SYNTHESIS AND CHARACTERIZATION OF WELL DEFINED ABC TYPE TRIBLOCK COPOLYMERS VIA ATOM TRANSFER AND STABLE FREE RADICAL POLYMERIZATION

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ATOM TRANSFER VE KARARLI SERBEST RADİKAL POLİMERİZASYONU İLE İYİ TANIMLANMIŞ ABC TİP TRİBLOK KOPOLİMERLERİN SENTEZİ VE KAREKTERİZASYONU

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January 2002 Tuba ERDOĞAN

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LIST OF SYMBOLS

M_n	: Number average molecular weight of polymers
M_w	: Weight average molecular weight of polymers
MWD	: Molecular weight distribution of polymers
PtBA	: Poly (tert-butylacrylate)
PMMA	: Poly (methyl methacrylate)
PSt	: Polystyrene
Cat	: Catalyst
k_a, k_d	: Rate constants of activation and deactivation steps of the initiation in radical polymerization
K_{eq},k_p	: Equilibrium rate constant and rate constant of propagation step in radical polymerization respectively
k_{tc}, k_{td}	: Rate constant of termination by combination and rate constant of termination by disproportionation respectively
EtOH	: Ethanol
Et_3N	: Triethylamine
I, M	: Initiator and monomer respectively
Ph	: Phenyl

SUMMARY

SYNTHESIS AND CHARACTERIZATION OF WELL DEFINED ABC TYPE TRIBLOCK COPOLYMERS VIA ATOM TRANSFER AND STABLE FREE RADICAL POLYMERIZATION

Accurate control of polymerization processes to give polymers with well-defined architecture is becoming an increasingly important aspect of polymer chemistry. The field of radical polymerization has exploded with the advent of controlled radical polymerization processes. Radical polymerization is a very important commercial process for preparing high molecular weight polymers. The only disadvantage of conventional radical polymerization is the poor control of macromolecular structures including end functionalities and polydispersities due to chain transfer and termination processes. Specifically, controlled architecture possesses some characteristics, which are molecular weight control, end group control, ability to form block copolymers, and a living nature. Recently, the controlled/'living' radical polymerizations have been utilized for the synthesis of well-defined, narrow polydispersity polymers. Among them stable free radical polymerization (SFRP) and copper catalyst mediated atom transfer radical polymerization (ATRP) are versatile methods for the controlled radical polymerization of various monomers. SFRP is based on the use of stable nitroxide free radicals, such as 2,2,6,6-tetrametylpiperydinyl-1-oxy (TEMPO), as thermally labile capping agents for the growing polymer chain, which leads to control of the polymerization. In 1995, Matyjaszevski et al. developed an alternative controlled/'living' free radical polymerization process using a copper (I)- catalyzed system. Atom transfer radical polymerization (ATRP) is a convenient method especially for the preparation of polymers and block copolymers because the 2-bromopropionate group, which is an efficient initiator of ATRP, can easily be introduced as the end group to different polymers.

One of the advantageous of controlled radical polymerizations such as SFRP and ATRP is that the molecular weight and the chain end functionality can be controlled. The wide range of functionality can be introduced into a polymer chain end using asymmetric difunctional initiator if one of the functional group remains intact during the polymerization. This has enabled the synthesis of well-defined block copolymers by a sequential two-step or one pot method without any transformation or protection of initiating sites.

In the present work, novel asymmetric double functional initiator, 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino) oxy] ethyl 2-bromopropanoate was synthesized and used in preparation of ABC type methylmethacrylate (MMA)-ter-butylacrylate (tBA)-styrene (St) triblock copolymer via ATRP-ATRP-SFRP route and vice versa. ^{1}H-NMR and GPC (Gel Permeation Chromatography) studies of the obtained polymers show that block copolymers are readily formed as a result of combination of ATRP and SFRP mechanisms.

ÖZET

ATOM TRANSFER VE KARARLI SERBEST RADİKAL POLİMERİZASYONU İLE İYİ TANIMLANMIŞ ABC TİP TRİBLOK KOPOLİMERLERİN SENTEZİ VE KAREKTERİZASYONU

İyi tanımlanmış mimariye sahip polimerlerin tam kontrollü polimerizasyon yöntemleriyle eldesi polimer kimyasında gittikçe artan bir öneme sahiptir. Radikal polimerizasyon alanı kontrollü radikal polimerizasyon yöntemlerinin keşfiyle büyük bir patlama yapmıştır. Radikal polimerizasyonu yüksek molekül ağılıklı polimerlerin eldesinde kullanılan çok önemli ticari bir yöntemdir. Klasik radikal polimerizasyonun tek dezavantajı zincir transfer ve sonlanma reaksiyonlarından dolayı makromolekülün yapısıyla birlikte fonksiyonalitesi ve polidispersitesi üzerinde düşük bir kontrole sahip olmasıdır. Kontrollü mimari denilince, molekül ağırlık kontrolü, uç grup kontrolü, blok kopolimer oluşturabilme ve yaşayan karakter akla gelmektedir. Son yıllarda, iyi tanımlanmış düşük polidispersiteye sahip polimerlerin sentezinde kontrollü/'yaşayan' polimerizasyon yöntemleri kullanılmaktadır. Bu yöntemler içinde en etkili olanı kararlı serbest radikal polimerizasyonu (SFRP) ve Cu(I) kataliz sistemli atom transfer radikal polimerizayonudur (ATRP). Kararlı serbest radikal polimerizasyonu (SFRP) kararlı serbest nitroksit radikalinin, 2,2,6,6-tetrametilpiperidinil-1-oksi (TEMPO), kullanımına dayanmaktadır ve bu sistemde TEMPO büyüyen zincirin sonunda ısısal olarak kopabilen bir uç grup olarak kontrollü polimerizasyona neden olmaktadır. Matyjaszwski ve grubu 1995 yılında Cu (I) kataliz sistemi kulanılan alternatif bir kontrollü/'yaşayan' polimerizasyon yöntemi geliştirmişlerdir. Atom transfer radikal polimerizasyonu (ATRP), özellikle blok kopolimerlerin eldesinde kullanılan çok yaygın ve uygun bir metotdur, çünkü ATRP için çok etkili bir başlatıcı olan 2-bromo propanoat farklı polimerlerin uç gruplarına kolaylıkla yerleştirilebilmektedir.

SFRP ve ATRP gibi kontrollü polimerizasyon tekniklerinin bir avantajı da elde edilen polimerlerin molekül ağırlıklarının ve zincir uç grubu fonksiyonalitesinin kontrol edilebilir olmasıdır. İki fonksiyonlu asimetrik başlatıcılar kullanılarak polimer zincir uç gruplarına çok çeşitli fonksiyonellikler kazandırılabilir ki bu da herhangi bir transformasyon reaksiyonu gerektirmeden düşük molekül ağırlık dağılımına ve kontrollü molekül ağırlıklarına sahip polimerlerin eldesine olanak tanır.

Bu çalışmada, iki fonksiyonlu asimetrik başlatıcı, 2-fenil-2-[(2,2,6,6-tetrametilpiperidinil)oksi]etil 2-bromo propanoat sentezlenmiş ve ATRP-ATRP-SFRP polimeriasyon sırası ve tersi kullanılarak ABC tipli metilmetakrilat-ter-butilakrilat-sitiren triblok kopolimer sentezi gerçekleştirilmiştir. ^{1}H-NMR ve GPC(Jel Geçirgenlik Kromatografisi) cihazlarından alınan sonuçlar doğrultusunda elde edilen blok kopolimerlerin gerçekten de ATRP ve SFRP tekniklerinin kombinasyonu ile oluştukları belirlenmiştir.

1.INTRODUCTION

The desire to control polymer properties through the synthesis block copolymers and complex macromolecular architectures is a continuing theme throughout polymer chemistry.

The free radical polymerization is the most important industrial process used to prepare high molecular weight polymers. A wide variety of monomers can be polymerized and copolymerized under simple experimental conditions. However, conventional free radical polymerization techniques are inherently limited in their ability to synthesize polymers with well-defined architectural and structural parameters. One of the drawbacks of the conventional radical polymerization is the lack of control in both the molecular weight and the structure of the resulting polymers due to the chain transfer and the termination processes [1]. Gaining control over radical polymerization to synthesize polymers with controlled molecular weight and well-defined architecture is one of the main aspects in contemporary polymer chemistry since the molecular weight and the molecular weight distribution of the polymer highly affect the final properties of the resulting materials. Generally, as the molecular weight increases the intermolecular forces also increase and this causes significant changes not only in mechanical and thermal properties, but also in process ability, electrical, optical and chemical properties.

In the past 20 years there have been several techniques aimed at controlling free radical polymerization including iniferters, nitroxide-mediated polymerization, atom transfer radical polymerization (ATRP) and the most recent one reversible addition-fragmentation chain transfer (RAFT).

Recent developments in the area of controlled radical polymerization processes opened new synthetic possibilities for the synthesis of well defined polymers from monomers polymerizing by radical mechanism. In many systems sequential polymerization could be succesfully conducted, leading to well defined block

copolymers, including block copolymers comprising blocks formed by different mechanism.

Synthesis of multi-functional initiators compatible with atom transfer (ATRP) and stable free radical (SFRP) polymerization techniques allows the polymer chemistry to get copolymers with controlled molecular weight and structure that leads to obtain well-qualified materials having the characteristics of different monomers. The basic concept behind this new approach to block copolymers is that a single bearing two or more functional groups can be used to sequentially initiate one type of polymerization, and then without further transformation steps the other original functional group, which is now at the chain end of the first polymer block can be used to initiate a second type of polymerization. The advantage of this method is the potential to form block copolymer from disparate monomer units without any intermediate deprotection or functionalization reaction.

In this work, the controlled radical polymerization techniques have been applied to the preparation of homopolymers as well as diblock and triblock copolymers of tert-butyl acrylate, methyl methacrylate and styrene monomers.

1.THEORETICAL PART

2.1. Free Radical Polymerization

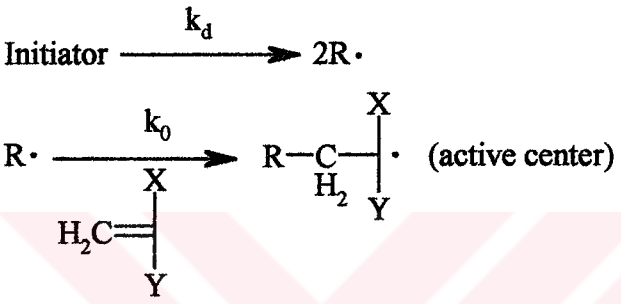
Free radical polymerization has been a very important industrial process due to low requirements on monomer and reactant purity, facile copolymerization, and the fact that polymerizations can be conducted in either emulsion or suspension using water as the medium [2]. The polymers obtained via this method are used in the manufacture of numerous products such as fabrics, surface coatings, plastics, paints, packaging, and contact lenses [3]. The importance of free radical polymerization can be summarized as follows;

- Free radical polymerization can be carried out under relatively undemanding conditions.
- It exhibits a tolerance of trace impurities.
- High molecular weight polymers can be produced without removal of the stabilizers present in commercial polymers.
- Trace amount of oxygen does not disturb the polymerization.
- Free radical reactions can be conducted in aqueous media.
- A variety of monomers can be polymerized via free radical polymerization route unlike to the ionic polymerization techniques.

