ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF BLOCK COPOLYMERS BY COMBINATION OF PHOTOINDUCED AND ATOM TRANSFER RADICAL POLYMERIZATION ROUTES

M.Sc. Thesis by

İrem EREL

515991031

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Supervisor (Chairman) : Prof. Dr. Yusuf YAĞCI

Co-Supervisor : Assoc. Prof. Dr. İ. Ersin SERHATLI

Members of the Examining Committee : Prof. Dr. Yusuf YAĞCI (İ.T.Ü.)
Assoc. Prof. Dr. İ. Ersin SERHATLI (İ.T.Ü.)
Dr. Ioan CIANGA (Petru Poni Institute)

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FOTOPOLİMERİZASYON VE ATOM TRANSFER RADİKAL POLİMERİZASYON YÖNTEMLERİNİN BİRLEŞTİRİLMESİ İLE BLOK KOPOLİMER SENTEZİ

YÜKSEK LİSANS TEZİ
İrem EREL
515991031

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Tez Danışmanı : Prof. Dr. Yusuf YAĞCI
Ortak Tez Danışmanı : Doç. Dr. İ. Ersin SERHATLI

Diğer Jüri Üyeleri : Dr. Ioan CIANGA (Petru Poni Enstitüsü)

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LIST OF ABBREVIATIONS

UV : Ultra violet
^{1}H-NMR : Proton Nuclear Magnetic Resonance Spectrospin
GPC : Gel Permeation Chromotography
GC : Gas Chromotography
ATRP : Atom Transfer Radical Polymerization
MMA : Methyl methacrylate
PMMA : Poly(methyl methacrylate)
Poly(MMA-b-St) : Block copolymer of methyl methacrylate and styrene
DMEA : N,N Dimethylethanolamine
St : Styrene
ACPA : 4,4' Azobis (4-cyanopentanoyl chloride)
ACPC : 4,4' Azobis (4-cyanopentanoic acid)
ACPO : 4,4' Azobis (4-cyanopentanoyl)
BDC : Benzyl-N,N Diethyl dithiocarbamate
XDC : Xsilen bis N,N Diethyl dithiocarbamate
THF : Tetrahydrofuran

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SYNTHESIS OF BLOCK COPOLYMERS BY PHOTOINDUCED AND ATOM TRANSFER RADICAL POLYMERIZATION ROUTES

SUMMARY

Block copolymers of methyl methacrylate (MMA) and styrene (St) were synthesized by combining photopolymerization and atom transfer radical polymerization (ATRP) methods.

The bromine ended poly(methyl methacryalate) (PMMA) which was then used as initiating system in ATRP was synthesized in two steps. In the first step; the MMA was photopolymerized in the presence of N,N-Dimethylethanolamine (DMEA) and benzophenone as an initiating system and the polymers containing final –OH groups, capable to participate in esterification reactions, were obtained. In the second step; these –OH functionalized polymers were esterified by 2-bromopropionyl bromide in the presence of triethylamine and bromine ended PMMA was synthesized.

The bromine functionalized polymers were used as initiators in ATRP of St carried out in bulk in conjuction with CuBr/2,2'-bipyridine as catalytic system providing block copolymers with a narrow polydispersity.

The unimodal shapes of the traces obtained at GPC and the ^{1}H-NMR spectrum prove that the copolymers were obtained. Almost the same values for copolymer compositions were obtained again from GPC and the ^{1}H-NMR analyses.

The good correlation between determined molecular weight with the calculated one, as well as the kinetic study indicates a fully controlled/living radical polymerization with obtaining block copolymers with narrow polydispersity.

FOTOPOLİMERİZASYON VE ATOM TRANSFER RADİKAL POLİMERİZASYON YÖNTEMLERİNİN BİRLEŞTİRİLMESİ İLE BLOK KOPOLİMER SENTEZİ

ÖZET

Bu çalışmada; fotopolimerizasyon ve atom transfer radikal polimerizasyonu (ATRP) yöntemleri kullanılarak metil metakrilat (MMA) ve stiren (St) kopolimerleri sentezlenmiştir.

ATRP'de makrobaşlatıcı olarak kullanılan –Br uç gruplu polimetilmetakrilatların (PMMA) sentezi 2 aşamada gerçekleştirilmiştir. İlk aşamada, farklı konsantrasyonlarda N,N-Dimethylethanolamine (DMEA) ve benzofenon başlatıcı sistemi kullanılarak farklı molekül ağırlıklarına sahip –OH uç gruplu PMMA sentezlenmiştir. İkinci aşamada ise, bu –OH fonksiyonel grubuna sahip polimerler 2-bromopropionil bromür ile trietilamin varlığında esterleştirilerek –Br uç gruplu PMMA elde edilmiştir.

Sentezlenen bu –Br uç gruplu polimerler, St'nin atom transfer radical polimerizasyonunda CuBr/2,2'-bipiridin katalizörleri eşliğinde makrobaşlatıcı olarak kullanılmıştır.

Deneyler neticesinde, GPC ve ^{1}H-NMR sonuçlarına dayanarak kopolimerler elde edildiği ispatlanmıştır. Ayrıca GPC ve ^{1}H-NMR sonuçlarından hesaplanan kopolimer bileşim değerlerinin birbirine yakınlığı, hedeflenen polimerlerin başarıyla sentezlendiğini desteklemiştir.

Teorik olarak hesaplanan molekül ağırlıklarının deney sonuçları ile uyumluluğu, polimerizasyon esnasında yapılan kinetik çalışma ve dar polidispersiteye sahip kopolimerlerin elde edilmesi çalışmalarımızda yaşayan/kontrollü polimerizasyonun yürüdüğünü göstermektedir.

1. INTRODUCTION

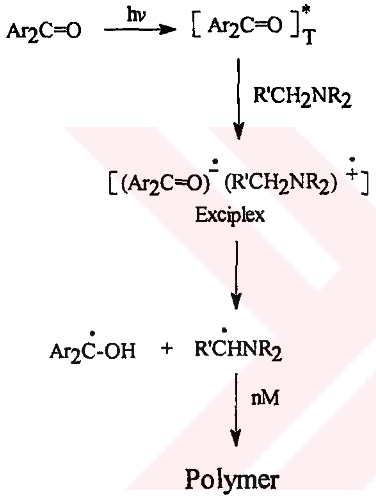
Block copolymers have become increasingly important in recent years. This importance is due to the fact that their special chemical structure yields unusual physical properties. Block copolymers are applied in various fields, they are used as surfactants, adhesives, fibres, thermoplastics, and thermoplastic elastomers.

A number of different techniques for the preparation of block copolymers have been developed. Among them the transformation polymerization is an elegant method which allows to combine various polymerization mechanisms. By using this way, many monomers with different chemical structure can be polymerized to yield block copolymers with novel properties. Many different modes of transformation polymerization have been reported and reviewed.

Free radical polymerization has several advantages over other polymerization methods, including less sensitivity toward impurities present in the reaction mixture and applicability to a wide range of monomers with various functional groups. Therefore, free radical polymerization is usually used as one of the polymerization mechanism of the transformation polymerization. However, there are numerous reports showing that a combination of two radically polymerized monomers to a block copolymer using radical-radical transformation polymerization.

In these examples, mostly initiators carrying two different radical forming sites were used as transformation agents, i.e., initiators containing groups of different thermal activity, thermal and photochemical activity, and redox and thermal activity. However, block copolymers prepared in such a manner were ill-defined and generally homopolymer formation was unavoidable. In recent years several methods for controlled polymerization such as atom transfer radical polymerization (ATRP), stable radical mediated radical polymerization (SFRP) and radical addition-fragmentation (RAFT) have been reported. More recently, several studies concerning combination of conventional radical polymerization with controlled radical polymerization methods have been reported. For example, appropriate bifunctional initiators were used for the preparation of block copolymers of styrene with various vinyl monomers using conventional radical polymerization and ATRP.

Photoinitiated polymerizations can also be used in transformation polymerization. Low temperature conditions, usually room temperature, prevents the side reaction leading to the formation of homopolymers and high block yields are attained. The types of photoinitiated free radical polymerization used in transformation polymerization include α-cleavage and bimolecular photoinitiating systems. The most recognized and practically used bimolecular free radical initiating system is the reduction of aromatic carbonyls, usually ketones, by a large variety of electron donor molecules, particularly amines. The general mechanism is represented below.



Selective and effiecient formation of block and graft copolymers may be accomplished by using such initiating system.

This study concerns about the combination of photoinduced and atom transfer radical polymerization (ATRP) routes for the synthesis of the block copolymer of methyl methacrylate and styrene [poly(MMA-b-St)]. The methyl methacrylate (MMA) which was photopolymerized by using DMEA (N,N-Dimethyl ethanolamine) and benzophenone initiating system, was then esterified with 2-bromo propionyl bromide. This bromine ended poly(methyl methacrylate) (PMMA) was used as macroinitiator after isolation and purification for the ATRP of styrene (St). By using ATRP, we obtained block copolymers of MMA and St with narrow polydispersity.

2. THEORETICAL PART

2.1 Free Radical Polymerization

2.1.1 Conventional Free Radical Polymerization

Free radical polymerizations are initiated by radicals and propagated by macroradicals. These radicals exhibit an unpaired electron. Traditionally, the free radical systems are characterized by 3 main steps: [1]

- Initiation
- Propagation
- Termination

2.1.1.1 Initiation:

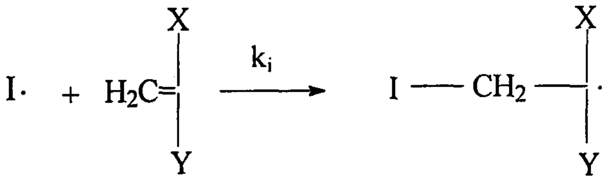
Initiating radicals are rarely formed by monomers themselves but rather thermally, electrochemically or photochemically from deliberately added initiators.

The initiation consists of two steps in a free radical polymerization:

1. A dissociation of the initiator to form two radical species.

$$\text{Initiator} \xrightarrow{k_d} 2\,\text{I}\cdot \qquad (2.1)$$

2. Addition of a single monomer molecule to the initiating radical (association step)



$$\text{I}\cdot + \text{H}_2\text{C}{=}\text{C}(\text{X})(\text{Y}) \xrightarrow{k_i} \text{I}-\text{CH}_2-\text{C}(\text{X})(\text{Y})\cdot \qquad (2.2)$$

k_d and k_i are the rate constants of decomposition and initiation steps.

