizable groups: the thiophene ring, with substitution at the 3-position, can be employed in oxidative polymerization while the vinyl group is useful for radical polymerization. The macromonomer, having an electroactive group, was polymerized oxidatively in the presence of $FeCl_3$ as an oxidant (reaction 4.6). The structure of the soluble part of the comb-like polymer obtained was characterized by ^1H-NMR. The decrease in the ratio of the integral peak area of the signals at 7.31-6.92 ppm corresponding to –CH protons of thiophene rings to that of ethylene oxide can be attributed to the fact that polymerization took place,most probably, at 2 and 5 positions of the thiophene rings (Figure 4.6b). Also, the vinylic double bond in chemical polymerization was not affected.



(4.6)

The macromonomer was also used in homopolymerization via vinylic terminus. The reaction involves the free radical polymerization of PEO in the presence AIBN as a thermal initiator. The reaction 4.7 indicates the reaction path. The structure of homopolymer was characterized by ^{1}H-NMR spectroscopy and GPC measurements. The disappearence of the signals at 5.7-6.1 ppm corresponding to vinylic protons and the apperance of the signal at 1.47 ppm corresponding to $-C\mathbf{H}_2C(CH_3CO\text{-})$ shows that the homopolymerization of macromonomer proceeded via the vinylic bond (Figuere 4.6c).



(4.7)

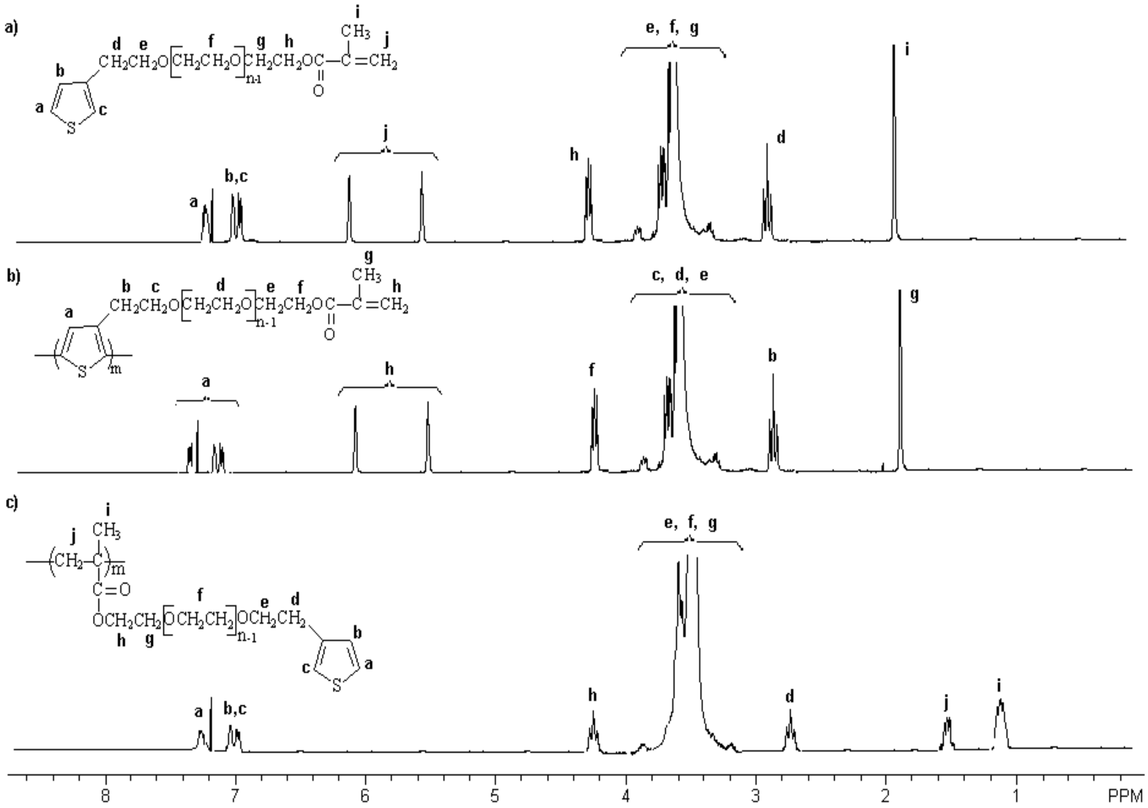


Figure 4.6. ^{1}H-NMR spectra of PEO macromonomer **(a)**; after oxidative polymerization **(b)**; after free radical polymerization **(c)**

Table 4.1. Molecular Weight Characteristics of PEO Macromonomer

Macromonomer	M_n[a]	M_w/M_n
Before polymerization	1250	1.09
After oxidative polymerization	13100	1.08
After free radical polymerization	12800	1.09

[a] Estimated by GPC based on polystyrenes standard.

The evidence for successful free radical and oxidative polymerization processes was obtained by GPC measurements. Chromatograms recorded with macromonomer, after oxidative and free radical polymerizations are shown in Figure 4.7. The peak corresponding to the macromonomer is shifted to higher molecular weight indicating the successful radical and oxidative polymerizations. After both free radical and oxidative polymerizations, the polydispersity of the macromonomer did not apparently changed. However, because of the highly branched or comb-like structure of the poly-macromonomers obtained, the values of M_n and the M_w/M_n, just calibrated with linear standard polymers, should be taken as the minimum estimatation [154, 165].

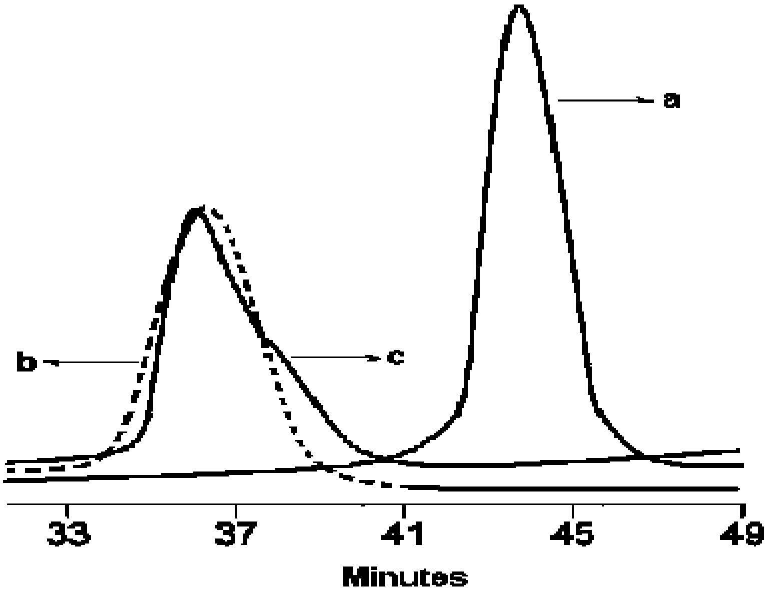
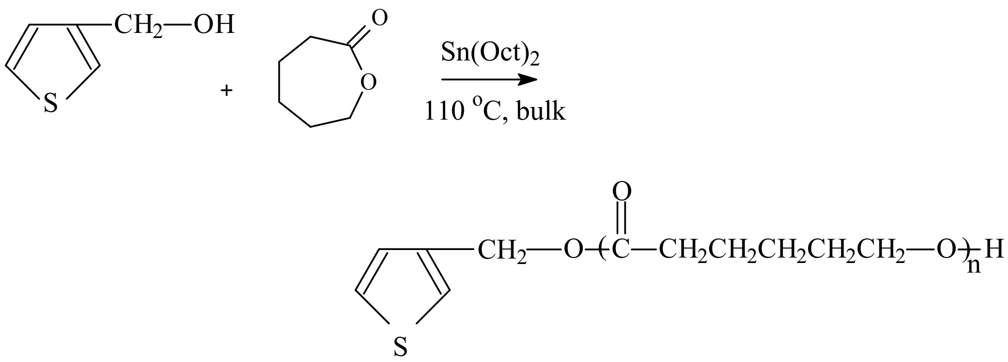


Figure 4.7. GPC traces of PEO macromonomer **(a)**; after oxidative polymerization **(b)**; after free radical polymerization **(c)**

Thus, a novel poly (ethylene oxide) macromonomer possessing methacryloyl and thiophene end groups was synthesized and employed in free radical polymerization through vinylic bond and in oxidative polymerization through thiophene moiety.

4.2.2 Poly(ε-Caprolactone) Macromonomers

The synthesis of macromonomer of poly(ε-caprolactone) depicted in the reaction 4.8 involved the reaction of thiophene methanol with ε-caprolactone (ε-**CL**) in the presence of stannous 2-ethyl-hexanoate (stannous octoate) in short $Sn(Oct)_2$ used as a catalyst. In view of the reported role of hydroxyl group as initiator in ring-opening polymerization, this reaction was expected to produce polymer containing a thiophene end group.



(4.8)

As can be seen from Table 4.2, the measured and calculated M_n values are in good agreement indicating that each thiophene molecule generates one growing end. The GPC trace in Figure 4.8 is also unimodal and narrow implying that no side reactions occurred.

Table 4.2. Synthesis of Poly (ε-Caprolactone)[a]

$[I]x10^{-2}$ ($mol.L^{-1}$)	Time (hour)	Conversion (%)	Mn_{theo}.	Mn_{GPC}	Mw/Mn	Mn_{HNMR}
41	140	100	2300	2100	1.37	2350

[a] Temp.110°C, [ε-CL]o = 8.50 $mol.L^{-1}$(in bulk),
[I]/[ε-CL]: 1/20 and [Sn(Oct)2]/ [I]: 1/400

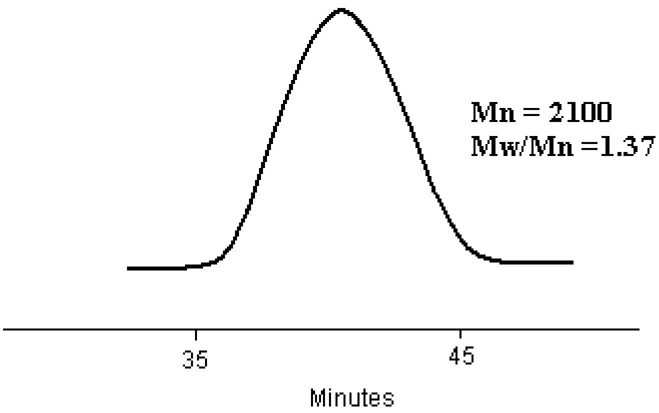


Figure 4.8. GPC chromatogram of poly (ε-Caprolactone)

In the ^{1}H-NMR spectrum of the polymer can be found not only the specific signals of poly(ε-caprolactone) (PCL), but also absorptions belonging to the rests of thiophene methanol. In Figure 4.9 is shown the ^{1}H-NMR spectrum of polymeric macromonomer in $CDCl_3$. The peak at **g** (5.1 ppm) implies the presence of protons of β methylene groups of thiophene. The peaks at **h, i, j** (7.0-7.3 ppm) observed correspond to three protons on thiophene rings. ^{1}H-NMR result clearly indicates the presence of the preassumed structure.

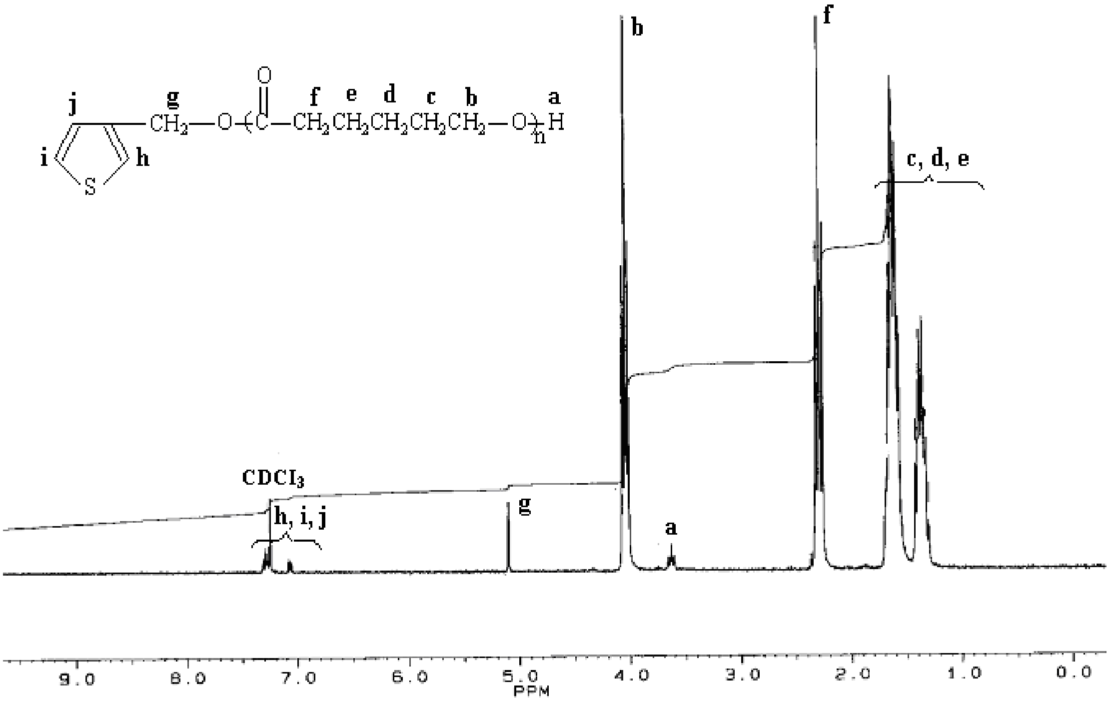
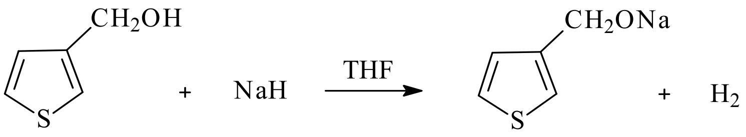


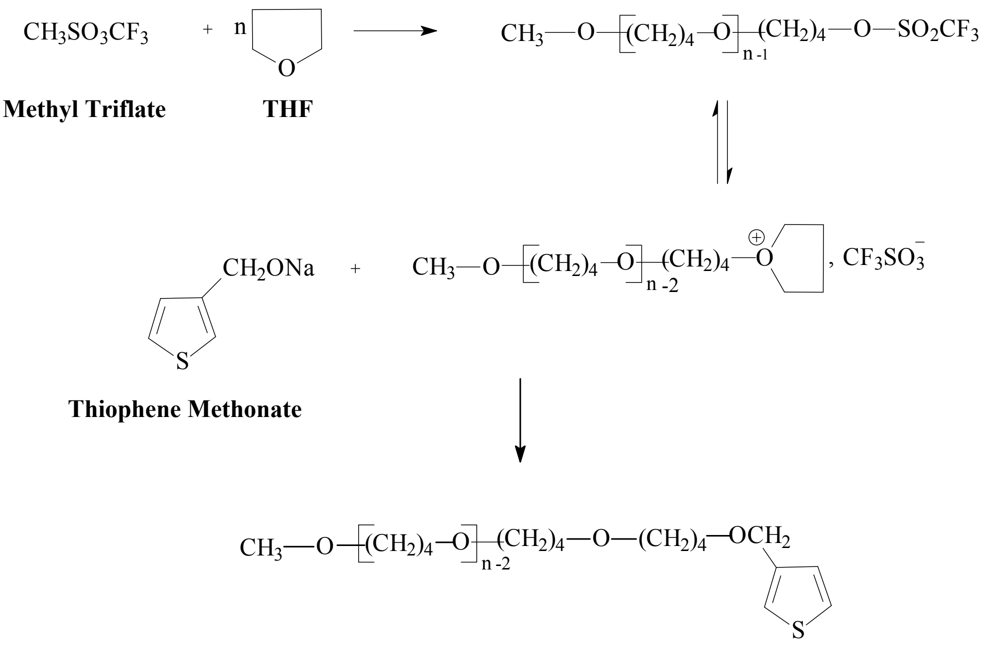
Figure 4.9. ^{1}H-NMR spectrum of Poly (ε-Caprolactone)

4.2.3 Poly(THF) Macromonomers

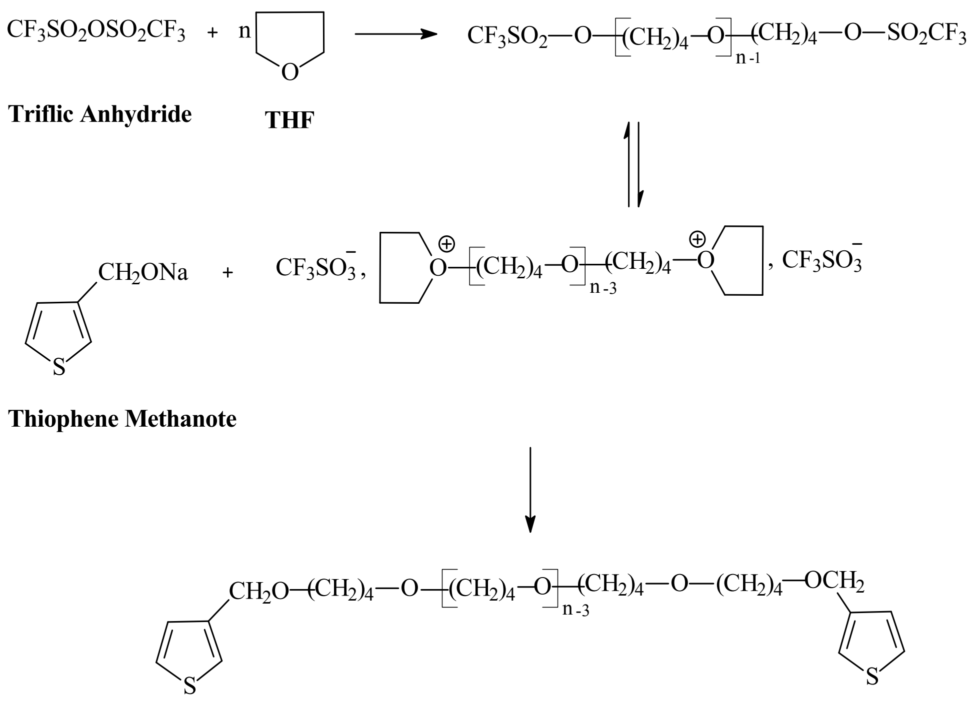
Living polymerization is a technique which allows the preparation of various well-defined polymers with functional end groups. Electrochemically polymerizable thiophene moeities can be incorporated into polymers by means of another controlled polymerization method, cationic polymerization. It has been shown that cyclic ethers such as tetrahydrofuran (THF) can be polymerized without chain transfer and termination under closely controlled conditions. Living ends of polytetrahydrofuran (PTHF) can react with nucleophiles and thus give rise to a variety of functional groups [166, 15, 11, 13, 89- 91]. Methyl trifluoromethanate sulfonate (methyl triflate) and trifluoromethanate sulfonic anhydride (triflic anhydride) have been described as initiators which lead to mono and bifunctional living polytetrahydrofurans respectively [87, 88].These initiators were employed in the polymerization of THF and subsequently electrochemically active mono and bi functional PTHF macromonomers were obtained by terminating the living end (s) of polymer chains with the sodium salt of thiophene methanol, according to following reactions (4.9, 4.10 and 4.11).



(4.9)



(4.10)



(4.11)

The living propagating chains were terminated with sodium salt of thiophene methanol. The results are summarized in Table 4.3. The Mw/Mn values of the polymers are between 1.2 and 1.3, which are commonly observed in cationic living polymerization.

Table 4.3. Synthesis of PTHF with Thiophene Moiety

Code	*Mn*(NMR)	*Mn*(GPC)[c]	*Mw*/*Mn*
TPTHF-I[a]	4050	9050	1.27
TPTHF-II[b]	11500	11400	1.22

[a] [THF], 12.22 M; [methyl triflate], 0.088 M; [sodium thiophenemethonate], 0.88 M ; 25 ^{0}C, 1 h.

[b] [THF], 12.25 M; [triflic anhydride], 0.044M; [sodium thiophenemethonate], 0.44 M; 25 ^{0}C, 1 h.