Free radical polymerization is initiated by radicals and propagated by macroradicals. These radicals exhibit an unpaired electron. Initiating radicals are rarely formed by monomers themselves but rather thermally, electrochemically or photo chemically from the homolytic chain cleavage of the deliberately added initiators. Free radical polymerization is a chain growth reaction and traditionally consists of three main steps: initiation, propagation and termination.

Initiation

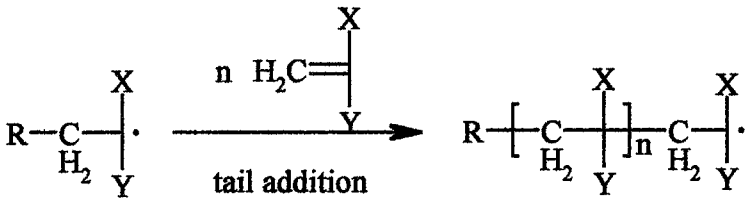
Initiation occurs from the reaction of an initiator-derived radical center with a monomer molecule. Firstly a couple of radical occurs by a homolytic cleavage of the initiator. If the radicals are formed in the presence of vinyl monomers, these radicals react with the double bond and generate a new radical. The first one is known as the dissociation and the second is the association step in the initiation of free radical polymerization. Since $k_d < k_0[M]$, the decomposition is the rate determining step in the initiation process [4].



(2.1)

Propagation

Propagation is the rapid addition of more monomer to the growing chain end, for example the rate constant of propagation is about 100-10000 [L/(mol*sec)]. These rates are very high compared to that of the other chemical reactions [5].



(2.2)

Termination

Termination is the disappearance of an active center by self-reaction of carbon-centered radicals, reaction of an active chain with an initiating radical or by chain transfers reactions.

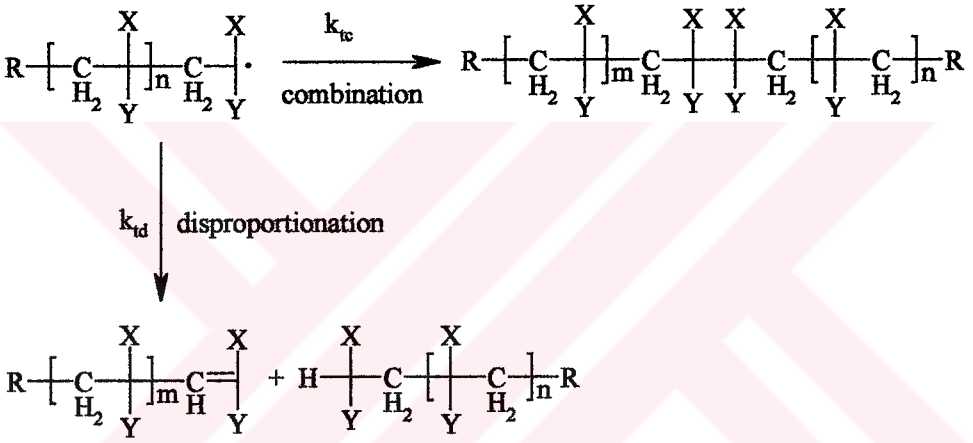
1) The self reaction of carbon-centered radicals

a) Combination

Termination by combination occurs when two propagating radical chains of arbitrary degrees of polymerization meet at their free radical ends.

b) Disproportionation

Termination by disproportionation results in two terminated chains. Because of hydrogen transfer, one terminated chain will have an unsaturated carbon group while the other one is saturated.



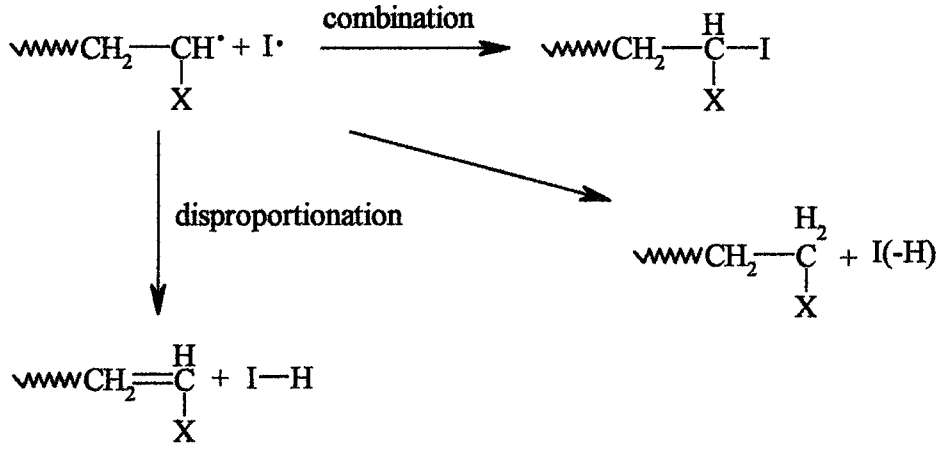
(2.3)

The rate of k_{tc} / k_{td} is dependent on the polymerization conditions and the type of monomers. For example, in normal conditions while styrene prefers termination by combination, methyl methacrylate chains are usually terminated by disproportionation.

2) Primary radical termination

Primary radical termination is the reaction of a propagating radical with a radical derived from the initiator. This type of termination gives products that may originate from either of three reaction; combination of the two radical species, hydrogen abstraction from the propagating radical by the initiator-derived radical or hydrogen abstraction from the initiator-derived radical by the propagating radical to give a

polymer with saturated chain end. The schematic representation of primary radical termination is seen in (2.4).



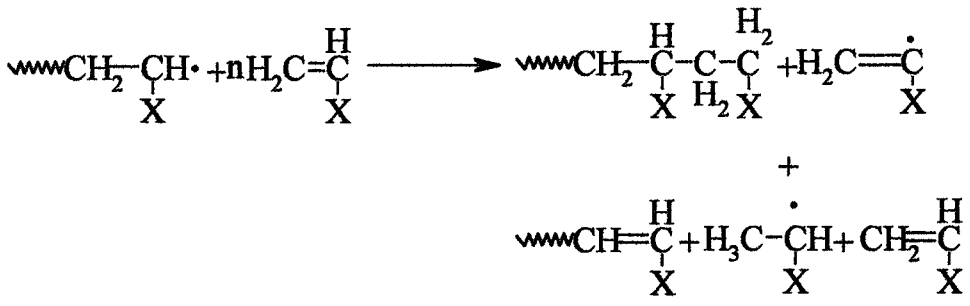
(2.4)

3) Chain transfer reactions

Chain transfer is the reaction of a propagating radical with a non-radical substrate to produce a dead polymer chain and a new radical capable of initiating a new polymer chain.

a) Transfer to monomer

If the generated monomer radicals become stable via resonance structure they do not initiate polymerization of a new chain. An example is given in (2.5)



(2.5)

b) Transfer to polymer chain

The transfer of an active center exist on a growing chain radical to the another polymer chain results in branching but it does not influence the length of the chain.

(2.6)

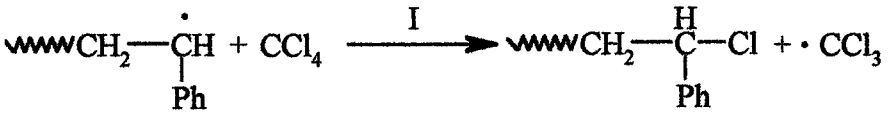
c) Transfer to initiator

Transfer to initiator involves the termination of a propagating radical by reaction of a molecule of initiator. The resulting polymer possesses two initiator-derived end groups, and in the process, a new primary radical is formed, which may initiate a new chain.

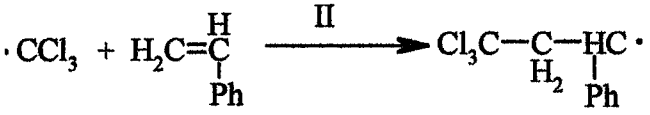
(2.7)

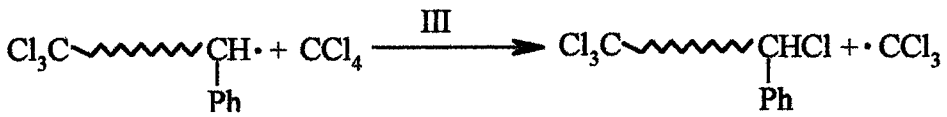
d) Transfer to solvent

The molecular weight of polymers obtained via a polymerization in a solvent is usually smaller than that of the polymers obtained in a solvent-free medium. This difference depends on the type of solvent used and the degree of the dilution.

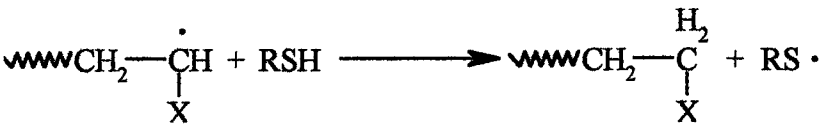


(2.8)





e) Transfer to modifier



(2.9)

4) Termination by impurities

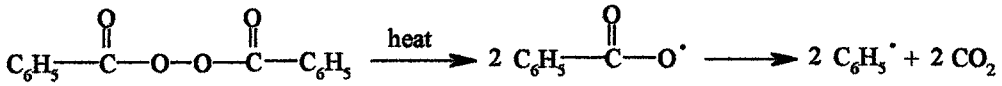
The impurities or oxygen react with the formed radical centers and so terminate the polymerization.

2.1.1. Free Radical Initiators

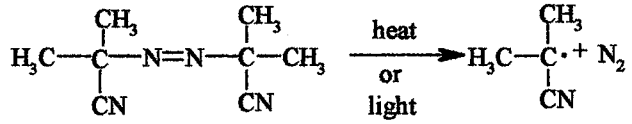
A good free radical initiator can be defined as a compound undergoing a homolytic chain cleavage when it is subjected to proper heat, radiation or chemical reaction and so resulting in formation of radicals whose activities are more than that of the monomer themselves. These radicals formed should be stable enough to be able to react with monomers and generate active centers.