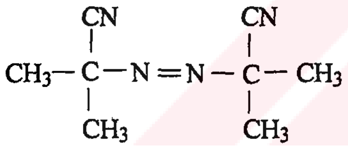
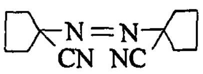
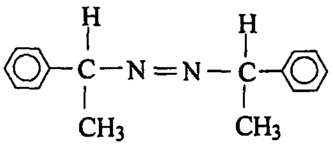
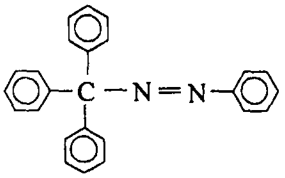
Initiation can be grouped into 3 as thermal initiation, initiation via electron transfer redox initiating systems and photo initiation. [1-2]

a) Thermal Initiation:

Thermolabile initiators are usually employed in a temperature range between 50°C and 140°C.In order to have high initiation rates, the activation energy of thermal initiators has to be on the order of 120-170kJ mol^{-1}.This activation energy brings about a strong temperature dependence of the dissociation, which is reasonable because initiators should have good storage stability at room temperature but produce radicals at slightly elevated temperatures.There are only a few functional groups meeting these demands. Of practical importance are especially azo compounds and peroxides. [3]

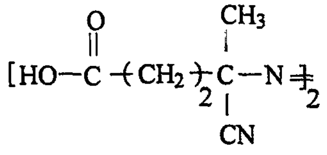
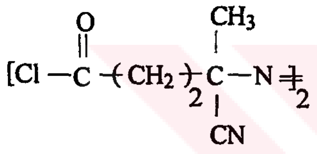
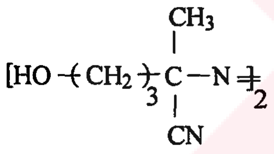
- **Azo Initiators**

Table 2.1. Decomposition Characteristics of Some Selected Azo Compounds

Azo Compound	E$_a$ kJ mol^{-1}	K$_d$ s^{-1}	Ref.
	142	1,7x10^{-4} (80°C)	[4]
	141	7,4x10^{-5} (80°C)	[5]
	136	5,4x10^{-5} (100°C)	[6]
	122	3,5x10^{-4} (55°C)	[7,8]

For converting these initiators into macroinitiators into, diamines, glycols or diisocyanates are often used. Block copolymers of amide and vinyl monomer blocks are easily produced when these macroinitiators are heated in the presence of a second monomer. [3]

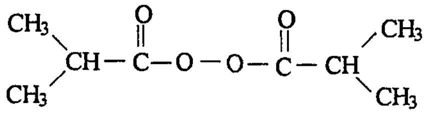
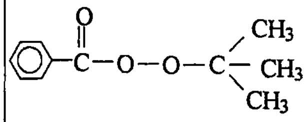
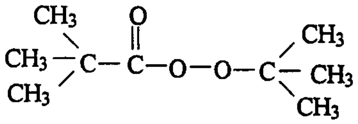
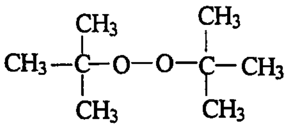
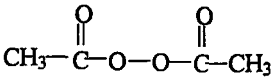
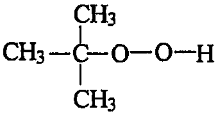
Table 2.2. Bifunctional Azo Compounds Used Frequently in Polycondensation and Addition Reactions

Formula	abbreviation	Ref. Synthesis
 $[HO-\overset{O}{\overset{\Vert}{C}}-(CH_2)_2-\underset{CN}{\overset{CH_3}{C}}-N=]_2$	ACPA	[9]
 $[Cl-\overset{O}{\overset{\Vert}{C}}-(CH_2)_2-\underset{CN}{\overset{CH_3}{C}}-N=]_2$	ACPC	[10,11]
 $[HO-(CH_2)_3-\underset{CN}{\overset{CH_3}{C}}-N=]_2$	ACPO	[12]

- **Peroxide Initiators**

The ease of radical formation is considerably influenced by the substituents at the peroxide group. For practical applicaitons, diacyl peroxides are used foremost; alkyl hydroperoxides and their esters, peroxyesters, and the salts of peracids are also of importance. In the case of peroxy initiators, there is often a considerable influence of solvent on the decomposition kinetics. [3]

Table 2.3. Selected Peroxy Compounds as Thermal Free-Radical Initiators:

Peroxy Compound	**Ref.**	**Peroxy Compound**	**Ref.**
	[13]		[14]
	[14]	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$	[15]
 $CH_3-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-CH_3$	[14]	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-H$	[16]

b) Radical Formation via Electron Transfer-Redox Initiating Systems

Redox initiators generate initiating radicals by the reaction of a reducing agent with an oxidizing agent. Such redox reactions require only a little activation energy. Oxidation agents, such as hydroperoxides or halides, in conjuction with electron donors, like metal ions, may form radicals via electron transfer:

$$H\text{-}O\text{-}O\text{-}H + Fe^{+2} \longrightarrow H\dot{O} + OH^{-} + Fe^{+3} \qquad (2.3)$$

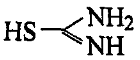
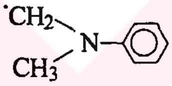
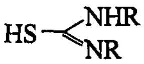
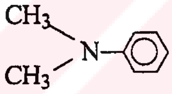
$$Fe^{+2} \longrightarrow Fe^{+3} + e^{-} \text{ (oxidation)} \qquad (2.4)$$

$$H\text{-}O\text{-}O\text{-}H + e^{-} \longrightarrow H\dot{O} + OH^{-} \text{ (reduction)} \qquad (2.5)$$

The initiator systems used in this type of polymezation are of two components: an oxidizing agent and a reducing agent. If hydrogen peroxides are used as the oxidizing agent and a reducing agent, one hydroxyl radical and one hydroxyl ion are formed, in contrast to direct thermal initiation where two hydroxyl radicals are generated. The hydroxyl ion formed in redox systems is stabilized by solvation. As a result, the thermal activation energy is relatively low, usually 60-80 kJ mol^{-1} lower than for the direct thermal activation.

Therefore, using redox systems, polymerizations can be conducted at low temperatures,which is advantageous in terms of energy saving and prevention of thermally induced termination depolymerization. [3]

Table 2.4. Some Iniating Systems in Redox Initiation

Oxidizing Agent	Initiating Radical	Reducing Agent	Ref.
H-O-O-H	HO·	Fe^{+2} NO_3^- NH_3 HSO_3^-/SO_3^{2-} 	[17] [18] [19] [20] [21]
R-O-O-R	RO· RO· + 	Fe^{+2}  	[22] [23] [24]

c)Photo Initiation:

Initiating radicals are formed by external stimulation such as light, heat, gamma-radiation and redox processes. Light induced photopolymerization has several advantages over the other methods. These low temperature conditions, usually room temperature, and controllability via selective wavelength irradiation and light intensity. Moreover, light can be focused onto a articular site, thus polymer can be formed only at desired places.

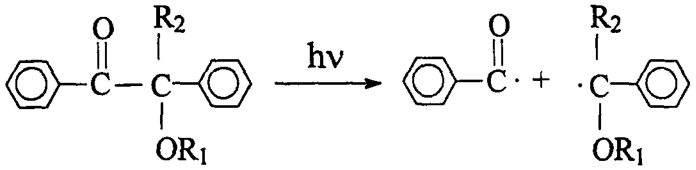
Photoinitiators for radical polymerization may be classed in two classes:

1.those which undergo intramolecular bond cleavage, notably acetophenone and derivatives, and

2.those which undergo intermolecular H-abstraction from a H-donor, benzophenone and derivatives.

1. **Intramolecular Bond Cleavage**

An important criterion for photoinitiators in this class is the presence of a bond with a dissociation energy lower than the excitation energy of the reactive excited state, on the other hand sufficiently high to provide thermal stability. Benzoin derivatives are the first class of photoinitiators utilized in photopolymerization applications. These compounds undergo photo-cleavage to produce benzoyl and hydroxybenzyl radicals as shown below:



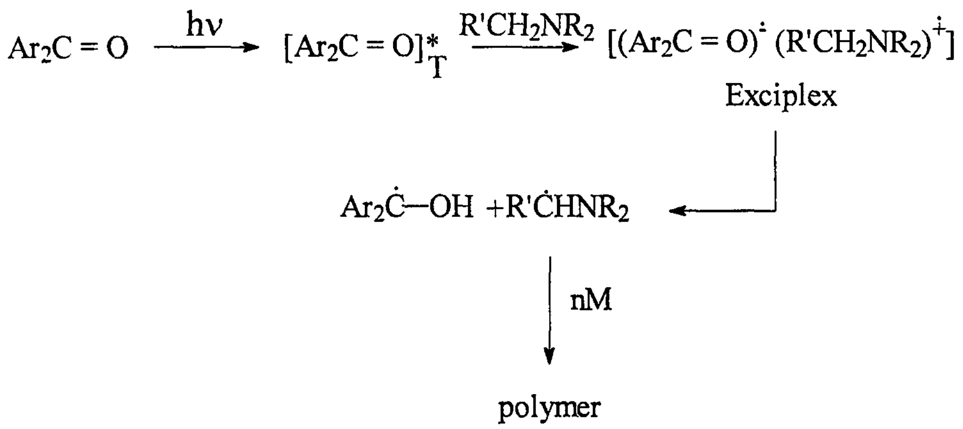
(2.6)

R_1 = H,Alkyl
R_2 = H,Alkyl

Although at different rated depending on the structure of the monomers employed, both radicals are capable of initiating free radical polymerization.

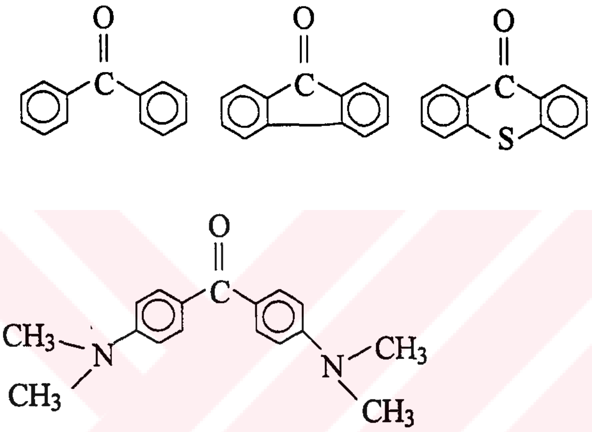
2. **Intermolecular H-abstraction**

Photoinitiators of this type include benzophenone and derivatives such as Michler's ketone, thioxanthones, 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 [25,26].



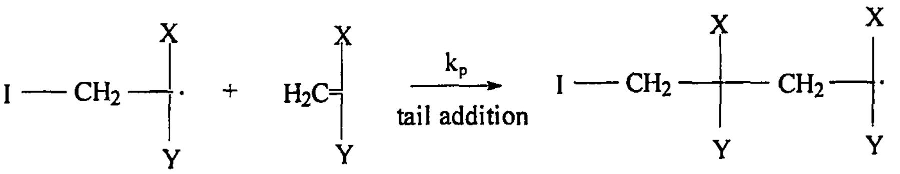
(2.7)

Ar$_2$C = O :



2.1.1.2 Propagation:

Propagation contains the growth of the monomer. By the successive of large numbers of monomers, it can be figured as shown below where k_p is the rate constant of propagation.