[c] Determined by GPC with the calibration using polystyrene standards by a conversion factor of 0.592 [167].

^{1}H-NMR spectra were taken with CDCl$_3$ and DMSO-d$_6$ as the solvents. ^{1}H-NMR spectra of both mono and bi functional PTHF macromonomers in CDCl$_3$ are shown in Figure 4.10 & 11 respectively. The signals at **f** (1.5 ppm) and **e** (3.5 ppm) arise due to the existence of two types of methylene protons in the structure, inner groups and

OCH_2 groups, respectively. Peak **d** (4.5 ppm) implies the presence of β methylene protone groups of thiophene. ^{1}H-NMR spectra of PTHF macromonomers were also taken in DMSO-d_6 in order to detect the peaks that were obscured by $CDCl_3$. Peaks **a**, **b**, **c** observed in DMSO-d_6 correspond to three protons on thiophene rings. ^{1}H-NMR results reveal that preassumed structures were obtained.

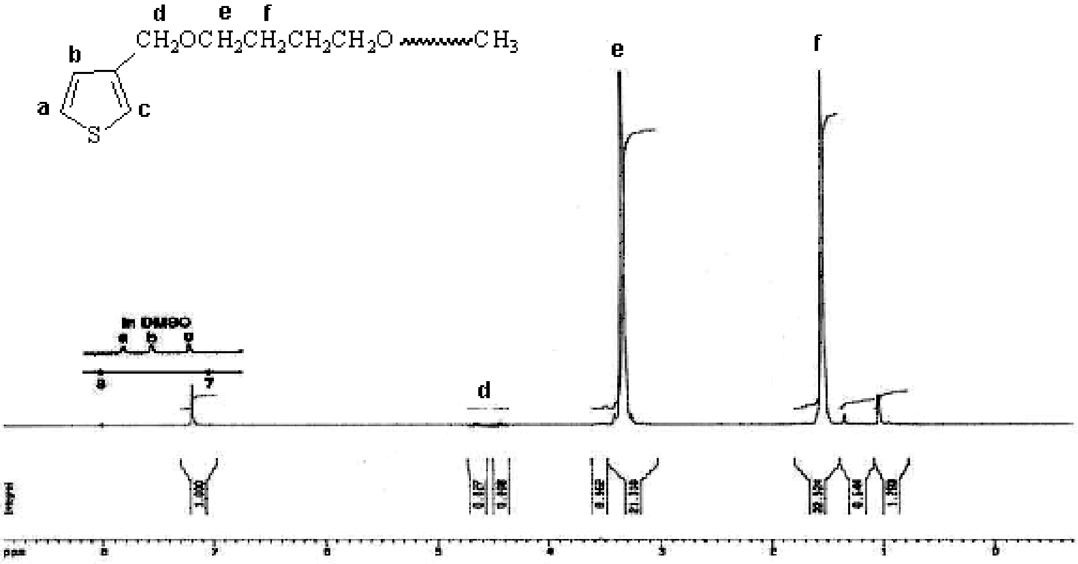


Figure 4.10. ^{1}H-NMR spectrum of PTHF possessing thiophene moiety at one end

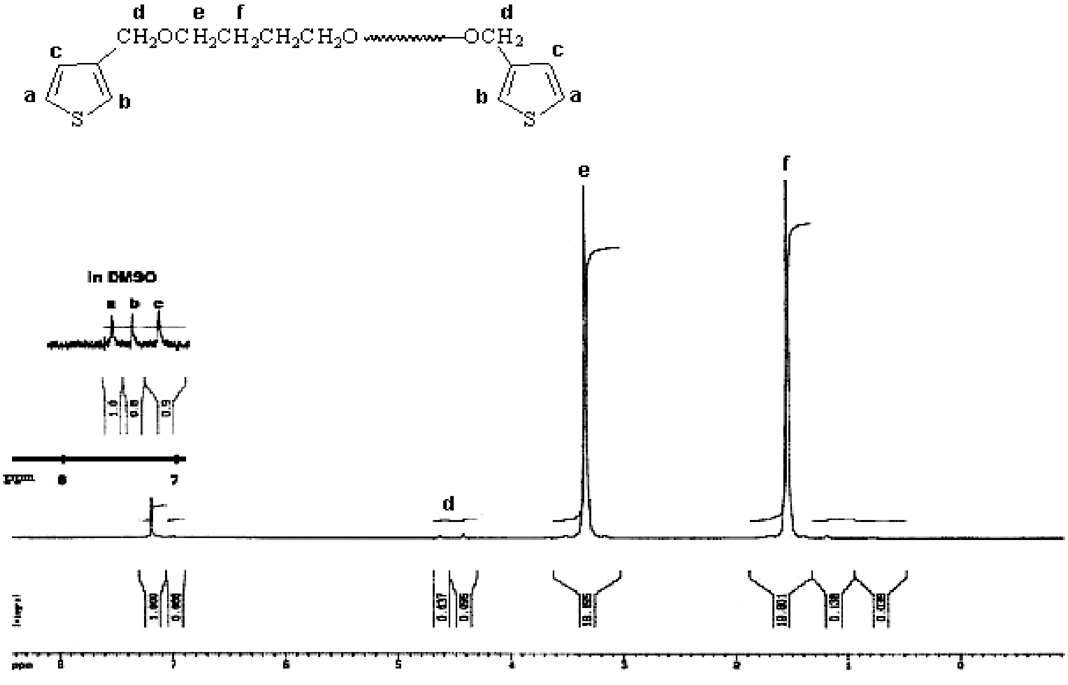


Figure 4.11. ^{1}H-NMR spectrum of Poly (THF) possessing thiophene moiety at both ends

4.3 Synthesis of Polymers Containing Side-Chain Thiophene Monomers

4.3.1 Synthesis of Block Copolymers of Methyl methacrylate and 3-Methylthienyl methacrylate (PMMA-*b*-PMTM)

Bulk polymerization of methyl methacrylate (reaction 4.12) was performed by DPE method in the presence of AIBN as initiator at 80 ^{0}C. The results are presented in Table 4.4. As presented in reaction 4.10 various complex reactions were proposed for the polymerization process [168].

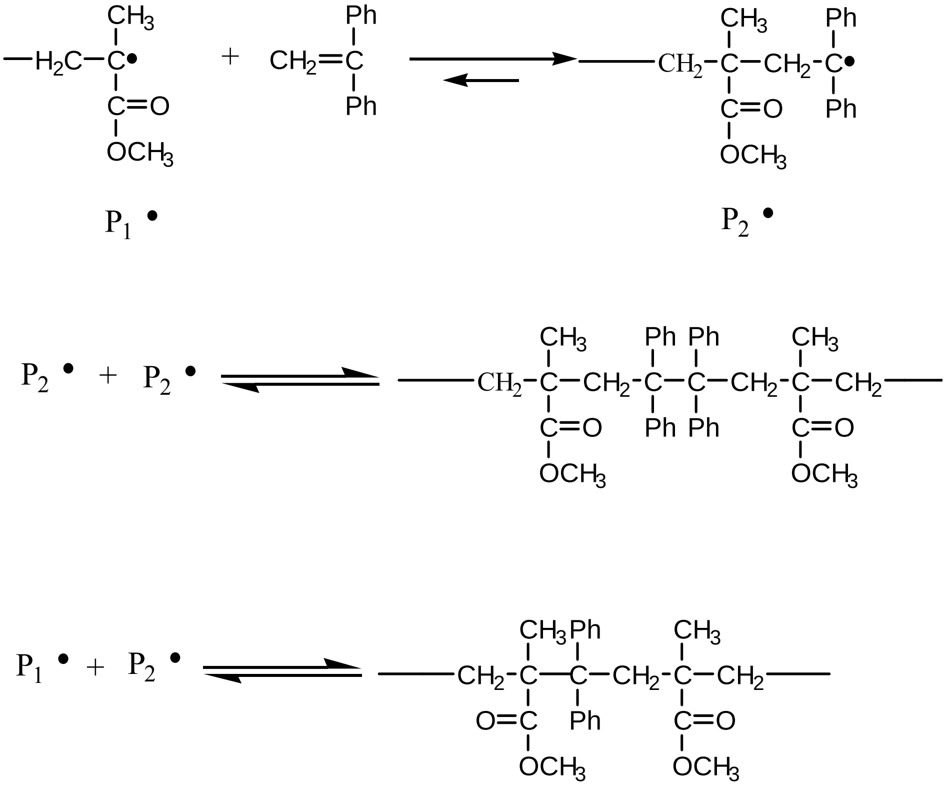
DPE reacts with growing chains and reduces their activity. The participation of DPE in radical polymerization leads to the formation of stable DPE radicals by resonance stabilization of the radical by two phenyl groups and a strong steric hindrance for the addition of any other monomer. The reversibility of the reaction would allow a certain level of $P_1^{\cdot}$ (reaction 4.12) to grow. Termination may occur by combination of the polymeric radicals of various type which would result in the formation of thermosensitive polymers. Obviously, this means that the termination steps are reversible [169, 170].

Table 4.4. Preparation of DPE-Containing Poly(methyl methacrylate)[a]

Code	Time (min)	Conversion (%)	*Mn*[b]	*Mw/Mn*
PMMA1	100	23	19100	1.44
PMMA2	200	35	21870	1.37
PMMA3	300	38	24600	1.26

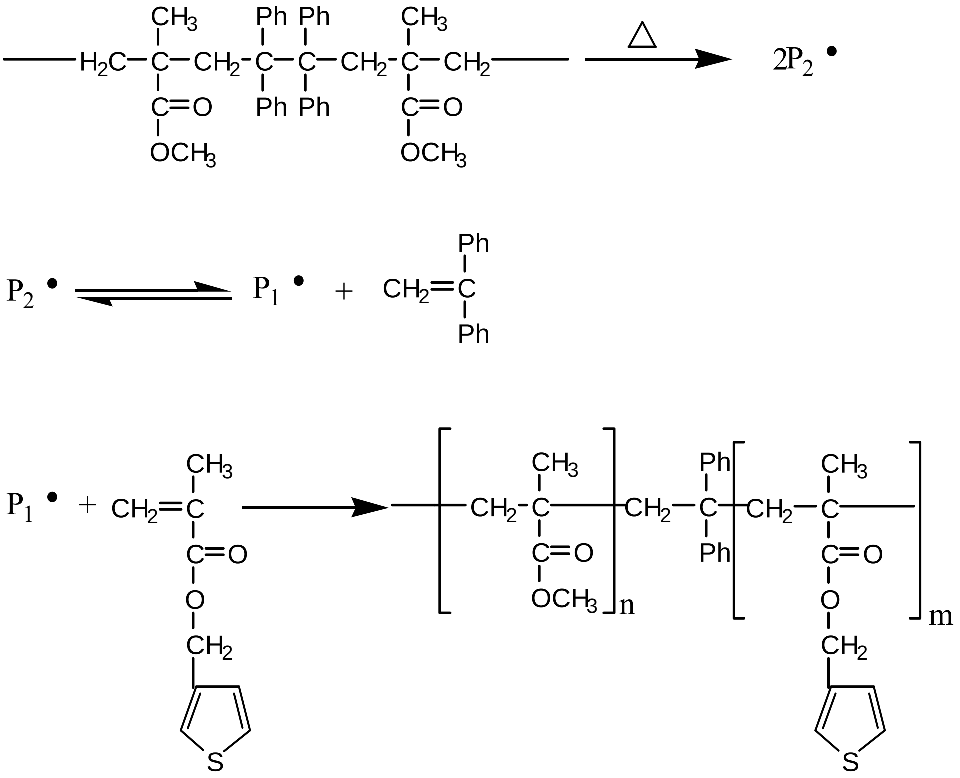
[a] [AIBN]/[DPE] = 1/1 = $2.8*10^{-2}$ molL^{-1}, [MMA] = 9.34 molL^{-1}, Bulk, Temp.= 80 ^{0}C.

[b] Determined by GPC according to polystyrene standards.



(4.12)

Homopolymer of methyl methacrylate, which was polymerized in the presence of DPE, can initiate the polymerization of a second monomer. Heating the DPE containing polymethyl methacrylate (PMMA) at 80 ^{0}C in the presence of electroactive 3-methylthienyl methacrylate monomer (MTM) yielded block copolymer (reaction 4.13).



(4.13)

Using DPE, block copolymers possessing thiophene containing segments have been synthesized. Polymerization conditions and the results are given in Table 4.5. Gel Permeation Chromatography (GPC) measurements show that the prepolymers were converted into block copolymers. Curve **a** in Figure 4.12 shows the segmental unit of homo poly(methyl methacrylate). Apparently this peak is shifted to higher molecular weight indicating successful blocking of 3-methylthienylmethacrylate segment. The Mw/Mn values of all the block copolymers are between 1.41 and 1.59 which are clearly below those observed in radical polymerization.

Table 4.5. Preparation of Block Copolymer of MMA and MTM by DPE Method[a].

Code	Precursor (g L^{-1})	Time (h)	Copolymer composition[b] PMMA-*b*-PMTM (Mol %)		Conversion (%)	*Mn*[c]	*Mw*/*Mn*
			PMMA	PMTM			
BC-1	PMMA1 (40)	3	33	67	57	39170	1.41
BC-2	PMMA2 (40)	3	37	63	53	47384	1.38
BC-3	PMMA3 (40)	3	35	65	55	43870	1.36
BC-4	PMMA1 (40)	6	27	73	47	54000	1.59

[a] Solvent DMF; Reaction time 3 h; Temp. 80 ° C

[b] Determined by ^{1}H-NMR

[c] Determined by GPC according to polystyrene standards

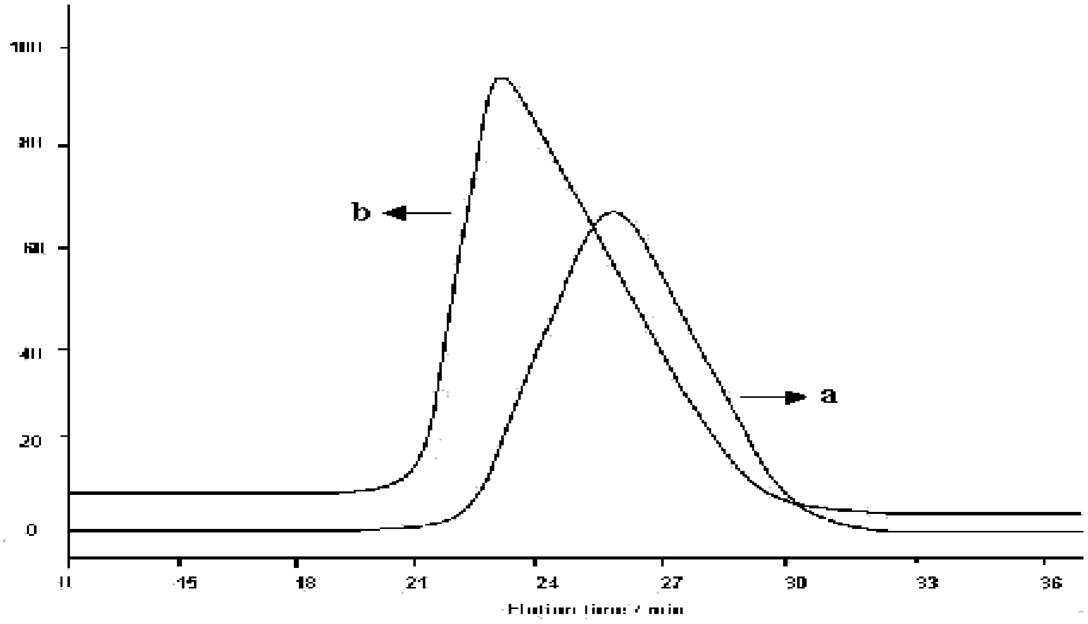


Figure 4.12. GPC curves of poly (methyl methacrylate) (PMMA1, M_n= 19100; M_w/M_n = 1.44) **(a)** and the block copolymer of poly(methylmethacrylate-*b*-3-methylthienylmethacrylate) (BC1, M_n= 39170; M_w/M_n = 1.41) **(b)**

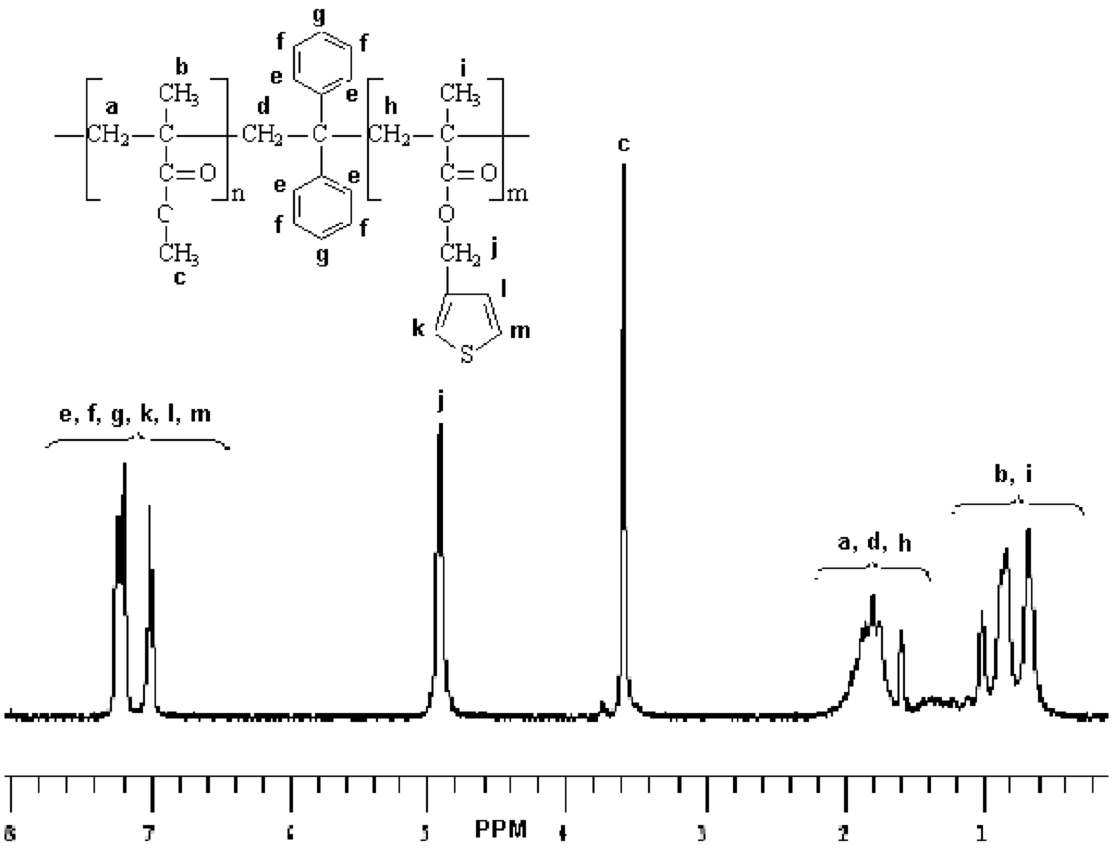
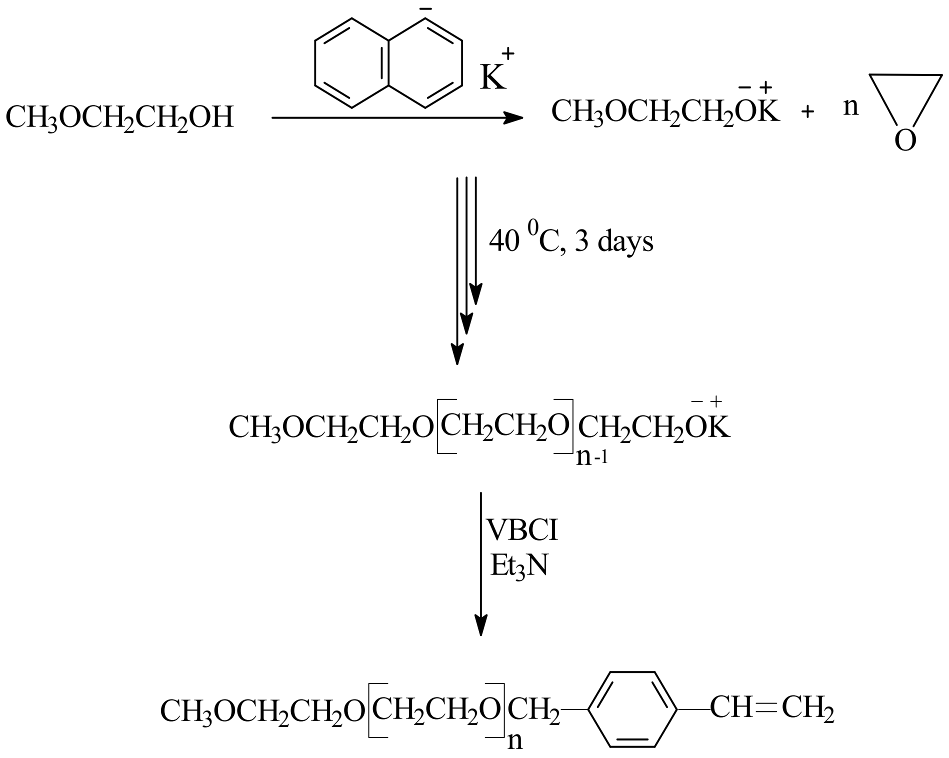


Figure 4.13. ^{1}H-NMR spectrum of **PMMA-*b*-PMTM** (BC1) in CDCl$_3$

The composition of the block copolymers determined by ^{1}H-NMR spectroscopy was calculated by comparing the integral peak area of the protons of Th-C**H**$_2$-O, exhibiting signals at 4.90 ppm, to that of COOC**H**$_3$, showing signals at 3.58 ppm in Figure 4.13.