2.1.1.1. Initiators giving radicals via homolytic chain cleavage of a covalent bond

Many organic compounds can produce free radicals for chain growth polymerization by absorbing thermal, photochemical, electrical or mechanical energy. Especially the thermal and photochemical chain breaking of an organic compound is the most widely used ones in the formation of free radicals. For example, organic peroxides and azo-compounds like dibenzoyl peroxide and 2,2-azobisizobutironitrile (AIBN) generate radicals either by heat or light. Two examples to the formation of radicals via this method are given in (2.10) and (2.11), decomposition of dibenzoyl peroxide and AIBN respectively.



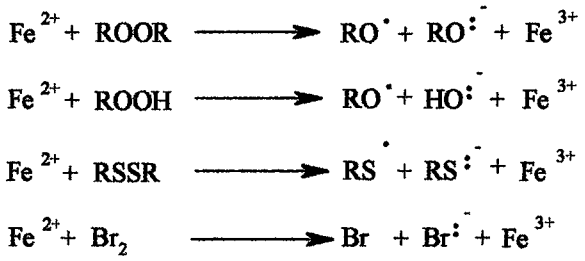
(2.10)



(2.11)

2.1.1.2. Initiators giving radicals by electron transfer

The most important one is the redox reactions.



$$Fe^{2+} + ROOR \longrightarrow RO^{\bullet} + RO^{:-} + Fe^{3+} \quad (2.12)$$

$$Fe^{2+} + ROOH \longrightarrow RO^{\bullet} + HO^{:-} + Fe^{3+}$$

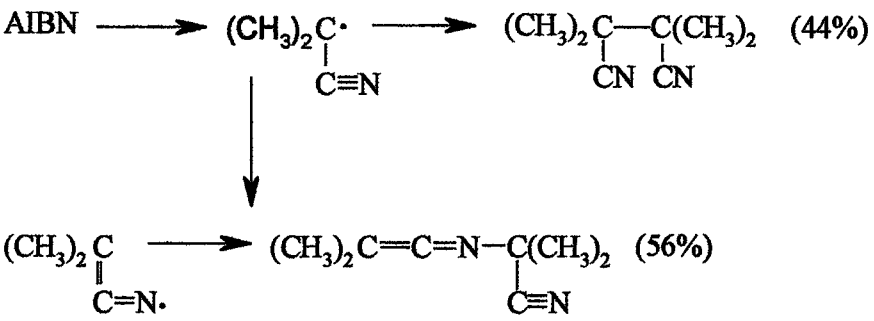
$$Fe^{2+} + RSSR \longrightarrow RS^{\bullet} + RS^{:-} + Fe^{3+}$$

$$Fe^{2+} + Br_2 \longrightarrow Br + Br^{:-} + Fe^{3+}$$

The pathway of the polymerization initiated by the electrochemically formed radicals usually undergoes over the anionic or cationic ions.

2.1.2. Initiator efficiency

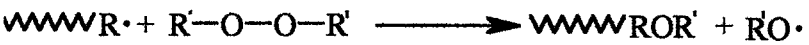
Although all of the initiator molecules are subjected to chain breaking in the polymerization medium, their efficiency to initiate the chain growth is rarely hundred percent. Some of the radicals formed cannot diffuse away due to the effect of solvent and hence react with each other. This is usually known as cage effect. An example to this kind of situation can be given as in the equation of (2.13).



$$AIBN \longrightarrow (CH_3)_2\underset{\displaystyle C\equiv N}{\underset{|}{C}}\cdot \longrightarrow (CH_3)_2\underset{\displaystyle CN}{\underset{|}{C}}-\underset{\displaystyle CN}{\underset{|}{C}}(CH_3)_2 \quad (44\%) \quad (2.13)$$

$$(CH_3)_2\underset{\displaystyle C=N\cdot}{\underset{\|}{C}} \longrightarrow (CH_3)_2C=C=N-\underset{\displaystyle C\equiv N}{\underset{|}{C}}(CH_3)_2 \quad (56\%)$$

Efficiency of the initiator is dependent on the type of solvent. Another reason reducing the effect of initiator is the reaction of some part of the initiator molecules with the active centers present in the polymerization medium.



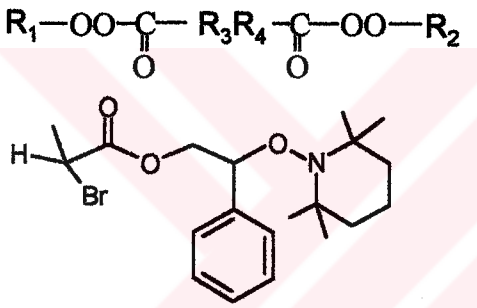
$$\sim\sim\sim R\cdot + R'-O-O-R' \longrightarrow \sim\sim\sim ROR' + R'O\cdot \quad (2.14)$$

As seen in (2.14) although one mole of initiator is used, as a result, the number of radicals is kept constant.

Because of the above reasons initiator efficiency is usually between 0,3 and 0,8 [6].

2.1.3. Bi-functional initiators

Bi-functional and multi-functional initiators have been synthesized in many applications. Their one important and successful use has been in the synthesis of block copolymers. Important examples to this group of initiators are bi-functional diperoxides and alkoxyamine based multi-functional initiators, for example 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo-propanoate, which was also used in this work, in the general structures of (2.15) respectively.



(2.15)

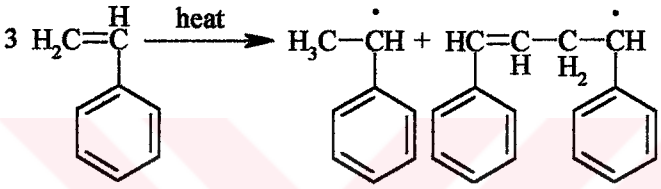
In free radical polymerization process, homo-polymers are unavoidably produced together with block copolymers, two radicals are created by the scission of peroxide and only one will be connected to the active polymer chain. Separation procedures are, therefore, necessary to isolate the block copolymer [3].

Due to the nature of free radical polymerization mechanism and kinetics, the rate of polymerization is inversely proportional to the chain length of the polymer formed. This means that increase in initiation rates will always be coupled with lowering of the molecular weight of the polymer produced. It has been shown that bi-functional free radical initiators with sequential decomposition kinetics modify the polymerization mechanism so as to allow faster reaction without lowering molecular weight of the polymer [7-8].

2.1.4. Thermal polymerization

Some of the monomers can initiate a polymerization without need of an initiator. In many cases, impurities exist in monomer, like peroxides and hydro-peroxides, formed due to the presence of oxygen, can initiate a polymerization by their thermal or photochemical degradations. The best examples to the thermally polymerizable monomers are styrene, methyl methacrylate and 2-vinyl tiyofen, 2-vinyl furan [9-10].

Although the exact mechanism is not known, the works done on this subject [11-12] shows that the thermal polymerization of styrene is initiated by two different mono-radicals in a termolecular reaction as seen in (2.16).



(2.16)

2.2. Controlled / "Living" Radical Polymerizations

Living polymerization was first defined as a chain growth process without chain breaking reactions (transfer and termination). Such a polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition. However, it does not necessarily provide for molecular weight control and narrow molecular weight distributions (MWD). Additional prerequisities to achieve these goals are that the initiator should be consumed at early stages polymerization and that exchange between species of various reactivities is fast in comparison with propagation. If these additional criteria are met, a controlled polymerization results. Polymerization can also be defined as controlled if side reactions occur, but only to an extent which does not considerably disturb the control of the molecular structure of the polymer chain.

Three types of radical polymerization have been called living;

Polymerizations where the normal termination process of radical-radical reaction is slow or absent because of the physical nature of the reaction medium or the

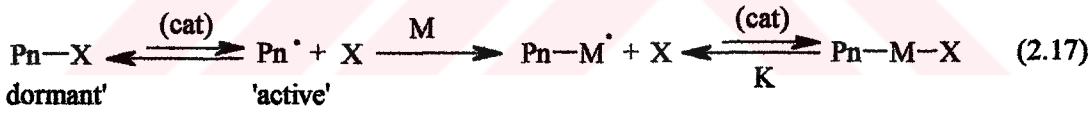
immediate environment of the reactive chain end. Systems in this class include precipitation polymerization, certain template polymerizations and polymerizations in inclusion complexes. Unfortunately these systems have little generality and do not have application in the synthesis of high purity block copolymers.

Systems with reversible termination where the bond formed by primary radical termination or chain transfer are stable. The aim of the first polymerization step is to synthesize a macro-initiator serving as precursor to a block co-polymer. Narrow polydispersities are not available by these techniques.

Systems with reversible termination where the bond formed by free radical termination or chain transfer is kinetically unstable under the reaction conditions. These polymerizations should be considered as true living polymerizations.

Only the latter class will receive detailed consideration in this work.

The latest developments in living free radical polymerizations of vinyl and cyclic monomers are base on the reversible protection of the growing chains in the form of inactive 'dormant' species exchanging reversibly with the active growing chain as seen in (2.17).



(2.17)

cat=Nu⁻, Lewis acids, hv, heat
X=protective group
Pn=polymer chin
M=monomer
K=equlibrium constant

Controlled polymerization requires a low proportion of deactivated chains, which can be achieved by keeping molecular weight sufficiently low. This necessitates a relatively high concentration of the initiator, or in other words, low $[M]_0 / [I]_0$ ratios. However when $[I]_0$ is high, since the termination is bi-molecular, contribution of termination becomes more significant when a large concentration of radicals [P.] is generated.

Therefore establishing an exchange between dormant and active species is necessary to solve this discrepancy. The concentration of dormant species can be equal to $[I]_0$, and the concentration of momentarily growing species to [P.]. The total number of growing chains will be equal to $[I]_0$, and radicals would be present at a very low stationary concentration, [P.], and therefore the contribution of termination should be very low. There are three possibilities to realize the concept of controlled radical polymerization.

1) Reversible homolytic cleavage of covalent species

$$P\text{—}R \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P^{\bullet} + R^{\bullet} \qquad (2.18)$$

An initiator with the structure of P-R is the adduct of the model of growing radical P., capable of propagation, and the scavenging or the dormant radical (R.), which ideally should react only with (P.) but not with the monomer itself.

This case probably the most postulated in controlled radical polymerization. As examples of (R.); Otsu and Yoshida [14] used dithiocarbamate radicals, Georges et al. [15-16] used nitroxyl radicals and Borsing et al. [17] used triaryl methyl species.

