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**BLOCK COPOLYMERS BY USING COMBINED
CONTROLLED RADICAL AND RADICAL
PROMOTED CATIONIC POYMERIZATION
METHODS**

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140058

JANUARY 2003

**KONTROLLÜ SERBEST RADİKAL
POLİMERİZASYON VE KATYONİK
POLİMERİZASYONA YÜKSELTGENME
YÖNTEMLERİYLE BLOK KOPOLİMER
SENTEZLENMESİ**

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Tezin Enstitüye Verildiği Tarih : 24 Aralık 2002
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December 2002

Mehmet Atilla TAĐDELEN

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LIST of ABBREVIATIONS

CRP	: Controlled Radical Polymerization
FRP	: Free Radical Polymerization
ATRP	: Atom Transfer Radical Polymerization
SFRP	: Stable Free Radical Polymerization
RAFT	: Reversible Addition-Fragmentation Chain Transfer Polymerization
DPE	: 1, 1-Diphenylethene
CTA	: Chain Transfer Agent
GPC	: Gel Permeation Chromotography
IR	: Infrared Spectrophotometer
NMR	: Nuclear Magnetic Resonance Spectroscopy
UV	: Ultra Violet
M	: Monomer
St	: Styrene
MMA	: Methyl methacrylate
CHO	: Cyclohexene oxide
MAN	: Acrylonitrile
AN	: Methacrylonitrile
AIBN	: 2, 2'-Azobisisobutyronitrile
THF	: Tetrahydrofuran
TEMPO	: 2, 2, 6, 6- Tetramethylpiperidinoxy
PSt	: Poly(styrene)
PMMA	: Poly(methyl methacrylate)
PCHO	: Poly(cyclohexene oxide)
On⁺	: Onium Salt
Ph₂I⁺PF₆⁻	: Diphenyliodonium hexafluorophosphate
Ph₃S⁺PF₆⁻	: Triphenylsulfonium hexafluorophosphate
EMP⁺PF₆⁻	: N-Ethoxy-2-methylpyridinium hexafluorophosphate

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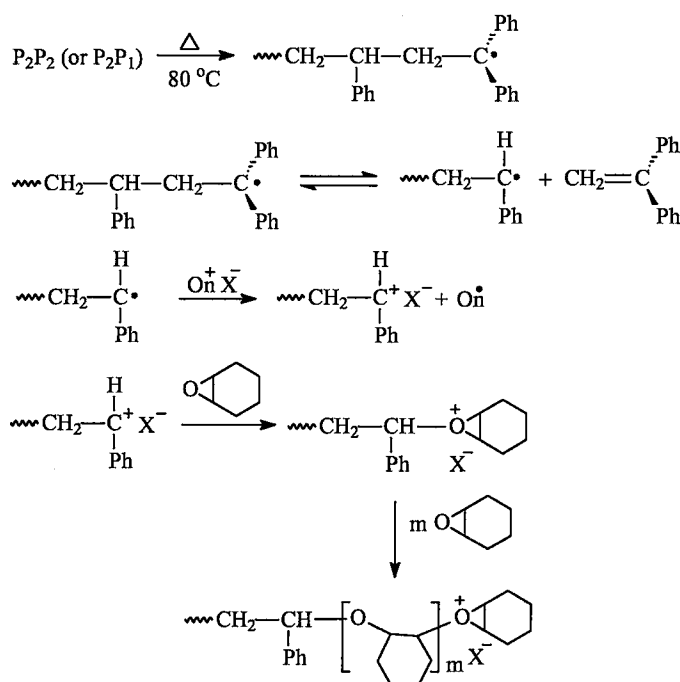
LIST of SYMBOLS

λ	: Wavelength
$h\nu$: Radiation
R^\cdot	: Radical
I	: Initiator
LGN	: Ligand
M	: Monomer
C^+	: Cation
$C^{+\cdot}$: Radical cation
C^-	: Anion
S	: Sensitizers
$E_{1/2}^{Ox}$: Oxidation potential
$E_{1/2}^{Red}$: Reduction 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_d	: Rate constant of decomposition step
k_i	: Rate constant of initiation step
k_p	: Rate constant of propagation step
k_t	: Rate constant of termination step
k_{tc}	: Rate constant of termination step by combination
k_{td}	: Rate constant of termination step by disproportionation
M_t^n	: Transition metal
DP	: Degree of polymerization
PDI	: Polydispersity
$Pn-T$: Dormant species
T^\cdot	: Stable nitroxyl radical
P_2P_2	: Tetraphenyl ethane unit
P_2P_1	: Triphenyl ethane unit

BLOCK COPOLYMERS BY USING COMBINED CONTROLLED RADICAL AND RADICAL PROMOTED CATIONIC POYMERIZATION METHODS

SUMMARY

Recent advances in controlled free radical polymerization have been applied to synthesis of wide range of well-defined specific polymer architectures. Several methods, such as atom transfer radical polymerization (ATRP), stable radical mediated radical polymerization (SFRP) and radical addition-fragmentation chain transfer (RAFT) process have been accepted to be most efficient. Nevertheless, no broad industrial application of these techniques took place due to some important disadvantages. These are the use of toxic metal catalysts, an unsatisfactory universality or the formation of thioles during the polymerization. It was demonstrated that many radical polymerizations became controlled if small amounts of 1, 1-diphenylethene (DPE) were added. The formation of block copolymers with numerous monomers became possible by simply heating a preformed polymer containing DPE units in the presence of a second monomer. DPE is commercially available, odorless, colorless and without known toxicity. It is known as a non polymerizable styrene derivative, which was useful only as molecular weight regulator. The radical polymerization of many common monomers in the presence of DPE shows the characteristics of a controlled polymerization and, therefore, this strategy opened a wide new field in polymer chemistry.



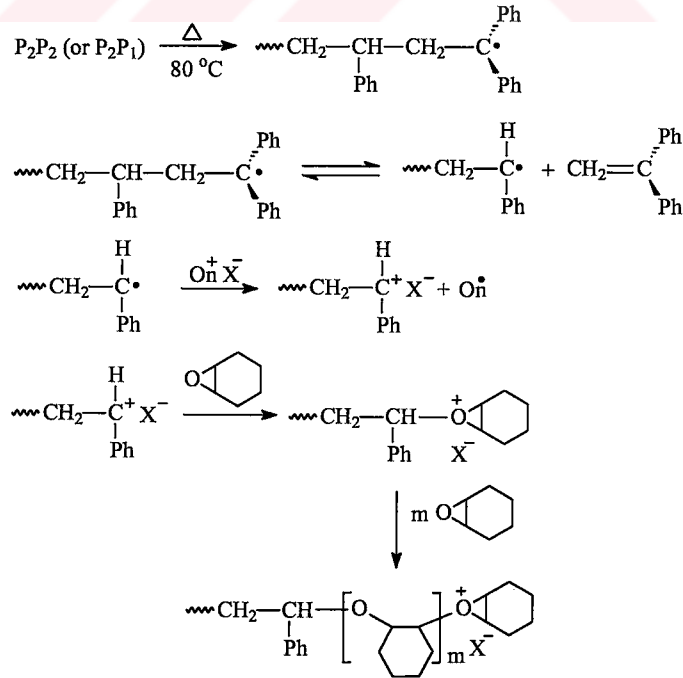
As continuation of this study, we now apply the DPE method to free radical promoted cationic polymerization so as to prepare block copolymers of monomers polymerize by different mechanisms. This thesis reports the preparation of block copolymers by combined system of controlled free-radical polymerization by using diphenyl ethylene as molecular weight regulator and free radical promoted cationic polymerization. Previously, it was presented that the 1,1-diphenylethene (DPE) method enabled to produce block copolymers by a free radical mechanism. In this thesis, First step, we prepared homopolymers of styrene (St) and methyl methacrylate (MMA) in the presence of DPE. Polydispersities of homopolymers are below 1.5 slightly. Second step, prepolymers possessing tetraphenyl ethylene groups were used as free radical generators. Upon heating the polymeric radicals formed were oxidized the corresponding cations by onium salts to initiate the cationic polymerization of cyclohexene oxide (CHO). The block copolymers of methyl methacrylate and styrene with cyclohexene oxide were obtained. The spectrum of the block copolymers of Pst-*b*-PCHO and PMMA-*b*-PCHO clearly show resonances characteristics of homopoly (styrene) (7.21 ppm), homopoly (cyclohexene oxide) (3.41 ppm) and homopoly (methyl methacrylate), (3.5 ppm).



KONTROLLÜ SERBEST RADİKAL POLİMERİZASYON VE KATYONİK POLİMERİZASYONA YÜKSELTGENME YÖNTEMLERİYLE BLOK KOPOLİMER SENTEZLENMESİ

ÖZET

Sentetik polimer kimyasında, polimerin kompozisyonunu, molekül ağırlığını ve molekül ağırlığı dağılımının kontrol edilebilmesi büyük önem taşımaktadır. Yaşayan iyonik sistemler dışında, kontrollü radikal polimerizasyon metoduyla yıldız, blok şeklinde özel polimer yapıları elde edilmiştir. Bu konuda bilinen üç method vardır: Kararlı Serbest Radikal Polimerizasyon (SFRP), Atom Transfer Radikal Polimerizasyon (ATRP) ve Dönüşümlü Katılma-Bölüşme Zincir Transfer Polimerizasyon (RAFT). Bir çok monomerlerin polimerleştirilememesi (SFRP), başlatıcılarının birçoğunun zehirli metallerden olması (ATRP), ditio grubunun verdiği renk, koku ve ortamdaki uzaklaştırılmaması (RAFT), bu yöntemlerin endüstride kullanılmasını kısıtlamaktadır. Radikal polimerizasyonda ortama küçük miktarda 1,1-difeniletan katıldığında polimerizasyonun kontrollü davranış gösterdiği saptanmıştır. 1,1-difeniletan (DPE) kokusuz, renksiz ve zehirsiz olmasından dolayı endüstride kullanılabilirliği ve birçok yaygın monomer ile kontrollü polimerizasyon yapabilmesinden dolayı polimer kimyasında yeni bir alan açmıştır.



1,1-difeniletan (DPE) yöntemi, klasik serbest radikal polimerizasyonu ile yaşayan anyonik polimerizasyonunun avantajlarını bir arada uygulama fırsatını verir. Bu şekilde yeni blok kopolimerler elde edilebilir. Sentezler organik çözücülerde, çözücüsüz ortamda veya suda yapılabilir. Bu tez çalışmasında difeniletan metoduyla katyonik polimerizasyona yükseltgenme metodunu birleştirerek farklı yapılarıdaki monomerleri kullanarak, bu monomerlerin kontrollü blok kopolimerleri elde edilmesi amaçlanmıştır. Çalışmanın ilk bölümünde stiren (St) ve metil metakrilat (MMA) monomerleri, klasik radikal polimerizasyon sistemine, başlatıcı (AIBN) ile birlikte DPE konularak kontrollü polimerleşmesi gerçekleştirilmiştir. Elde edilen homo polimerlerin molekül ağırlık dağılımları 1.5 altında bulunduğu saptanmıştır. Bu yöntemle elde edilen polimerler ısıtıldığında polimerik difenilmetil radikallerini oluşturur. İyodonyum ve piridinyum tuzları varlığında redoks reaksiyonu sonucu polimerik karbokasyonlar oluşturulur. Oluşan karbokasyonlar ile sikloheksen oksidin katyonik polimerizasyonu başlatılır. Sonuç olarak, her iki segmentin kontrolünün sağlandığı blok kopolimerler elde edildi. Elde edilen blok kopolimerlerin ¹H-NMR spektrumları incelendiğinde homopoli (stiren) (7.21 ppm), homopoli (metil metakrilat) (3.5 ppm) ve homopoli (sikloheksen oksid)'in (3.41 ppm) karakteristik rezonans spektrumları görüldü.



1. INTRODUCTION

Polymers are widely used in all walks of human life and play a vital role in shaping modern man's activities to be as important and comfortable as they are today. The advances in science and technology made in recent decades owe much to development of polymer science. The synthesis and design of new polymeric materials to achieve specific physical properties and specialized applications, and attempt to find interesting applications involving advanced structures and architectures, are in continuous development in the period of the polymer science.

Basically, a polymerization process is based on a repetitive reaction in which a monomer is converted into polymer segment. To achieve such a goal, polymer chemists have a variety of synthetic processes to choose from reactions with very high selectivity when planning a particular synthesis. However, each method has its strengths and its weaknesses, and often requires high-purity reagents and special conditions. Indeed, the need high-purity monomers and solvents, reactive initiators and pure conditions have dramatically limited the industrial application of many techniques.

Free radical polymerization is very important in the field of industrial polymer synthesis and is the preferred route to commercial polymers. It is very is adaptable to many types of monomer under mild conditions. However, the preparation of well-defined polymers from unsaturated monomers has been limited by the technology available for conventional free radical polymerization. Certainly, such processes inherently do not allow to control over molar masses and give broad polydispersity since not all the polymeric chains are initiated at the same time because of a lack of control over chain-breaking reactions; i.e., both termination and the transfer steps greatly limit ability to polymer architecture. Living polymerization is an essential technique for synthesizing polymers with controlled structure i.e. polymers with controlled molecular weight and narrow molecular weight distributions. Moreover, living polymerization techniques allow preparation of macromers, macroinitiators,

functional polymers, block and graft copolymers and star polymers. This way, the need for specialty polymers having a desired combination of physical properties can be fulfilled. Control of such complex architectures by living polymerization has largely achieved using living anionic or cationic and group transfer polymerization techniques. There are so many different methods to synthesize block copolymers.