4.3.2 Synthesis of Random Copolymers of 3-Methylthienyl methacrylate (MTM) and PEOVB (PMTM-*r*-PEOVB)

The anionic living polymerization of EO initiated by 2-Methoxyethanol-potassium naphthalene salt system was terminated with *p*-vinylbenzyl chloride (VBCI). The reaction path is represented in reaction 4.14 The structure of macromonomer was confirmed by ^{1}H-NMR measurements and GPC analyses. The molecular weight of the macromonomer calculated from ^{1}H-NMR spectrum is consistent with the molecular weight obtained from GPC spectrum. The molecular weight of PEO macromonomer which is taken into account for further calculations, was calculated by comparing the integral peak area of the protons of benzene to that of ethylene oxide. The ^{1}H-NMR spectrum of PEO macromonomer terminated by *p*-vinylbenzyl chloride exhibits signals in the range of 7.56-7.24 corresponding to –CH protons of benzene rings, 5.80-5.25 corresponding to vinyl protons, 6.83-6.65 ppm (PhC**H**) (Figure 4.14).



(4.14)

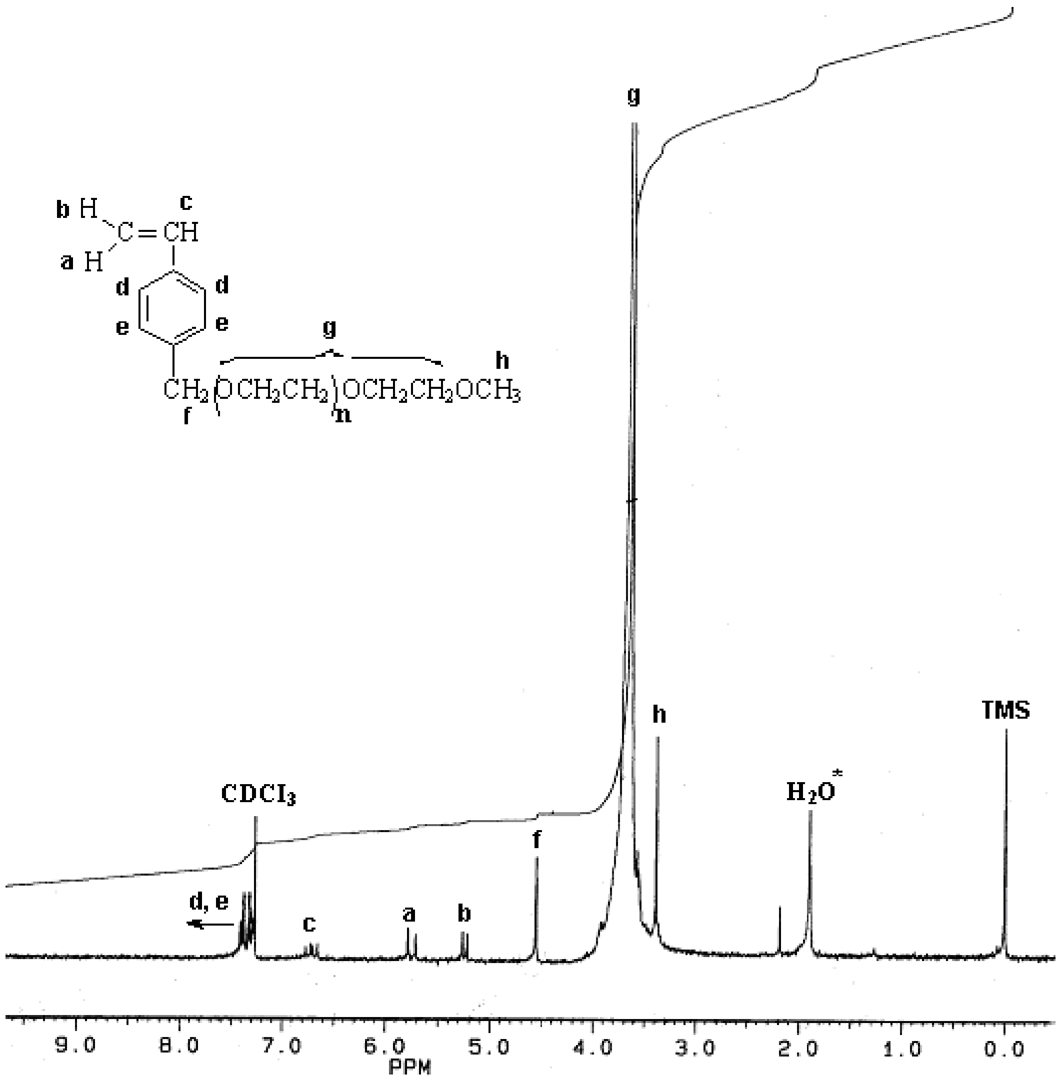
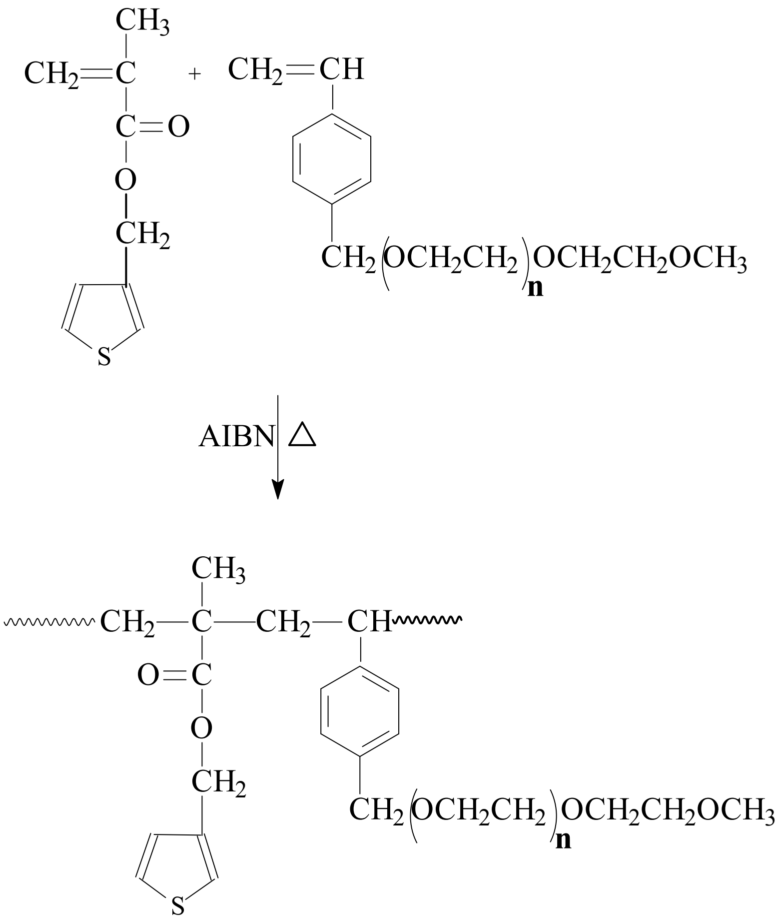


Figure 4.14. ^{1}H NMR spectrum of **PEOVB** macromonomer

* Indicates peak due to adsorbed water. The position and shape vary significantly according to its concentration and temperature depending on the extent of their hydrogen bonding.

PEOVB macromonomer was further used in copolymerization via vinylic terminus. Polymerization conditions and the results are presented in Table 4.6. The reaction involves the free radical polymerization of PEOVB with electroactive 3-methylthienyl methacrylate (MTM) monomer in the presence AIBN as a thermal initiator. The reaction 4.15 indicates the reaction path. The structure of random copolymer was characterized by GPC measurements and ^{1}H-NMR spectroscopy (Figure 4.15 & 16). The disappearence of the signals at 5.80-5.25 ppm corresponding to vinylic protons of PEOVB and the apperance of the signal at around 5 ppm corresponding to Thi-C$\mathbf{H}_2$ of MTM show that the random copolymers of PEOVB and MTM proceeded via the vinylic bonds.



(4.15)

Table 4.6. Preparation of Random Copolymer of MTM and PEOVB

[AIBN]= $2.8\text{x}10^{-2}$ molL^{-1}, [MTM] =$5.5\text{x}10^{-1}\text{molL}^{-1}$, Time = 3 hours, Temp.= 80 ^{0}C.

Code	Random Copolymer composition PMTM-r-PEOVB (Mol %)		Conversion (%)	*Mn*	*Mw*/*Mn*
	MTM	PEO-VB			
PMTM-*r*-PEOVB	91	9	62	13800	11.43

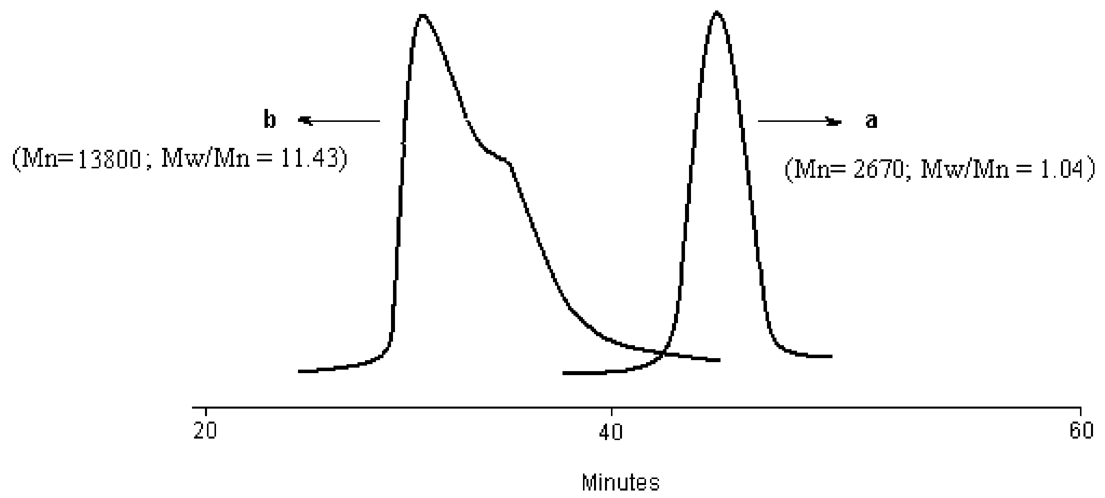


Figure 4.15. GPC traces of PEOVB macromonomer (M_n= 2670; M_w/M_n = 1.04) **(a)**; after random copolymerization with MTM (M_n= 13800; M_w/M_n = 11.43) **(b)**

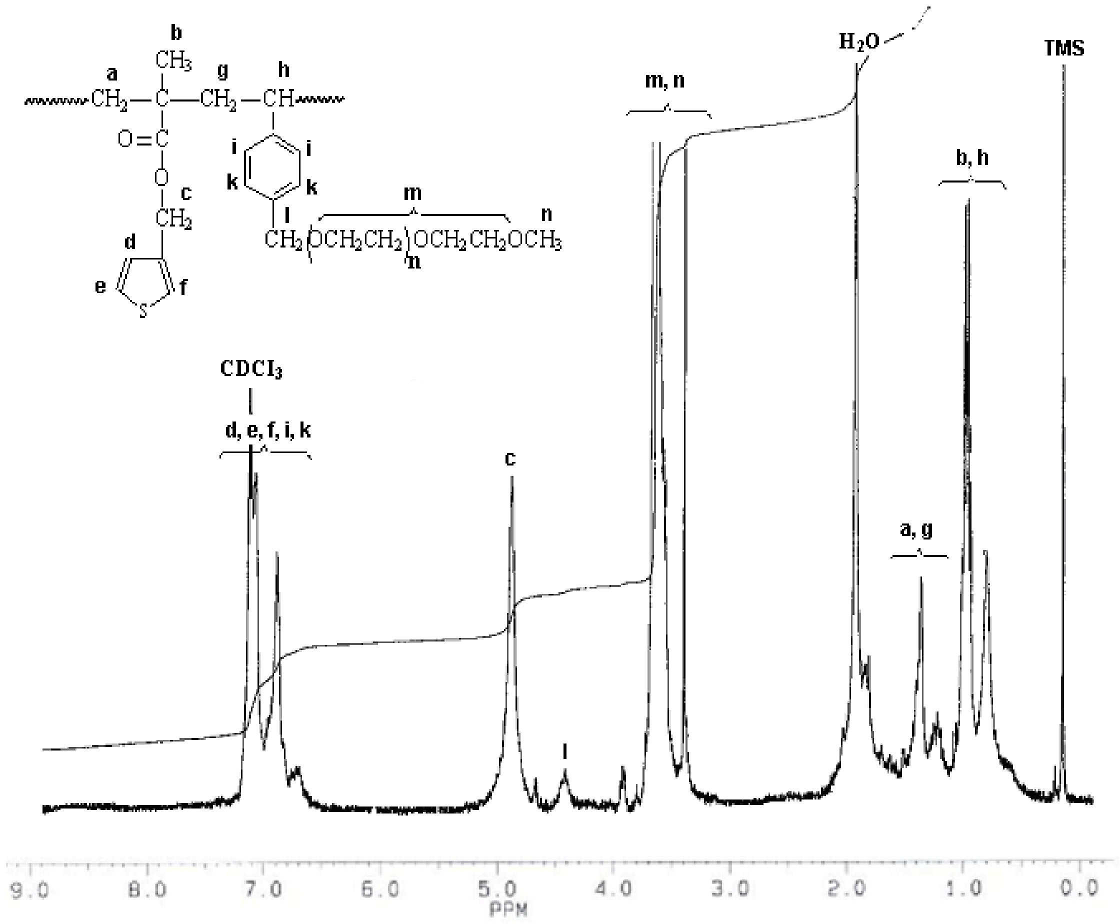


Figure 4.16. ^{1}H-NMR spectrum of random copolymers of 3-methylthienyl methacrylate and PEOVB

The composition of the random copolymers determined by ^{1}H-NMR spectroscopy was calculated by comparing the integral peak area of the protons of Th-C$\mathbf{H_2}$-O, exhibiting signals at around 5.00 ppm, to that of -Ph-C$\mathbf{H_2}$-, showing signals at 4.45 ppm in Figure 4.16.

4.3.3 Synthesis of Alternating Copolymers of N-(4-(3-thienyl methylene)-oxycarbonylphenyl)maleimide (MBThi) with Styrene (St) by Photopolymerization (PSt-*alt*-MBThi)

There is considerable interest not only in the synthesis of new types of plastic materials, but also in the modification of commodity polymers in order to improve their properties to meet requirements for new applications. One of the existing methods of improving polymer properties is the copolymerization.

Polymers of N-substituted maleimides and their derivatives can be classified into polyimides, important high-performance engineering plastics, being a class of rigid polymers because of the imide rings in the backbone. This provides the polymers with superior mechanical and thermal stability.

Maleimide-incorporated vinyl polymers have also gained current interest in several fields related to their dielectric [171] and nuclear magnetic relaxational characteristics [172], asymmetric induction polymerization [173], or Langmuir-Blodgett film-forming properties [174]. Copolymers of N-substituted maleimides were synthesized and investigated for their use as positive photoresists [175], or for non-linear optical (NLO) applications [176]. The peculiar homo- and copolymerization characteristics of the electron-deficient maleimide group make it an attractive monomer for designing special vinyl polymers. Although maleimide undergoes homopolymerization with great difficulty, it copolymerizes quite readily with a variety of vinyl monomers. Further, it is known to form alternating copolymers with electron-rich monomers. Apart from enhancing the thermal stability and glass transition temperature of the resultant copolymers, maleimide group can effectively serve as a vehicle for many functional groups for their predefined distribution in a vinyl polymer backbone through free radical copolymerization.

One of the main advantages offered by functional maleimides is the fact that new monomers with desired substituents to the imino nitrogen can be readily prepared. The 4-maleimidobenzoic acid, a very versatile reagent was often used in the last decade to obtain N-phenyl maleimide type monomers [146-151] or bismaleimides [151,152] with different functionalities.

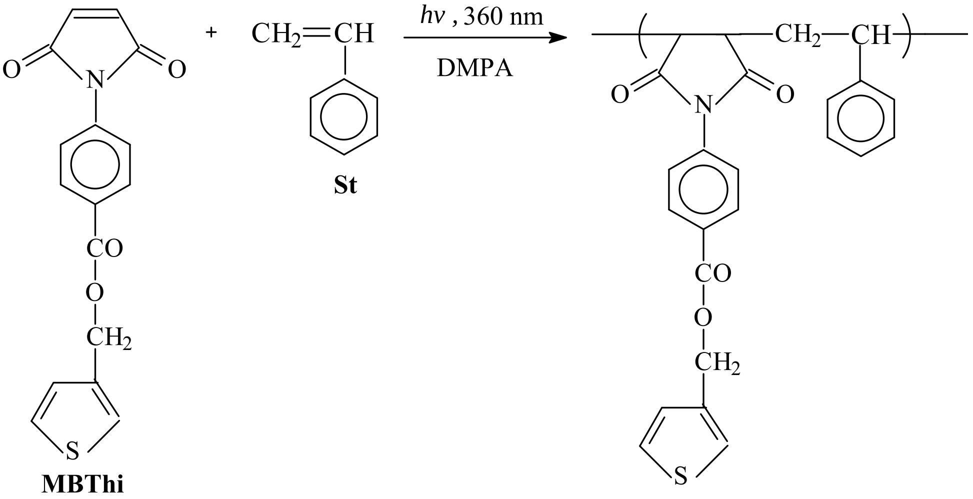
Photopolymerization is one of the most rapidly expanding processes for materials production. Photopolymerization have gained prominence in recent years for the pollution-free curing of polymer films as well as emerging applications in dental materials, conformal coatings, electronic and optical materials and high-resolution rapid prototyping of 3D objects. Near to the excellent properties of the obtained polymers (adhesion, abrasion resistance, chemical resistance, etc.) photopolymerization process itself affords advantages such as very high reaction rates at room temperature and spatial control of polymerization [177].

Recently, development of soluble and melt processible electrically conducting polymers based on 3-alkyl substituted polythiophenes and similar derivatives of polyheterocycles have opened a new direction in conducting polymer research. S. Edge *et al*, for the first time reported the preparation and characterization of polymaleimides which contain pendant 3-substituted thiophene rings [178] in order to obtain a processable conducting material *via* electro and oxidative polymerizations.