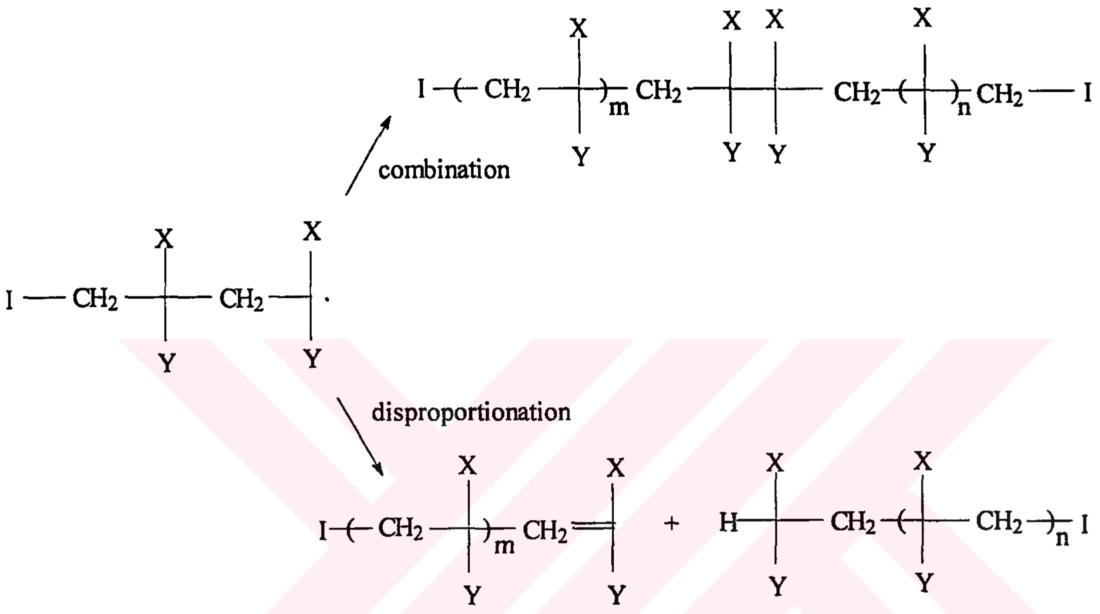


$$I-CH_2-\overset{X}{\underset{Y}{C}}\cdot + H_2C=\overset{X}{\underset{Y}{C}} \xrightarrow[\text{tail addition}]{k_p} I-CH_2-\overset{X}{\underset{Y}{C}}-CH_2-\overset{X}{\underset{Y}{C}}\cdot \qquad (2.8)$$

Propagation takes place very rapidly. The value of k_p for most monomers are in the range of $10^2 - 10^4$ liter/mole.sec. [1-2]

2.1.1.3 Termination

The propagating polymer chain stops growing and terminates.Two radicals react with each other by combination, or more rarely, by disproportionation in which hydrogen abstraction from one end to give two dead polymer chains, one is being an unsaturated and the other is saturated.



(2.9)

k_{tc} and k_{td} are the rate constants of termination by coupling and dispropotionation, respectively.

Typical termination rate consants are in the range of $10^6 - 10^8$ liter/mole.sec. [2]

2.1.2 Controlled Radical Polymerization

The term living polymerization was initially used to describe a chain polymerization in which chain breaking reactions were absent. In such an ideal system, after initiation is completed, chains only propagate and do not undergo transfer and termination. However, transfer and termination often occur in real systems. Thus, living polymerizations (no chain breaking reactions) and controlled polymerization (formation of well defined polymers) are two separate terms.

A controlled polymerization can be defined as a synthetic method for preparing polymers with predetermined molecular weights, low polydispersity and controlled functionality.

Transfer and termination are allowed in a controlled polymerization if their contribution is sufficiently reduced by the proper choice of the reaction conditions such that polymer structure is not affected. On the other hand, living polymerizations will lead to well defined polymers only if the following additional prerequisites are fullfilled:

-initiation is fast in comparison with propagation

-exchange between species of different reactivities is fast in comparison with propagation

-the rate of depropagation is low in comparison with propagation and the system is sufficiently homogeneous, in the sense of availability of active centers and mixing.

Well defined polymers may be formed in radical polymerization only if chains are relatively short and concentration of free radicals is low enough. There is apparent contradiction between these two requirements because usually a decrease of the concentration of radicals leads to higher molecular weights. However, the two conditions can be accommodated in systems with reversible deactivation of growing radicals. The controlled polymerization requires a low proportion of deactivated chains, which can be achieved by keeping molecular weights sufficiently low. This necessitates a relatively high concentration of the initiator or in other words, low $[M]_o$ / $[I]_o$ ratios. However, because termination is bimolecular, the contribution of termination becomes more significant at high $[I]_o$ when a large concentration of radicals, $[P\cdot]$ is generated. In order to solve the discrepancy between high $[I]_o$ and low [P·], it is necessary to establish an exchange between dormant and active species. The concentration of the dormant species can be equal to $[I]_o$ ($\approx[P\text{-}R]_o + [P\cdot]$), and radicals would be present at a very low stationary concentration. The covalent species P-R can reversibly and homolytically cleave to produce the growing radical P· capable of propagation and the dormant radical (scavenging radical) R· which ideally should react only with P· but not with monomer or itself to form inactive dimers. P· can react with M and R· but also with another P· , leading to termination. Because termination rate is proportional to $[P\cdot]^2$, and propagation rate to [P·], the contribution of termination and the proportion of deactivated chains increase with P·. This case is probably most frequently postulated in controlled radical polymerizations. As example of R· dithiocarbamate radicals, nitroxyl radicals and also bulky organic radicals such as triarylmethyl and substituted diarylmethyl species can be used. Another approach for controlled radical polymerization is to use persistent radical {P-X}· .

The persistent radical should only cleave homolytically to form P· and the specie X. X should be an inert compound capable only of reacting with P· (reversible deactivation of a growing radical with a non-radical species through the formation of a dormant persistent radical).

$$\{P\text{-}X\}\cdot \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P\cdot + X \tag{2.10}$$

X can be element of organic or organometallic species with an even number of electrons. Some success has been reported with group IIIA and VA elements such as aluminium and phosphorus as well as with organometallic derivatives of Co, Cr, and other transition metals. [27-28]

2.1.2.1 Iniferters

Disulfides are useful compounds in free radical polymerization of vinyl compounds. The S-S bond present in the molecule readily decomposes to form thinyl radicals, which act as both initiators and terminators. The disulfides are also used as chain transfer agents. These compounds are called iniferters by anomie to their roles in initiation, transfer and termination reactions.

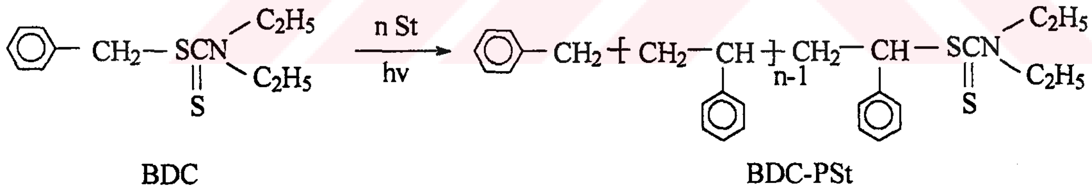
The concept of iniferter may be summarized as follows:

The polymer formation in the radical polymerization of a monomer (M) by an initiator (R-R') may be expressed as follows, by considering ordinary bimolecular termination [3]:

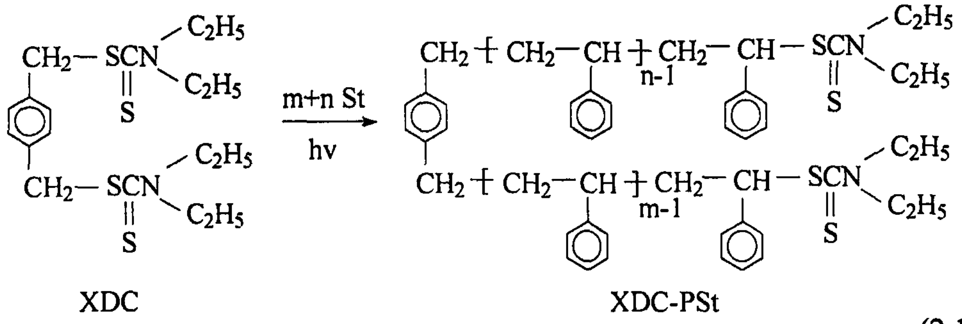
$$R\text{-}R' + xM \rightarrow R\text{-}(\text{-}M\text{-})_x\text{-}R' \qquad (2.11)$$

a) Photoiniferters:

BDC and XDC were used as monofunctional and bifunctional photoiniferters for the living polymerizaiton of styrene and methyl metacrylate, respectively [29]. Polymers having identical chain end groups were formed as follows:



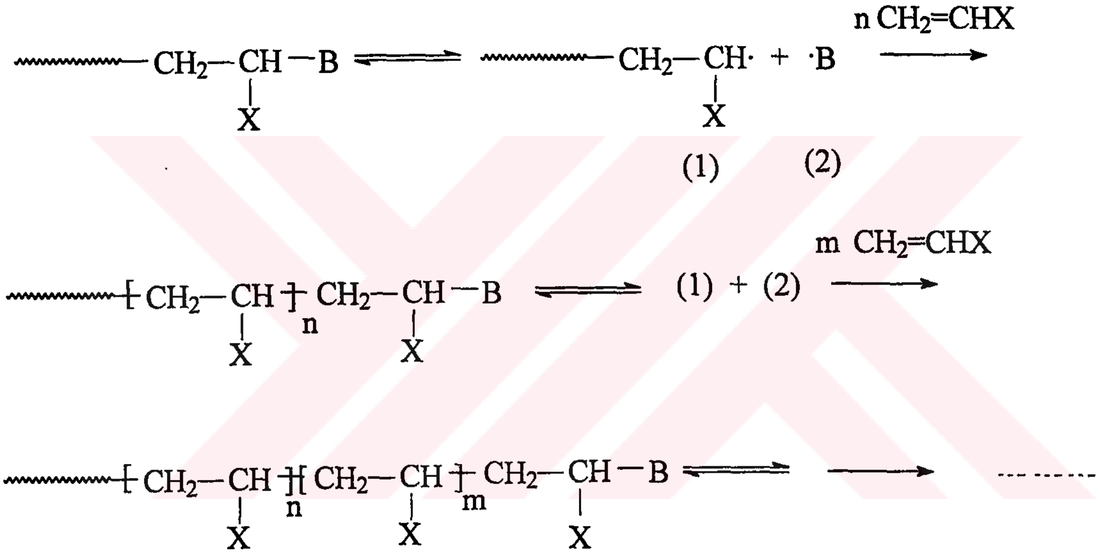
(2.12)



(2.13)

The yield and the molecular weight (M_n) of the polymers formed are observed to increase as a function of reaction time, indicating that the polymerization proceeds via a living radical mechanism in a homogeneous system [3].

To further confirm the living nature of these polymerization systems, Otsu [30] determined the number of end groups of the polymers produced in photopolymerization of St with BDC and XDC initiators. The number of $(C_2H_5)_2NCSS$- end groups per one polymer molecule are found to be almost constant (i.e., 1 and 2 for BDC and XDC, respectively), independent of the reaction time. The reaction mechanism is proposed as follows by Otsu [31]:



$$\sim\!CH_2-\underset{X}{CH}-B \rightleftharpoons \underset{(1)}{\sim\!CH_2-\underset{X}{CH}\cdot} + \underset{(2)}{\cdot B} \xrightarrow{n\,CH_2=CHX}$$

$$\sim\!\left[CH_2-\underset{X}{CH}\right]_n CH_2-\underset{X}{CH}-B \rightleftharpoons (1) + (2) \xrightarrow{m\,CH_2=CHX}$$

$$\sim\!\left[CH_2-\underset{X}{CH}\right]_n\left[CH_2-\underset{X}{CH}\right]_m CH_2-\underset{X}{CH}-B \rightleftharpoons \longrightarrow \cdots\cdots$$

(2.14)

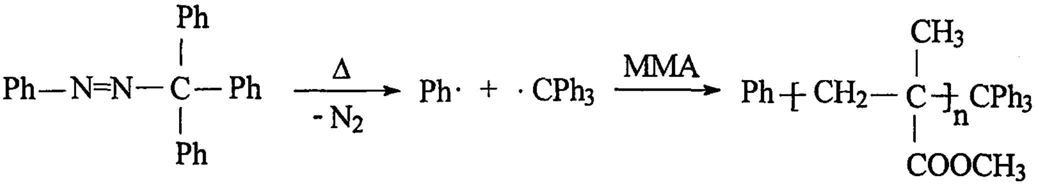
If the propagating chain end which can dissociate thermally or photochemically into a propagating radical (1) and a small radical (2), which must be stable enough noy to initiate a new polymer chain, and can recombine easily with a propagating radical anf if these dissociation, monomer addition, and recombination cycles are repeated, such a radical polymerization proceeds apparently via a living mechanism.