Among them, the transformation polymerization is an elegant method which allows to combine various polymerization mechanisms. It is one of the major methods to obtain well defined block copolymers. This way many monomers with different chemical structure can be polymerized to yield block copolymers with novel properties.

Recent advances in controlled free radical polymerization have been applied to synthesis of wide range of well-defined specific polymer architectures. Several methods, such as atom transfer radical polymerization (ATRP), stable radical mediated radical polymerization and radical addition-fragmentation chain transfer (RAFT) process have been accepted to be most efficient. Recently, Nuyken and co-workers have introduced a new additive for the controlled radical polymerization of numerous vinyl monomers. The addition of 1, 1-diphenylethene (DPE) to a conventional polymerization system consisting of initiator and monomer results in a controlled behavior of the polymerization. This method overcomes some problems observed in the existing controlled polymerization methods associated with high temperature conditions, catalyst removal and limited applicability to specific monomers. The aim of this thesis to apply recently developed DPE method in the preparation of block copolymers formed from structurally different monomers.

2. THEORETICAL PART

2.1. Free Radical Polymerization (FRP)

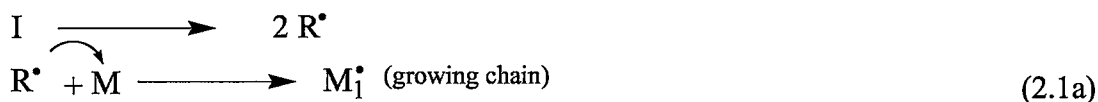
Free-radical reactions are of importance in a wide variety of commercial applications. Polymers prepared by free-radical means are used in the manufacture of numerous products, such as fabrics, surface coatings and paints, plastics, packaging, spectacle and contact lenses and surgical devices. Free radical polymerization 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. Steps of the Polymerization Process

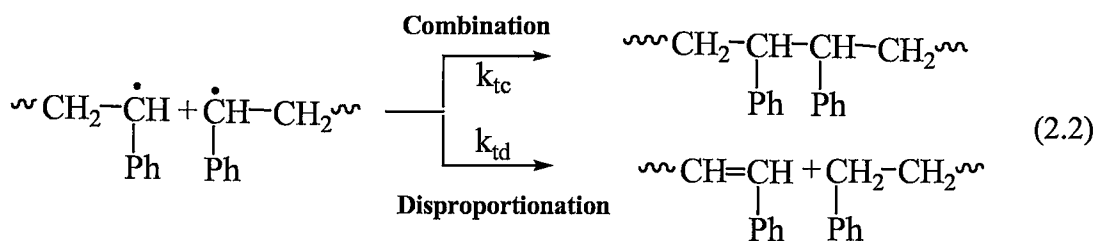
A typical free-radical polymerization comprises four elementary steps [1-2]:

1. initiation,
2. propagation,
3. chain transfer,
4. termination.

The first step, *initiation* is decomposition of the initiator molecule into primary radicals $R\cdot$. The actual initiation occurs when free radical react with a monomer (2.1a). The *propagation* or growth reaction consists of the (rapid) addition of monomer molecules to the radical species. In this step reaction is repeated many times (2.1b). 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.

Initiation**Propagation****Chain transfer to monomer or solvent****Reinitiation by transfer radicals****Termination**

In *termination*, growth of polymer chains is brought to an end by the destruction of propagating radicals (2.1e). Normally, in the absence of retarding species that destroy growing radicals, chain termination occurs by bimolecular interaction of radicals. These processes, analogous to those taking place with simple alkyl radicals, consist of radical combination or disproportionation (2.2).



Disproportionation leads to two polymer molecules, one saturated and one containing a terminal double bond. Many monomers show both types of termination: thus in methyl methacrylate, disproportionation is approximately twice as rapid as combination at room temperature and increases in importance as the temperature is raised. On the other hand, styrene and acrylonitrile radicals terminate preponderantly by combination (Table 2.1).

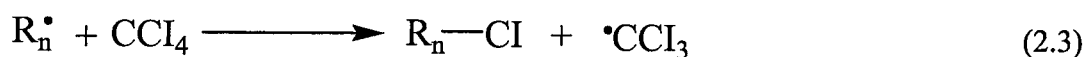
Table 2.1. Termination ratios of monomers

Monomer	k_{td}/k_{tc}	Temperature
Styrene	0.07	20
Styrene	0.10	118
MMA	0.62	90

It is possible to make some generalizations:

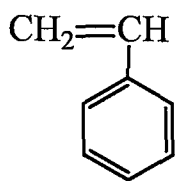
- Termination of polymerizations involving vinyl monomers involves predominantly combination.
- On the other hand, termination of polymerizations involving α – methylvinyl monomers always includes a measurable proportion of disproportionation.
- During disproportionation of radicals bearing an α – methyl substituent (for example, those derived from MMA), there is a strong preference for transfer of a hydrogen from the α – methyl group rather than the methylene group.
- Within a series of vinyl or α – methylvinyl monomers, k_{td} / k_{tc} appears to decrease according to the ability of the substituent to stabilize a radical center in the series $\text{Ph} > \text{CN} \gg \text{CO}_2\text{R}$.

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 (2.1c and d). 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. Transfer to carbon tetrachloride is illustrated in 2.3.

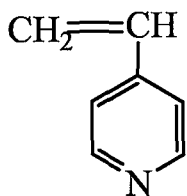


2.1.2. Monomers

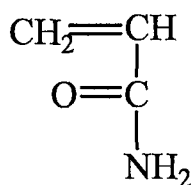
Most of vinyl and diene monomers (2.4) can undergo free radical polymerization.



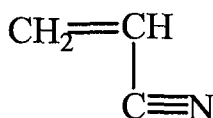
Styrene



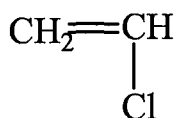
4-vinyl pyridine



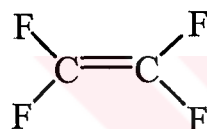
Acrylamide



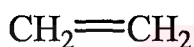
Acrylonitrile



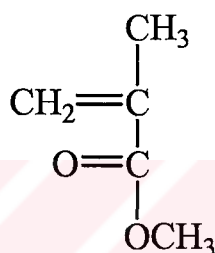
Vinyl chloride



Tetrafluoro ethylene



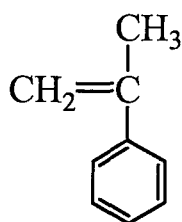
Ethylene



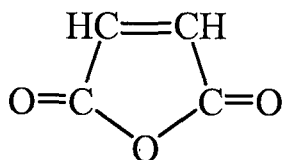
Methyl methacrylate

(2.4)

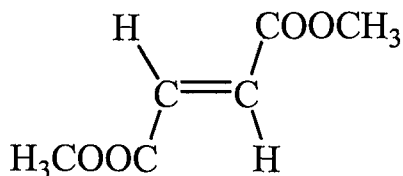
Some potential monomers do not form polymers under usual free radical polymerization conditions. Such as α -methyl styrene is involved in polymerization-depolymerization equilibrium above a ceiling temperature. Maleic anhydride and dimethyl fumarate (2.5) are symmetrically substituted ethylenes therefore, they can not be polymerize by free radical polymerization.



α -methyl styrene



maleic anhydride



dimethyl fumarate

(2.5)

2.1.3. Initiator

Polymerization of a reactive vinyl monomer is initiated by free radicals having sufficiently high activity. These may be generated from initiators in diverse ways, among which thermal or photochemical intramolecular bond cleavage, redox reactions, and photochemical hydrogen abstraction are the commonest, but other processes such as use of γ -radiation or electron beams find applications.

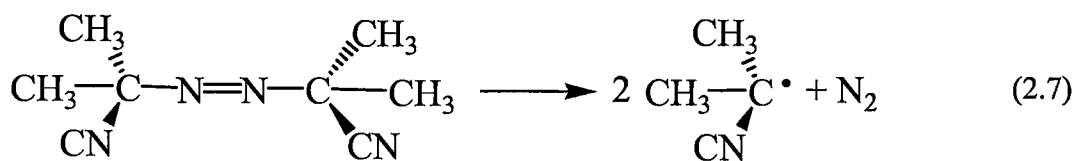
2.1.3.1. Thermal Initiators

Azo Initiators

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) (2.6).

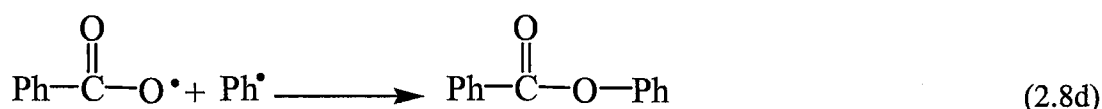
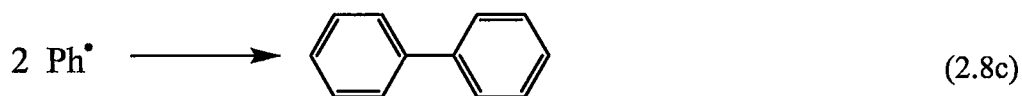
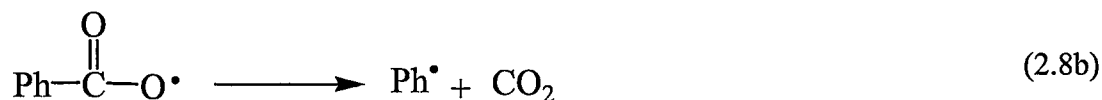
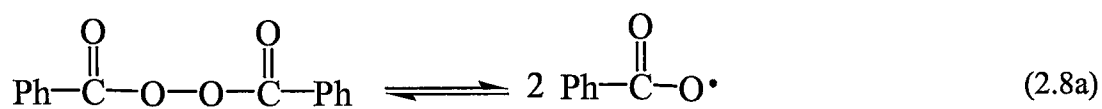


Azobisisobutyronitrile (AIBN) is very widely used initiator. Thermal decomposition of AIBN and its analogues is generally considered to produce cyanoisopropyl radicals (or analogues) according to the following reaction 2.7.



Peroxy Compounds

Benzoyl peroxide is a well-established initiator of polymerization. Like other peroxides, the primary step in the thermal decomposition is scission of the — O — O — bond to give two acyloxy radicals (2.8a). 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 (2.8b). Further, recombination reactions giving biphenyl and phenyl benzoate may then occur (2.8c and d).

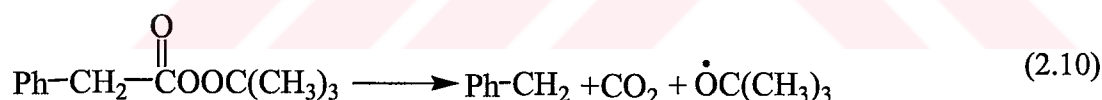


Peresters

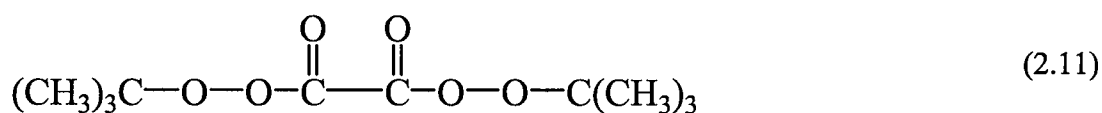
The thermolysis of *t*-butyl peresters has received detailed attention [3-5].



Evidence was adducted for the occurrence of concerted rupture of C — C and O — O bonds on thermolysis, for example with *t*-butyl phenylperacetate (2.10) [6].



Many of these peresters function as low-temperature initiators of free-radical polymerization. Although some of the stabilized radicals may not be effective initiators, the *t*-butoxy radical and its β -scission product, methyl, initiate readily (2.11). Di-*t*-butyl peroxyoxalate initiates well at 25°C. Di-isopropyl peroxydicarbonate is a familiar perester which initiates well at moderate temperatures [7].



2.1.3.2. Redox Initiators

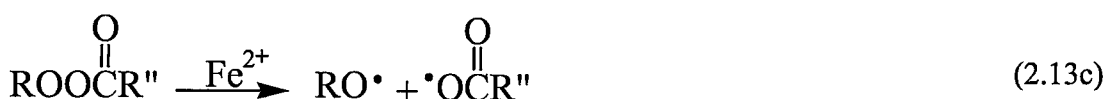
Many oxidation-reduction reactions produce radicals that can be used to initiate polymerization. This type of initiation is referred as *redox initiation*, *redox catalysis*, or *redox activation*. A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular redox system, including initiation at moderate temperatures of 0-50°C and even lower. This allows a greater freedom of choice of the polymerization temperature that is possible with the thermal homolysis of initiators [8].

Types of Redox Initiators

1- Peroxides in combination with a reducing agent are a common source of radicals, for example, the reaction of hydrogen peroxide with ferrous ion (2.12).