The problem with this method is that except nitroxyl radicals, the others may participate in side reactions leading to degenerative transfer

2) Reversible homolytic cleavage of persistent radicals

$$P^{\bullet} + X \rightleftharpoons (P\text{—}X)^{\bullet} \qquad (2.19)$$

The role of a scavenger radical may be also played by a neutral species. The persistent radical, (P-X)', should only cleave homolytically to form (P.) and the species X, but it should not react with monomer. X should be inert compound capable of reacting only with (P.). X may be elementoorganic or organometalic species with an even number of electrons. Some success have been reported with group XIII and XV elements such as aluminum [18] and phosphorus [19] as well as

with organometalic derivatives of Co [20], Cr [21], and other transition metals. In some cases not only radical but also ionic and coordinative polymerization may take place. The pathway of the polymerization is dependent on the nature of metal or elements, ligands and medium effects.

3) Degenerative transfer

$$Pn^{\bullet} + P1\text{-}R \xrightarrow{k_{tr}} P1\bullet + Pn\text{—}R \qquad (2.20)$$

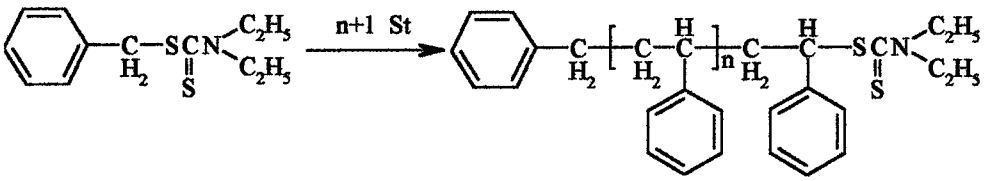
In this case growing radical (Pn.) reacts rapidly and selectively with a transfer agent (P1-R) to exchange the R group and form a dormant species (Pn-R) and a new radical (P1.), which is capable of chain growth. (P.) would be generated by a classical initiator such as AIBN, BPO and redox reactions. (P.) can react with monomer, for propagation, with (P-R), for degenerative transfer, and can also react one with another, for termination.

2.2.1. Initiation systems

Four main types of initiator have been used for the reversible deactivation of growing radicals in controlled free radical polymerization.

a) Organosulfides

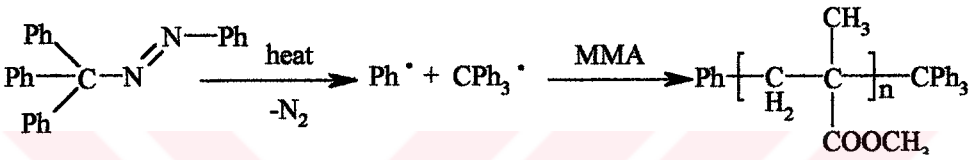
As discussed previously, the potential of organosulfides as initiators of living radical polymerization was first recognized by Otsu and Yoshida [14]. Living polymerization initiated by these species involves monomer insretion to C-S bond. BDC (Benxyl N,N-diethyl dithiocarbamate) and XDC (xylene bis (N-N diethyl dicarbamate), which are mono and di-functional fotointerferters, were used to initiate the living radical polymerizations of styrene and methyl methacrylate respectively [22]. As an example, living radical polymerization schematic of styrene with BDC is seen in (2.21).



(2.21)

b) Di and triarylmethyl derivatives

Otsu and Tezaki [23] reported on the use of tri phenyl methyl azo-benzene as an initiator of living polymerization. The phenyl radical initiates polymerization and the tri phenyl methyl radical reversibly terminates the chains.

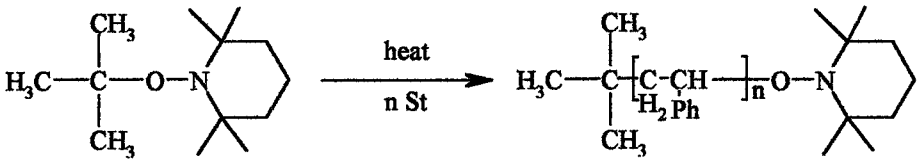


(2.22)

Living radical polymerization of methyl methacrylate in the presence of tri phenyl methyl azo-benzene is given in (2.22). The active end group of the initiator is reversibly decomposed over heating. The molecular weight of the polymer formed increases as the conversion increases and this is a one of the evidences of living radical polymerizations. Acar and Yagci [24] also used this initiator to prepare methacrylate block co-polymers.

c) Alkoxyamines

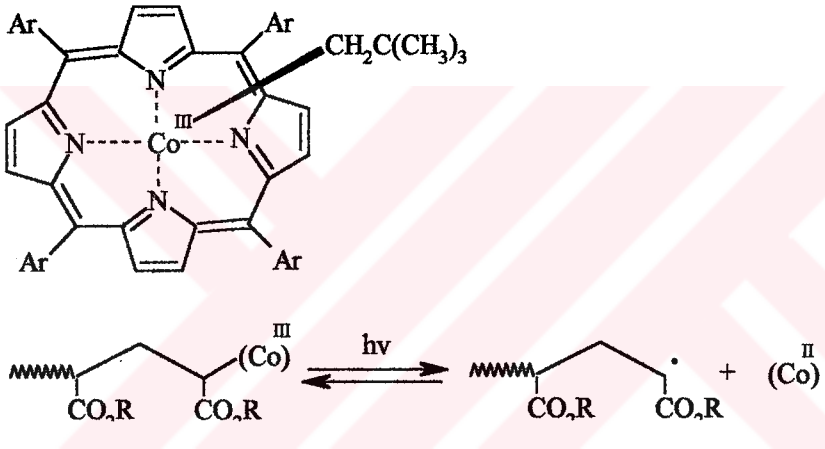
Rizzardo et al. [25] pioneered the use of alkoxyamines as initiators in living free radical polymerizations. The C-O bond is relatively weak and undergoes homolysis on heating to yield a reactive carbon-centered radical and a stable nitroxide. The carbon-centered radical initiates the polymerization and the nitroxide radical is inert towards monomer but they react with the propagating radicals by primary radical termination to form new oligo- or polymeric alkoxyamine initiator. Controlled radical polymerization of styrene with an alkoxyamine type of initiator synthesized by the decomposition of azobis (izobutyronitrile) (AIBN) in the presence of 2,2,6,6-tetra methyl piperidine-N-oxyl (TEMPO) is given in (2.23) as an example.



(2.23)

d) Organocobalt compounds

Organocobalt compounds may function as initiators of quasi-living polymerization. Wayland et al. [21] have demonstrated that it is possible to synthesize high molecular weight poly (methyl acrylate) with very narrow polydispersities (1,1-1,3) using this reagents. A schematic representation of the pseudo-living radical polymerization of methyl acrylate with an organocobalt compound is seen in (2.24).

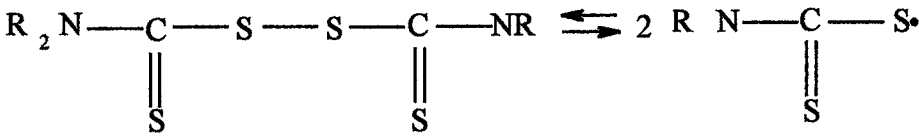


(2.24)

2.2.2. Iniferter method

Iniferters are initiators that induce radical polymerization that proceeds via initiation propagation, primary radical termination, and transfer to initiator. Because bimolecular termination and other transfer reactions are negligible, these polymerizations are performed by the insertion of the monomer molecules into the iniferter bond, leading to polymers with two iniferter fragments at the chain ends. The use of well-designed iniferters would give polymers or oligomers bearing controlled end groups. If the end groups of the polymers obtained by a suitable iniferter serve further as a polymeric iniferter, these polymerizations proceed by a living radical polymerization mechanism in a homogenous system. In these cases, the iniferters (C-S bond) are considered a dormant species of the initiating and propagating radicals. Iniferters can be classified into several types: thermal or

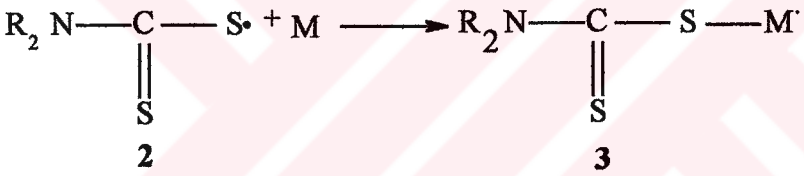
photoiniferters; monomeric, polymeric or gel iniferters; monofunctional, difunctional, trifunctional or polyfunctional iniferters; monomer or macro monomeriniferters.



(2.25)

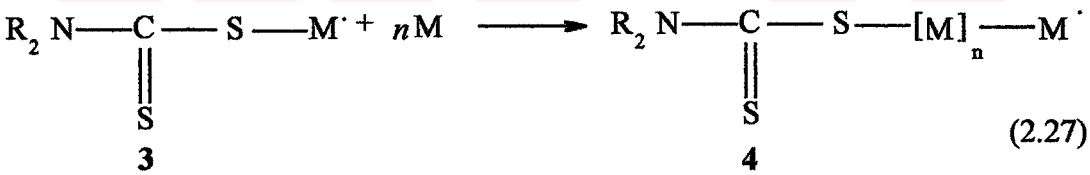
1 **2**

From the kinetic studies **1** in (2.25) was found to act not only as an initiator but also as a retarder, terminator, and transfer agent. Therefore, the polymerization of the monomer (M) with **1** in (2.25) proceeds via the dissociation of **1** (2.25), initiation, propagation, primary radical termination and chain transfer to **1** (2.25), according to eqs (2.25-2.29) respectively:



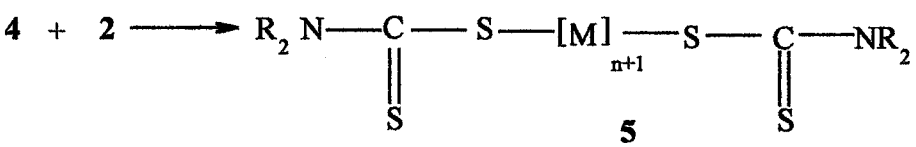
(2.26)

2 **3**



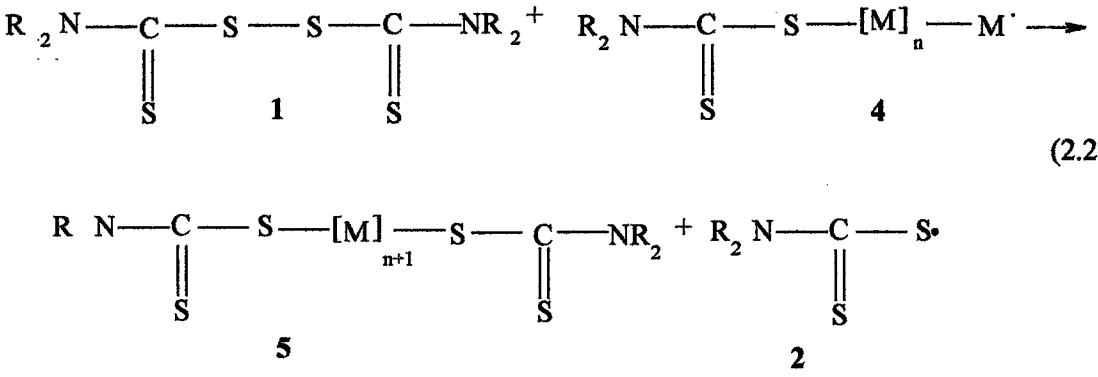
(2.27)

3 **4**



(2.28)

5



(2.29)

The ordinary bimolecular termination is neglected because primary radical **2** in (2.26) is less reactive for initiation and more reactive for primary radical termination. The chain transfer to **1** in (2.25) also occurs because the chain transfer constants are high values 0,72 for St and 0,48 MMA at 60°C, yielding a relatively low molecular weight polymer, **5** in (2.28), with two sulfide end groups.