b) Ultrasonic Irradiation:

Liu and his group have reported on the polymerization of St, initiated by a polymeric iniferter such as diethyl-thiocarbamate-terminated PSt under ultrasonic irradiation [32]. The ultrasonic polymerization of St in the presence of polymeric iniferter proceeded via living radical polymerization mechanism in which initiating polymeric radicals were generated by ultrasonic cleavage of the terminal groups of the iniferter. The degree of polymerization (DP) increased as a function of the reaction time. During the ultrasonic irradiation, the weaker linkage between the polymer chain and the end group in the polymeric iniferter dissociated producing a propagating radical and a stable radical. Under continuous ultrasonic irradiation, these dissociation, propagation and recombination processes would be repeated.

c) Thermal and Redox Systems:

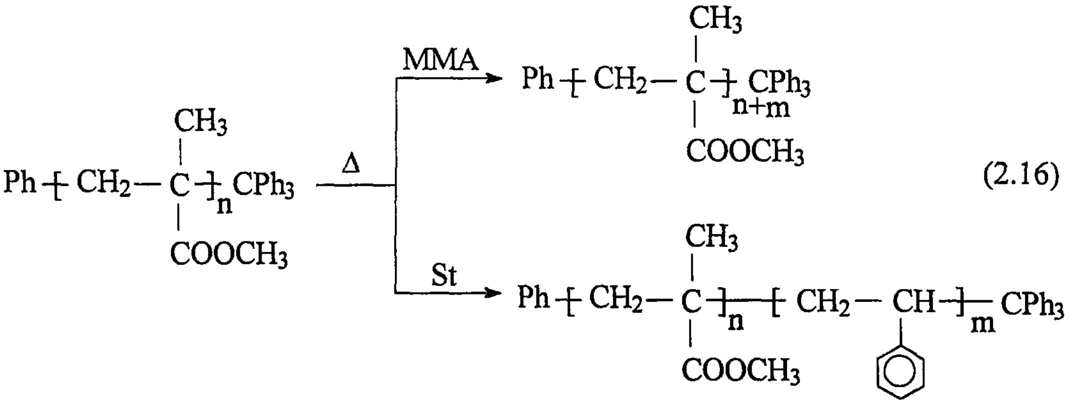
Otsu and Tazaki [33] showed that compounds of the phenylazotriphenylmethane type can act as a thermal iniferter, where the phenyl radical initiates the polymerization, and the triphenylmethyl (trityl) radical is a stable radical which couples with the growing chain, exhibiting a kind of living radical nature:



$$\mathrm{Ph{-}N{=}N{-}\underset{Ph}{\overset{Ph}{C}}{-}Ph} \xrightarrow[-\mathrm{N_2}]{\Delta} \mathrm{Ph\cdot} + \mathrm{\cdot CPh_3} \xrightarrow{\mathrm{MMA}} \mathrm{Ph}\left[\mathrm{CH_2}{-}\underset{\mathrm{COOCH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\right]_n\mathrm{CPh_3}$$

(2.15)

The trityl end-capped and isolated polymer can serve as a macroiniter for the subsequent polymerization which leads to chain extension and block copolymer formation: [3]

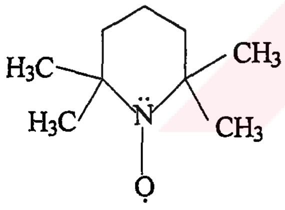


(2.16)

(2.17)

2.1.2.2 Stable Radical Polymerization

The concept of reversible termination by using a stable free radical has recently been shown to control growing free radical chains[3,34-35]. The stable nitroxide radicals such as 2,26,6-tetramethyl-1-piperidinyloxy (TEMPO) are known to act as strong polymerization inhibitors[3,36-37].



TEMPO (2,2,6,6-tetramethyl-piperidinyloxy)

According to an investigation of Solomon [38], a nitroxide radical adduct can be used to initiate polymerization, whereas the nitroxide moiety can reversibly terminate the growing chain, producing low molecular weight oligomers:

(2.18)

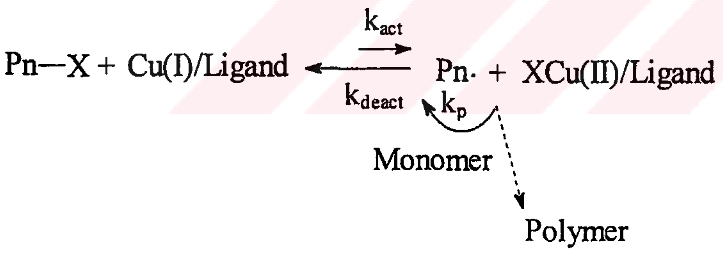
In this process, nitroxides function to form thermally transient adducts in a similar manner to the iniferters. Compared with the iniferter system, the use of nitroxides has the advantage of inhibiting but not initiating polymerization.

Consequently, the stable free radicals are not capable of initiating new chains late in the polymerization process, as they reversibly react with a propagating chain.
This polymerization system contains a monomer or monomer mixtures, free radical initiator, and a stable free radical and requires only heating at elevated temperatures. [3]

2.1.2.3 Atom Transfer Radical Polymerization (ATRP)

An ATRP system consists of an initiator, a copper(I) halide complexed with some ligand(s), and of course, monomer. ATRP occurs as a repetitive addition of a monomer to a growing radicals generated from dormant alkyl halides by a reversible redox process catalyed by transition metal compounds complexed by amine ligand.

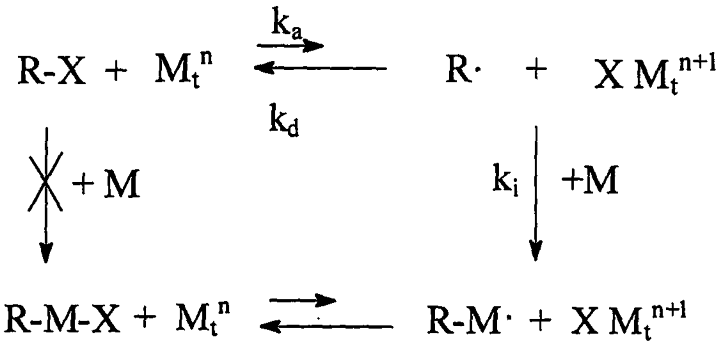
General Reaction:



(2.19)

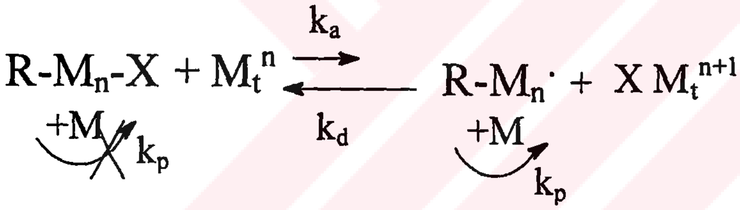
General Reaction Mechanism of ATRP:

Initiation



(2.20)

Propagation



(2.21)

Termination

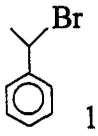
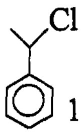
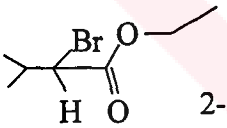
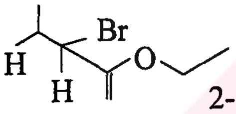
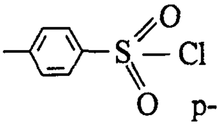
$$R\text{-}M_n^{\cdot} + R\text{-}M_m^{\cdot} \xrightarrow{k_t} R\text{-}M_{n+m}\text{-}R + R\text{-}M_nH / R\text{-}M_m^{=}$$

(2.22)

- **Initiators**

The initiator (organic halides) usually, but not always, should have a structure homologous to the corresponding polymer end group.

Table 2.5. Initiators Used in ATRP

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 2-Bromo ethyl isobutyrate	Methyl methacrylate
 2-Bromo ethyl propionate	Methylacrylate and other acrylates
 p-toluene sulphonyl chloride	Methyl methacrylate

- **Transition Metals Used in ATRP**

Basic requirements for the good catalyst are high selectivity towards atom transfer process and high ability of the resulting $X\text{-}M_t^{n+1}$ species (higer oxidation state of metal). The metal should participate in an one-electron process which would result in oxidative addition/reductive elimination but not in atom transfer process.

Additionally, the metal should have a high affinity for atom/group X, but a low affinity for hydrogens and alkyl radicals. Otherwise, transfer reactions (β-hydrogen elimination) and the formation of organometallic derivatives may be observed reducing selectivity of propagation and control of process.

The most important factors in selecting good ATRP catalyst are the equilibrium position, dynamics of exchange between dormant and active species. These parameters are related to the redox cycle M_t^n / M_t^{n+1} but it must be remembered that ATRP is not an electron transfer process but an atom transfer process. Thus, the inner coordination sphere of M_t^n must expand to accommodate a new X(halide) ligand. Expansion from tetra to pentacoordinated structure

Cu (I) / 2 ligand $\Rightarrow$ X-Cu(II) / 2 ligand or pentacoordinated structure

$X_2Fe(II)$ / $3PR_3$ $\Rightarrow$ $X_3Fe(III)$ / $3PR_3$ must be possible. The most important catalysts used in ATRP are given below:

Cu(I)Cl, Cu(I)Br, Ni(II), Ru(II) / $Al(OR)_3$, and Fe(II) / $3PR_3$ [27-28]

- **Ligand**

The role of ligands is three-fold. They affect the redox chemistry by their electronic effects. They control the selectivity by steric/electronic effects and they also solublize catalytic systems. The most effective ligands for ATRP are derivatives of 2,2-bipyridine. Other nitrogen based ligands such as N,N,N',N'',N'' pentamethyldiethylenetriamine (PMDETA), tetramethylethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetraamine (HMTETA), Tris[2-(dimethylamino)ethyl]amine (Me_6-TREN), and Alkylpyrdylmethanimines are also used.[27-28]

- **Monomers**

ATRP can be succesfully employed in the polymerization of a large variety of vinyl monomers such as styrenes, methacrylates, acrylates, acrylonitrile, acrylamides, metacrylamides, N-vinylpyrolidone, N-vinylpyridine and dienes. [3,39-46]

- **Kinetics of ATRP**

The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction is usually negative first order with respect to the deactivator (CuX_2 / Ligand).