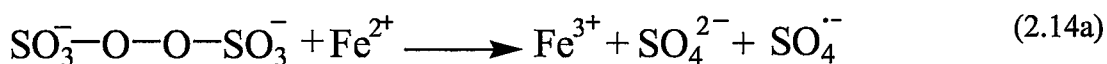


Ferrous ion also promotes the decomposition of a variety of other compounds including various types of organic peroxides (2.13).



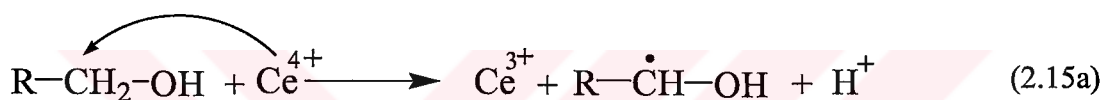
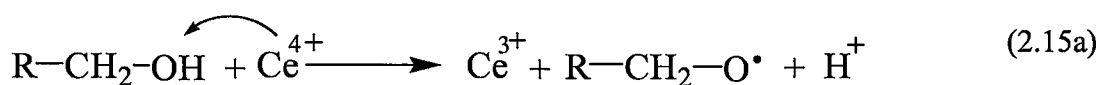
Other reductants such as Cr^{2+} , V^{2+} , Ti^{3+} , Co^{2+} , and Cu^+ can be employed in place of ferrous ion in many instances.

2- The combination of a variety of inorganic reductants and inorganic oxidants initiates radical polymerization, for example,



Other redox systems include reductants such as HSO_3^- , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, and $\text{S}_2\text{O}_5^{2-}$ in combination with oxidants such as Ag^+ , Cu^{2+} , Fe^{3+} , ClO_3^- , and H_2O_2 .

3- 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+} (2.15a and b).



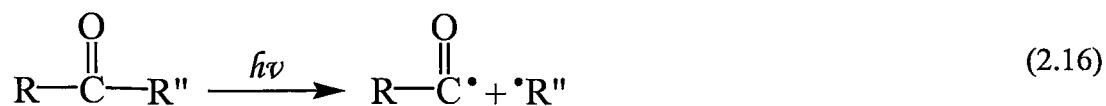
4- There are some initiator systems in which the monomer itself acts as one component of the redox pair. Examples are thiosulfate plus acrylamide or methacrylic acid and N, N-dimethylaniline plus methyl methacrylate.

2.1.3.3. Photoinitiators

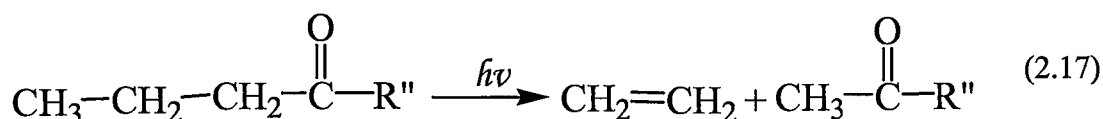
Photoinitiators for free-radical polymerization fall into two classes: those which on irradiation undergo intramolecular bond cleavage with radical generation and those which when photoexcited abstract hydrogen atoms from H-donors and so form radicals.

Photoinitiation by Intramolecular Bond Cleavage

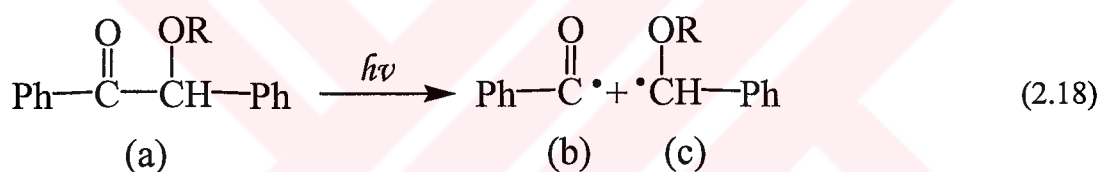
Most peroxy initiators yield radicals on photolysis and benzoyl peroxide has frequently been used as a photoinitiator [9,10]. They require shorter wavelengths than azo compounds (<300nm), a disadvantage since many monomers absorb in this region. The same remark applies to many simple ketones which photodissociate according to the Norrish type I mechanism (2.16) [11].



Ketones carrying alkyl chains three or more carbon atoms long may undergo the essentially nonradical Norrish type II fission (2.17):



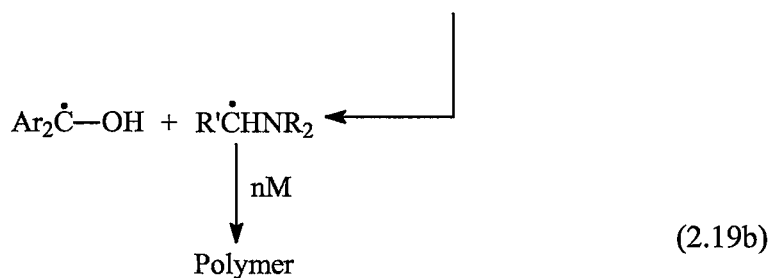
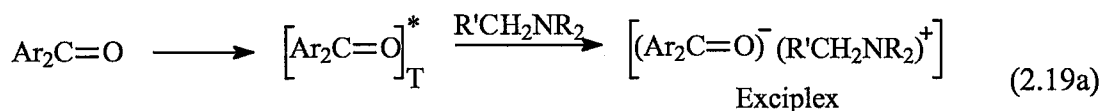
Benzoin is a well-known photoinitiator [12,13]. Benzoin ethers (a) which are much used in photocuring process undergo a type I photodissociation into two different radicals. It has been reported that both types of radicals can initiate the polymerization (2.18).



Photoinitiation by Hydrogen Abstraction

Photoinitiators of this type include benzophenone and derivatives such as Michler's ketone (14), thioxanthenes, benzyl and quinones. In contrast to cleavage type photoinitiators, which are capable of generating radicals independently, this type of initiators must undergo a bimolecular reaction with hydrogen donors. Tertiary amines with abstractable hydrogen atoms are particularly effective H-donors for UV curing of acrylate monomers [14,15].

The classical example is benzophenone, of which the photochemistry is well-known [16]. The lowest excited singlet (S_1) is of $n \rightarrow \pi^*$ character and yields by intersystem crossing the lowest excited triplet (T_1). In the presence of a hydrogen donor RH the following reaction occurs (2.19).



2.2. Controlled Radical Polymerization (CRP)

Free Radical polymerization (FRP) is a very important commercial process for preparing high molecular weight polymers because it 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 °C). In addition, many monomers can easily copolymerize radically leading to an infinite numbers of copolymers with properties dependent on the proportions of the comonomers. The only disadvantage to conventional radical polymerization is the poor control of macromolecular structures including degrees of polymerization, polydispersities, end functionalities, chain architectures and compositions. The synthesis of well-defined polymers has long been of great interest in polymer chemistry. Typically, living polymerization techniques are employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination. The development during the last decade of various processes for the control of free radical polymerizations (CRP) has lead to new ways of synthesizing polymers with low polydispersities, new architectures, compositions, functionalities and molecular composites (Figure 2.1) [17].

$$DP_n = 200 < M_n < 200,000 ; \Delta[M]/[I]_0 = 1.04 < M_w/M_n < 1.5$$

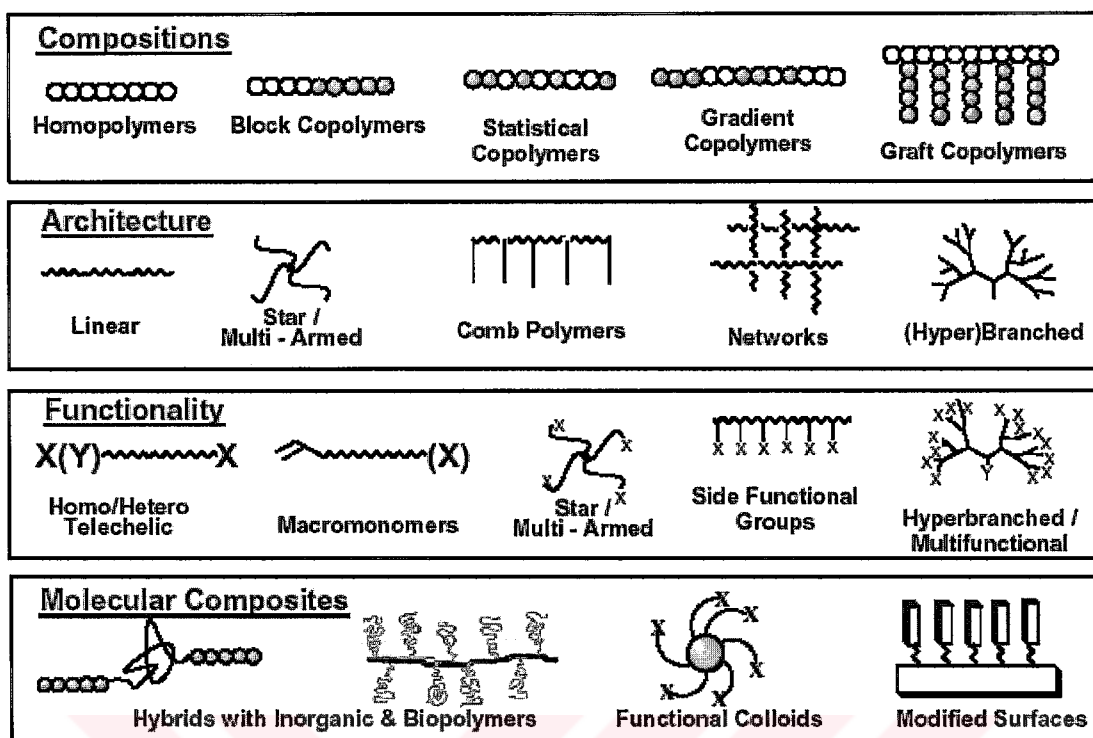


Figure 2.1. Products of Controlled Free Radical Polymerization

To be effective in controlling a radical polymerization, there are two necessary conditions. 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 accomplished, then conventional radical polymerization was converted to a controlled/living radical polymerization yielding polymers with a wide range of molecular weights and narrow MWDs is possible [18].

CRP has proved to be a versatile and robust method to prepare well-defined organic polymers. A major difference between conventional radical (i.e., azobis (isobutyronitrile) - or peroxide-initiated processes) and controlled radical polymerizations is the lifetime of the propagating radical during the course of the reaction. In conventional radical processes, radicals generated by decomposition of the initiator undergo propagation and bimolecular termination reactions within a

second. In contrast, the lifetime of a growing radical can be extended to several hours in a CRP, enabling the preparation of polymers with predefined molar masses, low polydispersity, controlled compositions, and functionality for the equilibrium as shown Figure 2.2 [19, 20].

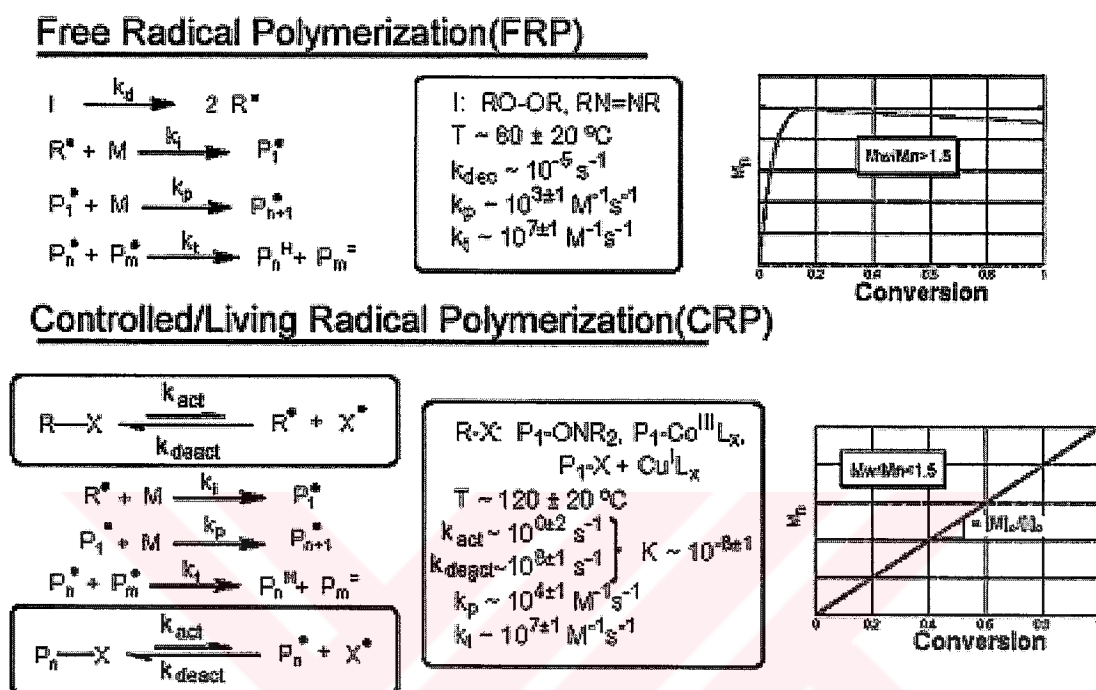


Figure 2.2. Comparison between FRP and CRP

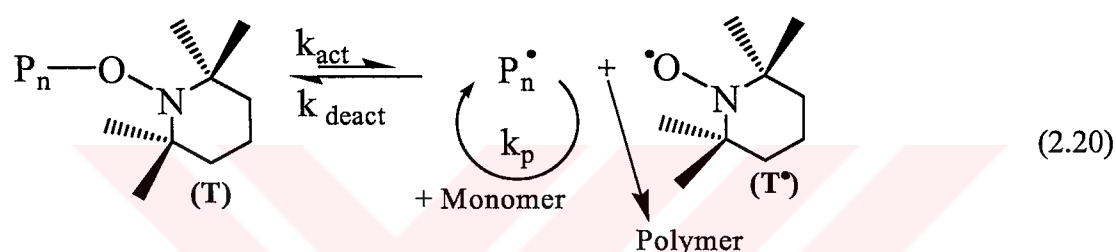
The mechanism invoked in CRP processes to extend the lifetime of growing radicals utilizes a dynamic equilibration between dormant and active sites with rapid exchange between the two states. Unlike conventional radical processes, CRP requires the use of persistent radical (deactivator) species, or highly 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}) [21].