This part of the study is based on previously reported results [17] and is devoted to the synthesis, characterization and copolymerization of a thiophene-containing maleimide monomer with styrene in order to improve solubility in suitable solvents for free radical polymerization and also decrease oxidation potential.

Free radical polymerization and copolymerization of styrene as electron-rich monomer with various N-substituted maleimides as electron-deficient monomers have been reported in many papers [146-151, 179, 180] and a nearly alternating copolymer was obtained through the formation of charge transfer complexes (CTCs), better called electron donor-acceptor complexes, EDA. A measure for the strength of the donor (D) – acceptor (A) interaction is the equilibrium constant of EDA complex formation, (K).

Weak complex formation is generally slightly exothermic and disfavored entropically and an increase in temperature would decrease the complex concentration [181]. Lower temperature is also expected to lead to a higher equilibrium constant for the complex formation [182] and increase of (K) will lead to an increase in copolymer stereoregularity [181]. We have, therefore, chosen photopolymerization at room temperature as a method for the synthesis of the alternating copolymers of MBThi with styrene (reaction 4.16).



(4.16)

The structure of the monomer **MBThi** (see reaction 4.1) is similar to already published monomer [17] having an AB-type structure and containing a dienophile group (maleimide) together with a dienic one (thiophene ring). Even though the dienic character of the thiophene heterocycle is the lowest comparing with furane and pyrrole [183], to avoid the competition between addition polymerization and thermal Diels-Alder polymerization [184], photopolymerization seemed to be the most convenient method for the obtainment of linear polymers.

Generally, the choice of a solvent for the polymerization of the maleimides is limited by the poor solubility of both monomeric and polymeric materials. Consequently, polar solvents are often used for the polymerizations, many of which are undesirable as solvents for free radical polymerization. It is therefore of interest to produce maleimide-based polymers of improved solubility in common solvents and of high molecular weight, both of which extend their use in industrial applications. The effect of varying reaction conditions on the stereochemistry of alternating copolymers of N-substituted maleimides with electron-donor co-monomers has been already studied [181, 185, and 186]. So, it is well known that the stereoregularity of this type of copolymers varies with copolymerization conditions as temperature, solvent, total concentration of the co-monomers, co-monomer concentration ratio at fixed total monomers' concentration and the donor-acceptor character of the co-monomers' pair. The results of our attempts are included in Table 4.7.

The copolymerizations of **MBThi** with St were conducted at room temperature by using a constant concentration of photoinitiator, ω,ω-dimethoxy-ω-phenylacetophenone (DMPA). Two solvents with different polarities (benzene and dichloromethane) were used at the same total concentration of the comonomers (C_t) in the feed. The initial ratio of the comonomers was chosen as 1:1 for which the EDA concentration is greatest and also the overall rate of polymerization (R_p) is maximum [183].

In our experiments the influence of the solvent and the total concentration of the comonomers, C_t, on the characteristics of the obtained polymeric materials was followed. In order to establish the influence of the C_t on the copolymers' characteristics, the copolymerization in benzene was conducted by using two different values of the above-mentioned parameter. The selection of the solvents for the polymerization was made considering that the equilibrium constant for EDA complex formation (K) is generally solvent dependent [187] and that the equilibrium can be perturbed if one or both of the complex participants is strongly solvated [181].

From this point of view, the non-polar benzene could be considerate as an "inert" solvent that promote the EDA complex formation in a high concentration. It has been suggested that, if an EDA complex participate in a copolymerization, some structural evidences related to the structure of the complex may be found in the copolymer [181, 185, 155, and 188]. It has been also suggested [189] that the relative amounts of the *cis* and *trans* linkage configurations at the succinimide rings in the copolymers are closely related to the quantitative role of the EDA complex in alternating copolymerization.

Table 4.7. Preparation of Copolymer of MBThi with Styrene[a] via Photo Induced Free Radical Polymerization.

Sample		Reactions conditions			Conversion (%)		MI(%) in Copolymer[b]	Ratio[b] Cis/trans	M_n[c] (x10^3)	M_w/M_n[c]
		Solvent	Irradiation time (h)	C_t						
COP1		CH_2Cl_2	72.0	0.35	92		50	2	91	1.50
COP2	COP2.1[d]	Benzene	0.50	0.35	41.4	71.8	47.5	nd*	nd	nd
	COP2.2[e]					14.9	48	4	3.3	2.40
	COP2.3[f]					13.3	50	6	12	3.09
COP3	COP3.1[g]	Benzene	0.20	0.18	22.6	72.3	50	4.7	34	1.61
	COP3.2[f]					27.7	55	1.5	3	2.52

[a] The concentration of photoinitiator DMPA was 0.008 mol/L

[b] Calculated from ^{1}H-NMR data

[c] Obtained by GPC measurements

[d] This fraction was obtained from the precipitated material during the polymerization, after was extracted with THF at room temperature for 24h

[e] This fraction represent the polymeric material resulted from the THF solution of above fraction after its concentration and precipitation in methanol.

[f] The fraction that remained soluble in benzene during the polymerization

[g] The precipitated fraction during the polymerization, soluble in THF and chlorinated solvents

nd: not determinated

C_t: Total concentration of monomers [M]

*The ^{1}H-NMR spectrum of COP2.1 being registered in DMSO-d_6, the *cis*:*trans* ratio was not possible to calculate due to the presence of water in the same range as the methine protons

COP: Alternating copolymer

K. Fujimori *et. al* [190] claimed that the presence of the *cis* linkage configuration of maleimide unit in the copolymers can be considered as a structural evidence for the participation of the EDA complex in the propagation step. In the case of our new copolymers the presence of the methine protons in the succinimide moiety in the *trans* and *cis* form was evidenced by ^{1}H-NMR investigations. The ^{1}H-NMR spectra of the copolymers COP1 and COP2.3 are presented in Figure 4.17 (A and B).

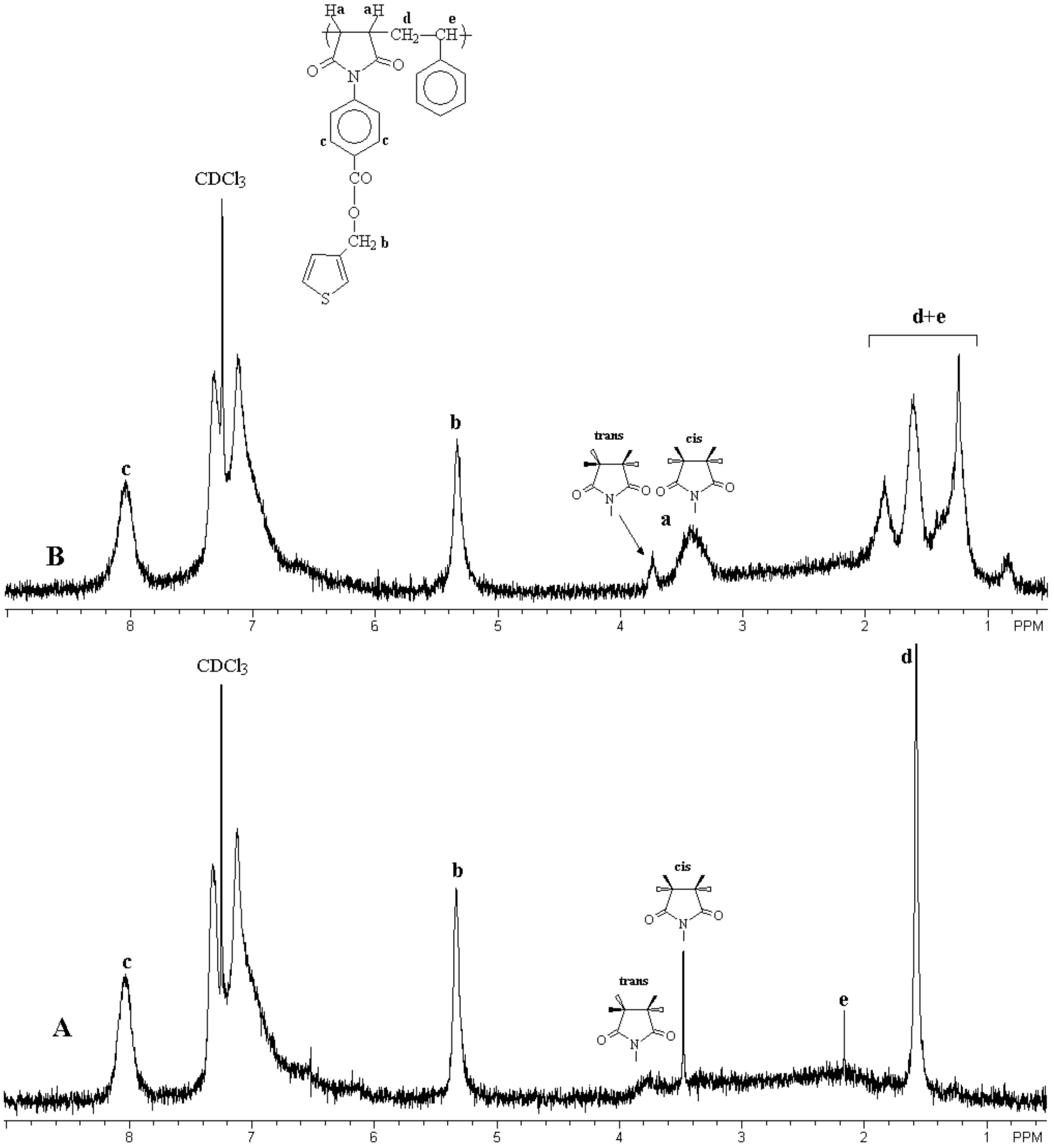


Figure 4.17.The ^{1}H-NMR spectra of copolymer COP1 **(A)** and copolymer COP 2.3 **(B)** in $CDCl_3$

Considering the results of Mormann and Schmaltz [191], we can conclude that the features of these spectra confirm the alternating structure of the synthesized copolymer with a preference for the *cis* form in both used solvents. The ratios between *cis* and *trans* configurations for the synthesized copolymers are presented in Table 4.7 and were calculated from the corresponding integrals in their ^{1}H-NMR spectra. The relative broad singlets usually situated between 3.0-3.6 ppm characterize the *cis* configuration. The peaks in the range 3.6-3.9 ppm were assigned to the *trans* configuration at the succinimide rings. From the values of these ratios we can conclude that the concentration of EDA complex is higher in benzene by comparing with dichloromethane and consequently a large proportion of the *cis* linkage configuration at the succinimide units was found in the former one.

It is expected that the *trans* linkage configuration will be formed overwhelmingly at the cyclic succinimide rings in the copolymers, if only free monomers react one at a time in the propagation step of the copolymerization. As can be seen from Table 4.7, the copolymers' composition is near 1:1 for all synthesized materials. Taking in account that the comonomer's ratio in the feed was 1:1, this result suggests that the bulky side chain in maleimide monomer sterically controls the addition of the styrene monomer to the growing chain end in the propagation step in the case of the free monomer addition.

The results of the *cis trans* ratio correlate well with the total monomer concentration, C_t, used in the experiments. Thus, by comparing the above mentioned ratio for the copolymers COP2.2, COP2.3, COP3.1 and COP3.2, the higher values were founded for the COP2s for which the C_t was higher (0.35, Table 1).

An influence of the solvent on the conversion, the number-average molecular weight (M_n), and the polydispersity index (M_w/M_n) could also be observed. The highest conversion was obtained in dichloromethane accompanied by the lowest value of polydispersity in connection with the highest M_n values that were accessible for the determination. In fact, the reactions performed in benzene were the precipitation copolymerizations since both monomers were soluble while the copolymers precipitated out during the polymerization. So, in the case of COP2.1, M_n and polydispersity values were not possible to establish since the copolymer is soluble only in high polar solvents such as DMSO, DMF and DMAc. Notably, insolubility can not be due to crosslinking as IR spectra of all the synthesized copolymers exhibited the similar feature. The insolubility in non-polar or low polar solvents is attributed to the increased polarity of the obtained copolymer induced by the high molecular weight. In this case it is possible to suppose that the highest M_n characterizes the COP2.1.

The influence of the C_t on the properties of the copolymers was also observed for the copolymerizations performed in benzene. By comparing COP2.1 with COP3.1 and COP2.3 with COP 3.2, a decrease of M_n concomitantly with the diminution of C_t could be observed. Thus, the copolymers COP3.1 and COP2.1 both precipitated out from the reaction mixture during the copolymerization and are insoluble in benzene. The solubility of COP3.1 in chloroform and THF could be explained by its lower number-average molecular weight comparing with that of the copolymer COP2.1.

Also, the IR spectrum of COP1 is given in Figure 4.18. It contains the bands at 769 and 3105 cm^{-1} related to C-Hα streching modes. The absorption bands due to the carbonyl group and to C-O-C streching are present at about 1714 and in the 1000-1272 cm^{-1} region respectively [149].

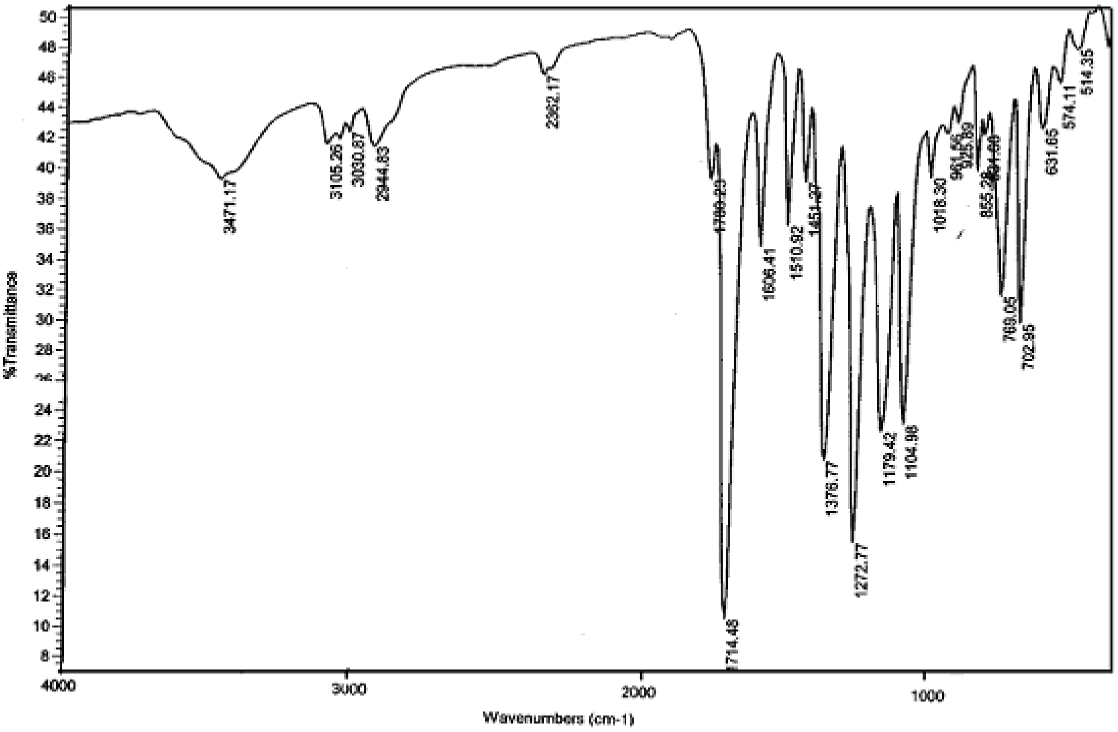


Figure 4.18. IR Spectrum of alternating copolymer (COP1)

The thermal behavior of the synthesized copolymers was investigated by means of the differential scanning calorimetry (DSC) and thermo-gravimetrical analysis (TGA) and is closely related to the copolymers' composition, more specifically to the maleimide content. The experimental data are included in Table 4.8.

Table 4.8. Thermal Properties of the Synthesized Copolymers

Sample		IDT[a,b] (°C)	T_g[c] (°C)	T_{W10}[b,.d] (°C)	Y_C[b,e] (%)
COP1		320	193	400	35
COP2	COP2.1	270	190	400	28
	COP2.2	279	192	401	28
	COP2.3	280	193	401	30
COP3	COP3.1	305	193	430	31
	COP3.2	252	196	401	35

[a] Initial degradation temperature (IDT)
[b] From TGA analysis
[c] From DSC analysis
[d] The temperature at which the weight loss is 10 % (Y_{W10})
[e] The percent of char yield at 800°C (Y_C)

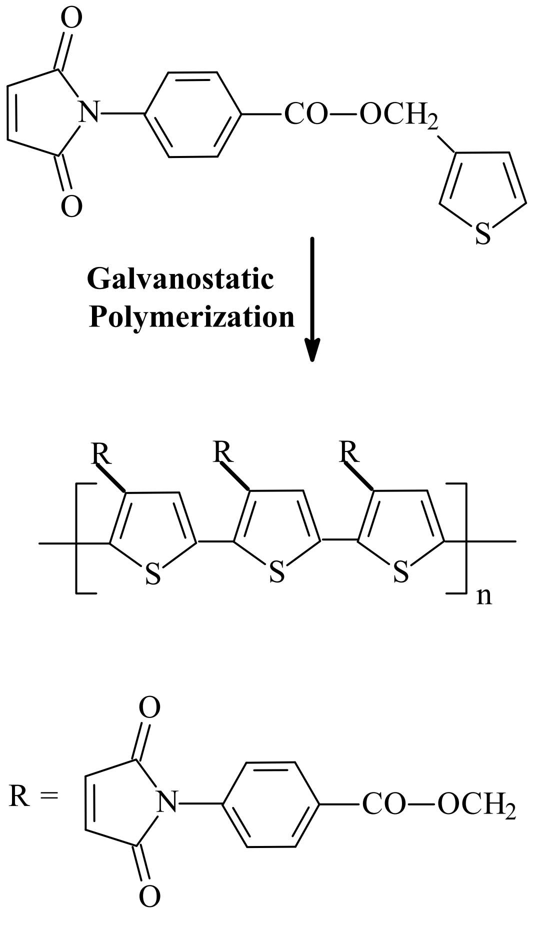
In general, glass transitions of polymaleimides are difficult to observe because they exhibit low changes in heat capacity [175a] and are very broad. Therefore, more material than usual and the scan rate at 40°C/min were used. As was reported [149] the glass transitions of copolymaleimides with St increas with the maleimide content in the copolymers. The similar behavior was observed in our case. The T_g values for copolymers range between 190 °C and 196 °C the highest value being registered for COP3.2, the maleimide content of which is 55 %. Table 4.8 also includes the values of the initial degradation temperature, (IDT), the temperature of 10% weight loss (T_{w10}) and the percent char yield (Y_c) at 800 °C for all synthesized materials.

Generally, the same relationship, as in the case of T_g, was observed between maleimide content of the copolymers and the IDT or Y_c values (see COP2.1, COP2.2 and COP1). Two exceptions were also observed. Thus, in the case of the copolymers having the same composition (COP1, COP2.3 and COP3.1) the values of IDT and Y_c are directly connected with the M_n values. On the other hand, the decreased value of IDT for COP 3.2 that have the highest maleimide content is also due to the low number-average molecular weight. For the T_{w10} nearly a constant value was found for all investigated materials. This fact suggests that up to 400 ^{0}C the maleimide content in the copolymers cannot influence the thermal stability.