When we consider polymer formation by radical polymerization, there are two extreme cases in regard to the activity of the initiators used :

Case1 is radical polymerization with the usual strong initiators leading to high MW polymers without controlled end groups because bimolecular termination occurs by combination or disproportionation. However, the bulk polymerization of St with benzoyl peroxide or AIBN gives a polymer with two initiator fragments, because the termination for St occurs only by combination.

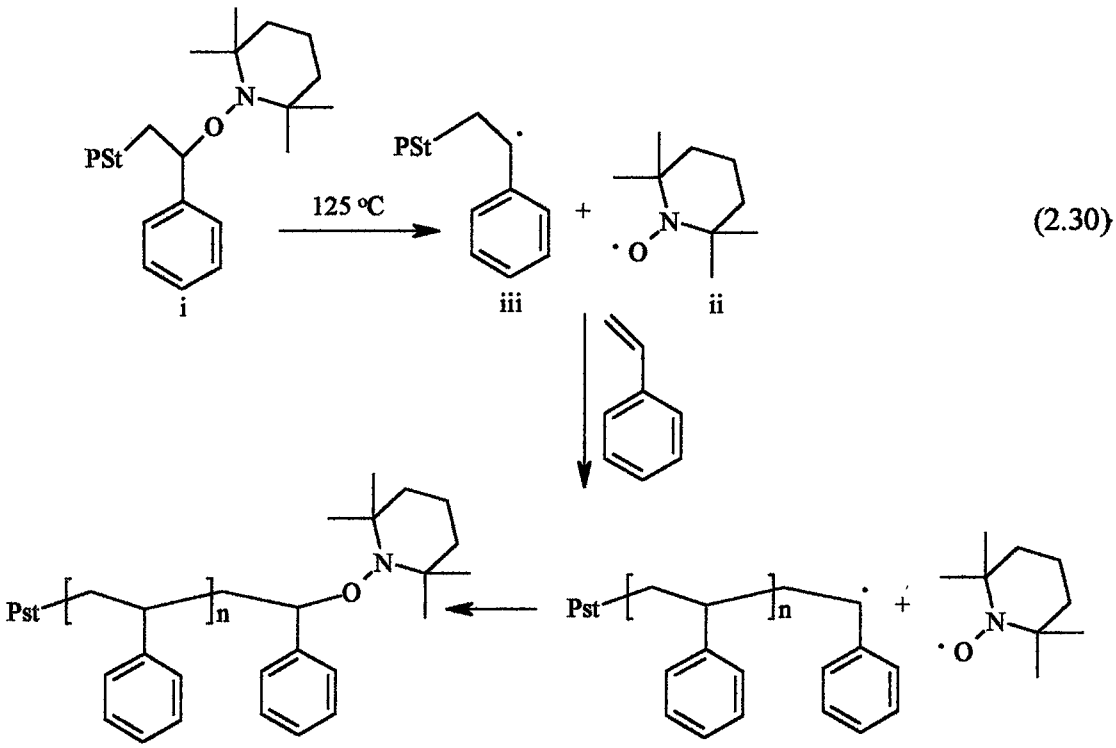
Case 2 involves weak initiators such as **1** in (2.25) or chain transfer agents in which bimolecular termination is negligible and the polymers with controlled ends are formed by primary radical termination and chain transfer reaction. These polymerizations proceed by an insertion of monomer, **5** in (2.28), and the MWs of the polymers do not change or increase with the reaction time. These polymerization might provide a new route for preparing specialty polymers. As described in Case 2 if the initiators such as **1** (2,25) induce such radical polymerization, polymers with two initiators fragments at their ends such as, **5** (2.28) are obtained as the result of monomer insertion. The use of well-designed initiators give various polymers with controlled end groups such as block polymers.

2.2.3. Stable free radical polymerization (SFRP)

Living free radical polymerization has gained in popularity as a result of the continued expansion of the stable free radical polymeriation (SFRP) process. Moad and Rizzardo [25] adopted a different approach and introduced the reversible end capping of the propagating chain ends by nitroxide free radicals, like 2,2,6,6-tetramethylpiperidinyl 1-oxy (TEMPO).

The use of TEMPO in living free radical polymerization was subsequently refined by Georges et al. who demonstrated that polystyrene with low polydispersity could be prepared using bulk polymerization conditions. These two seminal reports resulted in the true developments of living free radical procedures.

The origin of the unprecedented control in niroxide mediated living free radical polymerizations is believed to be the reversible termination of the growing polymeric radical to give a dormant, or inactive, species in which the nitroxide moiety is covalently bound to the polymer chain end. At lower temperatures, this trapping simply results in termination of the polymerization reaction, and infact nitroxides are good inhibitors for vinyl monomers. However, at elevated temperatures, typically 100 °C or greater, the C-ON bond of alkoxyamine type of initiator, as seen in (2.30) as (i), is homolytically unstable and undergoes fragmentation to regenerate the stable free nitroxide radical (ii) and the polymeric radical (iii). The polymeric radical can then undergo chain extension with monomer to yield a similar polymeric radical in which the degree of polymerization has increased. The recombination of this finally formed polymeric radical with nitroxide then gives again dormant species, which essentially has the same structure as (i) and the cycle of homolysis / monomer addition can repeated as seen in (2.30).



(2.30)

Since the mediating nitroxide free radical does not initiate the polymerization of vinyl monomers, no additional propagating centers are created. An extremely favorable consequence of the presence of significant amounts of covalent, or inactive, chain ends is that the overall concentration of reactive chain ends is decreased substantially. This lowers the occurrence of unwanted side reactions such as termination, disproportionation, or combination, which enables the polymer chain to grow in a controlled process. However it should be pointed out that the occurrence of these side reactions is not eliminated, in the strictest sense, the polymerizations are not truly living. The possible side reactions also include the auto polymerization, e.g. of styrene, because at elevated temperatures for example higher than 100°C, styrene polymerizes by self initiation via formation of Diels-Alder adduct, which is further aromatized, generating radicals.

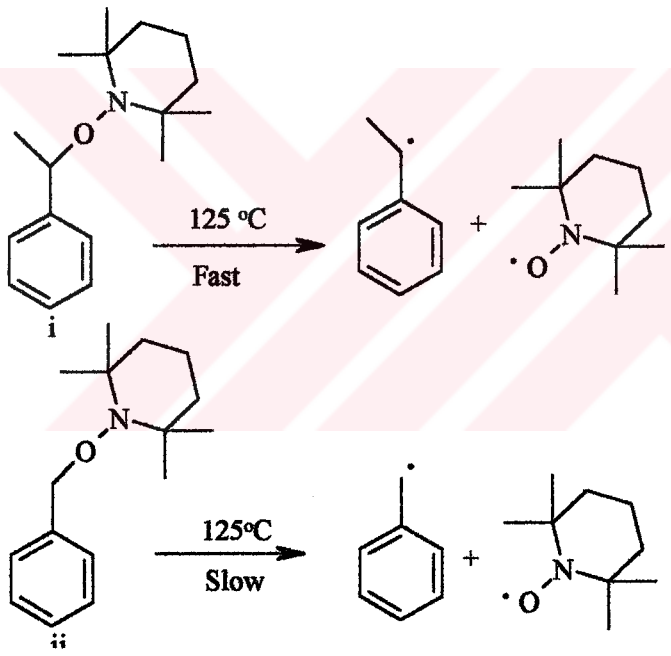
2.2.3.1. Mechanical considerations

1) Structural effects of unimolecular initiators

The alkoxyamine type of initiators, which on decomposition, gives an initiating benzylic radical and a nitroxide radical in the desired 1:1 stoichiometry. It has recently been shown that the strength of the C-ON bond in alkoxyamine-based

initiator is of crucial importance to the success of living free radical polymerization. If C-ON bond is too thermally stable then the homolysis is slow compared to the propagation, leading to uncontrolled polymerizations.

It was found that a variety of functional groups could be substituted on the aromatic ring, nitroxide unit or β-carbon without affecting the polymerization process deleteriously. However if the α-methyl group is removed to give parent benzyl-TEMPO derivative, as seen in (2.31) as (ii), a substantial loss of control over the polymerization is observed in the study of Malmstrom and Hawker (1998). The reasons for this dramatic change are shown in the same work as the difference in stability, or rate of formation, for the initiating benzylic radical.

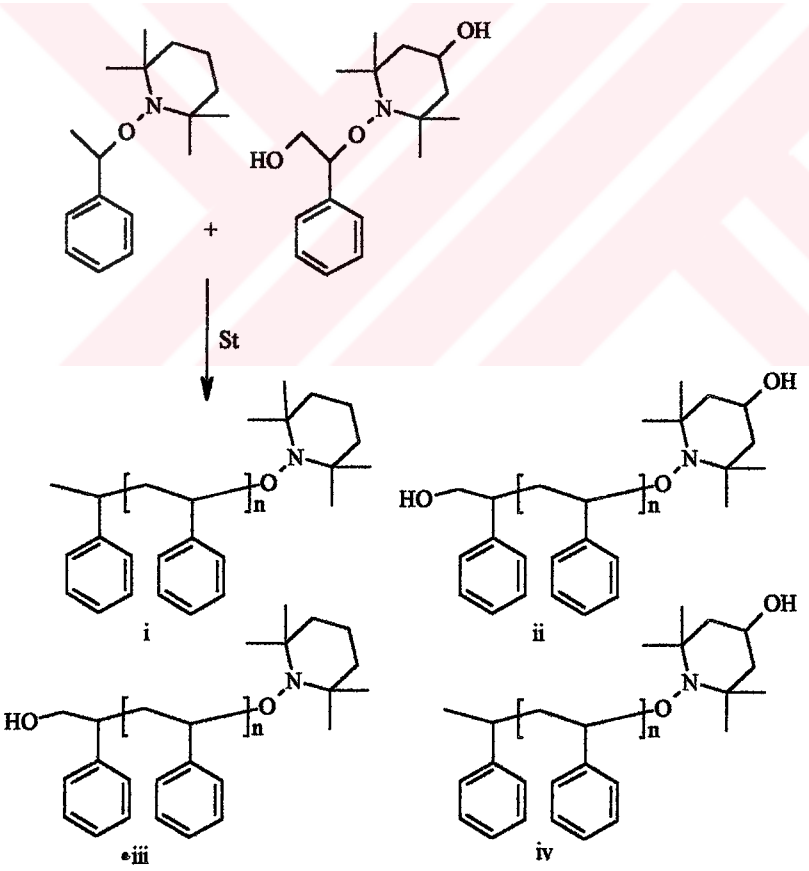


(2.31)

The steric or electronic nature of nitroxide can significantly increase the rate of polymerization [28]. For example Puts and Sogah [29] have shown that by replacement of two methyl groups with phenyl groups to give 2,5-dimethyl-2,5-diphenylpyrolidine-1-oxyl, instead of TEMPO, a significant increase in the reaction rates is observed, which allows the polymerization to be conducted at lower temperatures.