In the 1990s, several methods were developed that enable controlled radical copolymerization. These methods include stable free-radical polymerization (SFRP) [22], atom transfer radical polymerization (ATRP) [23], and reversible addition-fragmentation chain transfer (RAFT) [24] and Diphenylethene method (DPE) [25].

Using these polymerization methods, the molecular weight of the polymers linearly increases with conversion and the polydispersities are well below 1.5

2.2.1. Stable Free Radical Polymerization (SFRP)

The first such mechanism, SFRP (see (2.20)), is a polymerization with reversible termination by coupling with a persistent radical (e.g. nitroxide). Currently, the best example in this class is alkoxyamine-initiated or nitroxide-mediated polymerization first described by Rizzardo et al. [26], and later developed by Georges [27] and Hawker [28].



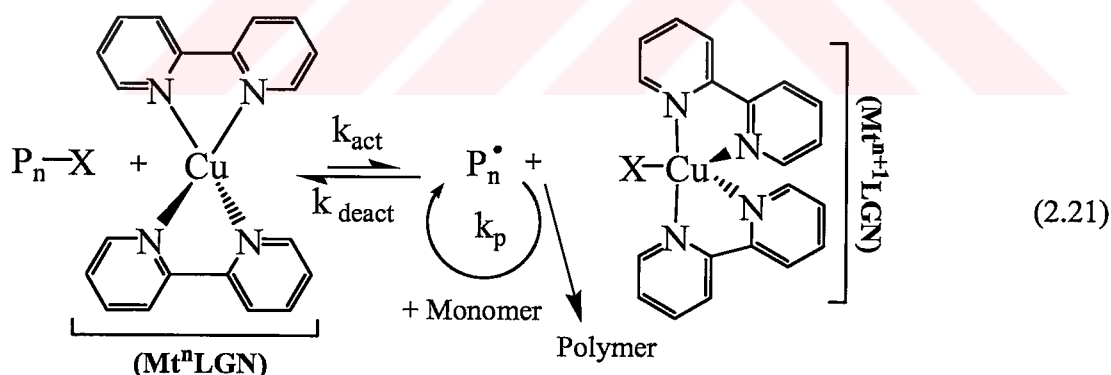
The key reactions in this system have been shown to be the alternating activation–deactivation process, in which the polymer-nitroxide adduct P_n-T (dormant species) is reversibly activated by thermal homolysis into the polymer radical ($P_n\cdot$) and the stable nitroxyl ($T\cdot$). This dramatically 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 [29]. These activation–deactivation cycles allow all the chains to propagate at nearly equal rate, thus controlling the chain length and its distribution. The most commonly used stable radicals have been nitroxides, especially 2, 2, 6, 6-tetramethylpiperidinoxy (TEMPO). TEMPO (2, 2, 6, and 6- tetramethylpiperidiny) is used for the reversible trapping of growing radicals. At a temperature below 100°C the resulting alkoxyamine is stable whereas at higher temperature the C-O bond undergoes homolytic cleavage thus allowing again the propagation. These systems have been shown to be efficient for controlled polymerization of styrene and substituted styrene.

Although SFRP is one of the simplest methods of controlled free radical polymerization (CRP), it has many disadvantages. Many monomers will not polymerize because of the stability of the dormant alkoxyamine that forms. Also, since the reaction is kinetically slow, high temperatures and bulk solutions are often required. Also, the alkoxyamine end groups are difficult to transform and require radical chemistry.

Recent work in SFRP has revolved around the synthesis and evaluation of new nitroxide radicals, chain end fictionalization, 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 [22].

2.2.2. Atom Transfer Radical Polymerization (ATRP)

The second mechanism, ATRP (2.21), is a radical polymerization with reversible deactivation by atom transfer. ATRP is based on the reversible transfer of halogen atoms between dormant alkyl halides and transition metal catalysts by redox chemistry.



This method utilizes a reversible halogen atom abstraction step, in which a lower oxidation state metal (M_t^n complex by a ligand LGN) reacts with an alkyl halide (P_n-X) to generate a radical (P_n^\bullet) and a higher oxidation state metal complex ($XM_t^{n+1}LGN$, 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}) [30, 31].

An ATRP system consists of an initiator, a catalyst, ligand(s), and of course, monomer. In ATRP, alkyl halide with an activating group at the α -position is used as an initiator. Its main role 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. ATRP is catalyzed by transition metal compounds complexes (Ru, Cu, Fe, Ni, and other transition metal complexes) by suitable ligands like bipyridyls, aryl phosphines, aliphatic amines, etc. ATRP has been mainly applied to styrene, (meth) acrylates and acrylates. However, it has also been used with other monomers like acrylonitrile and 4-vinyl pyridine. For each monomer, the reaction conditions are different since atom transfer equilibrium depends upon the combination of halide initiator and metal catalyst. Thus, metal complex and halide initiator are useful tools to fine tune ATRP [18]. ATRP is a multi-component system, so concentrations and the structures of all these compounds affect the polymerization rate and the properties of the resulting polymer. For each particular ATRP, a specific initiator, metal, ligands, deactivator, temperature, reaction time and solvent should be selected [19] Nevertheless, ATRP has a few limitations. High concentration of catalyst is required for acceptable rates of polymerization and its removal after the reaction, in homogeneous systems, is difficult. Most of the initiators are toxic. Also, due to the limitations of present-generation catalysts, ATRP cannot be used for polymerization of more reactive monomers like ethylene, olefins, and vinyl acetate and vinyl alcohol. Future work in this field includes the removal and recycling of the catalyst as well as the design of catalysts that react with a larger range of monomers [32].

2.2.3. Reversible Addition – Fragmentation Chain Transfer Reactions (RAFT)

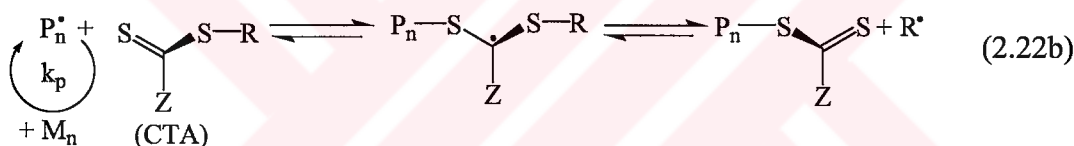
The third mechanism, RAFT, for achieving living character is free-radical polymerization with reversible chain transfer [24] The initiation system consists of a standard free-radical initiator and a suitable thiocarbonylthio compound, which acts as highly efficient reversible addition–fragmentation chain transfer agent (CTA agents) and provides the polymerization with living characteristics.

In RAFT, the CTA acts as so-called “trapping agent” because it is transferred between the active and the trapped chain. These trapped chain, usually called

dormant chains, are unable to propagate but also unable to terminate. Because chain termination is bimolecular reaction, so the termination rate is second order with respect to the radical concentration $[M_n^\bullet]$. While chain propagation is first order to the radical concentration $[M_n^\bullet]$ 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 [33, 34].



Chain Transfer (Addition/Fragmentation)

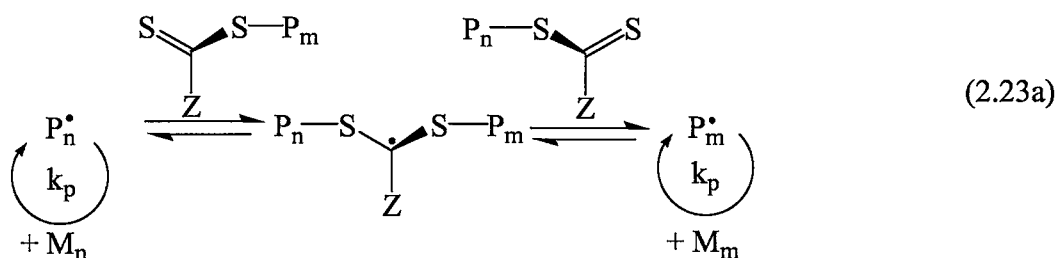


Reinitiation/Propagation

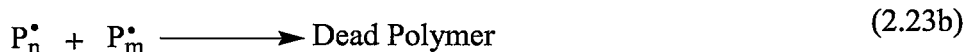


RAFT involves a reversible chain transfer in which a dithioester behaves as a chain transfer agent (CTA). The CTA reacts with either the primary radical or a propagating chain, forming a new CTA and eliminating R^\bullet , which re-initiated polymerization. The dithioester is transferred between the active and dormant chains, thus maintaining the living character of the polymerization. As seen from scheme (2.22), RAFT mechanism differs from normal free radical polymerization mechanism by having a chain transfer agent, which leads to addition-fragmentation, re-initiation/propagation and chain equilibrium between chain radical and a new CTA. Because the addition-fragmentation chain transfer process is reversible, so the process is called reversible addition-fragmentation chain transfer polymerization (RAFT) (2.23).

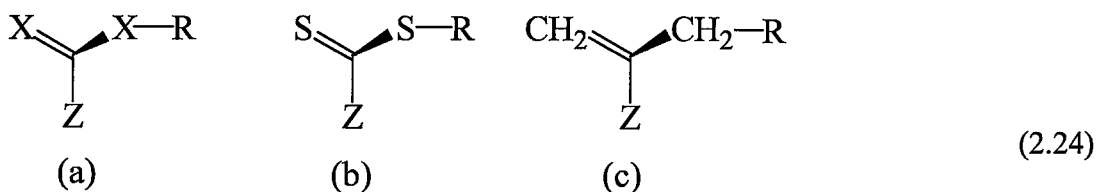
Chain Equilibration



Termination



A RAFT process is actually a kind of degenerative chain transfer reaction, in which activation and deactivation occur at the same time or an active site migrates from one chain to another. So the key to successful RAFT polymerization is to select highly efficient CTA (2.24a). The polymerization is carried out in the presence of thiocarbonylthio of general structure (2.24b) and results in the formation of end-functionalized polymers. Z should activate the C=S double bonds [24, 35]. 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 (2.24c), where X is CH₂ can also function as RAFT agents [36, 37, 38, and 39].



The greatest advantage to RAFT is the incredible range of polymerizable monomers practiced in both organic solvents and aqueous media (including water) 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 dithio end

groups left on the polymer give rise to toxicity, color, and odor and their removal or displacement requires radical chemistry. Also, the RAFT agents are expensive and not commercially available. Another drawback is that the process requires an initiator, which can cause undesired end groups and produce too many new chains which can lead to increased termination rates [32].

2.2.4. 1,1-Diphenylethene Additive Method (DPE)

The fourth 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 [25]. 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 [40].

2.2.4.1. Homopolymerization

The DPE systems show some characteristics which are different to a free radical polymerization. Figure 2.3 (left) shows the time-conversion plot for 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 2.3 (right) shows the molecular weight and the 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 [41].