4.4 Synthesis of Conductive Polymers by Electropolymerization

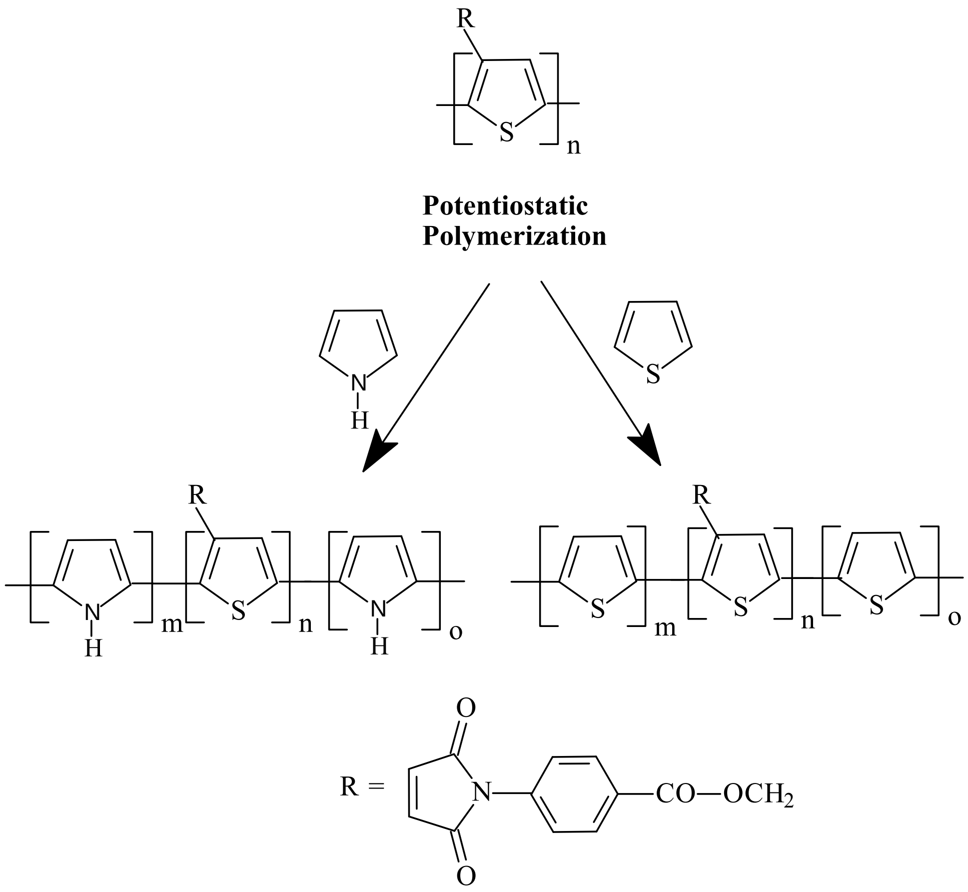
4.4.1 Electropolymerization of N-(4-(3-thienyl methylene)-oxycarbonylphenyl) maleimide (MBThi)

Homopolymerization of MBThi was accomplished by constant-current electrolysis technique (reaction 4.17).



(4.17)

The electropolymerization of PMBThi was achieved in the presence of pyrrole and thiophene by constant-potential electrolysis (reaction 4.18).



(4.18)

FTIR spectra of all the samples were recorded on a Nicolet 510 FTIR spectrophotometer. In the IR spectrum of the monomer (MBThi), the absorption bands at 764 and 3106 cm^{-1} arose from thienylene C-H α streching modes. The bands related to the carbonyl and C-O-C groups were observed at about 1720 and in the region of 1000-1213 cm^{-1}, respectively. Also the peak at 835 cm^{-1} was due to β-hydrogen in the thiophene ring. Additionally, the peaks at 1385 and 1282 cm^{-1} resulted from the C-N vibrations while the peaks at 1604 and 1512 cm^{-1} corresponded to C=C units (Figure 4.19). After the galvanostatic polymerization of the monomer (PMBThi), a new shoulder appeared at around 1611 cm^{-1} indicating the conjugation (Figure 4.20). The disappereance of the peaks at 3106 and 764 cm^{-1} also confirmed the evidence of polymerization from the 2 and 5 position of the thiophene ring. Moreover, the other characteristic monomer peaks conserved in the spectrum of PMBThi is attributed to the interaction of the monomer with Th. The electrochemically synthesized copolymer (MBThi/PTh) contains the absorption bands corresponding to carbonyl group. This indicates the presence of the monomer in the resultant polymers. Beside the carbonyl peak, the peak observed at 1614 cm^{-1} is a clear evidence of the polyconjugation.

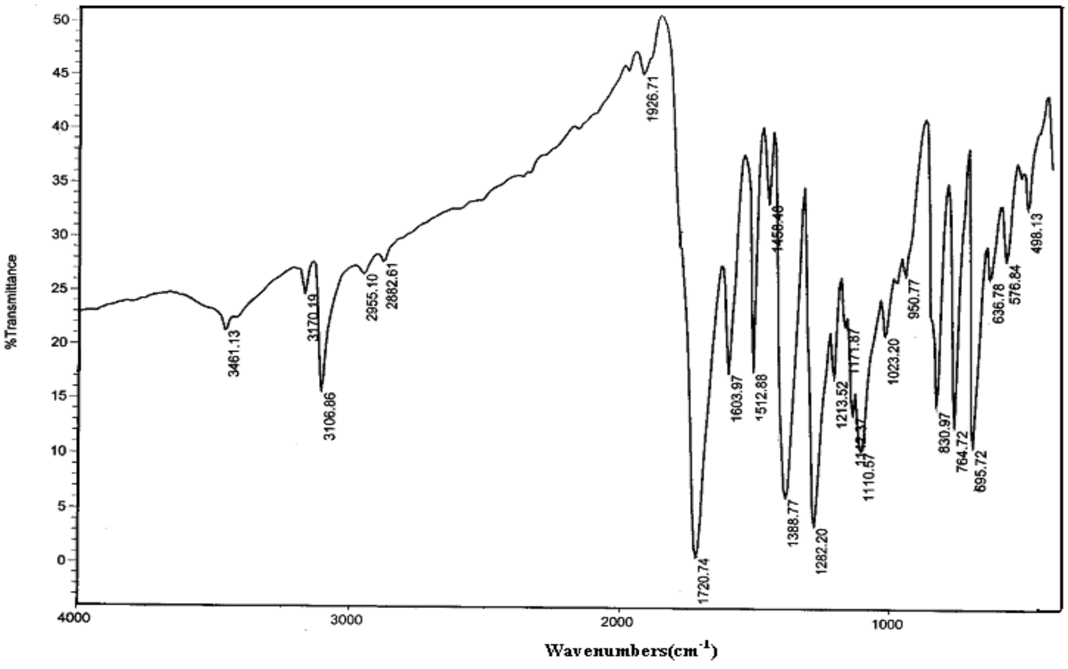


Figure 4.19. FTIR spectrum of **MBThi**

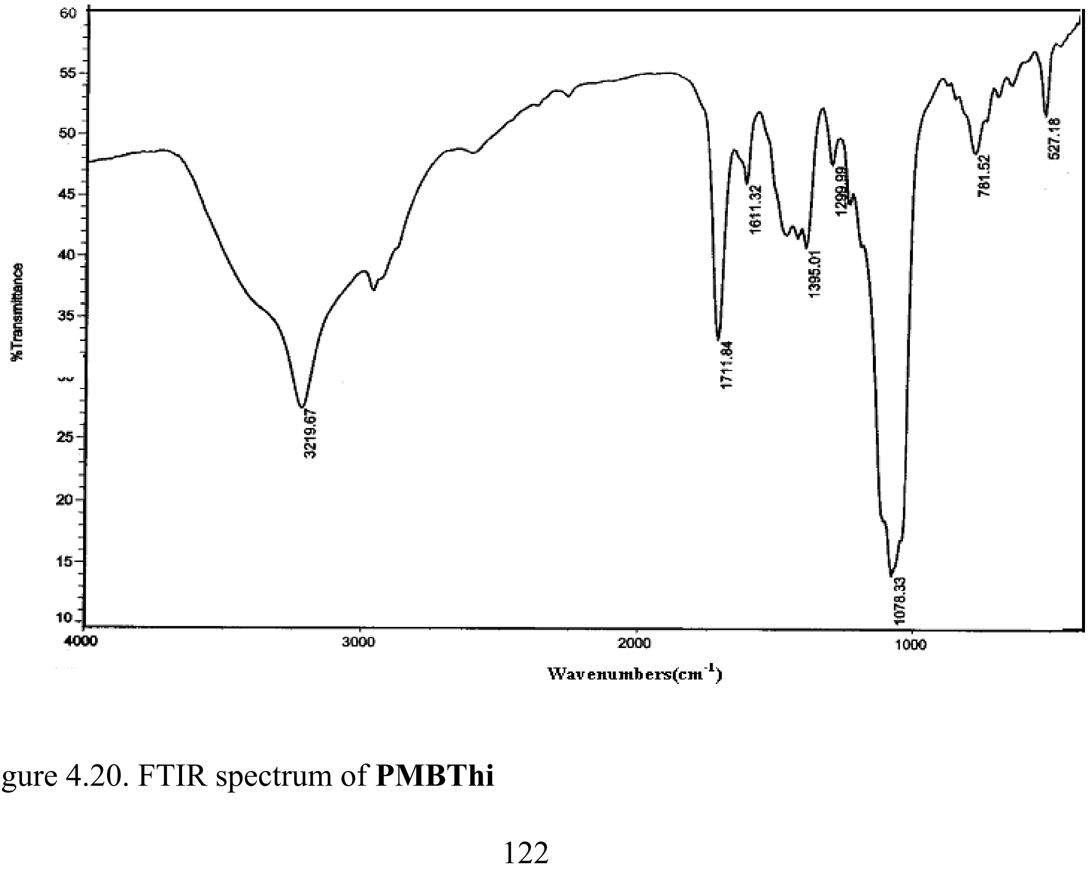


Figure 4.20. FTIR spectrum of **PMBThi**

CV studies were carried out in the presence of Py and Th in AN-TBAFB solvent – electrolyte couple under nitrogen atmosphere at room temperature. In the CV of the monomer an oxidation peak was obtained at +2.1 V (Figure 4.21). A decrease in peak intensities was obtained with continuous scan revealing a loss of electroactivity. However, in the presence of Th, increasing anodic and cathodic redox peaks appeared at + 1.5 V and + 0.57 V respectively. The potential values were somewhat different from the oxidation and reduction potentials of pure polythiophene which were obtained as +1.0 V and +0.7 V. This shift indicates the interaction between the monomer and Th. On the other hand there was no difference between voltammograms of pure PPy and MBThi/Py system. A clear conclusion regarding possible interaction between monomer and Py can not be drawn by CV, since the oxidation peak potentials of the monomer and pyrrole are quite different.

Thermal behavior of the resulting polymers was investigated by using using a Dupont 2000 Thermal Gravimetry Analyzer and Differential Scanning Calorimetry. The TGA thermogram of the monomer showed three weight losses; at 308, 437, and 547 ^{0}C (Figure 4.22) and in case of MBThi/PTh, the main weight loss was observed at 248 ^{0}C (Figure 4.23).

DSC of the monomer exhibited two transitions at 86 ^{0}C (Tm) and 307 ^{0}C (Figure 4.24). In the case of monomer/PTh, a transition at 116 ^{0}C resulted from the removal of solvent, and one at 308 ^{0}C from the evacuation of the dopant ion from polymer matrix were observed (Figure 4.25).

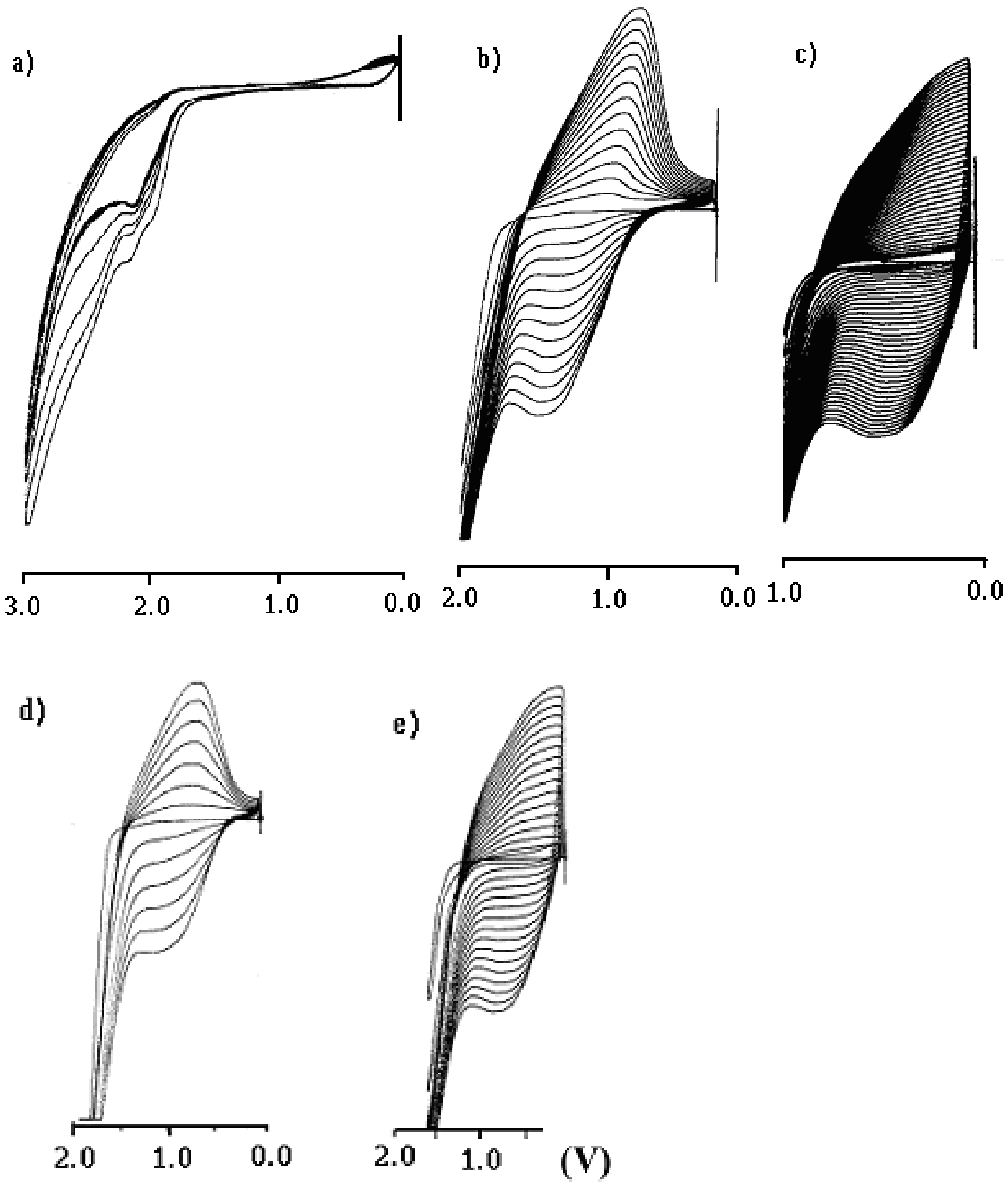


Figure 4.21 Cyclic voltammogram of **(a)** monomer (MBThi), **(b)** MBThi in the presence of thiophene, **(c)** MBThi in the presence of pyrrole, **(d)** thiophene on a bare Pt electrode, **(e)** pyrrole on a bare Pt electrode