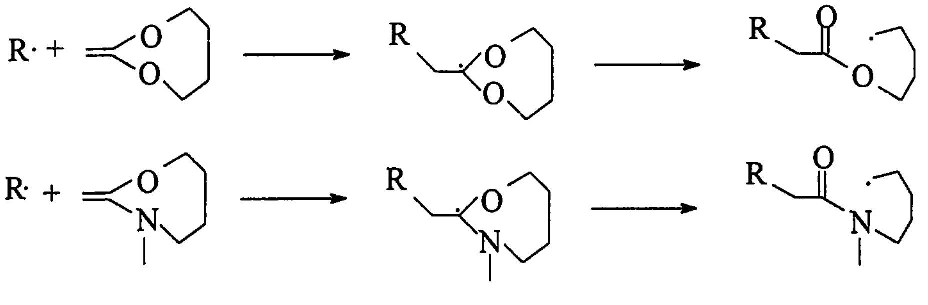
$$R_P = k_{app}[M] = k_p\,[P.]\,[M] = k_p\,K_{eq}\,[I]_0\,\frac{[Cu(I)]}{[Cu(II)X]}\,[M] \qquad \text{(Eq:2.1)}$$

The equilibrium constant (K_{eq}) depends on the monomer used, for example, in the bulk polymerization of styrene at 110°C using R-Br and CuBr/dNbipy the equilibrium constant is approximately $K_{eq} = k_{act} / k_{deact} = 4\text{x}10^{-8}$ [27-28]

2.1.2.4 Addition-Fragmentation Reactions

- **Free Radical Copolymerization of Vinyl Compounds with Unsaturated Heterocyclic Monomers:**

Free-radical ring opening polymerization of cyclic ketenacetals and their nitrogen analogous occurs via formation of carbonyl bond at the expense of a less stable carbon-carbon double bond as depicted below [47-53]:

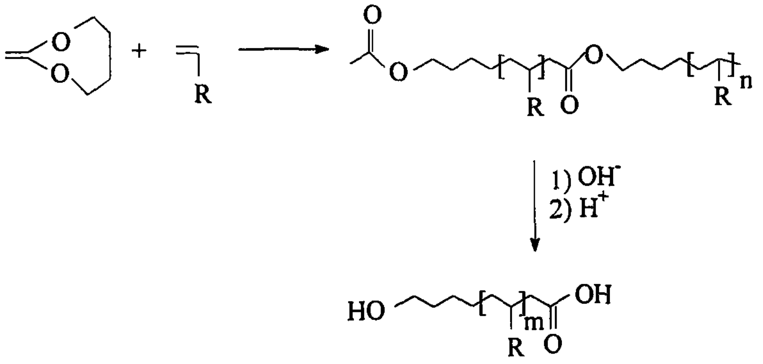


(2.23)

(2.24)

Functional polystyrene and polyethylene possesing hydroxy and carboxylic end groups in the same molecule were prepared by taking advantage of this type of so called addition-fragmentation reaction. For this purpose, 2-methylene-1,3-dioxepane was polymerized with excess styrene and ethylene [3].

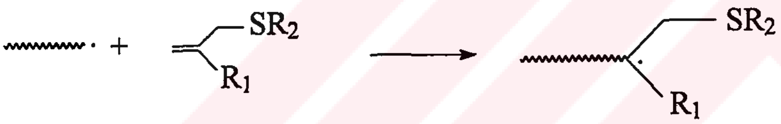
Hydrolysis of the resulting polymers yielded desired telechelics:



(2.25)

- **Allylic Sulfides:**

Among many other compouds which undergo addition-fragmentation reactions, appropriately substituted allylic sulfides have been shown to be efficient transfer agents in free radical polymerization [54-57].



(2.26)

(2.27)

$$R_2S\cdot \; + \; M \longrightarrow R_2S\sim\sim\sim\cdot \qquad (2.28)$$

Open chain ketenacetals, allylic peroxides and vinyl ethers also undergo addition-fragmentation reactions. [3]

2.2 Synthesis of Block Copolymers by Combination of Different Polymerization Routes

Advanced polymeric materials with specialized properties are of great interest. Block and graft copolymers are the most demanded advanced materials because of their diverse copolymer structures [58-60]. In most cases, the corresponding homopolymers do not form homogeneous phase. However, linear arrangement of the blocks by chemical bonds results in the realization of a stable structure with two phases seperated. Each segment exerts its character or function to the bulk of the copolymers. This way various properties that can be improved or combined to give possibility of using block copolymer comptabilizers, impact modifiers, surface modifiers, coating materials, antistatic agents and adhesives. [61-63]

A number of techniques for the preparation of block copolymers have been developed. Living ionic polymerization is an elegant method for the controlled synthesis of block copolymers. However, besides high purity requirements this technique is limited to ionically polymerizable monomers and exclude monomers that polymerize by other mechanisms.

In fact, there exits some limitations even for the ionically polymerizable monomers. Carrying out the block copolymerization of two ionically polimerizable monomers depends critically on the structure and relative reactivity of the ionic species and the monomers. [64-66]

In order to extend the range of monomers for synthesis of block copolymers, transformation approach was postulated in which the polymerization mechanism could be changed from one to another which is suitable for the respective monomers.[67-69]

All the research works performed in the area of polymerization transformation mechanism could be outlined in two main categories which are divided in subcategories within themselves as well:

- **Direct transformation reactions**

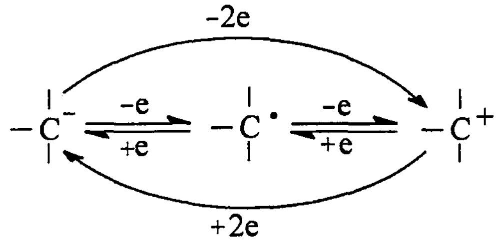
Cation to Anion Direct Transformation
Radical to Cation Direct Transformation

- **Indirect Transformation**

Transformations Involving Condensation Polymerization
Transformation of Anionic Polymerization to Radical Polymerization
Transformation of Cationic Polymerization to Radical Polymerization
Transformation of Radical Polymerization to Anionic Polymerization
Transformation of Radical Polymerization to Cationic Polymerization
Transformations Involving Anionic and Cationic Polymerizations
Transformations Involving Activated Monomer Polymerization
Transformations Involving Metathesis Polymerization
Transformations Involving Ziegler-Natta Polymerization
Transformations Involving Group Transfer Polymerization

2.2.1 Direct transformation reactions

The transformation of a polymerization mechanism is carried out at the end of the first block segment in the polymerization mixture, which means that the species initiated the polymerization mechanism of the first monomer by one mechanism was transformed to another mechanism by a redox process without termination and isolation as shown below:



(2.29)

2.2.2 Indirect Transformation Reactions

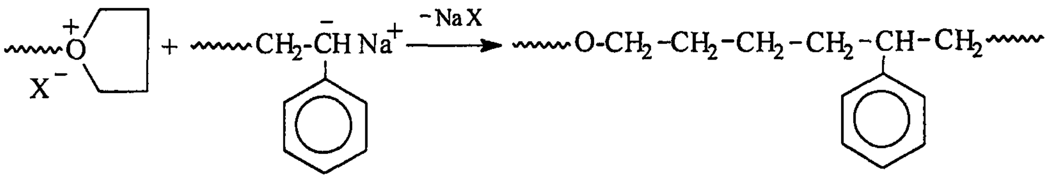
This type of transformation usually requires multistep reactions. The stable but potentially reactive functional group for the second polymerization mode is introduced to the chain ends either in the initiation or the termination steps of the polymerization of the first monomer. The polymer is isolated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

$$I + nM_1 \xrightarrow{\text{mechanism A}} I\!\left[M_1\right]_{n-1}\!M_1^* \xrightarrow{\text{termination}} I\!\left[M_1\right]_n\!F$$

$$I\!\left[M_1\right]_n\!F \quad + \quad mM_2 \xrightarrow{\text{mechanism B}} I\!\left[M_1\right]_n\!\textit{-block-}\!\left[M_2\right]_m$$

(2.30)

The coupling reactions in which the mutually reactive polymerizing ends are terminated with each other, i.e., cationic and anionic polymerization (2.31) are not considered as transformation reactions since the polarity of the propagating sites remains the same for the individual steps and transformation is not involved. In this connection it should be pointed out that the coupling reactions also yield block copolymers of monomers polymerizable with different modes.[70,71]



(2.31)

As a result; 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 built 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 possibilty of the various newly developped "living"/controlled polymerization mechanisms. It would be possible to design and synthesize materials having precise structures with desired properties by combination of such mechanisms.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

Benzophenone was a product of Fluka and used directly.

2-Bromopropionyl bromide was a product of Fluka, no further purification was applied.

2,2'-bipyridine was a product of Aldrich and used directly.

Copper(I) bromide was a product of Aldrich and used directly.

N,N-Dimethylethanolamine (DMEA) was a product of Aldrich and distilled with fractionation under calcium hydride.

Triethylamine was a product of Aldrich and distilled with fractionation under calcium hydride.

Methyl methacrylate (MMA) used as monomer, was a product of Fluka, purified by usual methods and distilled in vacuo from calcium hydride.

Styrene (St) used as monomer, was a product of Fluka, purified by usual methods and distilled in vacuo from calcium hydride.

Methylene chloride which was used as solvent in photopolymerization of methyl metacrylate and UV measurement of benzophenone was cleaned by sulfuric acid followed by water, %5 sodium hydroxide solution and water, and was dried with sodium sulfate and finally distilled from fractionation column.

Methanol (technical grade) was used in precipitation processes of polymers.

Tetrahydrofuran (THF) was dried over potassium hydroxide and finally distilled over sodium wire.

3.2 Equipments

3.2.1 Photo reactor

A merry-go-round type photoreactor, with 16 Philips 8W/06 lamps, emitting overhelmingly light at c.370nm was used.

3.2.2 UV Spectrophotometer

UV-Vis spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer.

3.2.3 Nuclear Magnetic Resonance Spectrospin (NMR)

H-NMR analysis were recorded on a Bruker 250 MHz NMR Spectrospin.

3.2.4 Gel Permeation Chromotography (GPC)

GPC analyses were performed with a setup consisting of a Waters pump and 3 Waters styragel HR3, HR4, HR4E columns with THF at a flow rate of 1mL/min and the detection was carried out with a differential refractometer. Molecular weights were calculated with the aid of polystyrene standards.

3.2.5 Gas Chromotography (GC)

Conversion of the monomer when samples were taken during the reaction in atom transfer radical polymerization (ATRP) experiments was calculated against an internal standard (brombenzene) by using GC with a OV-1 column.

3.3 Photopolymerization of Methyl methacrylate

Methylene chloride solutions of MMA as a monomer, benzophenone and DMEA as initiating system were introduced into a glass tube followed by bubbling through nitrogen gas which was passed through firstly from molecular sieve, secondly from P_2O_5 and lastly from silica-gel and H_2SO_4. The photopolymerizations were performed in a merry-go-round type photo reactor. Tubes were taken from the photo reactor according to the adjusted time durations. The resulting polymers were precipitated in methanol. The solid parts were collected after filtration and dried at 40°C in vacuum overnight. In several experiments, a second fraction with different molecular weight and polydispersity was obtained by adding more methanol.

3.4 Esterification of poly(methyl methacrylate) with 2-Bromo-propionylbromide

A solution of 2-Bromopropionyl bromide (0,13mmol) in 10 mlt THF was added dropwise to a solution of poly(methyl methacrylate) (PMMA) (0,1mmol) and triethylamine (0,3mmol) in 10 mlt THF under nitrogen for 1 hour at 0°C while stirring, subsequently the temperature was allowed to rise to room temperature. The reaction was continued for 24 hours. The solution was filtered, half of the solvent was evaporated and the bromine ended PMMA macroinitiator was precipitated in cold methanol.