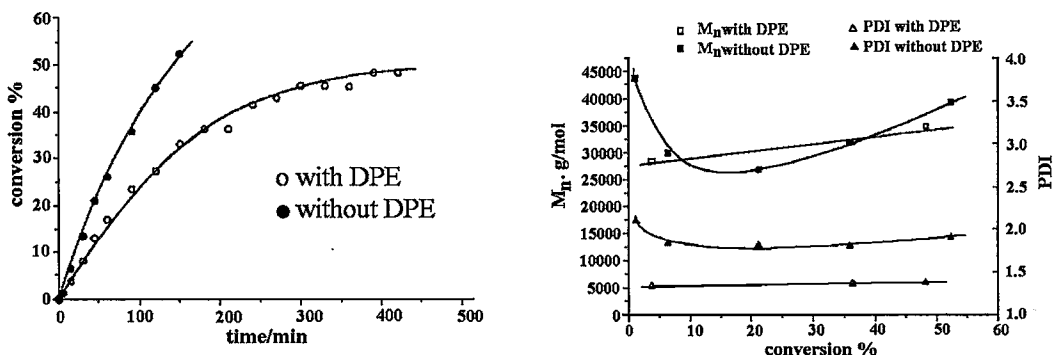


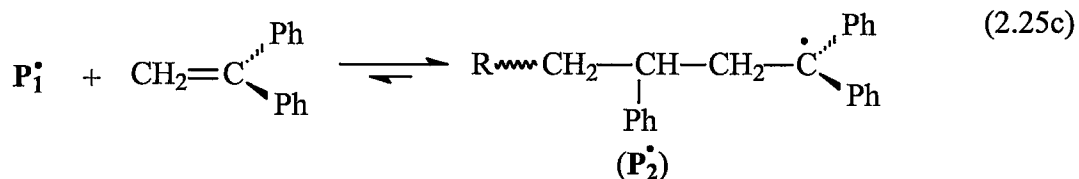
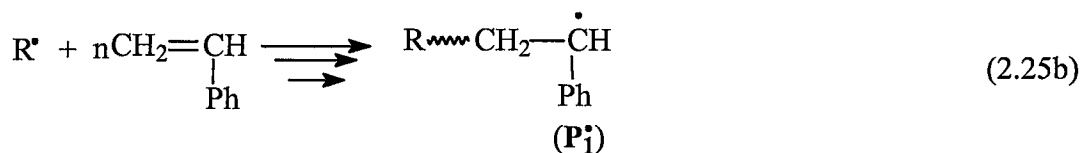
Figure 2.3. Time-conversion plot (left), Molecular weight and PDI versus conversion plot (right), polymerization of styrene in the presence of DPE and with out DPE.

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.

2.2.4.2. Block Copolymerization

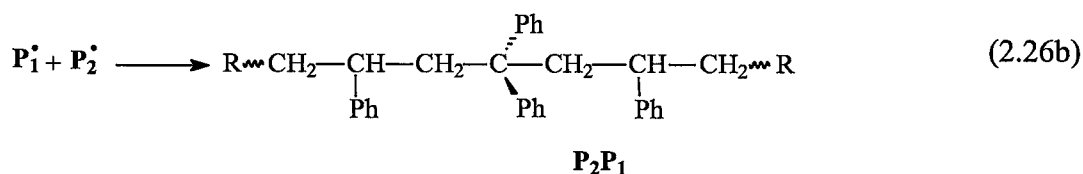
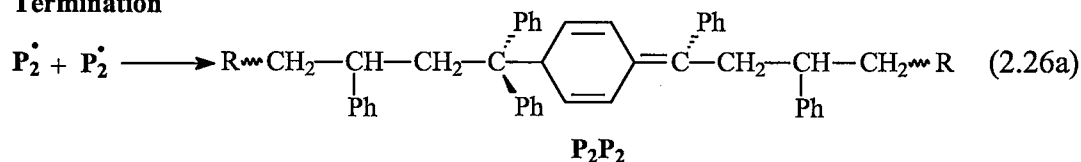
The DPE-system is very useful for the synthesis of various block copolymers. Polymers, which have been synthesized in the presence of small amounts of DPE are able to initiate the polymerization of second monomer if certain temperature is exceeded. The system seems to be quite universal with regard of the block formation. The yield of block copolymers varies for different monomers.

Initiation



The reaction shows how the copolymerization and reinitiation occurs. The first step is the formation of an active chain end P_1^\bullet common radical initiation (2.25a, b). P_1^\bullet reacts with a DPE molecule under formation of a stable diphenylmethyl radical P_2^\bullet (2.25c). This radical is a kind of a dormant species which can avoid transfer reactions. If the formation of P_2 is reversible all needs for equilibrium is required for all controlled polymerizations.

Termination



The final dormant species is built by combination of two P_2 radicals to a tetraphenylethane unit (2.26). Such units are thermolabile, as have been shown by different authors [42-44]. The tetraphenylethane unit will be a quinone like structure as have been shown for hindered tetraphenylethanes [45].

Figure 2.4 shows the $^1\text{H-NMR}$ spectrum of DPE containing PMMA where the characteristic signals of the quinone protons are visible.

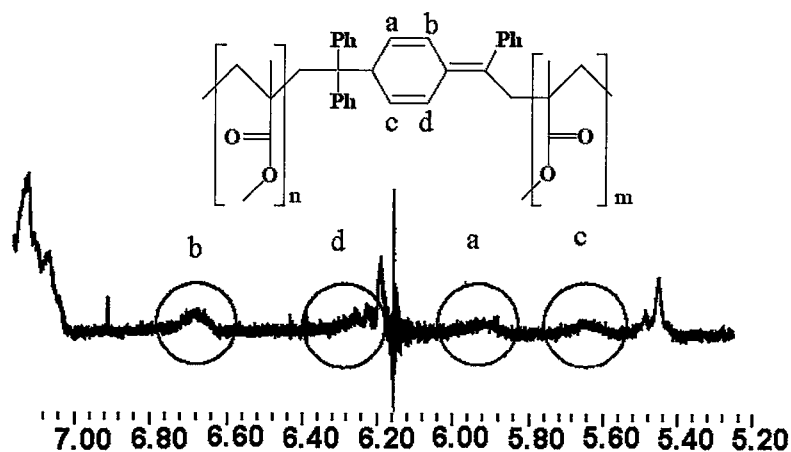
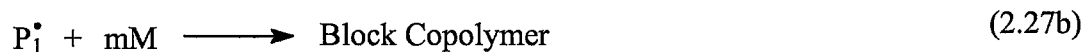
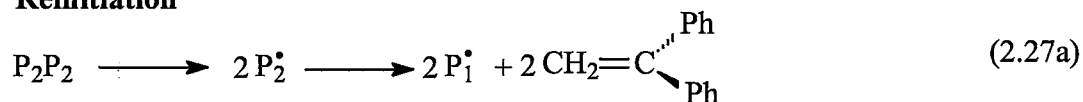


Figure 2.4. $^1\text{H-NMR}$ spectrum of PMMA ($M_n=4450$ g/mol) which has been synthesized in the presence of DPE

If the polymers with tetraphenylethane units along the chain will be heated in the presence of second monomer, they split into two P_2 radicals. The P_2 radicals split into P_1 and free DPE. P_1 can initiate the polymerization of second monomer (M_m) whereby block copolymers are formed (2.27).

Reinitiation



The polymerization control is not as good as in the other established systems like ATRP, SFRP, or RAFT, but the versatility of the DPE method makes it interesting especially for synthesis of block copolymers even industrial field [40]. The DPE method is surprisingly flexible with respect to choice of monomers and the 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 usual ones for conventional free-radical polymerization, which is beneficial for industrial implementation of the DPE method. DPE is commercially available, odorless, colorless and without known toxicity. It is known as a non polymerizable styrene derivative, [46] which was useful only as molecular weight regulator [47]. 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. Moreover, most of the applied monomers could not yet be polymerized in a controlled way by other radical pathways. Furthermore, the successful application of DPE-containing prepolymers for the synthesis of block copolymers, which allow many combinations, is particularly attractive since many of these block copolymers are not available yet.

2.3. Block Copolymers

Block copolymers have become increasingly important in recent decades. The reason for this importance is due to the fact that their special chemical structure yields

unusual physical properties, especially as far as solid state properties are concerned. The block copolymers find application in diverse fields: as thermoplastic elastomers, pressure sensitive adhesives, impact modifiers, compatibilisers etc. In solutions, their surfactant properties are exploited in foams, oil additives, solubilisers, thickeners and dispersion agents. The block copolymers may have potential applications in medicines, nanotemplating and nanotechnology. When two different types of monomers are joined in the same polymer chain, the polymer is called a copolymer. Block copolymers can be considered as a combination of two or more monomers joined end to end. The several of copolymers were illustrated as Figure 2.5.

Block copolymers can be synthesized by sequential addition reactions using :

- Ionic initiators where an active site kept , 'alive' on the end of the initial block, which is then capable of initiating chain growth of second monomer on the end of the first chain
- Coupling of different blocks with functional terminal units, either directly or through a reaction involving a small intermediate molecule
- Bifunctional radical initiators where a second potentially active site is incorporated at one end of the first chain grown, which can initiate at later stage a new chain from the macroradical produced [48].

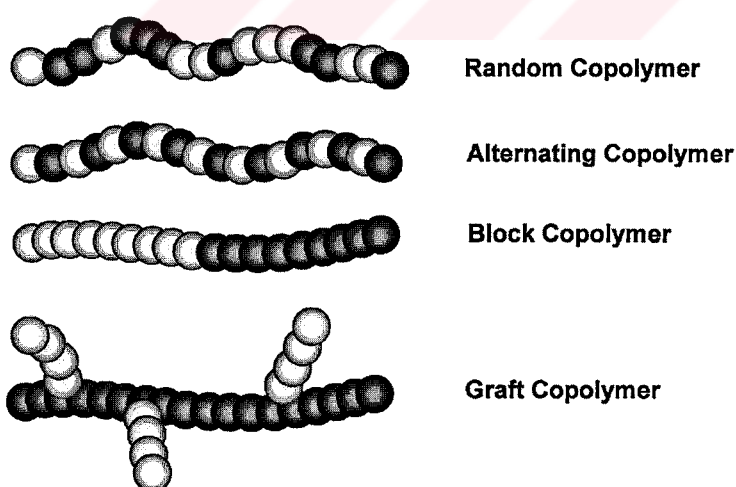


Figure 2.5. Types of copolymers

2.4. Methods to Preparation of Block Copolymers

A number of techniques for the preparation of block copolymers have been developed and generalized in 2.3 [49-51]. Living ionic polymerization is elegant method for the controlled synthesis of block copolymers. However, besides high purity requirements this technique is limited to ionically polymerizable monomers and excludes monomers that polymerize by other mechanisms. In fact there exists some limitations even for the ionically polymerizable monomers. Whether the block copolymerization of two ionically polymerizable monomers can or can not be carried out is critically dependent on the structure and relative reactivity of the ionic species and the monomers. For example only a few monomers are suitable for the preparation of block copolymers by anionic polymerization. A similar situation is valid for cationic polymerization. Furthermore, the synthesis of block copolymers between structurally different polymers i.e. condensation and vinyl polymers, by a single polymerization method is rather difficult due to the nature the respective polymerization mechanisms.

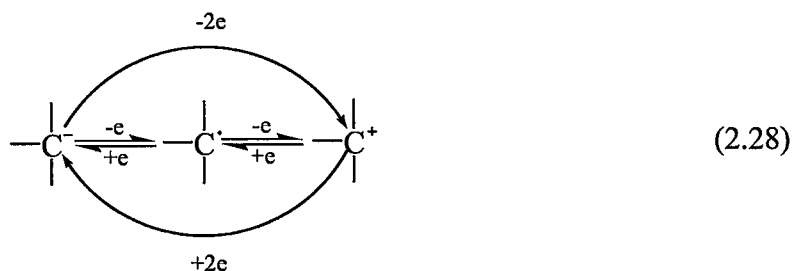
2.4.1 Transformation Reactions

In order to extend the range of monomers for synthesis of block copolymers, transformation approach was postulated by which the polymerization mechanism could be changed from one to another which is suitable for the respective monomers [52-54]. All the research works performed in the area of polymerization transformation mechanism could be outlined in two categories:

2.4.1.1 Direct Transformation Reactions

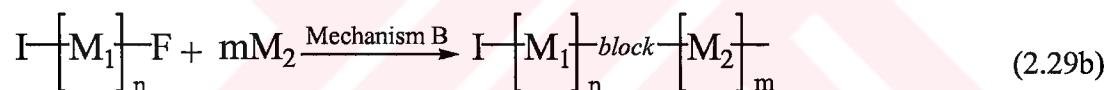
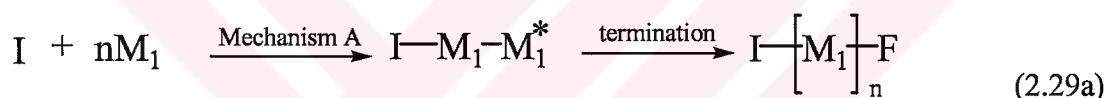
The transformation of a polymerization mechanism is carried out at the end of the first block segment in the polymerization mixture that means the species which initiated the polymerization mechanism of the first monomer by one mechanism was transformed to another mechanism by a redox process without termination and isolation [55].

- Cation to Anion Direct Transformation
- Radical to Cation Direct Transformation



2.4.1.2 Indirect Transformation Reactions

This type of transformation usually requires multistep reactions. The stable but potentially reactive function group for the second polymerization mode is introduced to the chain ends either in the initiation or the termination steps of the polymerization the first monomer. The polymer is isolated and purified, and finally the functional groups are converted to another kind of species by external stimulation such as photoirradiation, heating or chemical reaction [55].