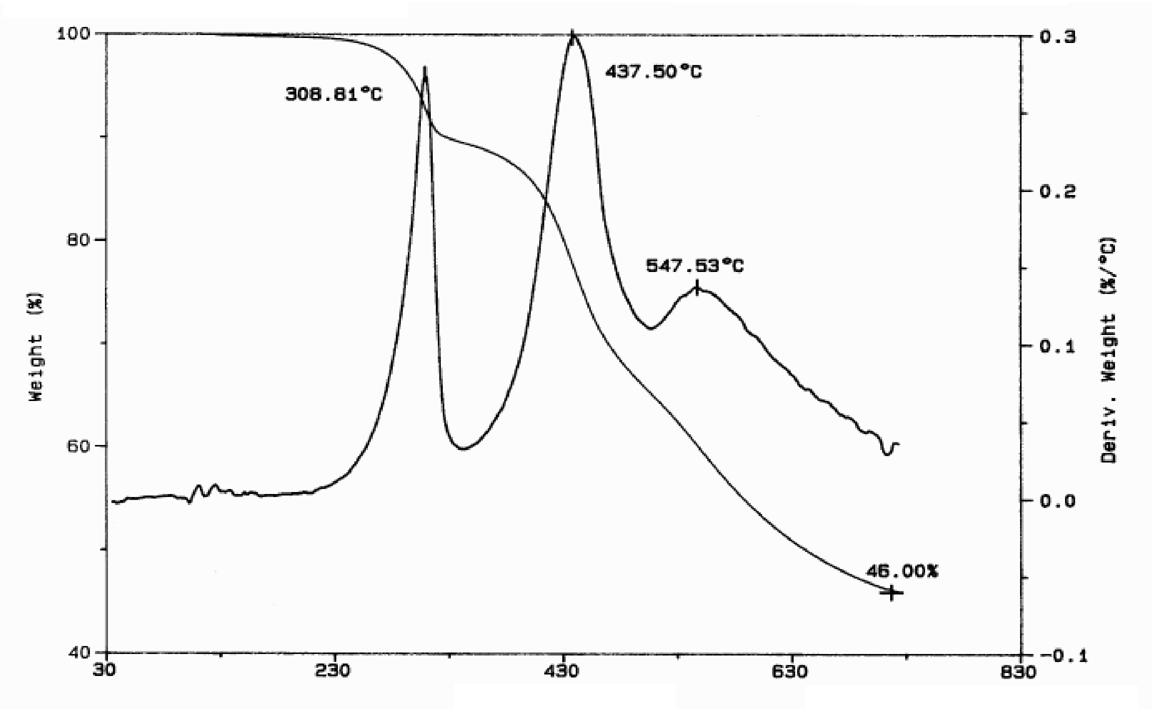


Figure 4.22. TGA curve of **MBThi**

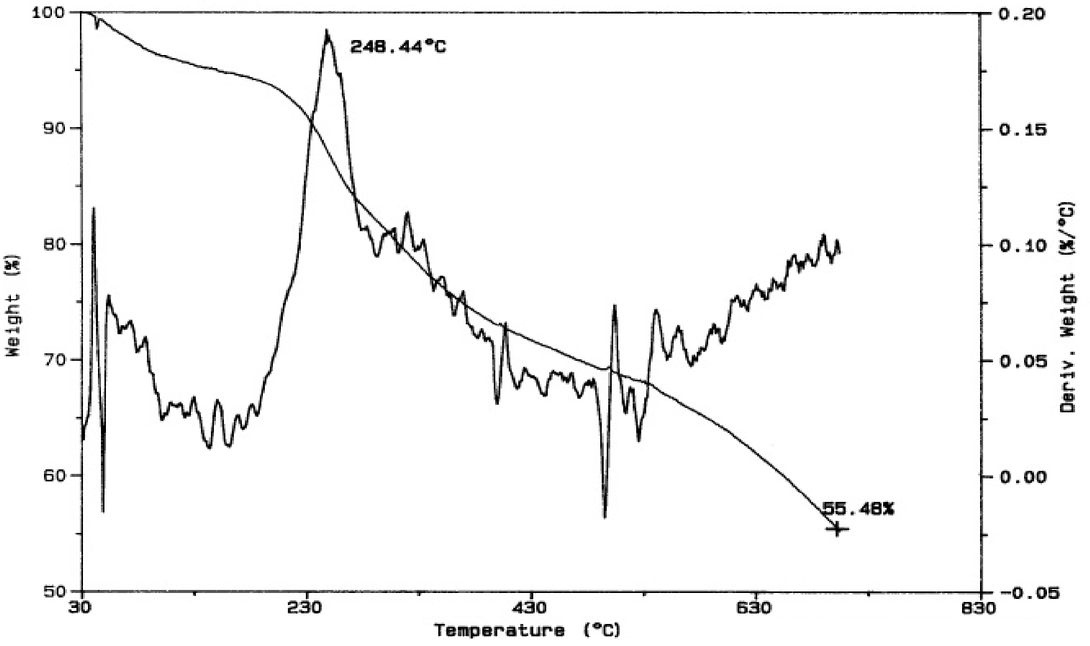


Figure 4.23. TGA curve of **MBThi/PTh**

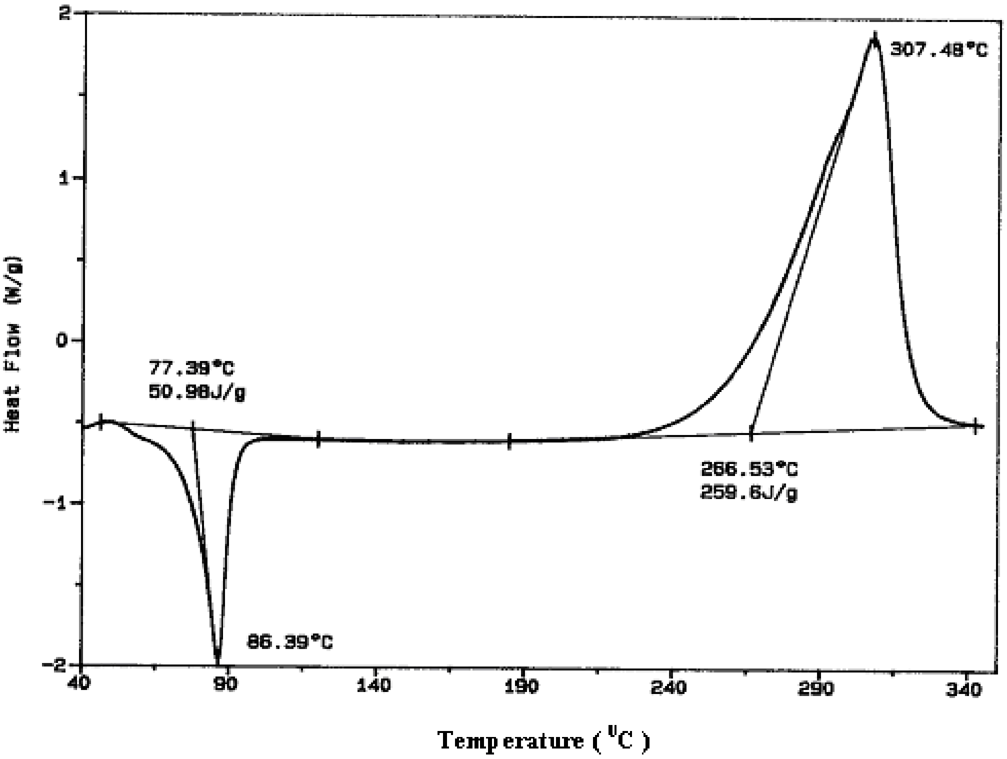


Figure 4.24. DSC curve of **MBThi**

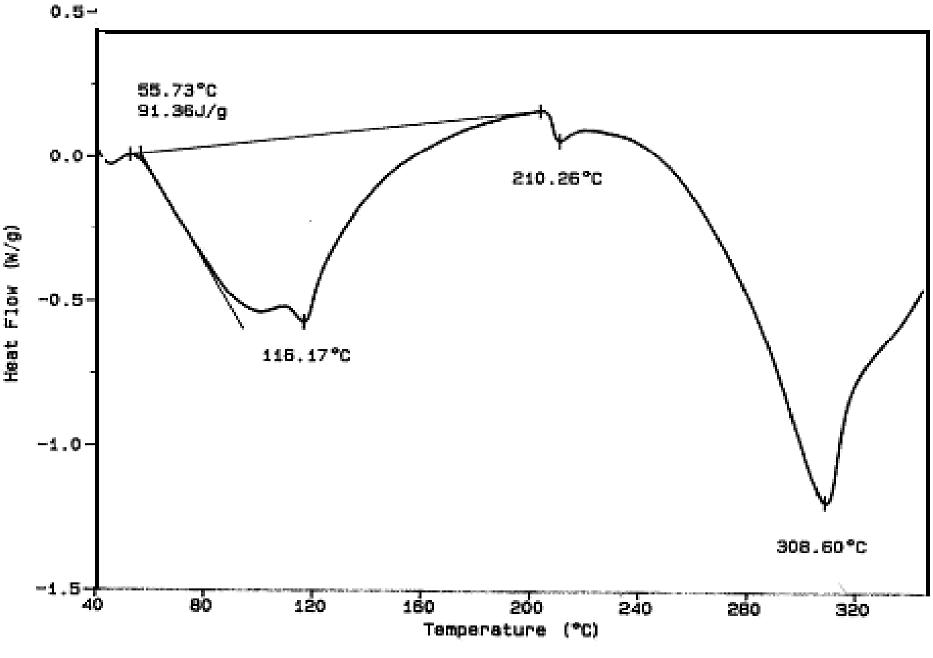


Figure 4.25. DSC curve of **MBThi/PTh**

The four probe technique was utilized in order to measure the electrical conductivities of the samples. The same order of magnitude in the conductivities of both the electrode and the solution sides indicates the homogeneity of the films. The results of conducting measurements are shown in Table 4.9.

Table 4.9. Conductivities of the Films (S/cm)

Polymer	Conductivity
MBThi/PTh ($BF^-{}_4$-doped)	1.1×10^{-1}
PMBThi/PTh ($BF^-{}_4$-doped)	4.4×10^{-2}
PMBThi/PPy1 (PTS^- doped)	1.3
PMBThi/PPy2 ($BF^-{}_4$-doped)	1.6

The morphologies of the films were investigated with a JEOL JSM-6400 scanning electron microscope. The micrograph of PMBThi/PPy1 and PMBThi/PPy2 were significantly different from that of pure PPy's cauliflower microsturucture. In the case of PMBThi/PTh copolymer, again no resemblence was found with respect to pure PTh sturucture. All these results point out that PMBThi is chemically bonded to both PPy and PTh chains (Figure 4.26).

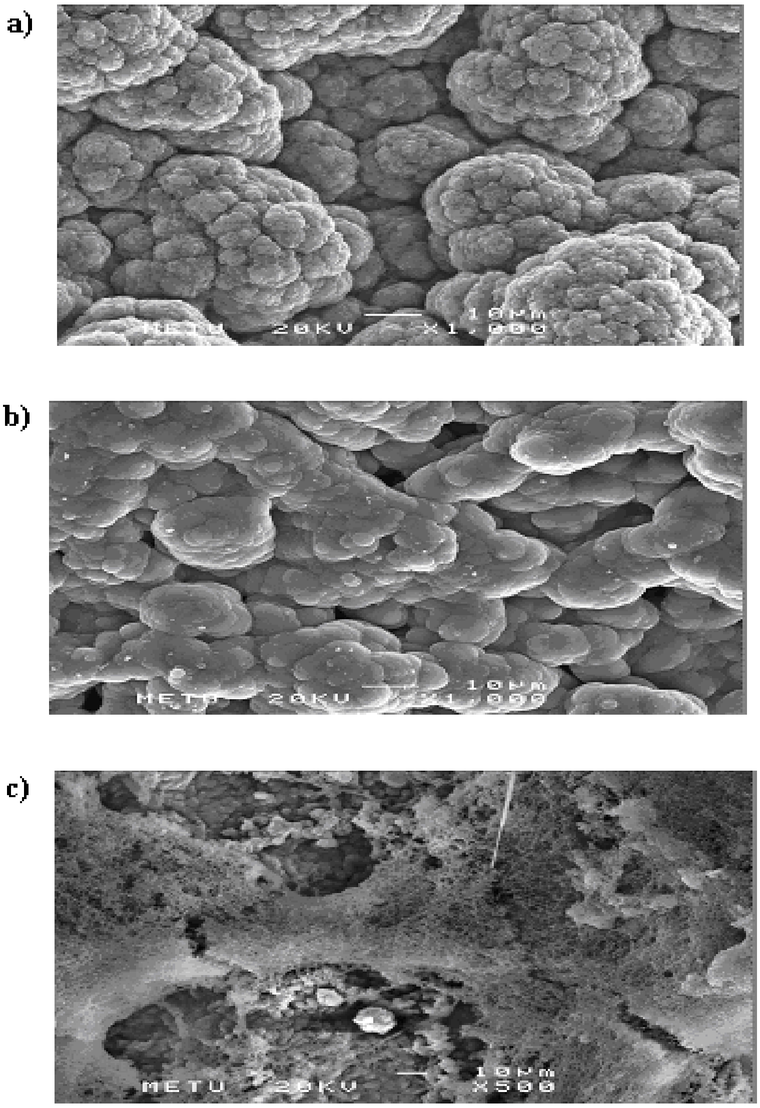


Figure 4.26. SEM micrographs of **(a)** MBThi/PTh film (BF^-_4-doped) **(b)** PMBThi/PPy1 film (PTS^- doped) and **(c)** PMBThi/PTh film(BF^-_4-doped)

5. CONCLUSIONS

In this thesis, reactive intermediates based on monomeric and polymeric structures possessing thiophene moieties were prepared and subsequently the attempts were made to demonsrate their possible use in electropolymerization through thiophene groups.

New mono, di, tri, and tetra thienyl functional monomers (**MBThi**, **TOET**, **TOPT**, and **TOTPT**) were synthesized by the esterification reaction of MBA with thiophene methanol (TM) and by the condensation reactions of thiophene carboxylic acid (TCA) with ethylene glycol (EG), glycerol (G), and pentaeritritol (PE), respectively and characterized by spectral methods.

Novel well-defined end(s) functional macromonomers of **PEO**, **PTHF** and **PCL** were prepared by controlled/living polymerization methods. α-ω-heterofunctional **PEO** macromonomers possessing thiophene moiety at one end and methacrylate group at the other end were prepared by anionic ROP method. Then, PEO macromonomers were successfully employed in free radical polymerization through vinylic bond and in oxidative polymerization through thiophene moiety. Electrochemically polymerizable thiophene moeities were incorporated into the living ends of **PTHF** via cationic ROP polymerization. Using 3-thiophene methanol, **PCL** macromonomers with the desired functionality were obtained by ROP in conjunction with the stannous-2-ethylhexanoate ($Sn(Oct)_2$) as a catalyst.

In addition, the block copolymers of **PMMA-*b*-PMTM** were prepared by DPE method. Upon heating a preformed PMMA containing DPE units in the presence of the second monomer (MTM) resulted in the block copolymers of MMA with MTM. The GPC spectrum of (**PMMA-*b*-PMTM**) clearly confirmed that the prepolymers were converted into block copolymers. The polydisperties of all the block copolymers obtained were below those observed in common radical polymerization. These studies clearly demonstrated that conventional radical polymerization can be converted to a controlled process to some extend and thus block copolymers can be synthesized in the presence of DPE. Also, side chain thiophene functional alternating and random copolymers were prepared. Alternating copolymers of styrene (St) and MBThi (**PSt-*alt*-MBThi)** were synthesized via photopolymerization by taking the advantage of electronic structure of the corresponding monomers. Successful alternating copolymerization has been proved by NMR spectral measurement. Random copolymers of MTM and PEOVB (**PMTM-*r*-PEOVB**) were prepared by free radical polymerization with the use of AIBN as the initiator.

Mono thienyl functional MBThi monomer was subsequently used in electropolymerization to yield electrically conducting copolymers.

We have presented the successful synthesis of side- and end-chain thiophene functional polymers. Syntheses were facilitated by using a variety of conventional and controlled/living polymerization techniques. A series of electrochemical and oxidative grafting and blocking of these functional polymers with pyrrole and thiophene may be further attempted. Obviously, the copolymers thus formed would have two fold benefits: To control the conductivity and obtain better mechanical and physical properties with respect to pure polythiophene (PTh) and polypyrrole (PPy).

REFERENCES

[1] **Skotheim, T.A., Elsenbaumer, R.L. and Reynolds, J.R.**, 1998. Handbook of Conducting Polymers, 2nd ed.; Marcel Dekker, New York.

[2] **Kraft, A., Grimsdale, A.C. and Holmes, A.B.**, 1998. Electroluminescent conjugated polymers - seeing polymers in a new light, Angew. Chem., Int.Ed., **37**, 402-428.

[3] **Killian, J.G., Coffey, B.M, Gao, F., Pochler, T.O. and Searson, P.C.**, 1996. Polypyrrole composite electrodes in an all-polymer battery system, *J. Electrochem. Soc.* **143**, 936.

[4] **Leventis, N.**, 1995. Polymers in Electrochromics, *Polym. News*, **20**, 5-18.

[5] **Barisci, J.N., Conn, C. and Wallace, G.G.,** 1996. Conducting polymer sensors *Trends Polym. Sci.* **4**, 307-311.

[6] **Olmeda, L., Hourquebie, P. and Jousse, F.,** 1993. Microwave absorbing materials based on conducting polymers, *Adv. Mater.* **3**, 373-377.

[7] **Beck, F. and Michaelis, R.J.,** 1992. Strongly adherent, smooth coatings of polypyrrole oxalate on iron, *Coat.Technol,* **64 (808)**, 59-67.

[8] **Mishra, M.K.**, 1994. Macromolecular Design: Concept and Practice, Polym. Frontiers Int. Inc., New York, , part 1.

[9] **Depoli, M.A., Waltman, R. J., Diaz, A.F. and Bargon, J.,** 1985. An electrically conductive plastic composite derived from polypyrrole and polyvinyl-chloride, *J.Polym Sci Polym Chem Ed.,* **23 (6)**, 1687-1985.

[10] **Wang, H.L., Toppare, L. and Fernandez, J.E.,** 1990. Conducting polymer blends: polythiophene and polypyrrole blends with polystyrene and poly(bisphenol A carbonate), *Macromolecules,* **23**, 1053.

[11] **Kizilyar, N., Toppare, L., Onen, A. ve Yagci, Y.,** 1999. Synthesis of Conducting PPy/PTHF Copolymers, *J. Appl. Polym. Sci*., **71**, 713.

[12] **Yagci, Y. and Toppare, L.,** 2000, Synthesis of conducting block and graf copolymers containing polyether segments, *Macromol. Symp*., **157**, 29.

[13] **Kizilyar, N., Toppare, L., Onen, A. and Yagci, Y.,** 1998. Synthesis of conducting polypyyrole/polytetrahydrofuran copolymers, *Polym. Bull.*, **40**, 639.

[14] **Cirpan, A., Alkan, S., Toppare, L., Hepuzer, Y. and Yagci, Y.,** Conducting graft copolymers of Poly(3-methyl thienyl methacrylate) with pyrrole and thiophene, 2002. , *J. Polym. Sci., Polym. Chem. Ed.*, **40**, 4131.

[15] **Alkan, S., Toppare, L., Hepuzer, Y and Yagci, Y.,** 1999. Block bopolymers of thiophene-capped poly(methyl methacrylate) with pyrrole, *J. Polym. Sci., Polym. Chem. Ed.*, **37**, 4218.

[16] **Alkan, S., Toppare, L., Hepuzer, Y. and Yagci, Y.,** 2001. Synthesis and characterization of conducting block copolymers of thiophene-ended polystyrene with pyrrole, *Synt. Met.*, **119**, 133.

[17] **Cianga, L. and Yagci, Y.,** 2002. Synthesis and characterization of poly(N-phenyl maleimide) polymers with pendant thiophene rings by photoinduced radical polymerization, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 995.

[18] **Lowe, J. and Holderoft, S.,** 1995. Synthesis and photolithography of polymers and copolymers based on poly(3-(2-(methacryloyloxy)ethyl)thiophene), *Macromolecules*, **28**, 4608.

[19] **Labaye, D.E, Jerome, C., Geskin, V.M., Louette, P., Lazzaroni, R., Martinot, L. and Jerome, R.,** 2002. Full electrochemical synthesis of conducting polymer films chemically grafted to conducting surfaces, *Langmuir*, **18 (13)**, 5222-5230.

[20] **Cirpan, A, Yilmaz, F, Toppare, L. and Yagci, Y.,** unpublished results.

[21] **Malenfant, P.R.L. and Frechet, J.M.J.,** 2000. Dendrimers as solubilizing groups for conducting polymers: Preparation and characterization of polythiophene functionalized exclusively with aliphatic ether convergent dendrons, *Macromolecules*, **33**, 3634.

[22] **McCarley, R.L and Willicut, R.J.,** 1998. Tethered monolayers of poly((*N*-pyrrolyl)alkanethiol) on Au, *J. Am. Chem. Soc.*, **120 (36)**, 9296-9304.

[23] **Smela, E.,** 1998. Thiol-modified pyrrole monomers: 4. electrochemical deposition of polypyrrole over 1-(2-Thioethyl)pyrrole, *Langmuir*, **14 (11)**, 2996-3002.

[24] **Sayre, C.N. and Collard, D.M.,** 1995. Self-assembled monolayers of pyrrole-containing alkanethiols on gold, *Langmuir*, **11 (11)**, 302-3002.

[25] **Lang, P., Mekhalif, Z. And Garnier, F.J,** 1992. Blocking and chemical pretreatments of platinum-electrode for the electropolymerization of thiophenes, *J. Chem. Phys.*, **89 (5),** 1063-1070.

[26] **Nuesch, F., SiAhmed, L, Francois, B. and Zuppiroli, L.,** 1997. Derivatized electrodes in the construction of organic light emitting diodes, *Adv. Mat.,* **9 (3)**, 222.

[27] **Simon, R., Ricco, A., Wrighton, M.,** 1982. Synthesis and characterization of a new surface derivatizing reagent to promote the adhesion of polypyrrole films to N-type silicon photoanodes: N-(3-(trimethoxysilyl)propyl)pyrrole, *J. Am. Chem. Soc.,* **104**, 2031.

[28] (a) **Kovacic, P. and Jones, M.B.,** 1987. Dehydro coupling of aromatic nuclei by catalyst-oxidant systems: poly(p-phenylene), *Chem. Rev.,* 87 (2), 357-379, (b) **Patil, A.O., Heeger, A.J. and Wudl, F.,** 1988. Optical properties of conducting polymers, *Chem. Rev.,* 88 (1) 183-200, (c) **Reynolds, J.R.,** 1988. Electrically conductive polymers, *Chemtech.*, 18 (7) 440-447, (d) **Billingham, N.C. and Calvert, P.D.,** 1989. Electrically conducting polymers - a polymer science viewpoint, *Adv. Poly. Sci.,* **90** 1, (e) **Roncali, J.,** 1997. Synthetic principles for bandgap control in linear π-conjugated systems, *Chem, Rev., **97***(**1),** 173-206.

[29] **Bauerle, P. and SCHEIB, S.,** 1993. Molecular recognition of alkali-ions by crown-ether-functionalized poly(alkylthiophenes), *Adv. Mater.,* **5 (11)**, 848-853.

[30] **Kovacic, P. and McFarland, K.N.,** 1979. Polymerization of aromatic nuclei. XIX. Polymerization of thiophene by aluminum chloride, *J. Polym. Sci., Polym. Chem. Ed.,* **17**, 1963-1976.

[31] **Yamamoto, T., Sanechika, K. and Yamamoto, A.,** 1980**.** Preparation of thermostable and electric-conducting poly(2,5-thienylene), *J. Polym. Sci.: Polym. Lett. Ed.,* **18 (1)**, 9-12.

[32] **Lin, J. and Dudek, L.P.,** 1980. Synthesis and properties of poly(2,5-thienylene), *J. Polym. Sci.: Polym. Chem. Ed.,* **18 (9)**, 2869-2873.

[33] **Kossmehl, G. and Chatzitheodorou, G.,** 1981. Electrical conductivity of poly(2,5-thiophenediyl)-AsF_5-complexes, *Makromol. Chem. Rapid. Commun.,* **2**, 551-555.

[34] **Blomquist, A.T. and Ferris, A.F.,** 1951. The Kinetics of the thermal decomposition of peresters. I. The effect of perbenzoate concentration on the decomposition of t-Butyl perbenzoate, *J. Am. Chem. Soc.,* **73**, 3408.

[35] **Blomquist, A. T. and Berstein, I.A.,** 1951. The Kinetics of the thermal decomposition of peresters. III. The effect of p-substituents on the unimolecular decomposition of t-Butyl perbenzoates, *J. Am. Chem. Soc*., **73**, 5546.

[36] **Bartlett, P.D. and Rüchardt, C.,** 1959. *P*eresters. IV. Substituent effects upon the concerted decomposition of t-Butyl phenylperacetates, *J. Am. Chem. Soc*., **82**, 1756.

[37] **Bartlett, P.D., Benzing, E.P. and Pincock, R.E.,** 1960. Peresters. V. Di-t-butylperoxyoxalate, *J. Am. Chem. Soc*, **82**, 1762.