2) Mobility of nitroxide radical

The propagation step in nitroxide living free radical polymerization may either occur via an associative, or insertion type, mechanism or by dissociative mechanism, in which the nitroxide completely dissociates from the growing polymer chain end. To determine which of these are operating, Malmstrom and Hawker (1998) conducted series of experiments in the standard living polymerization conditions and in the presence of two similar initiators, which differ from each other in the presence of, or absence of hydroxyl groups. Theoretically if an insertion type occurs only two products should be formed, seen in (2.32) as (i) and (ii). However, nitroxide is free to diffuse into polymerization medium and undergoes exchange with other propagating chain ends and so as a result, (iii) and (iv) types of products could also be obtained.



(2.32)

3) Role of auto-polymerization

Since the stable free radical polymerizations are conducted at relatively high temperatures, auto-polymerization should not be ignored. To gain a better understanding of auto-polymerization a series of experiments, in which styrene was heated at 125°C in the absence of initiator, but in the presence of a nitroxy radical, TEMPO, was conducted by Malmstrom and Hawker (1998). At the end of the experiments polymers having low polydispersities and molecular weights that corresponded to the theoretically calculated ones were obtained. This shows that unexpectedly high degree of control occurred meaning that chains are being initiated by auto-polymerization, with the role of nitroxide being to control the polymerization. The radicals are slowly formed during the polymerization. The radicals formed by self-initiation are initially trapped by the scavengers and then when the concentration of the scavengers is low enough and the concentration of the growing radicals is high enough polymerization starts. This is evidenced by long induction period. As a result, according to Matyjaszevski it is not necessary to use radical initiators in SFRP of styrene.

The studies on the SFRP techniques generally show that;

a) Rate of the polymerization is dependent firstly on the monomer and then the alkoxyamine concentration.

b) Molecular weights increase linearly as the conversion and good control over the polymerization is obtained up to the molecular weights of 30000.

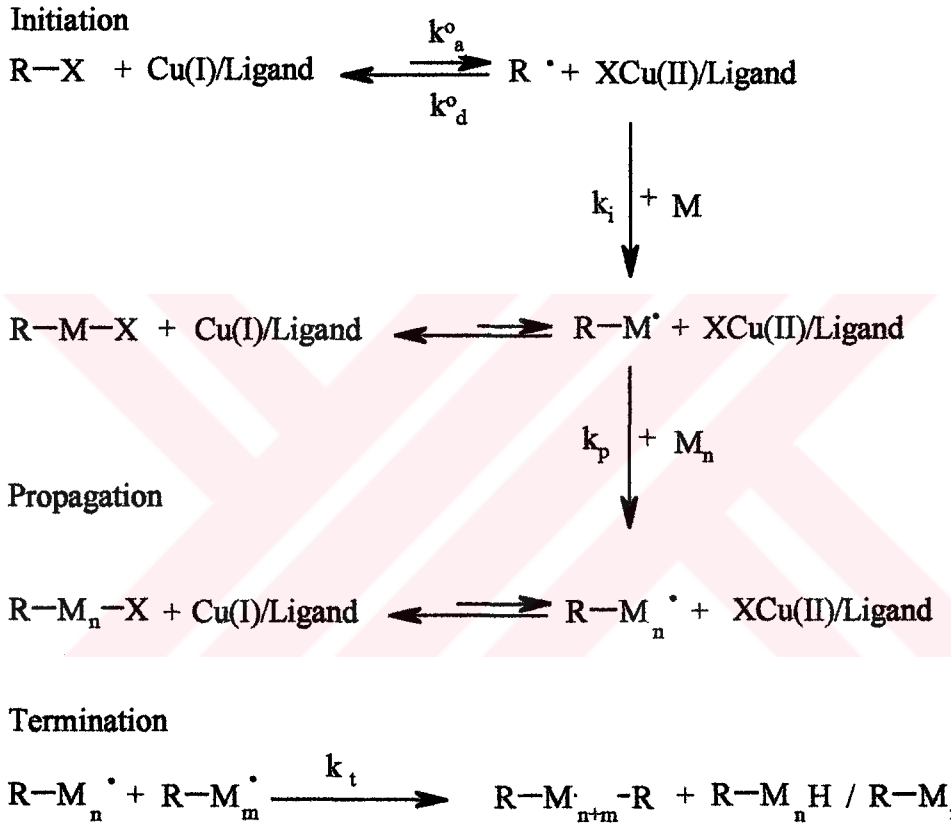
c) Polydispersities of smaller than 1,5 can be achieved.

d) The concentrations of TEMPO during the polymerization is about %0,1 –1 of that of TEMPO in the beginning.

2.2.4. Atom transfer radical polymerization (ATRP)

Atom transfer radical polymerization is one of the most widely used living free radical polymerization techniques and seems to be the most versatile one. This technique can successfully be applied to the living radical polymerization of methyl methacrylate, acrylate and styrene monomers with well-controlled molecular weights and well-defined structures [30-33]. A typical ATRP system consists of alkyl halides,

as initiators, copper (I) halides complexed with some ligand(s), and of course monomer. Cu / Ligand complex behaves as a halogen atom transfer agent between the active and the dormant chains. By using an activated alkyl halide as an initiator, all of the chains can start growing at the same time. Furthermore, the equilibrium between the active and the dormant chains ensures a low concentration of propagating radicals and thus reduces the probability of termination. The schematic representation of the mechanism of ATRP is given in (2.33).



(2.33)

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.

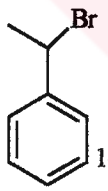
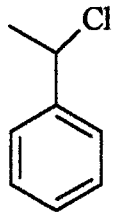
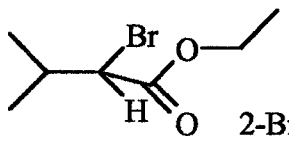
2.2.4.1. Initiators

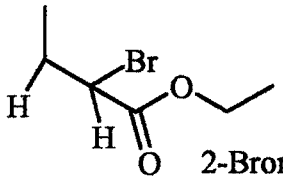
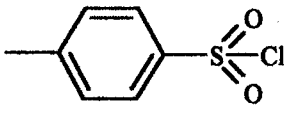
Organic halides, initiators, may either be a small molecule or a macromolecule. Hence, a variety of halogenated initiators and macro initiators activated by various types of aryl, sulfonyl and carbonyl groups can be used in ATRP systems.

A fast equilibrium between the active and the dormant chains is needed to observe low polydispersities in controlled or living radical polymerizations. In ATRP both effective initiation and good control of the polymerization rely heavily on the position of the equilibrium in both the initiation and the propagation steps, and also on reactivities of the radicals generated in the initiation step. Thus, choosing a suitable organic halide and Cu(I) halide is necessary for the controlled polymerization.

The initiator usually, but not always, should have a structure homologous to the corresponding polymer end group. The most frequently used initiator types in ATRP systems are given in Table 2.1.

Table 2.1 Types of initiators used in ATRP sytems

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 2-Bromo ethyl isobutyrate	Methylmethacrylate

 2-Bromo ethyl propionate	Methacrylate and other acrylates
 p-toluene sulphonyl chloride	Methylmethacrylate

2.2.4.2. Transition metals used in ATRP

Basic requirements for the good catalyst are high selectivity towards atom transfer process and high lability of the resulting X-Mt $^{n+1}$ species (higher oxidation state of metal). The metal should participate in a one-electron process, which should result in oxidative addition / reductive elimination but not in atom transfers 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 the 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 Mt ^{n} / Mt $^{n+1}$ but it must be remembered that ATRP is not an electron transfer process but an atom transfer process. Thus the inner coordination sphere of Mt ^{n} must expand to accommodate a new X (halide) ligand. Expansion from tetra to penta-coordinated structure Cu (I) / 2 ligand → X-Cu (II) / 2 ligand or penta-coordinated structure X_2Fe (II) / $3PR_3$ → X_3Fe (III) / $3PR_3$ the most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, Ni(II), Ru(II) / Al $(OR)_3$ and Fe(II) / $3PR_3$.

2.2.4.3. 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 make the catalytic system soluble. The most widely used ligands for ATRP systems are the

derivatives of 2,2-bipyridine and nitrogen based ligands such as N,N,N',N'',N'' pentamethyldiethylenetriamine (PMDETA), Tetramethylethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetraamine (HMTETA), tris[2-(dimetylamino) ethyl]amine (Me-TREN) and Alkylpyrdylmethanimines are also used.

Among all these ligands, amine ligands have been attracting the interest of the scientist in recent years. Since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper bipy complexes, the employment of the simple amines in ATRP may lead to faster polymerization rates [32]. The study of Xia and Matyjaszevski (1997) also shows that when bipy or TMEDA is used as ligand, a copper(I) to ligand ratio is usually selected as 1:2, while in the case of PMDETA is chosen as the ligand the ratio of 1:1 is sufficient to achieve maximum rates and control of polymerization. The low polydispersities can be ascribed to the less sterically hindered copper(II)-PMDETA complex, which facilitates the deactivation process

2.2.4.4. Monomers

In ATRP, a variety of monomers, such as styrenes, (meth)-acrylates, acrylonitrile, acrylamides, methacrylamides, N-vinylpyridine and diens can be used to obtained well-defined polymers. The polydispersities of the polymers obtained via ATRP techniques should be between 1,05 and 1,5.

2.2.4.5. Effects of other parameters

At higher temperatures ATRP usually gives better results, because $K\ °_{eq}$ and k_p, equilibrium and rate of propagation constants in ATRP respectively, increase as the temperature increases. The activation energy in the propagation step is much more higher than that in termination, either by disproportionation or combination, step resulting in higher k_p / k_t ratios leading to better control of polymerization at elevated temperatures. On the other hand, since the possibility of occurrence of the termination and the side reactions at high temperatures becomes more significant, it is necessary to make an optimization depending on the molecular weight and the functionality that the resulting polymer wanted to have.