3.5 Atom Transfer Radical Polymerization (ATRP) of Styrene

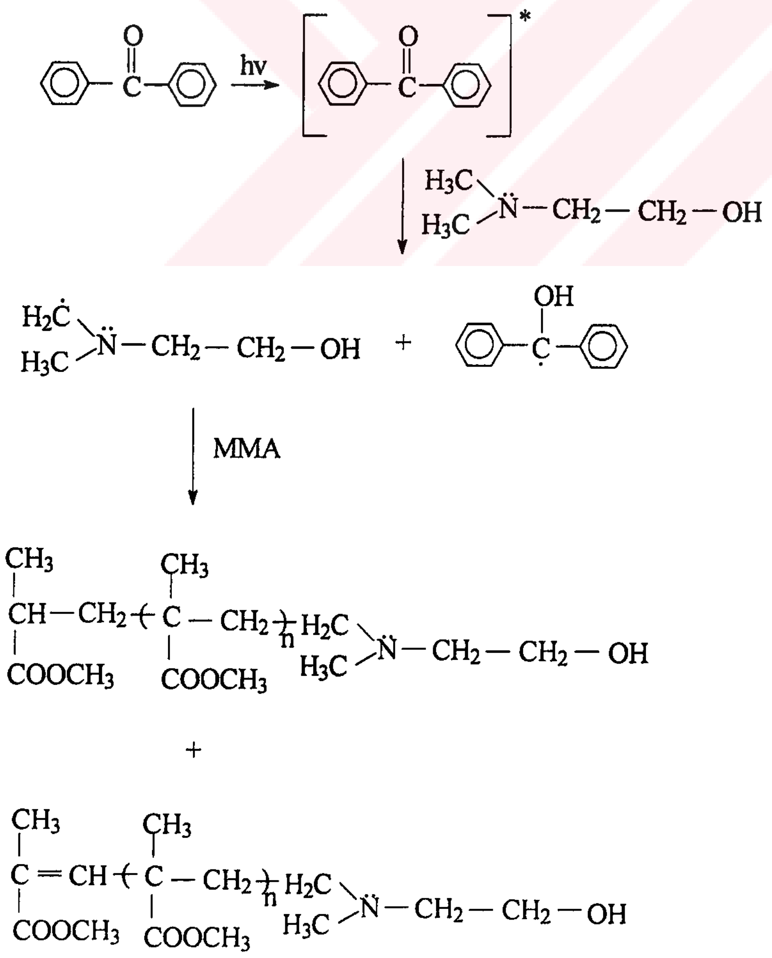
A round bottom-flask equipped with magnetic stirrer and a lateral neck with tap were used. The system was vacuumed and back-filled with dry nitrogen several times. The catalyst (CuBr), ligand (bipyridine), initiator (brominated PMMA) and monomer (styrene) were mixed in the round bottom-flask under nitrogen. The flask was placed in an oil bath which was heated to 110°C and stirred at this temperature for a determined time.

After stopping the reaction, the mixture was diluted with THF and poured into ten-fold methanol. The solid which is a block copolymer of MMA and St [poly(MMA-b-St)] was collected after filtration and dried at 40°C in vacuum overnight.

4. RESULTS AND DISCUSSION

4.1 Photopolymerization of Methyl methacrylate

Several experiments of photopolymerization of MMA in the presence of DMEA and benzophenone were performed using different reaction conditions. This step indicates the reaction shown below (4.1). The mechanism involves hydrogen abstraction by the photoexcited benzophenone from DMEA. The carbon centered radical stemming from the amine is able to initiate the free radical polymerization of MMA.



(4.1)

A control experiment in the absence of DMEA under identical experimental conditions was also carried out. In this case only a little amount of PMMA with high molecular weight was formed indicating negligible contributions of self-absorption by the monomer or hydrogen abstraction of the excited benzophenone from the monomer or solvent. (Table 4.1, exp. No:7)

The reaction conditions and results are presented in Table 4.1.

In order to obtain higher yield for ATRP experiments, the amount of the reactants was increased by modifying the benzophenone and DMEA concentrations and keeping the monomer concentration of experiment 3 (with the highest conversion) same in the further photopolymerization reactions (Table 4.2).

In several cases, by precipitating in methanol, initial high molecular weight fractions were obtained and after several days, lower molecular weight fractions were seperated by adding more methanol, too. The last ones showed lower polydispersities than those of the high molecular weight polymers.

The obtained polymers are expected to contain terminal OH groups since alkanol amines, such as DMEA are very efficient in hydrogen abstraction reactions and excited benzophenone triplets are usually three orders of magnitude more reactive towards tertiary amines than towards alcohols [72]. As the α- amino radicals are able to initiate the polymerization of MMA and propagating methyl methacrylate radicals terminate mainly by disproportionation each polymer chain can have one hydroxyl group.

Table 4.1. Photopolymerization Conditions and Results of MMA

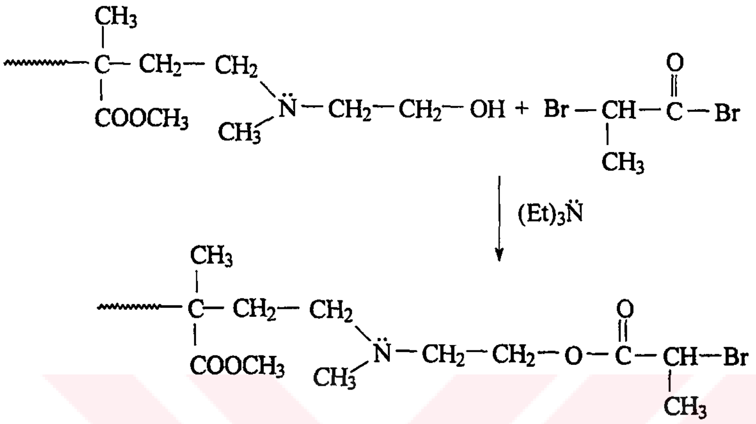
Exp No	**Sample**	**[Monomer] (Mol/lt)**	**[Benzophenone] (Mol/lt)**	**[N,N DMEA] (Mol/lt)**	**time (min.)**	**%conversion**	**M_n**	**P.D.**
1	PMMA 1	7,041	5.10^{-3}	10^{-2}	60	9,34	29029	1,80
2	PMMA 2	7,041	$1,5.10^{-2}$	$4,5.10^{-2}$	60	13,595	12452	1,80
3	PMMA 3	7,041	$4,5.10^{-2}$	$1,35.10^{-1}$	60	18,3049	9443	2,27
4	PMMA 4	7,041	$4,5.10^{-2}$	$1,35.10^{-1}$	30	5,0780	11760	2,72
5	PMMA 5	7,041	$4,5.10^{-2}$	$1,35.10^{-1}$	17	3,539	17393	3,03
6	PMMA 6	4,7	$4,5.10^{-2}$	$1,35.10^{-1}$	60	7,482	16615	2,88
7	PMMA 7	9,388	9.10^{-2}	-	60	1,042	80859	2,21

Table 4.2. Photopolymerization Conditions and Results of MMA with Increasing Amounts of Reactants

Exp No	**Sample**	**[Monomer] (Mol/lt)**	**[Benzophenone] (Mol/lt)**	**[N,N DMEA] (Mol/lt)**	**Time (min.)**	**%conversion**	**M_n**	**P.D.**
8	PMMA 8	7,041	$1,35.10^{-1}$	$4,05.10^{-1}$	60	15,9	**PMMA 8A** 11548 **PMMA 8B** 3785	**PMMA 8A** 2,33 **PMMA 8B** 1,45
9	PMMA 9	7,041	$6,75.10^{-2}$	$2,02.10^{-1}$	60	20,94	9475	2,20
10	PMMA 10	7,041	$4,5.10^{-2}$	$1,35.10^{-1}$	60	15,77	**PMMA10A** 12298 **PMMA10B** 3977	**PMMA 10A** 2,59 **PMMA10B** 1,56
11	PMMA 11	7,041	$4,5.10^{-2}$	$1,35.10^{-1}$	60	13,79	10,001	1,82

4.2 Synthesis of Bromine ended PMMA

The bromine ended PMMA can be obtained by an esterification reaction between the OH functionalized PMMA and 2-bromopropionyl bromide which then can be used as macroinitiator for ATRP . The reaction can be shown as below:



(4.2)

The molecular weights and polydispersities of the polymers obtained after the esterification reaction are presented in Table 4.3.

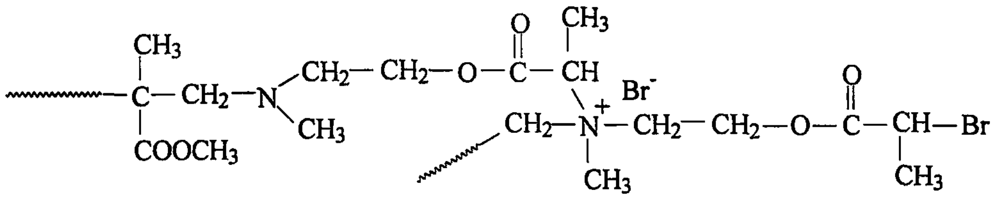
Table 4.3. Esterification Results of PMMA by Using 2-Bromopropionyl bromide

Exp No	Sample	PMMA Used	M_n*	M_w/M_n*
12	CND 3	PMMA 3	20946	3,45
13	CND 8-B	PMMA 8-B	6000	1,33
14	CND 9	PMMA 9	19983	1,71
15	CND 10-A	PMMA 10-A	19143	1,90
16	CND 10-B	PMMA 10-B	5500	1,46
17	CND 11	PMMA 11	17440	1,44

*Determined from GPC, based on PS standards.

As seen from the Table 4.3, the molecular weights are almost twice higher in every case. Even with higher molecular weights, the precipitation in methanol was more difficult at this polymers than at the corresponding initial ones. These observations determined us to suppose that some associations between two macromolecules are possible.

It is may be due to quarternization reactions with forming of macromolecular salts as shown below:



Another explanation would be that only high molecular weight macromolecules precipitated after the esterification reaction.

The ^{1}H-NMR spectrum of one of the bromine ended PMMA is presented below in Figure 4.1:

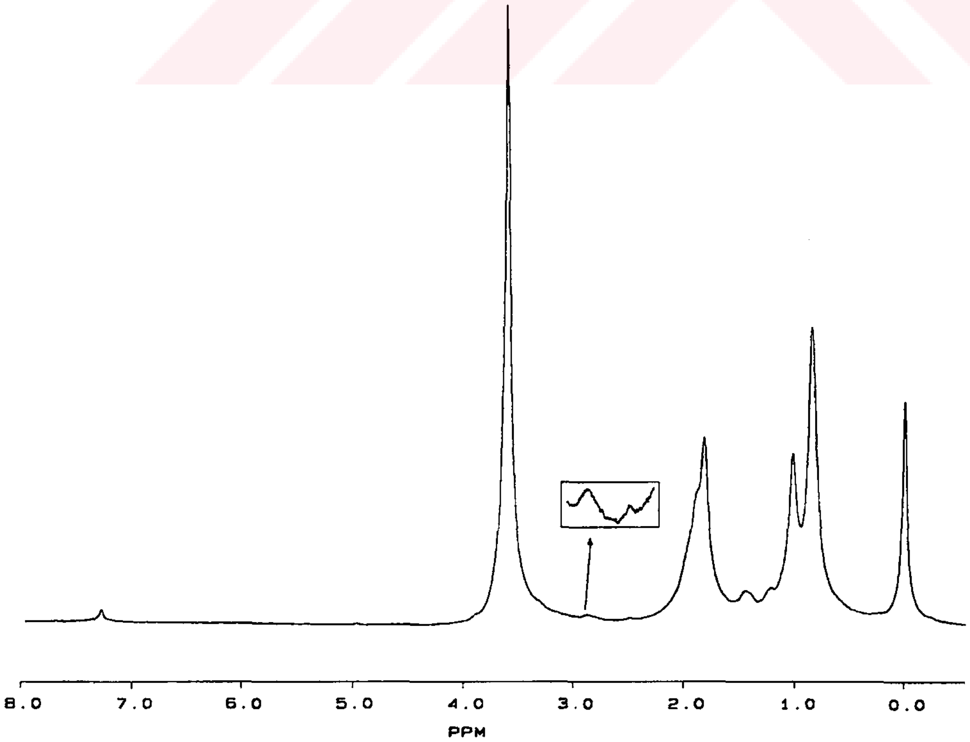


Figure 4.1. ^{1}H-NMR spectra of bromine ended PMMA of Exp.No.16

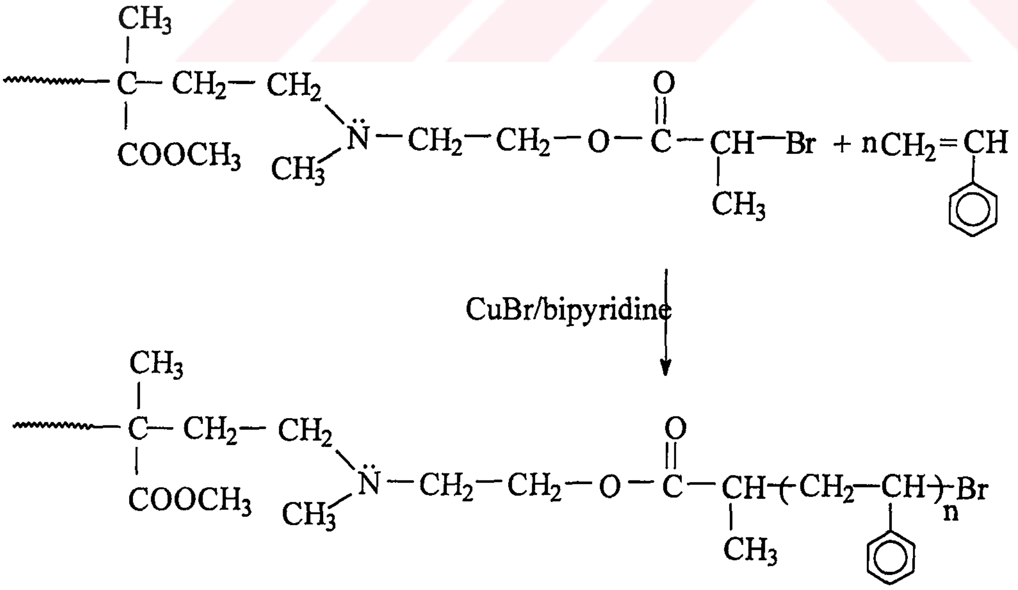
From the final groups of macroinitiator, only the -CH_2- protons linked to nitrogen atom could be identified in the ^{1}H-NMR spectrum at about 2.8 ppm, the others being covered by MMA peaks (Figure 4.1). Molecular weights of the polymer can be estimated by following the formula:

$$\overline{M}_{n,H-NMR} = 100\frac{2I_{3.6}}{3I_{2.8}} \qquad \text{(Equation 4.1)}$$

where $I_{3.6}$ and $I_{2.8}$ are the intensities of the peaks corresponding to O-CH_3 protons of MMA units and the above mentioned ones, respectively (Figure 4.1). The value of about 6000 calculated by this method is close to that determined from GPC (5500).

4.3 Poly (MMA-b-St) by ATRP

ATRP of St was carried out in bulk by using bromine ended PMMA as initiator and CuBr/bipyridine as catalytic system. The reaction can be shown as below:



(4.3)

The conversions were determined gravimetrically or by gas chromotography when samples were collected during the experiment. The composition of the copolymers was estimated from ^{1}H-NMR data by using the ratio of the peak intensities at 3,6ppm ($-OCH_3$ from MMA units) and 6,5-7 ppm (aromatic protons of styrene).The theoretical molecular weights ($M_{n,th}$) were calculated by using the following equation:

$$\overline{M}_{n,th} = \frac{[M_0]}{[I_0]} \, . \, 104 \, . \, (\text{conversion}) + \overline{M}_{n,PMMA} \qquad \text{(Equation 4.2)}$$

where M_0 and I_0 are the initial molar concentrations of the monomer and bromine ended PMMA respectively and the $M_{n,PMMA}$ is the molecular weight of the PMMA after the esterification reaction.

4.3.1 ATRP 1

The reaction conditions of ATRP 1 were presented in Table 4.4.

Table 4.4. Reaction Conditions of ATRP 1

Sample	Initiator used	[Monomer] (Mol/lt)	[Initiator] (Mol/lt)	Initiator/CuBr/bpy	Time (hour)	Temperature (°C)
ATRP 1	CND 11	8,75 (bulk)	0,01	1/1/3	16,5	110

Using sample CND11 as the initiator, the conversion was 66% and the copolymer with M_n = 77900 and polydispersity of 1.45 was obtained after 16,5 h of reaction. The theoretical molecular weight calculated with equation 4.2 is 77500, very close to that obtained from GPC measurements. The composition of copolymer calculated from GPC indicates 76,9% and from ^{1}H-NMR, 75% styrene content (Table 4.5).

Table 4.5.Results of ATRP 1

Sample	%conversion	M_n	M_n/M_w	$M_{n,th}$	%styrene in copolymer **GPC	%styrene in copolymer ** ^{1}H-NMR
ATRP 1	66	77900	1,45	77500	76,9	75

**refering to repeating units

The GPC traces of CND11 before and after copolymerization are shown below (Figure 4.2) . No signal shoulders attributed to the either starting PMMA or termally formed polystyrene were observed. Moreover, the trace corresponding to the block copolymer is unimodal and narrow. As the composition calculated from ^{1}H-NMR (Figure 4.3) is in reasonably good agreement with that resulted from GPC and the obtained molacular weight is close to the calculated theoretical one, we can conclude that the formation of copolymer is a result of ATRP mechanism.

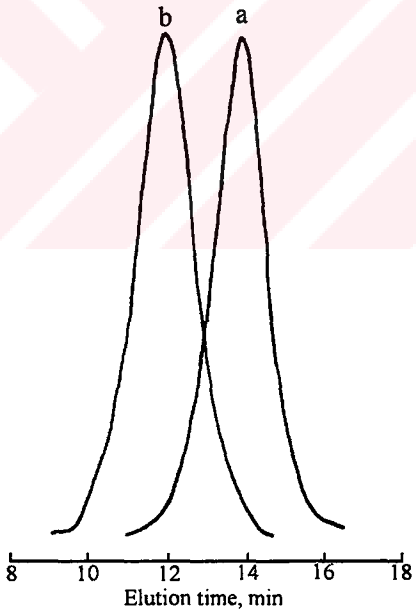


Figure 4.2. The GPC traces of bromine ended PMMA before and after copolymerization

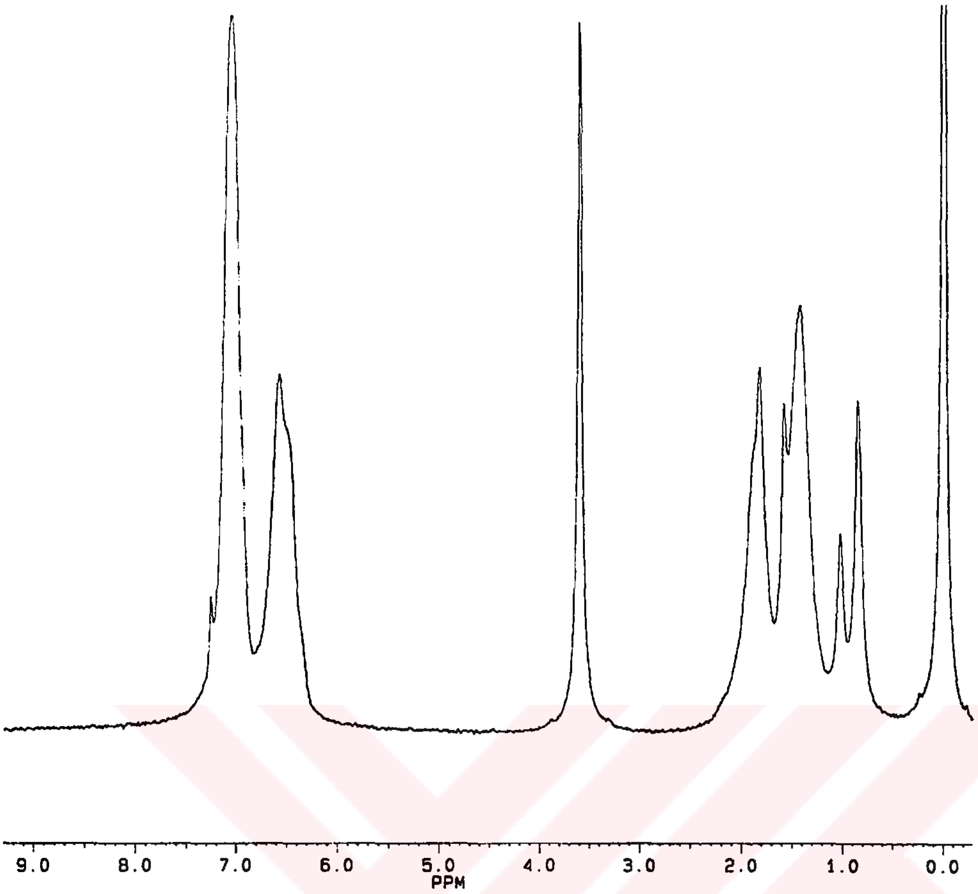


Figure 4.3. ^{1}H-NMR spectrum of the (MMA-b-St) of ATRP 1

4.3.2 ATRP 2

CND 8-B was used as macroinitiator and 4 different samples were taken during the experiment in order to see the increment of the molecular weight with time. The reaction conditions are presented in Table 4.6.

Table 4.6. Reaction Conditions of ATRP 2

Sample	Initiator Used	[Monomer] (Mol/lt)	[Initiator] (Mol/lt)	Initiator/CuBr/bpy	Time (hour)	Temperature (°C)
ATRP 2	CND 8-B	8,75 (bulk)	0,025	1/1/2	3	110

The kinetic plot of polymerization of styrene using CND8-B as initiator is presented in Figure 4.4. Gas chromotography data were used for calculating conversions in this case (Table 4.7).

Table 4.7. Gas Chromotography data

	Time (hour)	%conversion
Sample 1	½	5
Sample 2	2	10
Sample 3	2	20
Sample 4	3	26

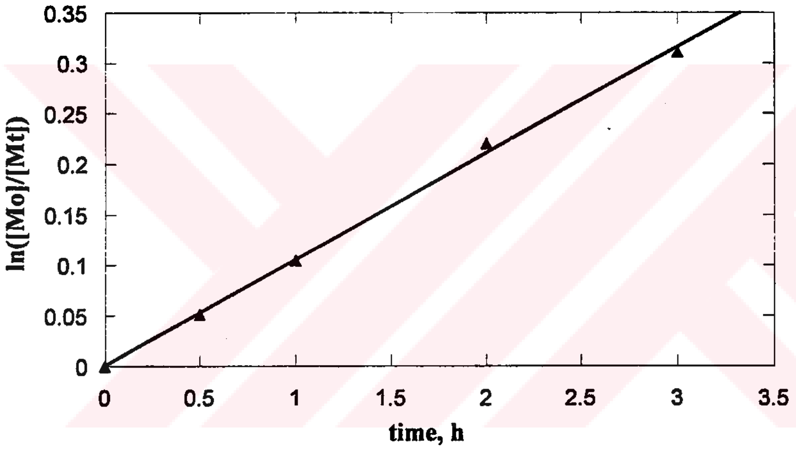


Figure 4.4. The kinetic plot of polymerization of styrene in ATRP 2

The linearity of the semilogarithmic plot of ln ($[M_0]$ / [M]) vs time indicates that the polymerization was first order with respect to monomer and the concentration of the growing radicals remained constant. No induction period was observed, indicating a fully controlled radical process.

4.3.3 ATRP 3

This polymerization was performed by using CND 10-B as macroinitiator. The reaction conditions are presented below (Table 4.8).