[38] **Bartlett, P.D. and Pincock, R.E.,** 1960. **Peresters**. VI. Ethyl, benzyl, p-Nitrobenzyl and p-Methoxybenzyl t-Butyl-peroxyoxalates, *J. Am. Chem. Soc.*, **82**, 1769.

[39] **Cohen, S.G. and Sparrow, D.B.,** 1950. Some reactions of diisopropyl peroxydicarbonate, *J. Am. Chem. Soc.*, **72**, 611.

[40] **Odian, G.,** 1992. *Principles of polymerization,* Third Edition, John Wiley & Sons, Inc., N.Y., 198-267.

[41] **Flory, P. J.,** 1953. *Principles of polymer chemistry,* Cornell University Press, Ithaca.

[42] **Bamford, C. H., Barb, W. G., Jenkins, A. D. and Onyon, P. F.,** 1958. *The kinetics of vinyl polymerization by radical mechanisms,* Butterworths, London.

[43] www.che.rochester.edu.

[44] **Blyth, J. and Hoffmann, A.W.,** 1845. *Ann.*, **53**, 292.

[45] **Dietliker, K.,** 1991. *Chemistry and technology of UV and EB formulations for coatings, inks and paints,* Sita Technology Ltd., London.

[46] **Walling, C.,** 1957. *Free radicals in solution,* Wiley, New York, 273.

[47] **Turro, N.J.,** 1978. *Modern molecular photochemistry,* The Benjamin/Cummerings Publishing Co., Inc. Menlo Park Ca, 368.

[48] **Murov, S.L.,** 1973. *Handbook of photochemistry,* Marcel Dekker, Inc., New York.

[49] **Patten, T.E. and Matyjaszewski, K.,** 1998. Atom transfer radical polymerization and the synthesis of polymeric materials, *Adv. Mater.,* **10 (12)**, 901-915.

[50] **Matyjaszewski, K.,** 1998. *Controlled Radical Polymerization, **685**,* ACS Symposium Series, American Chemical Society, Washington DC.

[51] **Matyjaszewski, K.,** 2000. *Controlled/Living Radical Polymerization, **768**,* ACS Symposium Series, American Chemical Society, Washington DC.

[52] **Matyjaszewski, K. and Pyun, J.,** 2001. Synthesis of nanocomposite organic/inorganic hybrid materials using controlled/"living" radical polymerization, *Chem. Mater.*, **13,** 3436.

[53] **Hawker, C. J., Bosman, A.W. and Harth, E.,** 2001. New polymer synthesis by nitroxide mediated living radical polymerizations, *Chemical Reviews,* ASAP, **101 (12)**; 3661-3688.

[54] **Matyjaszewski, K. and Xia, J.,** 2001. **Atom** Transfer Radical Polymerization, *Chem. Rev.,* **101,** 2921.

[55] **Mayadunne, R.T.A., Rizzardo, E., Chiefari, J., Chong, Y.K., Moad, G. and Thang, S.H.,** 1999. A more versatile route to block copolymers and other polymers of complex architecture by living radical polymerization: The RAFT process, *Macromolecules,* **32,** 2071.

[56] **Wieland, P.C., Raether, B. and Nuyken, O.,** 2001. A New Additive for Controlled Radical Polymerization, *Macromol. Rapid Commun.*, **22 (9)**, 700-703.

[57] **Wang, J. S. and Matyjaszewski, K.,** 1995. Living/controlled radical polymerization. Transition-metal-catalyzed atom transfer radical polymerization in the presence of a conventional radical initiator, *Macromolecules,* **28,** 7572-3.

[58] **Kato, M., Kamigaito, M., Sawamoto, M. and Higashimura, T.,** 1995. Polymerization of methyl methacrylate with the carbon tetrachloride/dichlorotris- (triphenylphosphine) ruthenium(II) / methylaluminum bis(2,6ditertbutylphenoxide) initiating system: possibility of living radical polymerization. *Macromolecules,* **28**, 1721-3.

[59] **Solomon, D.H., Rizzardo, E. and Cacioli, P.,** 1986. Free radical polymerization and the produced polymers *U.S. Patent* 4,581,429.

[60] **Georges, M. K., Veregin, R. P. N., Kazmaier, P. M, Hamer G. K.,** 1993. Narrow molecular weight resins by a free-radical polymerization process. *Macromolecules,* **26,** 2987.

[61] **Hawker, C. J.,** 1999. Molecular weight control by living free radical polymerization process, *J. Am. Chem. Soc*., **121,** 3904.

[62] **Fukuda, T., Goto, A. and Ohno K.,** 2000. Mechanisms and kinetics of living radical polymerizations, *Macromol Rapid Commun*., **21**, 151-65.

[63] **Mayadunne, R.T.A., Rizzardo, E., Chiefari, J., Krstina, J., Moad, G., Postma, A. and Thang, S.H.,** 2000. Living polymers by the use of trithiocarbonates as reversible addition-fragmentation chain transfer (RAFT) agents: ABA triblock copolymers by radical polymerization intwo steps, *Macromolecules,* **33 (2),** 243-245.

[64] **Goto, A., Sato, K., Tsujii, Y., Fukuda, T., Moad, G., Rizzado, E. and Thang, S. H.,** 2001. Mechanism and kinetics of RAFT-based living radical polymerizations of styrene and methyl methacrylate**,** *Macromolecules,* **34 (3),** 402-408.

[65] **Chiefari, J., Chong Y.K., Ercole, F., Krstina, J., Jeffery, J., Le, T.P.T., Mayadunne, R.T.A., Meijs, G.F., Moad, C.L., Moad, G., Rizzardo, E. and Thang, S.H.,** 1998. Living free-radical polymerization by reversible addition-fragmentation chain transfer: The RAFT process, *Macromolecules*, **31 (16)**, 5559-5562.

[66] **Krstina, J., Moad, G., Rizzardo, E., Winzor, C. L., Berge, C. T. and Fryd, M.**, 1995. Narrow polydispersity block copolymers by free-radical polymerization in the presence of macromonomers, *Macromolecules*, **28 (15)**, 5381-5385.

[67] **Krstina, J., Moad, G., Rizzardo, E., Winzor, C.L., Berge, C.T. and Fryd, M.**, 1996. A new form of controlled growth free radical polymerization, *Macromol. Symp.* **111**, 13-23.

[68] **Moad, G., Moad, C. L., Rizzardo, E. and Thang, S.H.,** 1996. Chain transfer activity of ω-unsaturated methyl methacrylate oligomers, *Macromolecules* **29 (24),** 7717-7726.

[69] **Moad, G., Ercole, F., Johnson, C. H., Krstina, J., Moad, C. L., Rizzardo, E., Spurling, T.H., Thang, S. H. and Anderson, A. G.,** 1998. *ACS Symp Series* 685, Ed by Matyjaszewski, K, American Chemical Society, Washington DC, 332.

[70] **Fischer, J. P.,** 1972. Kinetik der radikalischen copolymerisation α-substituierter styrole mit styrol. 2. Teil. Copolymerisation von styrol mit 1.1-diphenyläthylen, *Makromol. Chem.* **155**, 227-238

[71] **Rief, U., McKee G.E.**, DE 19719061, BASF AG, 1998, Chem. Abs. **129**, 343812

[72] **Nuyken, O., Wieland, P. C., Heischkel, Y. and Raether, B.,** 2002. New concepts for controlled radical polymerization: the DPE-system, *Polym. Preprints,* **43 (2)**, 84.

[73] **Borsig, E., Lazar, M., Capla, M. and Florian, S.,** 1969. Reinitiation reactions of poly(methyl methacrylate) with labile bound fragments of initiator, *Angew. Makromol. Chem.*, **9 (1)**, 89-95

[74] **Tharanikkarasu, K. and Radhakrishnan, G.J.,** 1997. Tetraphenylethane iniferters: Polyurethane-polystyrene multiblock copolymers through “ living” radical polymerization, *Appl. Polym. Sci.* **66 (8)**, 1551-1560.

[75] **Braun, D.** 1994. **Alkane als initiatoren zur radikalischen polymerization,** *Angew. Makromol. Chem.,* **223**, 69-79.

[76] **Beckhaus, H.D., Schaetzer, R. and Rüchardt, C.** 1983. The dimer of 2-methyl-1,1-diphenylpropyl radicals and its reactivity, *Tetrahedron Lett.,* **24 (32)**, 3307-3310.

[77] **Raether, B., Nuyken, O., Wieland, P. and Bremser, W.,** 2002. Free-radical synthesis of block copolymers on an industrial scale, *Macromol. Symp.*, **177 (1)**, 25-42.

[78] **Duda, A. and Penczek, S.,** 1994. Determination of the absolute propagation rate constants ın polymerization with reversible aggregation of active-centers, *Macromolecules,* **27 (18),** 4867-4870.

[79] **Kricheldorf, Hr., Kreiser-Saunders, I. and Boettcher, C.,** 1995. Polylactones.31. Sn(II)octoate-initiated polymerization of L-lactide - a mechanistic study, *Polymer,* **36 (6),** 1253-1259.

[80] **Degée, P., Dubois, P. and Jérôme, R.,** 1997. Bulk polymerization of lactides ınitiated by aluminium isopropoxide. 3. Thermal stability and viscoelastic properties, *Macromol. Chem. Phys.*, **198 (6),** 1985-1995.

[81] **Johns, D., Lenz, R.W. and Luecke, A.,** 1984. Lactones, in Ring-Opening Polymerization, 1, 464 Ivin K.J., Saegusa, T., Eds, Elsevier, London.

[82] **Löfgren, A., Albertsson, A.C., Dubois, P. and Jérôme, R.,** 1995. Recent advances in ring-opening polymerization of lactones and related-compounds, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **C35 (3),** 379-418.

[83] **Mecerreyes, D., Jérôme, R. and Dubois, P.,** 1999. Novel macromolecular architectures based on aliphatic polyesters: relevance of the "coordination-insertion" ring-opening polymerization, *Adv. Polym. Sci.,* **147,** 1-59.

[84] **Kricheldorf, H.R. and Kreiser, S.I.,** 1996. Polylactides - synthesis, characterization and medical application, *Macromol. Symp.,* **103,** 85-102.

[85] **Saegusa, T., Kobayashi, S. and Hayashi, K.,** 1978. Polymerization via zwitterion 171 alternating copolymerization of 2-phenylimino-1,3-dioxolane with beta-propiolactone, *Macromolecules,* **11 (2),** 360-361.

[86] **Mark, H. F., Bikales, N. M., Overberger, C. G. and Menges, G.,** 1985. *Encyclopedia of Polymer Science and Engineering,* pp.708-803, Eds. Kroschwitz, J. I., Vol. 13, Second Edition, John Wiley & Sons, Inc., N.Y.

[87] **Stanke, D., Hallensleben, M.L. and Toppare, L.,** 1995. Oxidative crosslinking polymerization of poly [(methyl methacrylate)-co-(2-(n-pyrrolyl)ethyl methacrylate)] with iron chloride in nitromethane, *Macromol. Chem. Phys.*, **196 (5),** 1967-1703.

[88] **Dhaese, F. and Goethals, E.J.,** 1988. Synthesis and reactions of polytetrahydrofuran with thiolanium end groups, *British Polym. J.,* **20 (2)**, 103-108.

[89] **Tezuka, Y. and Goethals, E.J.,** 1982. Synthesis and reactions of poly-tetrahydrofuran with azetidinium salt end-groups, *Eur. Polym. J.,* **18 (11)**, 991-998.

[90] **Hizal, G., Yagci, Y. and Schnabel, W.,** 1994. N-Alkoxy pyridinium ion terminated polytetrahydrofurans. Synthesis and their use in photoinitiated block copolymerization, *Polymer*, **20**, 4443.

[91] **Onen, A., Yagci, Y. and Schnabel, W.,** 1996. Synthesis of benzoin terminated polytetrahydrofuranes, *Angew. Makromol. Chem.*, **243**, 143.

[92] **Penczek, S.,** 2000. Cationic ring-opening polymerization (crop) major mechanistic phenomena, *J. Polym. Sci. Polym. Chem.,* **38 (11),** 1919-1933.

[93] **Kubisa, P. and Penczek, S.,** 1999. Cationic activated monomer polymerization of heterocyclic monomers, *Prog. Polym. Sci.,* **24 (10),** 1409-1437.

[94] **Penczek, S. and Slomkowski, S.,** 1987. Progress In Anionic Ring-Opening Polymerization, in "*Recent Advances In Anionic Polymerization,* Chap 19, 275, Hogen, E.T., Smid, J., Eds, Elsevier, New York.

[95] **Jedlinski, Z., Kurcok, P. and Kowalczuk, M.,** 1985. Polymerization of beta-lactones initiated by potassium solutions, *Macromolecules,* **18 (12),** 2679-2683.

[96] **Lundberg, R.D. and Cox, E.F.,** 1969. Lactones, in *Ring-Opening Polymerization,* Frish, K., Reegen, S., Eds, 2:247 Marcel Dekker,New York.

[97] **Duda, A., Florjanczyk, Z., Hofman, A., Slomkowski, S. and Penczek, S.,** 1990. Living pseudoanionic polymerization of epsilon-caprolactone - poly(epsilon-caprolactone) free of cyclics and with controlled end groups, *Macromolecules,* **23 (6),** 1640-1646.

[98] **Bero, M., Czapla, B., Dobrzynski, P., Janeczek, H. and Kasperczyk.,** 1999. Copolymerization of glycolide and epsilon-caprolactone - 2 - random copolymerization ın the presence of tin octoate, *J. Macromol. Chem. Phys.,* **200 (4).** 911-916.

[99] **Dubois, P., Ropson, N., Jérôme, R. and Teyssie, P.,** 1996. Macromolecular engineering of polylactones and polylactides.19. Kinetics of ring-opening polymerization of epsilon-caprolactone initiated with functional aluminum alkoxides, *Macromolecules,* **29,** 1965-1975.

[100] **Kricheldorf, H.R. and Meier, H.J.,** 1993. Polylactones.22. ABA triblock copolymers of L-lactide and poly(ethylene glycol), *Macromol. Chem.* **194 (2),** 715-725.

[101] **Kowalski, A., Duda, A. and Penczek, S.,** 1998. Kinetics and mechanism of cyclic esters polymerization ınitiated with tin(II) octoate, 1. Polymerization of epsilon-caprolactone, *Macromol. Rapid. Commun.* **19 (11),** 567-572.

[102] **Kowalski, A., Duda, A. and Penczek, S.,** 2000. Kinetics and mechanism of cyclic esters polymerization ınitiated with tin(II) octoate. 3. Polymerization of l,l-dilactide, *Macromolecules,* **33 (20),** 7359-7370.

[103] **Kricheldorf, H.R., Kreiser, S.I. and Stricker, A.,** 2000. Polylactones 48. Sn(Oct)$_2$-ınitiated polymerizations of lactide: a mechanistic study, *Macromolecules,* **33 (3),** 702-709.

[104] **Quirk, R. and Lee, B.,** 1992. Experimental criteria for living polymerizations, *Polym. Int.,* **27 (4),** 359-367.

[105] **Kricheldorf, H.R., Boettcher, C. and Tönnes, K.U.,** 1992. Polylactones.23. Polymerization of racemic and meso D,L-lactide with various organotin catalysts stereochemical aspects, *Polymer,* **33 (13),** 2817-2824.

[106] **Kowalski, A., Libiszowski, J., Duda, A. and Penczek, P.,** 2000. Polymerization of l,l-dilactide ınitiated by tin(II) butoxide, Macromolecules, **33 (6),** 1964-1971.

[107] **Mclain, S.J. and Drysdale, N.E.,** 1991.*Us Patent*, 5 028 667.

[108] **Mclain, S.J. and Drysdale, N.E.,** 1992. Living Ring-Opening Polymerization Of Epsilon-Caprolactone By Yttrium And Lanthanide Alkoxides *Abstr. Pap. Am. Chem. S* **203,** 160-Poly Part 3.

[109] **Preiner, G. and Matejcek, K.,** 1984. *Ger. Pat. Appl*. De 3433654, Assigned To Wacker Chemie.

[110] **Shirakawa, H., Louis, E.J., MacDiarmid, A.G., Chiang, C.K. and Heeger, A.J.,** 1977. Synthesis of electrically conducting organic polymers - halogen derivatives of polyacetylene, (CH)X, *J. Chem. Soc., Chem. Commun.,* **16,** 578-580**.**

[111] **Chiang, C.K., Fincher, C.R., Park, Y.W, Heeger, A.J, Shirakawa, H., Louis, E.J., Gau, S.C. and MacDiarmid, A.G.,** 1977. Electrical-conductivity in doped polyacetylene, *Phys. Rev. Lett.,* **39 (17)**, 1098-1101.

[112] **MacDiarmid, A.G. and Heeger, A.J.,** 1979. Organic metals and semiconductors: The chemistry of polyacetylene, $(CH)_x$, and its derivatives, *Synth. Met.,* **1**, 101-118.

[113] **Wegner, G.,** 1981. polymers with metal-like conductıvıty - a review of their synthesis, structure and properties, *Angew. Chem. Int. Ed.,* **20 (4)**, 361-381.

[114] **Wynne, K.J. and Street, G.B.,** 1982. I&EC Product Research and Development, **21**, 23.

[115] **Baughman, R.H.,** 1984. In: Vanderberg EJ (ed) Contemporary Topics in Polymer Science, **5**.

[116] **Greene R.L. and Street, G.B.,** 1984. *Science*, 226.

[117] **Dall'Olio, A., Dascola, G., Varacca, V. and Bocchi, V.,** 1968. *R. Acad. Sci. C.,* **267**, 433.

[118] **Diaz, A.F., Kanazawa, K.K. and Gardini, G.P.,** 1979. Electrochemical polymerization of pyrrole, *J. Chem. Soc., Chem. Commun.,* 14, 635-636.

[119] **Kanazawa, K.K., Diaz, A.F., Geiss, R.H., Gill, W.D., Kowak, J.F., Logan, J.A., Rabolt, J.F. and Street, G.B.**, 1979. Organic metals - polypyrrole, a stable synthetic metallic polymer, *J. Chem. Soc., Chem. Commun.,* **19**, 854-855.

[120] **Wynne, K.J. and Street, G.B.,** 1985. Poly(pyrrol-2-ylium tosylate), electrochemical synthesis and physical and mechanical properties, *Macromolecules*, **18 (12)**, 2361-2368.

[121] **Diaz, A.F. and Bargon, J.,** 1986. Handbook of Conducting Polymers. Skotheim TA (ed) Marcel Dekker Inc, New York, 81.

[122] **Street, G.B.,** 1986. Handbook of Conducting Polymers. Skotheim TA (ed) Marcel Dekker Inc, New York, p. 265.

[123] **Malhotra, B.D., Kumar, N. and Chandra, S.**, 1986. Recent studies of heterocyclic and aromatic conducting polymers, *Progr. Polym. Sci.,* 12:179-218.

[124] **Saunders, B.R., Fleming, R.J. and Murray, K.S.,** 1995. Recent advances in the physical and spectroscopic properties of polypyrrole films, particularly those containing transition-metal complexes as counteranions, *Chem. Mater., **7*** **(6)**, 1082-1094.

[125] **Novak, P.,** 1992. Limitations of polypyrrole synthesis in water and their causes, *Electrochim. Acta.,* **37 (7)**, 1227-1230.

[126] **Bartlett, P.N. and Birkin, P.R.** 1993. The application of conducting polymers in biosensors, *Synth. Met.* **61**, 15-21.

[127] **Letheby, H.,** 1862. *J. Chem. Soc.,* **15**, 161.

[128] **Mohilner, D.M., Adams, R.N. and Argersinger, Jr, W.J.,** 1962. Investigation of the kinetics and mechanism of the anodic oxidation of aniline in aqueous sulfuric acid solution at a platinum electrode, *J. Am. Chem. Soc.,* **84 (19)**, 3618-3622.

[129] **Jozefewicz, M., Yu, L.T, Belorgey, G. and Buvet, R.,** 1967. *J. Polym. Sci., Part C,* **16**, 2931.