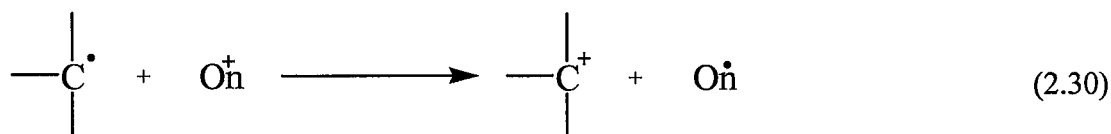
The methods will be classified according to the nature of the propagating centers involved in the transformation polymerization (Table 2.2). Using transformation reactions, i.e., combining different polymerization mechanisms, novel polymeric materials may be synthesized from new and existing monomers. A full range of possible block and graft copolymers builds from monomers with different chemical structure are accessible through transformation reactions. It is clear that the transformation reactions will continue to attract interest in the near future because of the possibility of the various newly developed “living”/controlled polymerization mechanisms. It would be possible to design and synthesize materials having precise structures with desired properties by combination of such mechanisms [55].

Table 2.2. Transformation Reactions Used for Block Copolymer Synthesis

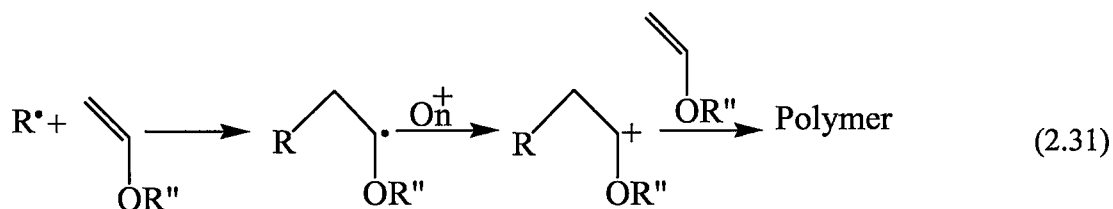
Transformation Types	References
1- Transformations Involving Condensation Polymerization	[56]
2- Transformation of Anionic Polymerization to Radical Polymerization	[57-59]
3-Transformation of Cationic Polymerization to Radical Polymerization	[60-62]
4- Transformation of Radical Polymerization to Anionic Polymerization	[63, 64]
5- Transformation of Radical Polymerization to Cationic Polymerization	[65-67]
6- Transformations Involving Anionic and Cationic Polymerizations	[68,69]
7- Transformations Involving Activated Monomer Polymerization	[70-72]
8- Transformations Involving Metathesis Polymerization	[73,74]
9- Transformations Involving Ziegler-Natta Polymerization	[75,76]
10- Transformations Involving Group Transfer Polymerization	[77,78]

2.5. Free Radical Promoted Cationic Polymerization

Free radical promoted cationic polymerization is an elegant method to initiate cationic polymerization by the use of free radical initiators [79, 80]. It was reported that the oxidation of electron donor radicals to corresponding cations may conveniently be used to promote cationic polymerization of monomers such as epoxides, cyclic ethers, and alkyl vinyl ethers [81,82]. Electron donor radicals can be generated thermally, photochemically and by other means such as electron beam irradiation. The photochemical generation of radicals can be applied even at low temperatures. Being photolyzed with high quantum yields, benzoin derivatives are so far the most effective photoinitiators for the free radical promoted cationic polymerization [83]. The other suitable free radical promoters include benzilketals [83], acylphosphineoxides [84, 85], azo compounds [83], benzophenone and certain dyes in conjunction with hydrogen donor compounds [86] and substituted vinyl halides [87]. The overall process may be represented by reaction (2.30) and useful oxidants include onium salts such as diaryliodonium salts.



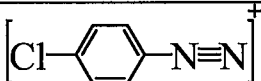
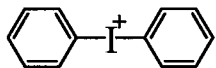
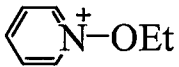
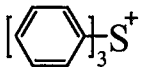
In the case of vinyl ether monomers, electron donor radicals are obtained by the addition of the radicals to the monomer and subsequent oxidation would then pursue the initiation of cationic polymerization (2.31).



This way the availability of a wide range of free radical photoinitiators is benefited and cationic polymerization can be activated by the free radical chemistry. Free radical and free radical promoted radical combined polymerizations can be performed both thermally and photochemically [88]. It should also be noted that the success of the free radical promoted cationic polymerization is related to the acceptor strengths of the cationic salts employed in the system which are known from their reduction potentials. The efficiency of onium salts as oxidizing agents is related to their electron affinity. The higher the oxidation power of the onium salt, the higher (more positive) is the reduction potential $E_{\text{red}}^{1/2}(\text{On}^+)$. The efficiency of onium salts in this mode of polymerization rises in the order of trialkyl sulphonium salts < alkoxy pyridinium salts < diaryliodonium salts < aryldiazonium salts (see Table 2.3).

Aryldiazonium salts are the most suitable for the oxidation of radicals. However, their practical application is hampered by the lack of thermal stability. Diphenyliodonium salts have also a relatively high reduction potential. Being very suitable for the oxidation of free radicals, these salts have been most frequently used for the oxidation of photo generated free radicals. On the other hand, triphenylsulphonium salts have only limited potential for radical induced cationic polymerizations due to their low reduction potential. However, some highly nucleophilic radicals could be oxidized with sulphonium salts.

Table 2.3. Reduction Potential and Triplet Excitation Energies of Onium ions

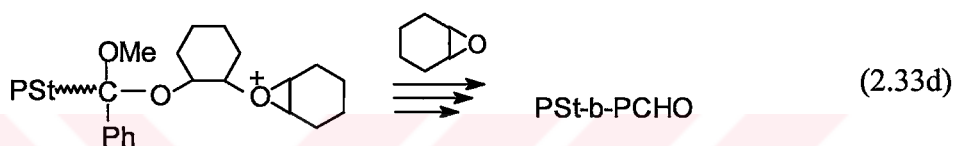
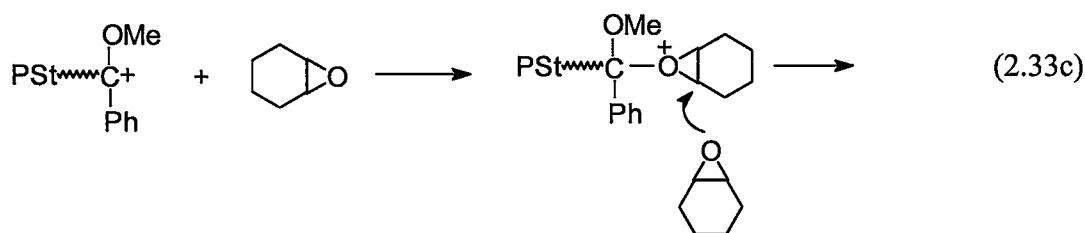
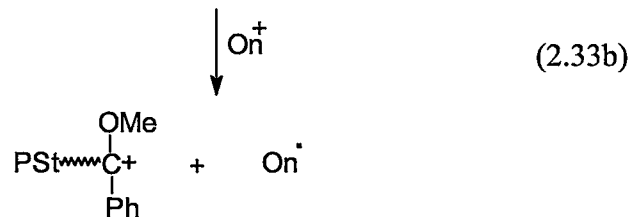
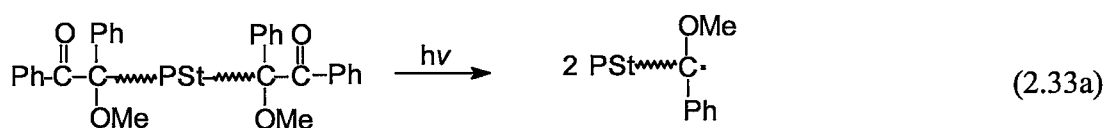
Onium Cation	$E_{1/2}^{\text{red}}$ (V) (vs SCE)	E_t^* (kJ mol ⁻¹)	References
 Aryldiazonium	0.35	-	[89]
 Diaryliodonium	-0.2	268	[90]
 Alkoxy pyridinium	-0.7	-	[83]
 Triaryl sulphonium	-1.1	314	[91]

Provided the oxidation and reduction potentials of the free radical and the onium ion, respectively, are known, it can be estimated on the bases of the Rehm-Weller equation (2.32) whether a radical can be oxidized by a given onium salt or not.

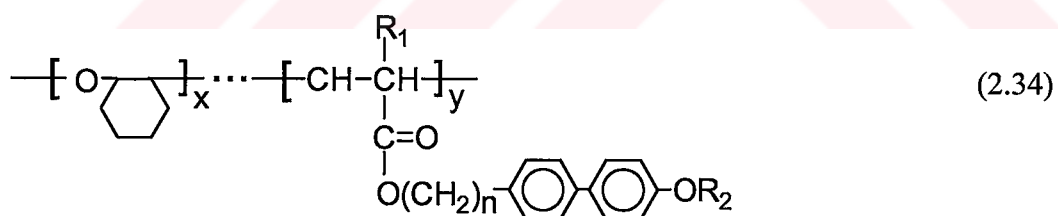
$$G = F [E_{\text{ox}}^{1/2} (\text{R}\cdot) - E_{\text{red}}^{1/2} (\text{On}^+)] \quad (2.32)$$

However, the calculation of G is usually not feasible since the exact oxidation potentials $E_{\text{ox}}^{1/2} (\text{R}\cdot)$ of most radicals involved in radical promoted polymerizations are unknown.

According to Yagci et al. [67] irradiation of benzoin terminated polymers in conjunction with pyridinium salts as oxidants in the presence of cyclohexene oxide (CHO) makes it possible to synthesize block copolymers of different chemical nature (2.33).



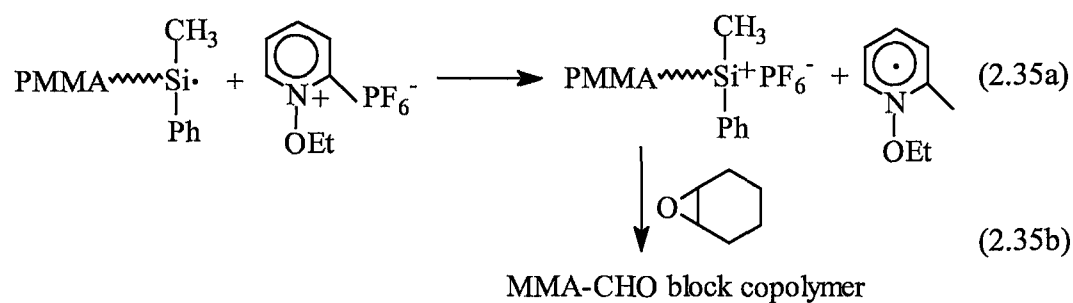
For the practical value of this process, we have prepared [92] block copolymers of crystalline and liquid crystalline segments of the following structure by using the same synthetic strategy (2.34).



Polyepichlorohidrin functionalized with benzoin groups with AM polymerization were also used in such promoted cationic polymerization to yield epichlorohidrine and cyclohexene oxide block copolymers.

Previously, the cationic polymerization of CHO is initiated upon UV irradiation of solutions containing alkoxy pyridinium salt and polysilane [93, 94]. A plausible explanation mechanism involves oxidation of silyl radicals by pyridinium ions formed would add to CHO, the resulting oxonium ion would initiate chain propagation (2.35). The same reaction principle was applied for the polymerization

of CHO using remaining polysilane units in PMMA, obtained by the partial photodegradation polysilane, and pyridinium ions [95].



Although block copolymers are formed, a considerable amount of homopolymers was also formed which may be due to extensive degradation of polysilane units during irradiation. Moreover, the character of initiation mechanism, which needs further investigation, may contribute to the formation of non-blocked component.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Initiators and Other Chemicals

2, 2'-Azobisisobutyronitrile (AIBN) (Aldrich)

2, 2'-Azobisisobutyronitrile was recrystallized from ethanol.

1, 1-Diphenylethene (DPE) (Aldrich)

1, 1-diphenylethene was distilled before use.

Diphenyliodonium hexafluorophosphate⁸ ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) (Fluka)

Symmetrical diarylsulphonium salts are obtained by a reaction of aromatic compounds with potassium iodate in the presence of sulfuric acid and acetic anhydride [96, 97]. Since the products possess nucleophilic counter anions, the anion has to be changed for a less nucleophilic one.

N-ethoxy-2-methyl pyridinium hexafluorophosphate ($\text{EMP}^+\text{PF}_6^-$)

N-ethoxy-2-methyl pyridinium salts are obtained with relatively high yields by a reaction of pyridine N-oxides with a triethyloxonium salt in methylene chloride or chloroform [98].

3.1.2 Monomers

Cyclohexene oxide (CHO) (Fluka)

Cyclic monomer was vacuum distilled from calcium hydride (CaH_2) before use.

Methyl methacrylate (MMA) (Aldrich)

Methyl methacrylate was washed with 5% aq. NaOH solution, dried over CaCl₂ and vacuum distilled from CaH₂ prior to use.

Styrene (St) (Fluka)

Styrene was washed with aq. 5% NaOH to remove inhibitors, then water, dried with CaH₂ several hours and distilled under reduced pressure (50 °C / 25 mm Hg). Middle fraction was collected and immediately used.

3.1.3 Solvents

Dichloromethane (CH₂Cl₂) (Lab-scan)

Methylene chloride was used as solvent for dissolving polymers. It was first washed with conc. H₂SO₄ until the acid layer remained colorless, then washed with water, aq. %5 NaOH and then water again. It was pre-dried with CaCl₂ and distilled from CaH₂.

N-hexane (Aldrich)

N-hexane was used without further purification.