Table 4.8. Reaction Conditions of ATRP 3

Sample	Initiator Used	[Monomer] (Mol/lt)	[Initiator] (Mol/lt)	Initiator/CuBr/bpy	Time (min)	Temperature (°C)
ATRP 3	CND 10-B	8,75 (bulk)	0,035	1/1/3	490	110

As in ATRP 2, the polymerization of styrene was performed with taking samples during the experiment, but this time, the conversions were calculated gravimetrically. The data obtained in ATRP 3 were presented in Table 4.9

Table 4.9.Results of ATRP 3

Sample	Time (min)	%Conversion	M_n	M_n/M_w	$M_{n, th}$	% St in copolymer ** (GPC)	% St in copolymer **(^{1}H-NMR),
A	70	3	5950	1.68	6250	7.2	6
B	190	7	7450	1.36	7250	22	18
C	310	14	8500	1.28	9000	35	31
D	490	17	9700	1.2	9750	41	39

**refering to repeating units

The conversion were calculated by weighing the resulting copolymers. Theoretical molecular weights were calculated using the equation 4.2. It is also interesting to note that the molecular weight distributions of the copolymers were narrower than the initial macroinitiator. This was due to the well-defined blocks prepared by ATRP in the second step.

The composition of the copolymers was estimated from ^{1}H-NMR (Figure 4.5) by using the ratio of the peak intensities at 3.6 ppm (-OCH$_3$ from MMA units) and 6.5-7 ppm (aromatic protons of styrene).

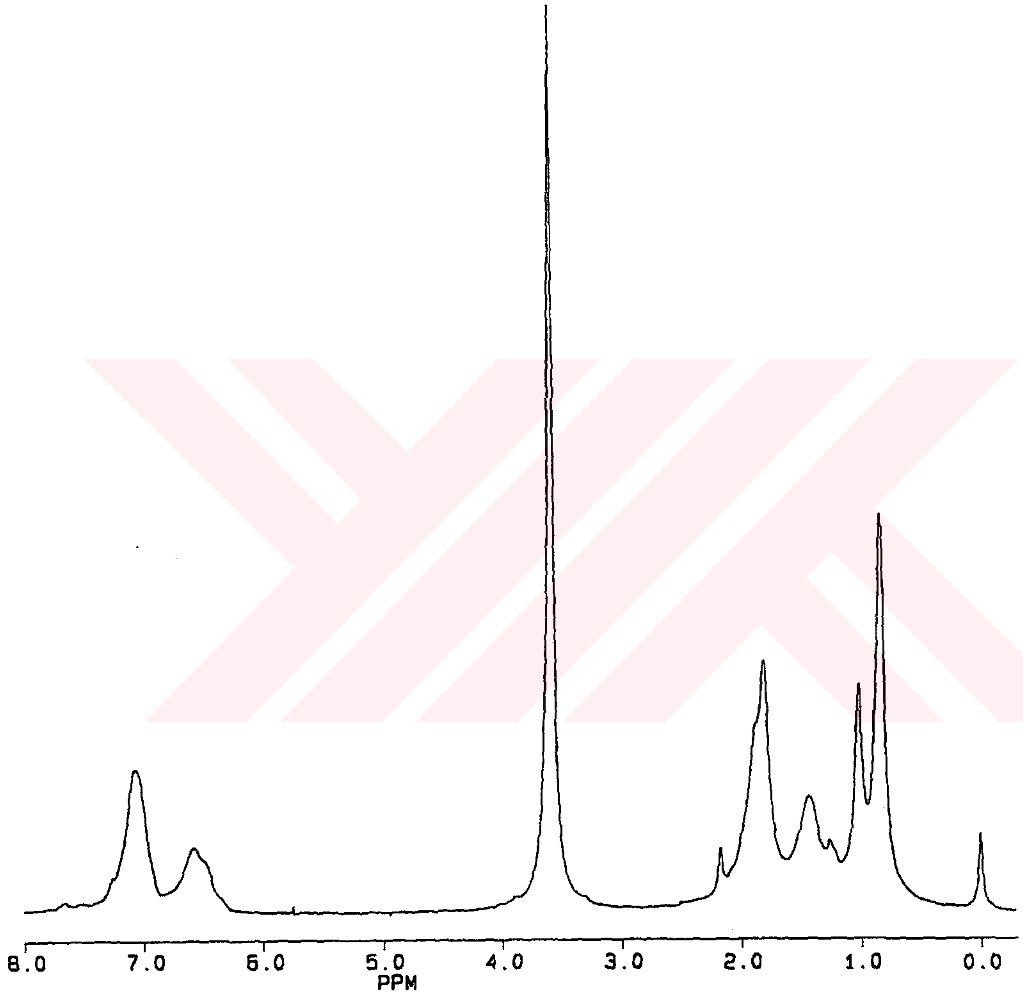


Figure 4.5. ^{1}H-NMR of the poly(MMA-b-St) in ATRP 3

In this experiment we also noticed the linearity of the semilogarithmic plot $\ln([M]_0/[M_t])$ vs time indicating that the polymerization was first order with respect to monomer and the concentration of the growing radicals remained constant.(Figure4.6)

The molecular weight increases linearly with the conversion indicating controlled radical process (Figure 4.7). The unimodal GPC curves (Figure 4.8) and the ^{1}H-NMR spectra prove the formation of copolymers.

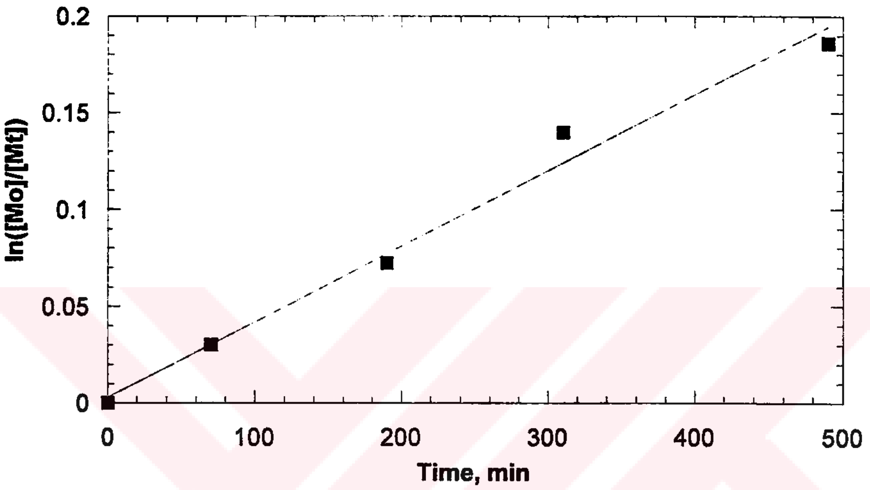


Figure 4.6. The kinetic plot of polymerization of styrene in ATRP 3

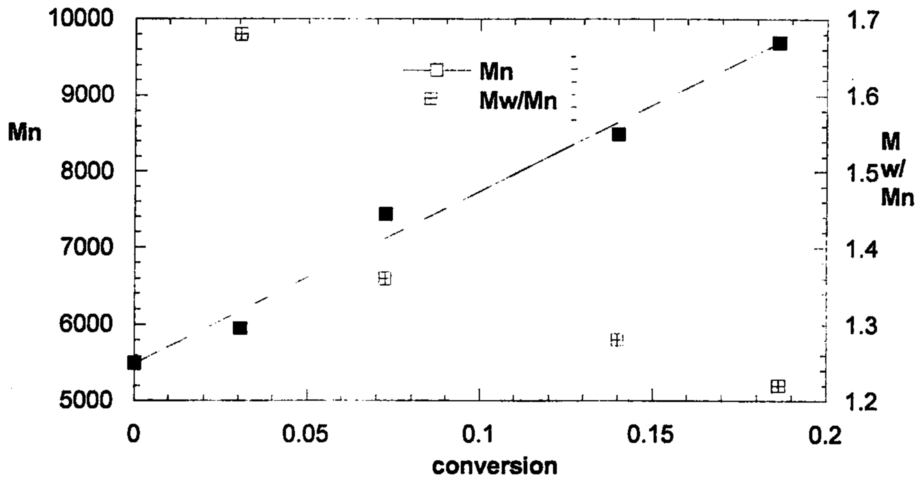


Figure 4.7. The molecular weight vs conversion plot of ATRP3

The peak pertaining to the initial polymer (Figure 4.8) is shifted to higher elution volumes after starting the ATRP.

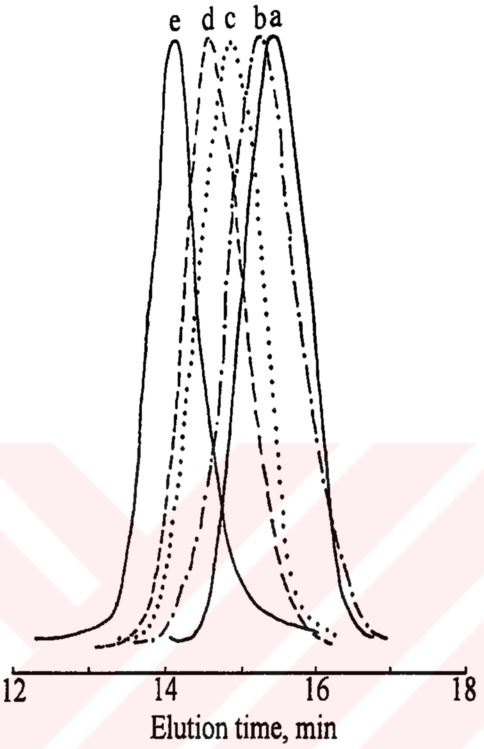


Figure 4.8. GPC traces of PMMA after condensation reaction (a) and block copolymers (MMA-b-St) at different conversions; 0.03 (b), 0.07 (c), 0.14 (d) and 0.17 (e) in ATRP 3

5.CONCLUSION AND SUGGESTIONS

In conclusion, the synthesis of block copolymers by combination of conventional free radical photopolymerization and ATRP has been demonstrated.

The macroinitiator was prepared by photoinitiated polymerization of MMA in the presence of DMEA and benzophenone as the initiating system. Although the light induced free radical polymerization has enormous commercial importance and many advantages, it is too difficult to control the molecular weight and obtain polymers with lower polydispersities by using this method. Because of this reason, the PMMA obtained in the first step showed the characteristics of the conventional free radical polymerization and homogeneity of living/controlled polymerization were not observed.

This process was followed by the esterification of the resulting polymers with 2-bromopropionyl bromide. These experiments were not succeeded very efficiently due to the difficulty in performing organic reaction in macromolecular chain ends.

The –Br functionalized polymers obtained in the second step were then used as macroinitiators in the ATRP of St. The unimodal shape of the trace obtained at GPC and the ^{1}H-NMR spectrum prove that a copolymer was obtained. Almost the same values for copolymer composition were obtained from ^{1}H-NMR and GPC analyses. The good correlation between determined molecular weight with the calculated one, as well as the kinetic study and the decrease in the polydispersities of the resulting polymers indicates a fully controlled / "living" radical polymerization.

From all these, we can conclude that the block copolymers, which can not be prepared by other methods or requires multisteps under stringent conditions, can be synthesized by using such combination. ATRP used in the second step is an easily applicable polymerization system that can polymerize a wide variety of monomers with a high degree of control.

Alternatively, an initiator having both dimethylamine and bromine end groups on each side would allow formation of block copolymers by two step photoinduced and ATRP methods without requirement of additional condensation reaction on bromine ended PMMA.

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BIOGRAPHY

İrem Erel was born in Istanbul in 1977. She graduated from Çavuşoğlu High School in 1995 and Istanbul Technical University, Department of Chemistry in 1999.

She was registered as a M.Sc. student to the Institute of Science and Technology of Istanbul Technical University in 1999.

During her M.Sc. study, she was financially supported by Tubitak. She is the co-author of a research paper submitted to 'Polymer'.