[130] **Honzl, J. and Tlustakova, M.,** 1968. *J. Polym. Sci., Part C,* **22**, 451.

[131] **Jozefewicz, M., Yu, L.T., Perichon, J. and Buvet, R.,** 1969. J. Polym. Sci., Part C, **22,** 1187.

[132] **MacDiarmid, A.G. and Epstein, A.J.,** 1989. Polyanilines - a novel class of conducting polymers, *Faraday Discuss Chem. Soc.* **88**, 317.

[133] **Epstein, A.J. and Macdiarmid, A.G.,** 1991. Novel concepts in electronic polymers - polyaniline and its derivatives, *Makromol Chem, Macromol. Symp.,* **51**, 217-234.

[134] **MacDiarmid, A.G.,** 1997. Polyaniline and polypyrrole: Where are we headed?, *Synth. Met.,* **84 (1-3)**, 27-34.

[135] **Reddinger, J.L. and Reynolds, J.R.,** 1999. Molecular engineering of pi-conjugated polymers, *Adv. Polym. Sci.,* **145**, 57-122.

[136] **Heinze, J.,** 1990. I*n Topics in Current Chemistry*, Springer-Verlag, Berlin, , **152**, 2.

[137] **Lyons, M.E.G.,** 1997. In Advances in Chemical Physics, Polymric Systems, Eds. I. Prigogine, S. A. Rice, John Wiley & Sons, New York, **94**, 297.

[138] **Genies, E., Bidan, G. and Diaz, A.F.,** 1983. Spectro electrochemical study of polypyrrole films, *J. Electroanal. Chem*., **149 (1-2)**, 101-113.

[139] **Ambrose, J.F. and Nelesn, R. F.,** 1968. *J. Electrochem. Soc.,* **115**, 1161.

[140] **Adams, R.N.,** 1969. *Acc, Chem. Res.,* **175**, 2.

[141] **Zotti, G., Schiavon, G., Berlin, A. and Pagani, G.,** 1993. Thiophene oligomers as polythiophene models. 1. Anodic coupling of thiophene oligomers to dimers: a kinetic investigation, *Chem. Mater.,* **5 (4)**, 430-436.,

[142] **Okada, T., Ogata, T. and Ueda, M.,** 1996. Synthesis and characterization of regiocontrolled poly(2,5-di-*n*-butoxy-1,4-phenylene) by oxovanadium-catalyzed oxidative coupling polymerization, *Macromolecules,* **29 (24),** 7645-7650.

[143] **Yoshino, K., Hayashi, R. and Sugimoto, R.,** 1984. Preparation and properties of conducting heterocyclic polymer-films by chemical method, *Jpn. J. Appl. Phys.,* **23 (2)**, 899-900.

[144] **Toshima, N. and Hara, S.,** 1995. Direct synthesis of conducting polymers from simple monomers, *Prog. Polym. Sci.,* **20 (1)**, 155-183.

[145] **Dobis, P., Barakat, I., Jerome, R. and Teyssie, P.,** 1993. Macromolecular engineering of polylactones and polylactides.12. Study of the depolymerization reactions of poly(epsilon-caprolactone) with functional aluminum alkoxide end-groups, *Macromolecules,* **26 (17),** 4404-4412.

[146] **Oishi, T. and Fujimoto, M.,** 1992. Synthesis and polymerization of n-[4-n'-(alpha-methylbenzyl)aminocarbonylphenyl]maleimide, *Polym. Chem,* **30 (9),** 1821-1830.

[147] **Oishi, T., Osubo, Y., Matsuaki, K. and Fujimoto, M.,** 1993. Synthesis and polymerization of n-[4-(cholesteroxycarbonyl)phenyl]maleimide, ***Polymer*****, 34 (7), 1504-1511.**

[148] **Cirpan, A., Alkan, S., Toppare, L., Hepuzer, Y. and Yagci, Y.,** 2002. Conducting graft copolymers of poly(3-methyl thienyl methacrylate) with pyrrole and thiophene, *J. Polym. Sci. Part A: Polym. Chem.,* 40, 4131.

[149] **Oishi, T., Sase, K. And Tsutsumi, H.,** 1998. Syntheses and thermostabilities of N-[4-(N '-substituted aminocarbonyl)phenyl]maleimide polymers, *J. Poly. Sci. Part A: Polm. Chem.,* **36 (12)**, 2001-2012.

[150] **Ahn, K.D. Kim, J.M., Lee, C.W. and Han, D.K.,** 2000. Synthesis and radical polymerization of bifunctional maleimides with different functional reactivities, *J. Macromol. Sci. Pure. Appl. Chem.,* **37 (1-2)**, 117-131.

[151] **Cianga, L. and Olaru, N.,** 2000. Synthesis and characterization of new optically active monomers based on 4-maleimidobenzoic acid, *Des. Monom. Polym.,* **3 (2)**, 209-230.

[152] **Sun, F., Yang, Y. And Ottenbrite, R.M.,** 1991. Synthesis of new bismaleimides and their copolymerization with bisdienes via diels-alder reaction, *Polym. Prepr.(Am Chem Soc Div Polym Chem),* **32**, 188.

[153] **Yamamoto, Y., Nakao, W., Atago, Y., Ito, K., and Yagci, Y.,** 2003. A novel macroinimer of polyethylene oxide: synthesis of hyper branched networks by photoinduced H-abstraction process, *Eur. Polym. J.,* 39 (3), 545-550.

[154] **Shen, R., Akiyama, C., Senyo, T. and K. Ito.,** *Macromolecules,* submitted.

[155] **Takeoka, S., Ohno, H. and Tsuchida, E.,** 1993. Recent advancement of ion-conductive polymers, *Polym. Adv. Technol.,* **4**, 53-73.

[156] **Armand, M.,** 1994. The history of polymer electrolytes, *Solid States Ionics,* **69 (3-4)**, 309-319.

[157] **Lauter, U., Meyer, W.H. and Wegner, G.,** 1997. Molecular composites from rigid-rod poly(*p*-phenylene)s with oligo(oxyethylene) side chains as novel polymer electrolytes, *Macromolecules*, **30** (7), 2092-2101.

[158] **Baum, P., Meyer, W.H., Wegner, G.,** 2000. Novel cation conductors based on rigid-rod poly(p-phenylene)s, *Polymer,* **41 (3)**, 965-973.

[159] **Bo, Z.S, Rabe, J.P. and Schluter, A.D.,** 1999. A poly(para-phenylene) with hydrophobic and hydrophilic dendrons: Prototype of an amphiphilic cylinder with the potential to segregate lengthwise, *Angew. Chem. Int. Ed*., **38** (16), 2370-2372.

[160] **Bo, Z., Zhang, C.M., Severin, N., Rabe, J.P. and Schluter, A.D.,** 2000. Synthesis of amphiphilic poly(*p*-phenylene)s with pendant dendrons and linear chains, *Macromolecules*, **33 (7)**, 2688-2694.

[161] **Huang, C., Huang, W., Guo, J. and Yang, C.Z.,** 2002. Color-variable, fast response light-emitting electrochemical cells based on ionic conductive poly(phenylene vinylene) derivatives, *Polym. Prep.*, **41**, 1271.

[162] **Pei, Q. and Yang, Y.,** 1996. Efficient Photoluminescence and Electroluminescence from a Soluble Polyfluorene, *J. Am. Chem. Soc.*, **118 (31)**, 7416-7417.

[163] **Yang, Y. and Pei, J.,** 1997. Efficient blue-green and white light-emitting electrochemical cells based on poly[9,9-bis(3,6-dioxaheptyl)-fluorene-2,7-diyl], *J. Appl. Phys*, **81(7)**, 3294-3298.

[164] **Stephan, O., Collomb, V., Vial, J.C. and Armand, M.,** 2000. Blue-green light-emitting diodes and electrochemical cells based on a copolymer derived from fluorene, *Synth. Met.*, **113 (3)**, 257-262.

[165] **Ito, K., Tomi, Y. and Kawaguchi, S.,** 1992. Poly(ethylene oxide) macromonomers. 10. Characterization and solution properties of the regular comb polymers with polystyrene main chains and poly(ethylene oxide) side chains, *Macromolecules*, **25 (5)**, 1534-1538.

[166] **Baskan, A., Hizal, G. and Yagci, Y.,** 2000. Block Copolymers by Transformation of Living Ring Opening Polymerization into an Initer Process , Eur. Polym., **36**, 1373.

[167] **Dawkins, J.V.,** 1972. Polym. J., **4**, 87.

[168] **Wieland, P.C., Raether, B. and Nuyken, O.,** 2001. A New additive for controlled radical polymerization, *Macromol. Rapid Commun.*, **22 (9)**, 700-703.

[169] **Braun, D. and Bledzki, A.,** 1986. Initiation of polymerization with substituted ethanes, *Macromol. Chem.,* **187 (11)**, 2599-2608.

[170] **Braun, D., Linder, H.J. and Tretner, H.,** 1989. Initiation of polymerization with substituted ethanes .12. Free-radical polymerization of methyl-methacrylate and styrene initiated with 3-methoxycarbonyl-3-methyl-2,2,5,5-tetraphenylhexanedinitrile, *Eur. Polym. J.,* **25 (7-8)**, 725-730.

[171] **Block, H., Lord, P.W. and Walker, S.M.** 1975. Structure and molecular relaxatıon of alternatıng copolymers of styrene and n-substıtuted maleımıdes, *Polymer,* **16 (10)**, 739-744.

[172] **Romero Colomer, F., Meseguer Duenas, J.M., Gomez Ribelles, J.L., Barrales-Rienda, J.M. and Bautista de Ojeda, J. M.,** 1993. Side-chain liquid crystalline poly(N-maleimides). 5. Dielectric relaxation behavior of liquid crystalline side-chain and amorphous poly(N-maleimides). A comparative structural study, *Macromolecules*, **26 (1)**, 155-166.

[173] **Oishi, T., Onimura, K., Isobe, Y., Yanagihara, H. and Tsutsumi, H.,** 2000. Asymmetric anionic polymerization of maleimides bearing bulky substituents, *J. Polym. Sci. Part A Polym. Chem.*, **38 (2)**, 310-320.

[174] **Tebbe, H., Van Ackern, F. and Tieke, B.,** 1995. New amphiphilic copolymers of n-phenylmaleimides and vinyl ethers - thermal-properties, langmuir and langmuir-blodgett-fılms, gas permeation, *Macromol. Chem. Phys.*, **196 (5)**, 1475-1486.

[175] **Chiang, W.Y. and Lu, J.Y.,** 1994. Preparation and properties of new photo-functional polymers .1. n-substituted maleimide styrene copolymers containing pendant para-nitrobenzyl groups, *Macromol. Chem. Phys.*, **195 (2)**, 591-600.

[176] **(a) Noordegraaf, M.A., Kuiper, G.J., Marcelis, A.T.M. and Sudholter, E.J.R.** 1997. Rigid maleimide-alt-vinylpyridine copolymers with pendant chromophores. Synthesis, characterization and monolayer formation, *Macromol. Chem. Phys.*,**198 (11)**, 3681-3697, **(b) Serhatli, I.E., Yagci, Y., Haltemer, E., Zentel, R., Schmalzlin, E., Hohenadl, S., Brauchle, C. and Meerholz, K.,** 2001. Crosslinkable maleimide copolymers for stable NLO properties, *J. Polym. Sci. Part A Polym. Chem.*, **39 (10)**, 1589-1595.

[177] **Kohli, P., Scranton, A.B. and Blanchard, G.J.,** 1998, Co-polymerization of maleimides and vinyl Ethers: A structural study, *Macromolecules*, **31 (17)**, 5681-5689.

[178] **(a) Edge, S., Charlton, A., Varma, K.S., Underhill, A.E., Hansen, T.K., Becher, J., Kathirgamanathan, P., and Khosravii, E.,** 1992. The synthesis and characterization of a poly(maleimide-ether) containing pendent thiophene rings, *J. Polym. Sci. Part A Polym. Chem.*, **30 (13)**, 2773-2780, (b) **Edge, S., Charlton, A., Varma, K.S., Hansen, T.K., Underhill, A.E., Kathirgamanathan, P., Becher, J. and Simonson, O.,** 1993. The preparation and properties of maleimide derivatives of 3-(2-aminoethyl)thiophene, *Synth. Met.*, **53 (3) ,** 315-324.

[179] **Oishi, T., Kagawa, K. and Nagata, H.,** 1997. Synthesis and polymerization of maleimide containing an L-menthyl group, *Polymer*, **38 (6)**, 1461-1469.

[180] **Hagiwara, T., Kawashima, N., Hamna, H. and Narita, T.,** 1997. Polymerization of N-(2,3,4,5,6-pentafluorophenyl)-maleimide, *Macromol. Rapid Commun.*, **18 (4)**, 303-311.

[181] **Olson, K.G.; Butler, G.B.,** 1984. Stereochemical evidence for the participation of a donor-acceptor complex in alternating copolymerizations. 2. Copolymer structure, *Macromolecules*, **17 (12)**, 2486-2501.

[182] **Schmidt-Naake, G., Drache, M. and Leonhardt, K.,** 1998. The influence of charge-transfer complexes on the copolymerization behavior of cyclic maleic acid derivatives with donor monomers, *Macromol. Chem. Phys.,* **199 (3)**, 353-361.

[183] **Gandini, A. and Belgacen, M.N.,** 1997. Furans in polymer chemistry, *Prog. Polym. Sci .,* **22 (6)**, 1203-1379.

[184] **Gousse, C. and Gandini, A.** 1998. Synthesis of 2-furfurylmaleimide and preliminary study of its Diels-Alder polycondensation, *Polym. Bull .,* **40 (4-5)**, 389-394.

[185] **Olson, K.G. and Butler, G.B.,** 1983. Stereochemical evidence for the participation of a comonomer charge-transfer complex in alternating copolymerization, *Macromolecules*, **16 (4)**, 707-710.

[186] **Butler, G.B., Olson, K.G. and Tu, C-L.,** 1984. Monomer orientation control by donor-acceptor complex participation in alternating copolymerization, *Macromolecules*, **17 (9)**, 1884-1887.

[187] **Andrews, L.J. and Keefer, R.M.,** 1964. In “Molecular Complexes in Organic Chemistry”; Holden-Day, Inc.: San Francisco,.

[188] **Olson, K.G. and Butler, G.B.,** 1984. Stereochemical evidence for participation of a Donor-acceptor complex in alternating copolymerization. 1. Model compound synthesis, *Macromolecules*, **17 (12)**, 480-2486.

[189] **Brown, P.G. and Fujimori, K.,** 1995. solvent effects on the opolymerızatıon of p-methoxystyrene wıth maleıc-anhydrıde - an ınvestıgatıon ınto the mechanısm of alternatıng copolymerızatıon, *Polymer*, **36 (5)**, 1053-1059.

[190] **Hao, X. and Fujimori, K.,** 1999. Alternating copolymerization of N-phenyl maleimide and styrene, *Polym. Prep.*, **40 (2)**, 476.

[191] **Mormann, W. and Schmaltz, K.,** 1994. Polymers from multifunctional isocyanates .9. alternating copolymers from 2-propenyl isocyanate and maleic-anhydride, Macromolecules, **27 (24)**: 7115-7120.

AUTOBIOGRAPHY

Faruk Yılmaz was born in 1970 and grew up in Istanbul where he graduated from Fatih Vatan High School in 1987. In the same year he was admitted to Boğaziçi University, Faculty of Education in Teaching Chemistry.

After receiving his diploma in 1993, he had worked as Chemistry and English Teacher between1993-1998 years. In 1998, he was appointed as a Research Assistant at Fatih University, Faculty of Science and Arts, Department of Chemistry and started to carry out M.Sc study in the area of trace element analysis. He completed M.Sc. degree successfully in 2000.

He was registered as a Ph.D. student to Istanbul Technical University, Polymer Science and Technology Program in 2000.

He is married with two children.

He is co-author of the following 14 scientific papers published / submitted in international journals.

1 Natural radioactivity in soil samples of Kocaeli basin, Turkey

B.Karakelle, N.Öztürk, A.Köse, A.Varinlioglu, A.Y.Erkol, **F.Yilmaz**
J. Radioana.Nucl.Ch., 254 (3), 649 (2002)

2. Trace Elements in Soils Samples of Kocaeli Basin and Its Surroundings By EDXRF

B. Karakelle, N. Ozturk, A.Bassari, A.Y. Erkol, **F.Yilmaz**,
Fresen. Environ. Bull., 11 (12B), 1127 (2002)

3. Heavy Metal Concentration in Surface Soils of Izmit Gulf Region, Turkey

F.Yilmaz, Y.Z.Yilmaz, M.Ergin, Y.Erkol, A.E.Muftuoglu, B.Karakelle
J. Trace Microprobe T. 21 (39), 523 (2003)

4. Removal of Basic Blue 41 from Aqueous Solutions by Bituminous Shale

   A.E.Muftuoglu, B.Karakelle, M.Ergin, A.Y.Erkol, **F.Yilmaz**
   Adsorpt. Sci. Technol., 21 (8), 751 (2003)

5. Synthesis and Characterization of a-є Heterofunctional Polyethylene Oxide Macromonomers

   F. Yilmaz, I.Cianga, K.Ito, T.Senyo, Y.Yagci
   Macromol. Rapid Commun., 24 (4), 316 (2003)

6. Controlled Synthesis of Block Copolymers Containing Side Chain Thiophene Units and Their Use in Electropolymerization with Thiophene and Pyrrole

   F.Yilmaz, O. Sel, A. Cirpan, L. Toppare, Y. Hepuzer, Y. Yagci,
   J. Macromol. Sci. Pure & Appl.Chem., A41 (8), 403 (2004)

7. Synthesis, Characterization and Electrochromic Properties of Conducting Copolymers of 2-[(3-thienylcarbonyl)oxy]ethyl 3-thiophene carboxylate with Thiophene and Pyrrole

   U. Bulut, S. Alkan, **F. Yilmaz**, Y. Yagci, L. Toppare
   J. Macromol. Sci. Pure & Appl.Chem., A41 (8), 1-11 (2004)

8. Synthesis and Characterization of Thiophene Capped Polytetrahydrofuran Conducting Copolymers,

   E.Ünür, L.Toppare, **F.Yilmaz**, Y.Yagci
   *J. Applied Poly. Sci.,*accepted

9. Synthesis, Characterization and Electrochromic Properties of Conducting Copolymers of 3-[(3-thienylcarbonyl)oxy]-2,2-bis{[(3-thienylcarbonyl)oxy]} propyl 3-thiophene carboxylate with Thiophene and Pyrrole

   U.Bulut, **F.Yilmaz**, Y.Yagci, L.Toppare
   React. Funct. Poylm., accepted

10. Synthesis and Characterization of Alternating Copolymers of Thiophene-Containing N-Phenyl Maleimide and Styrene by Photoinduced Radical Polymerization and Their Use in Electropolymerization

F. Yilmaz, L. Cianga, Y. Guner, L. Topppare, Y. Yagci.
Polymer, accepted.

11 Synthesis, Characterization and Electrochromic Properties of Conducting Copolymers of 2,3-bis-[(3-thienylcarbonyl)oxy]propyl 3-thiophene carboxylate with thiophene and pyrrole

U. Bulut, L. Toppare**, F. Yilmaz**, Y. Yagci
Eur. Polym. J., accepted.

12 Conducting Copolymers of Polytetrahydrofuran and Their Electrochromic Properties

E. Unur, L.Toppare, **F. Yilmaz,** Y.Yagci
Mater. Lett., Submitted

13. Conducting Copolymers of 3-Methylthienyl Methacrylate and Polyethtleneoxide Vinyl Benzene (PEOMTM) and Their Electrochromic Properties

H. B. Yildiz, S. Kiralp, L. Toppare, **F. Yilmaz,** Y. Yagci, K. Ito,T. Senyo
Polym. Bull., Submitted

14. Thiphene Ended Poly-ε- Caprolactone and Its Conducting Copolymers

İ. Kerman, L. Toppare, **F. Yilmaz**, Y. Yagci,
Eur. Polym. J., Submitted