Methanol (Technical)

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

3.2 Equipments

3.2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

¹H-NMR analysis was recorded on a Bruker 250 MHz NMR Spectrometer.

3.2.2 Infrared Spectrophotometer (IR)

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

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3.2.3 Gel Permeation Chromatography (G.P.C)

Gel permeation chromatography (G.P.C) analyses were performed with a set up consisting of an Agilent 1100 RI apparatus equipped with three Waters ultrastyrigel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min and a refractive index detector. Molecular weights were calculated by using monodisperse polystyrene standards.

3.3 Preparation Methods

3.3.1. Homopolymerization of St or MMA by DPE Method

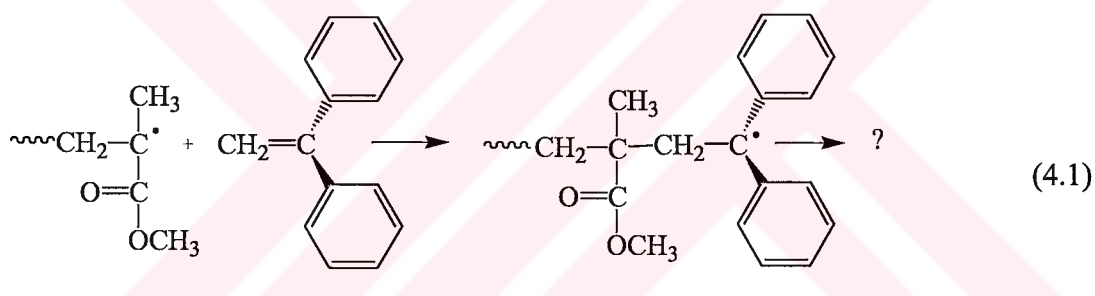
The reported procedure was followed [25]. Bulk monomers (St or MMA) containing a known amount of AIBN and DPE in glass tubes were degassed by bubbling dry nitrogen. The tubes were then immersed in a constant-temperature bath at 80 °C. At the end of given time the reaction mixtures were cooled to room temperature and poured into a 10-fold excess methanol. The precipitated polymers were then dried in a vacuum oven. The conversion of the polymerization was determined gravimetrically.

3.3.2. Promoted Cationic Block Copolymerization

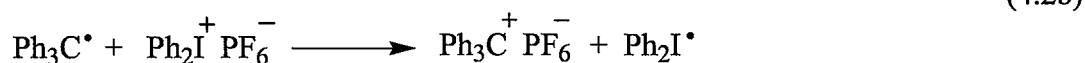
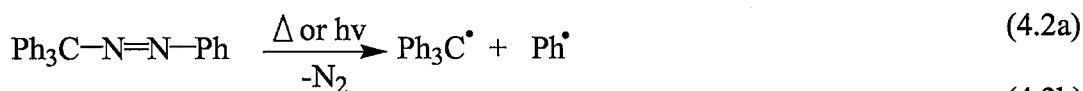
Appropriate solutions of CHO in dichloromethane containing above obtained polystyrene or poly (methyl methacrylate) and onium salts were degassed as described above and heated in a bath at 80 °C. The block copolymers formed during reaction were separated from the reaction mixture by precipitation into methanol and dried in a vacuum oven. A conversion of CHO was determined gravimetrically after subtracting the weight of the precursor polymers. Homopoly (cyclohexene oxide) was extracted with n-hexane.

4. RESULTS and DISCUSSION

Contrary to anionic [99–101] and cationic [102–108] polymerizations, the role of 1, 1-diphenylethene (DPE) in radical polymerization is still not yet understood in all details today. 1, 1-diphenylethene is well known for its inability to undergo homopolymerization [109], but it can participate in radical copolymerizations [110–119]. The participation of DPE in radical polymerization leads to the formation of stable DPE radicals (Scheme 4.1) by resonance stabilization of the radical by the two phenyl groups and a strong steric hindrance for the addition of any other monomer. Thus, DPE has drastic effects in radical polymerization.



In order to understand the influence of monomer structure and radical stability on free radical copolymerization, DPE was frequently chosen as a model monomer. Copolymerizations of DPE with various vinyl and acrylic monomers like acrylonitrile (AN) [110, 120], methacrylonitrile (MAN) [110, 120], methyl acrylate (MA) [116], methyl methacrylate (MMA) [116], acrylamide [120], styrene [112] and substituted butadienes [116] have been studied. The calculated reactivity ratios of DPE with almost all comonomers confirmed the impossibility of DPE to homopolymerize. In case of copolymerization with AN, MAN and acrylamide, the reactivity ratios of DPE are very close to zero [116, 112]. These results confirm that DPE acts as retarder during radical copolymerizations and hence, DPE was also frequently used in radical polymerization in order to control the molecular weight [118, 121].



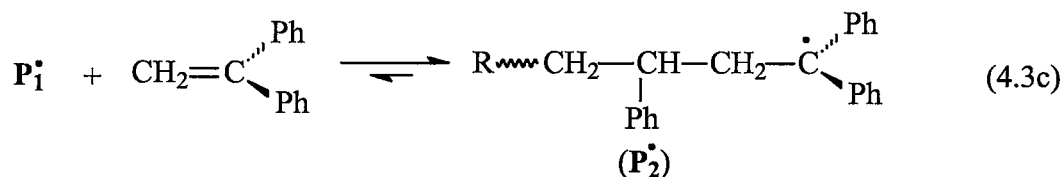
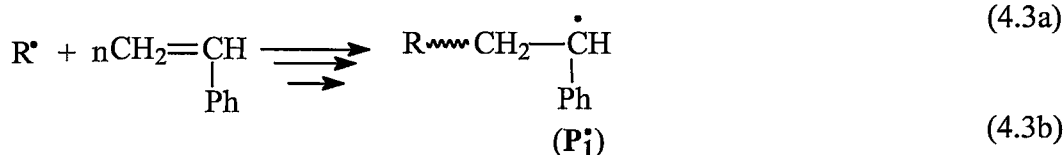
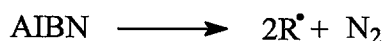
Poly (styrene) and poly (methyl methacrylate) possessing diphenylethyl units in the main chain were prepared by taking advantage of controlled radical polymerization using DPE as an additive. The results are shown in Table 1. As can be seen, polymers with relatively low polydispersity ($1.26 < M_w/M_n < 1.5$) were obtained. It is known [122] that triphenyl methyl radicals, produced thermally or photochemically from the related azo initiator (reaction 4.2a), may readily be oxidized to the corresponding carbocations by onium salts having suitable redox potentials (reaction 4.2b).

Table 4.1. Polymerization^{a)} of St and MMA in bulk in the presence of DPE

Monomer	Time (min)	Conversion (%)	^{b)} $M_n \times 10^{-3}$	M_w/M_n	Polymer
St	100	25	16.2	1.50	PSt-1
St	200	35	19.6	1.41	PSt-2
St	300	44	21.6	1.39	PSt-3
MMA	100	23	19.1	1.44	PMMA-1
MMA	200	35	21.9	1.37	PMMA-2
MMA	300	38	24.6	1.26	PMMA-3

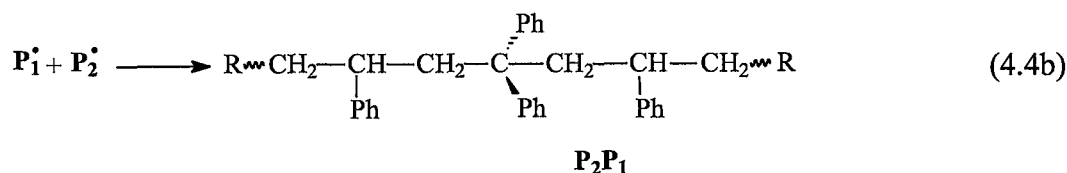
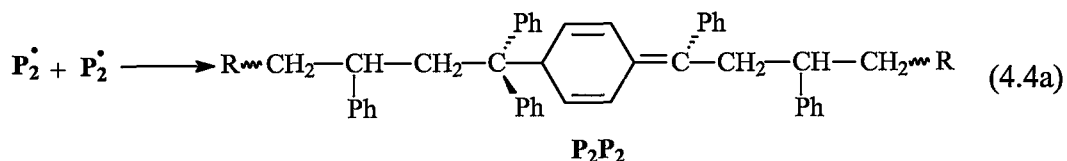
^{a)}Temp = 80 °C, [AIBN]/[DPE]: 1/1, [AIBN] = 2.61 x 10⁻² mol/L, [DPE] = 2.61 x 10⁻² mol/L

^{b)}Determined by GPC

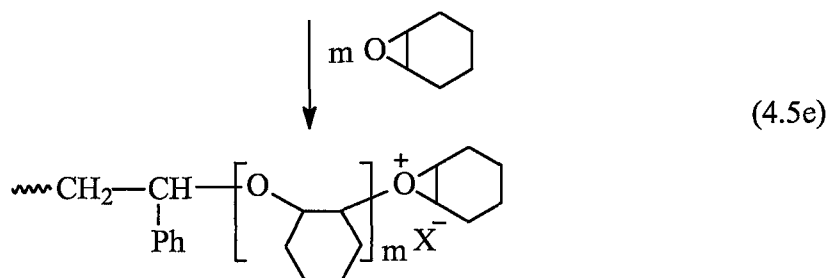
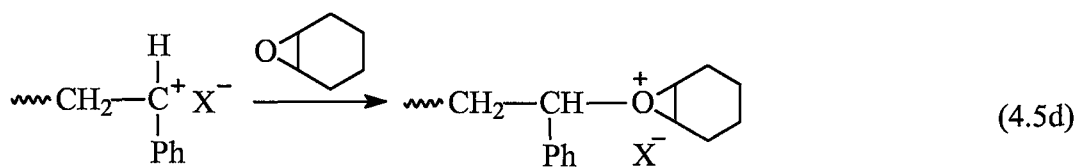
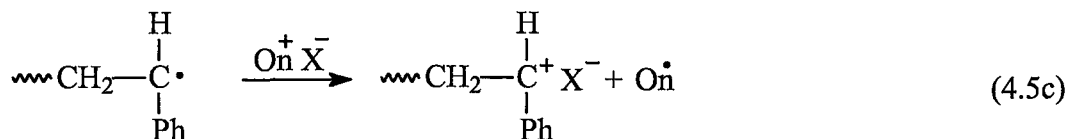
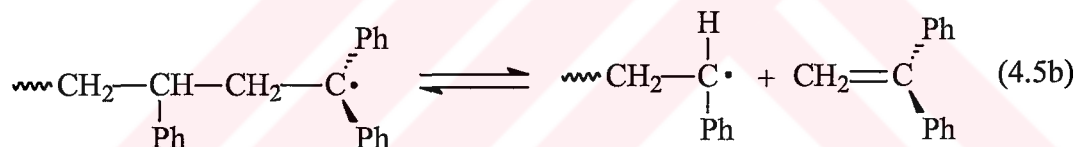
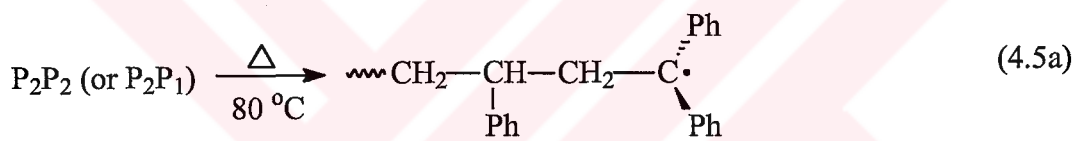


The first step is the formation of an active chain end P_1^\bullet common radical initiation (4.3a, b). P_1^\bullet reacts with a DPE molecule under formation of a stable diphenylmethyl

radical P_2^\bullet (4.3c). The final dormant species is built by combination of two P_2 radicals to a tetraphenylethane unit (4.4).



Since polymers obtained by the DPE method possess thermolabile diphenylethyl units in the main chain (structures P_2P_1 and P_2P_2), upon heating structurally similar polymeric alkylidiphenylmethyl radicals are expected to be formed (reaction 4.5a, b).



If the thermolysis is carried out in the presence of CHO and an onium salt such as $\text{Ph}_2\text{I}^+\text{PF}_6^-$ or $\text{EMP}^+\text{PF}_6^-$, the polymer attached diphenylmethyl radical is converted to the initiating cations to generate block copolymers according to the reactions (4.5 c, d and e). Typical results concerning block copolymerization via promoted cationic polymerization are presented in Table 2. It is interesting to note that the molecular weights of the block copolymers are usually lower than those of the precursor polymers. This is expected since the thermolysis of the initial polymers causes scission and polymeric radicals with shorter chain length are formed. The chain growth of the second block proceeds from the short chain cationic centers formed as a result of radical to cation transformation. A different situation was encountered in the case of free radical blocking reactions. In this case, complex scission and coupling reaction result in the formation of block copolymers with higher molecular weights. Termination via combination may also contribute to this observation.