2.2.4.6. 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 usually negative first order with respect to the deactivator (CuX_2 / Ligand).

The rate equation of ATRP is obtained by the aid of some assumptions such that the contribution of termination on the rate of the polymerization is ignored, the initiating molecules are completely consumed in the initiation step and fast equilibrium, which is necessary for getting low polydispersities, is ensured. The rate of polymerization is formulated in discussed conditions and given in (2.34).

$$R_p = k_{app}[M] = k_p[P.][M] = k_p K_{eq}[I]_O \frac{[Cu(I)]}{[Cu(II)X]}[M] \qquad (2.34)$$

Control of the polymerization and thus the resulting polymer depends not only on the concentration of the growing radicals but also on the rate of propagation and deactivation steps in atom transfer radical polymerization. If the deactivation does not occurs, if it is too slow ($k_p >> k_d$), there will be no difference between ATRP and the classical redox reactions and the termination and transfer reactions may be observed. To gain better control over the polymerization, addition of one or a few monomers to the growing chain in each activation step is desirable. Molecular weight distribution for ATRP is given in (2.35).

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_d[RX]_0}{k_p[XCu^{II}]}\right)\left(\frac{2}{p} - 1\right) \qquad (2.35)$$

p= poymerization yield
$[RX_0]$=concentration of the functional polymer chain
$[XCu^{II}]$=concentration of the deactivators
k_d=rate of deactivation
k_n=rate of propagation

When a hundred percent of conversion is reached, in other words p=1, it can be concluded that;

a) For the smaller polymer chains, higher polydispersites are expected to be obtained because the smaller chains include little activation-deactivation steps resulting in little control of the polymerization.

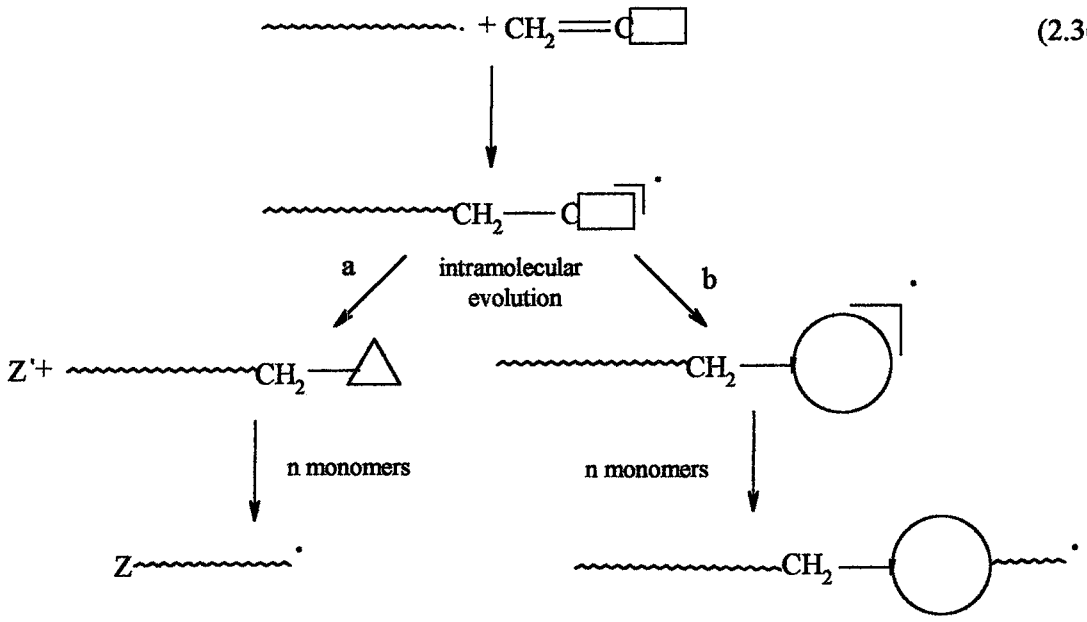
b) For the higher ratios of k_p / k_d, higher polydispersities (molecular weigh distributions) are usually obtained.

c) Resulting molecular weight distribution decreases as the concentration of the deactivators decreases.

As a result, atom transfer radical polymerization (ATRP) is a powerful technique allowing the polymerization of a variety of monomers with a high degree of control over the molecular weights and the molecular weight distributions of the resulting polymers. Additionally, since the polymerization conditions are relatively simple, various types of macromolecular structures can be achieved with a simple polymerization system via this method.

2.2.5. Addition –fragmentation process

An addition-fragmentation process is said to occur in free radical polymerization whenever a growing polymer chain reacts with a compound bearing both an activated site of unsaturation and a weak bond located somewhere else in the molecule. The intermediate radical formed by the addition of propagating radical on the transfer agent undergoes fragmentation involving the weak bond generating another radical which can enter the polymerization cycle. Such a process occurs with the formation of a functional group on the backbone of the polymer (which carried also radical, (2.36a) or at the end of the polymer chain (the radical resting another molecule (2.36b). The former case involves the use of an addition-fragmentation monomer and the latter the introduction of an addition-fragmentation chain transfer agent in the polymerization medium (2.36).



(2.36)

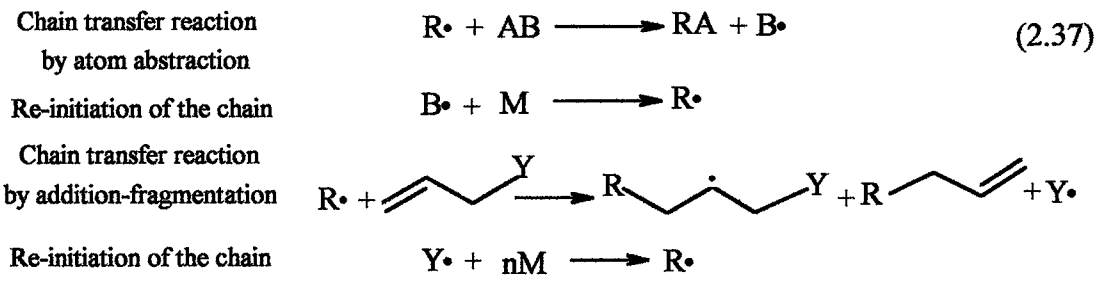
(2.36a) (2.36b)

Many monomer and transfer agents based on these types of skeleton have already been developed. However the actual use of an addition-fragmentation chain transfer agent or of an addition-fragmentation monomer in industrial applications is still limited at the present time, because of various problems arising from their synthesis, polymerizability and properties, although such compounds could inherently be useful in most industrial applications.

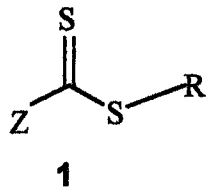
The control of molar mass in free radical polymerization is usually achieved by the addition of a chain transfer agent in the polymerization medium[1]. When a chain carrying radical is trapped by another specific compound XY to produce a radical Y• which is also reactive, this radical Y• can re-initiate a new radical chain. In this case XY is called a chain transfer agent. Two kinds of chain transfer agents can be distinguished according to their mode of action:

1. Atom or group transfer agents operating by an abstraction pathway (2.37). These additives are generally solvents such as CCl_4, mercaptans, substituted disulfides which react in the medium as atom donors to the growing macro radicals, thus terminating the polymer chain and generating, respectively a trichloromethyl a thiyl radical, able to re-initiate polymerization [34-35]

2. Addition-fragmentation chain transfer agents (2.37). The chain transfer agents which fallow the addition-fragmentation mechanism are particular interest in organic and polymer chemistry. Recently many studies have shown that ally, acrylyl and allenyl transfer to alkyl halides represent powerful synthetic tolls to prepare sophisticated molecules. Such a process was also identified as an effective means for controlling the molar mass of vinyl polymers, avoiding the use of conventional chain transfer agents based on thioderivatives.

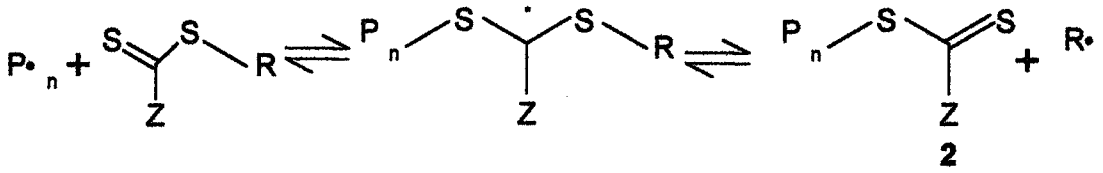


Thiocarbonylthio compounds of general structure **1** in (2.38) confer living characteristics to radical polymerization [36-37]. These reagents function by establishing a dynamic equilibrium between propagating radicals ($P_n^{\bullet}$) and dormant chains **2** in (2.38) by a mechanism of reversible addition –fragmentation chain transfer (raft) as shown in (2.38). RAFT agents **1** in (2.38) function effectively only when the substituent on sulfur (R) is good homolytic leaving group when compared to the polymer chain P_n. With appropriate choice of the RAFT agent **1** in (2.38) a wide range of polymers of predetermined MW and narrow polydispersity can be prepared [36-37-38]. The versatility and convenience of this process offer distinct advantages over other forms of living radical polymerization [39-40].

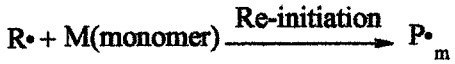


1

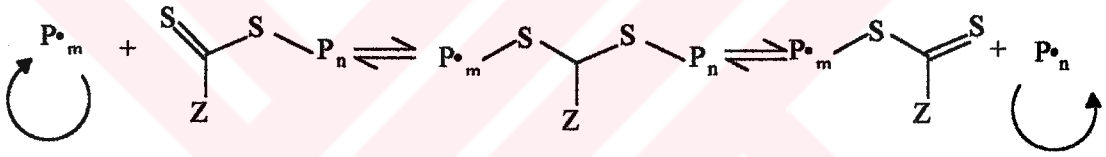
(2.38)



2



Equilibration



2.3. Copolymers

Homopolymers are derived from one species of monomer whereas copolymers are composed of two or more monomer units. Copolymers from two, three, four species of monomers are called bipolymers, terpolymers, quater polymers etc. Copolymers are subdiveded into block, gradient, random, periodic, segmented and graft copolymers.

Block copolymers are polymers which consist of two or more monomers that are segregated into separate regions of the polymer chain of the polymer chain, but are covalently bound to each other. Gradient copolymers exhibit a compositional gradient along the chain: one end of a bipolymer is enriched in first monomer unit and the other end in second monomer unit. Random copolymers have no continuous change in instantaneous compositon. In periodic copolymers, monomeric units are arranged in periodic sequences. Multiblock copolymers with short block lengths are

known as segmented copolymers. In graft copolymers, the block are connected to the main chain as side-chains. Schematic representation of the compositon in block, gradient, random, periodic, segmented and graft copolymers, in which the open circles denote monomer 1 and the closed circles denote monomer 2 is given in (2.39).