Table 4.2. Block Copolymerization^{a)} of PSt and PMMA with CHO in CH_2Cl_2

Prepolymer (g/L)	Onium Salt (5×10^{-3} mol/L)	Time (h)	Con. (%)	^{b)} $M_n \times 10^{-3}$	M_w/M_n	Composition of block copolymers PCHO (mol %)
PSt-1 (0,15)	$\text{Ph}_2\text{I}^+ \text{PF}_6^-$	7	13.52	13.7	2.08	12.3
PSt-1 (0,15)	$\text{EMP}^+ \text{PF}_6^-$	7	17.50	18.0	1.61	12.3
PSt-1 (0,15)	$\text{EMP}^+ \text{PF}_6^-$	12	28.62	13.7	1.81	29.3
PMMA-1 (0,07)	$\text{Ph}_2\text{I}^+ \text{PF}_6^-$	7	3.70	23.2	1.33	53.3
PMMA-1 (0,07)	$\text{EMP}^+ \text{PF}_6^-$	7	6.80	12.8	1.78	53.3
PMMA-3 (0,07)	$\text{EMP}^+ \text{PF}_6^-$	7	5.80	14.4	1.93	52.2

^{a)} $[\text{CHO}] = 4,93 \text{ mol/L}$, Temp: 80 °C,

^{b)}Determined by GPC

The block copolymer structure was assigned by means of IR and NMR spectral measurements. IR spectra of purified block copolymers show characteristic ether bond of the PCHO segment at 1090 cm^{-1} in addition to the respective PSt (Ar-H and C-H $2900\text{-}3100\text{ cm}^{-1}$, C-C $1400\text{-}1600\text{ cm}^{-1}$, C-H $600\text{-}1000\text{ cm}^{-1}$) and PMMA (carbonyl group 1750 cm^{-1}) bands (Figures 4.1 and 4.2).

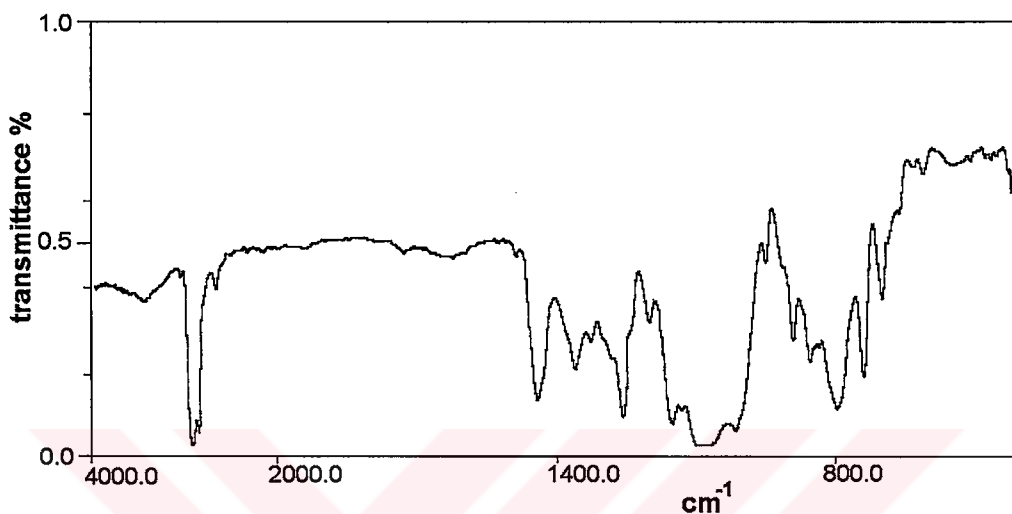


Figure 4.1. IR spectra of the PSt-*b*-PCHO block copolymer

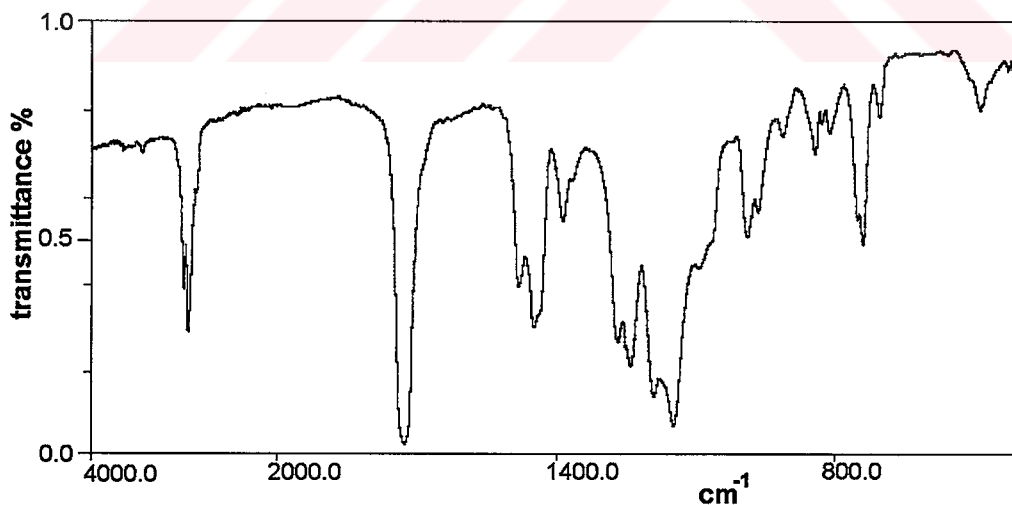


Figure 4.2. IR spectra of the PMMA-*b*-PCHO block copolymer

The NMR spectra of the block copolymers display signals of both segments. However, the spectrum of the block copolymer of Pst-*b*-PCHO and PMMA-*b*-PCHO clearly show resonances characteristic of homopoly(styrene), homopoly(cyclohexene oxide) and homopoly (methyl methacrylate), at 7.21, 3.41 and 3.5 ppm, respectively (Figure 4.3 and 4.4).

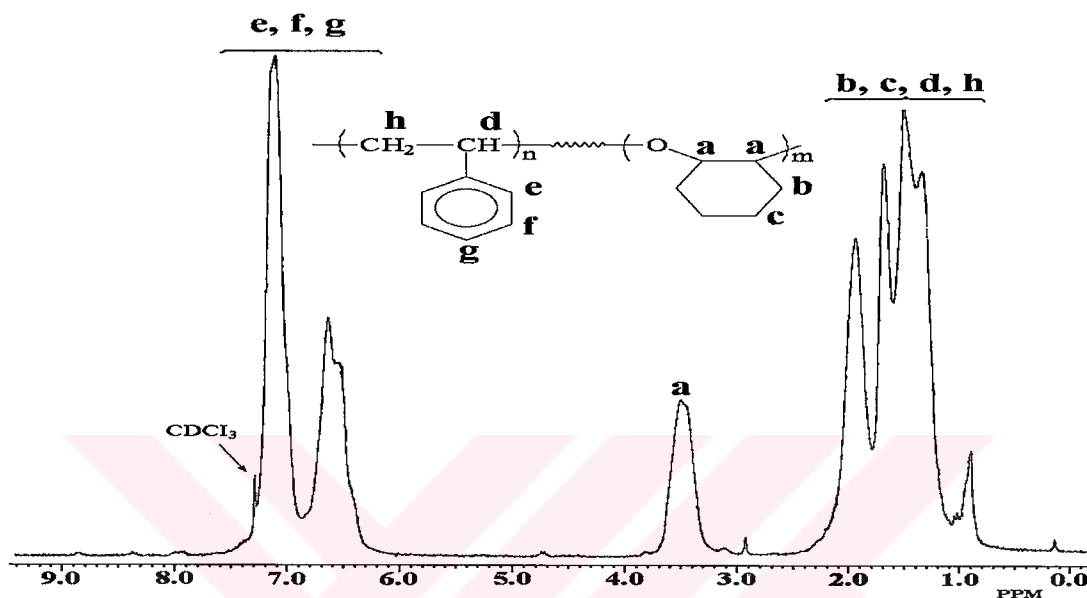


Figure 4.3. ¹H-NMR spectrum of PSt-*b*-PCHO block copolymer in CDCl₃.

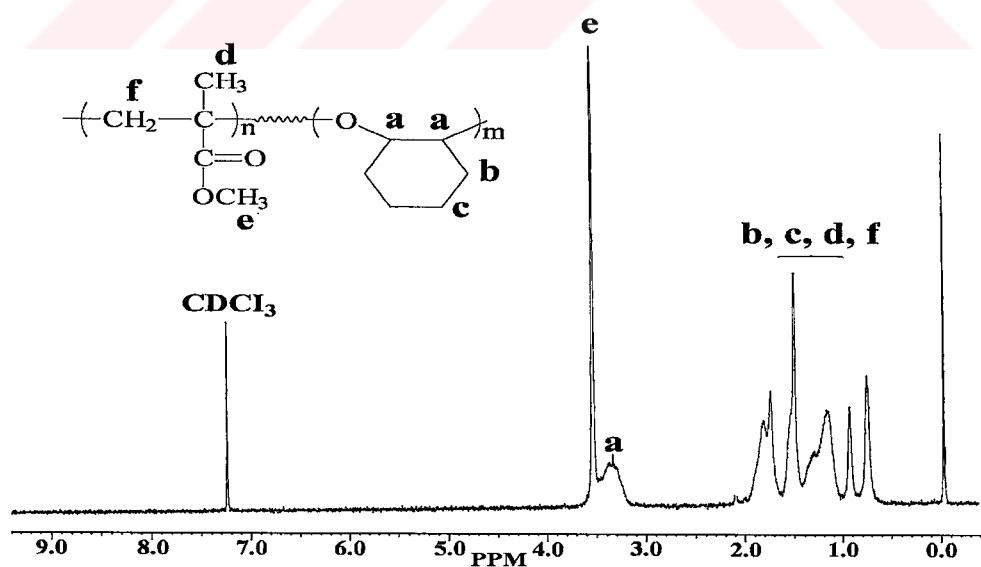


Figure 4.4. ¹H-NMR spectrum of PMMA-*b*-PCHO block copolymer in CDCl₃.

Moreover, dual detection by refractive index and UV measurements provides clear evidence for the successful block copolymerization. As can be seen from figure 4.5, gpc traces of PCHO-PSt block copolymer measured by UV ($\lambda=274$ nm) and refractive index appear at the same elution volume. The GPC traces of the polymerization products are shown in Figure 4.6 The trace **a** as for the prepolymer , the traces **b** and **c** are block copolymer and mixture , respectively.

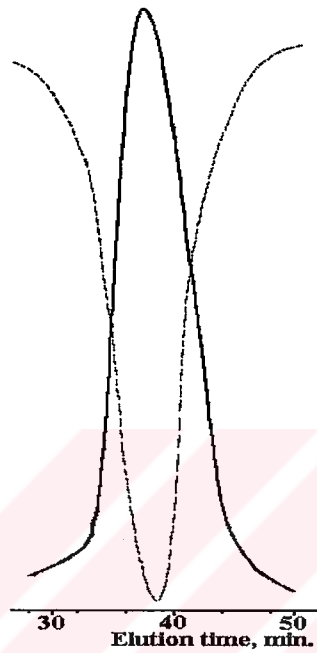


Figure 4.5. GPC trace of PSt-*b*-PCHO block copolymer: refractive index signal (-) and UV signal at $\lambda=274$ nm (--)

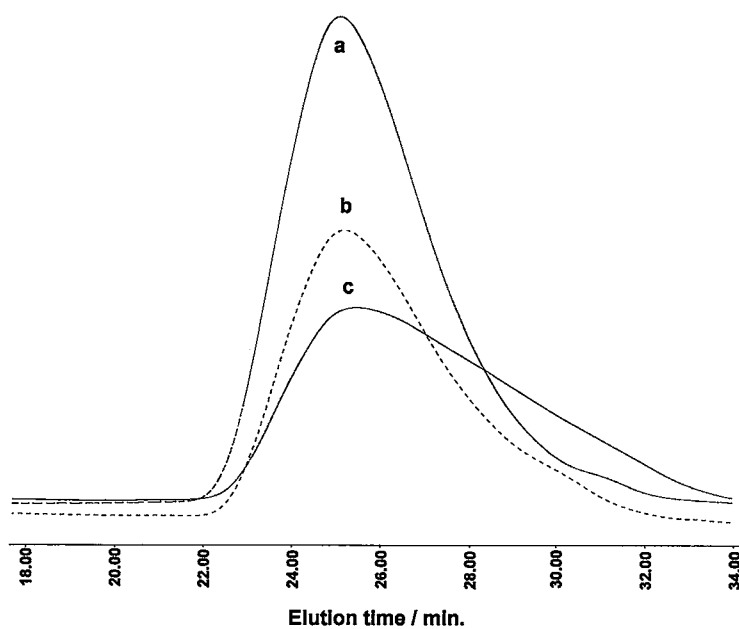


Figure 4.6. GPC traces of the prepolymer (a), block copolymer (b) and mixture (c).

In conclusion, although additional investigation is certainly needed to explore the generality of the method described, it is clear that the combination of free radical polymerization by using DPE and free radical promoted cationic polymerization provides a versatile route for the preparation of block copolymers with different polymerizability.



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1. Block Copolymers by Using Combined Controlled Radical and Radical Promoted Cationic Polymerization Methods
Taşdelen, M. A., Degirmenci, M., Yagci, Y. and Nuyken, O., 2002.
Polym. Bull.

Scientific Activities

2002- 17th National Chemistry Symposia
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