Block

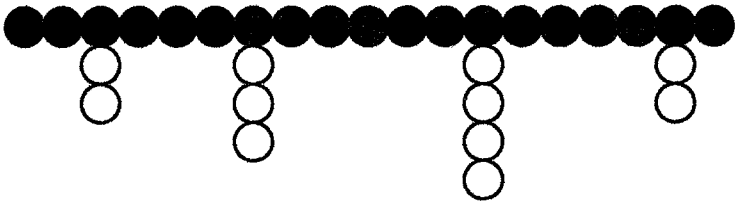
Gradient

Random

Periodic (2.39)

Segmented

Graft



The synthesis of block copolymers is often difficult or impossible in conventional free radical polymerization because the required functionality control is limited. During the last decade, various methods have been proposed and used for the synthesis of well defined block copolymers. These methods include (a) the sequential living polymerization of monomer units (b) coupling of preformed living chain ends (c) the transformation approach, in which the first monomer is polymerized to produce a polymer with a functional group that is capable of initiating polymerization of another monomer by a different mechanism. However, the transformation route may be somewhat less convenient if any intermediate protection or further functionalisation is required [41]. In recent years, controlled/ "living" radical polymerizations, such as atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization and reversible addition-fragmentation chain transfer (RAFT) polymerization, have considerable widened the oppurtunities for block copolymer stynthesis. This expansion is primarily due to the use of free radical intermediates during the polymerization, thus a large range of vinyl monomers may be utilized and the polymerization can take place under nonexating reaction conditions.

Synthesis of multi-functional initiators compatible with atom transfer (ATRP) and stable free radical (SFRP) polymerization techniques allows the polymer chemistry to get copolymers with controlled molecular weight and structure that leads to obtain well-qualified materials having the characteristics of two different monomers. The basic concept behind this new approach to block copolymers is that a single bearing two or more functional groups can be used to sequentially initiate one type of polymerization, and then without further transformation steps the other original functional group, which is now at the chain end of the first polymer block can be used to initiate a second type of polymerization. The advantage of this method is the potential to form block copolymer from disparate monomer units without any intermediate deprotection or functionalization reaction.

3. EXPERIMENTAL PART

3.1. Chemicals used

a) Monomers

MMA (99% Aldrich), tBA (99% Aldrich), and St (99% Aldrich) were passed through basic alumina column to remove inhibitors and then dried over CaH_2 and distilled under vacuum prior to use.

b) Solvents

Tetrahydrofuran (THF, 99.8%, J.T. Baker HPLC grade) was dried and distilled over lithium aluminium hydride. Dichloromethane was purchased from Aldrich and used after distillation over P_2O_5. All other reagents were purchased from Aldrich and used as received.

c) 2-Phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]-1-ethanol

It was synthesized according to the procedure of Hawker [42]. (92%). ^{1}H-NMR ($CDCl_3$) δ 1.15-1.58 (m, 18H), 3.72 (d of d, J=2.5 and 12 Hz, 1H, CH_2), 4.22 (d of d, J=9.5 and 12 Hz, 1H, CH_2), 5.31 (d of d, J=2.5 and 9.5 Hz, 1H, CH), 5.89 (br s, OH), 7.29-7.36 (m, 5H, ArH). ^{13}C-NMR ($CDCl_3$) δ 17.25, 20.66, 25.64, 32.20, 34.21, 39.99, 40.52, 61.03, 67.93, 84.23, 126.96, 127.83, 128.31, 139.1

3.2. Synthesis of 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo propanoate,(1)

To a round bottom flask were added 2-Phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]-1-ethanol (2,24 g, 3,06 mmol), triethylamine (Et_3N) (1,84 ml, 13,14 mmol), and 30 ml of dry tetrahydrafuran (THF). To the reaction mixture, stirred at room temperature under nitrogen was added drop wise 2-bromopropanoyl bromide (1,4 ml, 13,21 mmol) in 20 ml of dry THF over a period of one hour. The reaction mixture was stirred at room temperature overnight. The salt

was removed by filtration and after THF evaporation, the crude product was dissolved in dichloromethane (CH_2Cl_2) and washed successively with excess K_2CO_3 aqueous solution and water. Then dried over anhydrous Na_2SO_4, CH_2Cl_2 was removed and the crude ester was passed through a column of silica gel using hexane as the eluent. The resulting material was obtained as a pale yellow oil (1,8 g, 54%)

3.3. Synthesis of Poly(tert-butyl acrylate) and Polystyrene Macroinitiators

Poly(tert-butyl acrylate) (PtBA) macroinitiator was prepared by ATRP of t-butylacrylate in bulk using CuBr / N,N,N',N'',N'',-pentamethyldiethylenetriamine (PMDETA) as catalyst and **1** as initiator at 80°C. To a Schlenk tube equipped with magnetic stirring bar, the degassed monomer, ligand, catalyst, initiator were added in the order mentioned. Tube was degassed by three freeze-pump-thaw cycles, left under vacuum and placed in a thermostated oil bath at given temperature. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and unreacted monomer was evaporated under reduced pressure. The resulting polymer was dissolved in THF, precipitated from excess of methanol/water (80/20; v/v). After decantation, the polymer was dissolved in minimum amount of dichloromethane (approximately 30 ml) and dried over Na_2SO_4. Finally, the dichloromethane was removed by evaporation.

Polystyrene (PSt) macroinitiator was prepared by SFRP in the presence of **1**. The reaction mixture was degassed by three freeze-pump-thaw cycles and polymerized at 125°C for given time. The polymerization mixture was diluted with THF and precipitated in methanol.

3.4. Synthesis of Diblock Copolymers

General procedure for the synthesis of poly(tBA-b-MMA) diblock copolymer using ptBA as macroinitiator

The procedure for the synthesis of diblock copolymers are as follows; the polymerization of MMA was carried out in a Schlenk tube equipped with magnetic stirring bar. A given amount of MMA, CuCl, PMDETA, diphenylether (DPE) (MMA/DPE = 1; v/v) and ptBA as macroinitiator was added to the tube in the order

mentioned. Tube was then subjected to freeze-pump-thaw cycles three times to remove dissolved gas. The polymerization was conducted at 80°C for given times. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and unreacted monomer was evaporated under reduced pressure. The resulting polymer was dissolved in THF, precipitated in a 10 fold excess of methanol/water (80/20; v/v) and then isolated by vacuum filtration.

General procedure for the synthesis of poly(St-b-tBA) diblock copolymer using polystyrene as macroinitiator

Poly(St-b-tBA) block copolymer was prepared by ATRP of tBA using CuBr/PMDETA as catalyst and polystyrene as macroinitiator. The polymerization was carried out at 80°C under degassed condition for given times. The purification was as described above for the diblock copolymers.

3.6. Synthesis of Triblock Copolymers

The synthesis of poly(St-b-tBA-MMA) was accomplished by SFRP of St using DPE as solvent (monomer/solvent = 1; v/v) and poly(tBA-b-MMA) diblock copolymer as macroinitiator. The reaction mixture was degassed and polymerized at 125°C for given times. The reaction mixture was diluted with THF and precipitated in a 10 fold excess methanol.

Triblock copolymer possessing same monomer structure but synthesized by SFRP-ATRP-ATRP route was achieved by ATRP of MMA using CuCl/PMDETA as catalyst and Poly(St-b-tBA) diblock copolymer as macroinitiator under degassed condition at 80°C for given times. The polymer was recovered and purified as described above for diblock copolymers.

3.7. Characterization

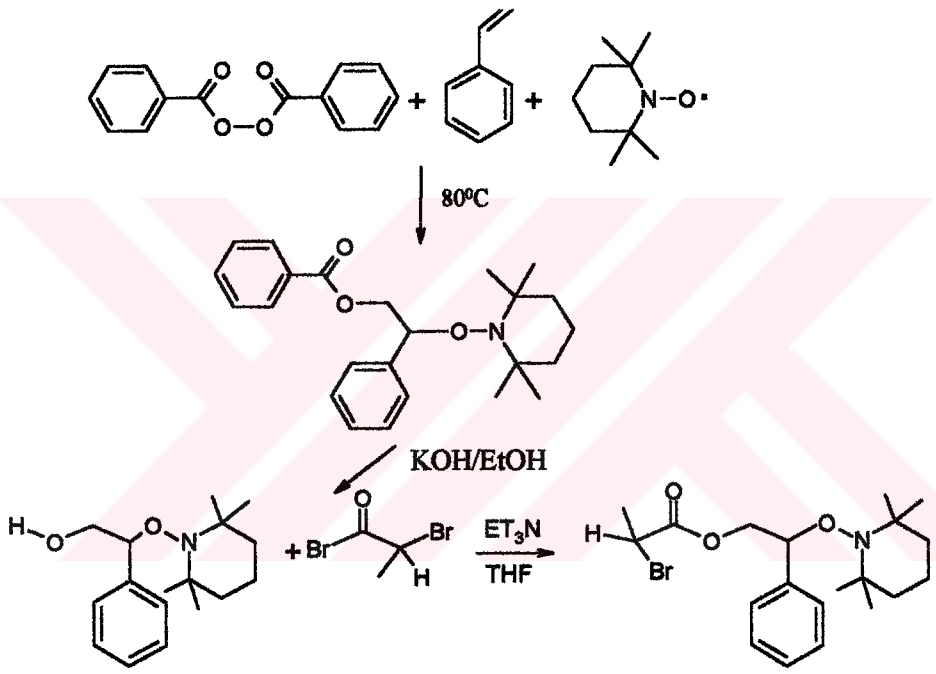
The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer (250 MHz for proton and 62.86 MHz for carbon) in $CDCl_3$. Gel permeation chromatography (GPC) analyses were performed with an Agilent Model 1100 instrument consist of pump and RI detector and three Waters Styragel columns (HR

4, HR 3, and HR 2). THF was used as eluent at a flow rate of 0.3 mL /min at 30°C. The molecular weight of the polymers was calculated with the aid polystyrene standards. All polymers obtained were dried under vacuum for 24h and the conversions were determined by gravimetrically.

4. RESULTS AND DISCUSSIONS

4.1. Synthesis of Initiator

4.1.1. Synthesis of 2-phenyl-2-[(2,2,6,6- tetramethylpiperidino)oxy]ethyl 2-bromo propanoat, (1)



Scheme 4.1 Synthesis of 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo propanoat, (1)

1-(benzyloxy)-2-phenyl-2-(2',2',6',6'-tetramethyl-1-piperidinooxy)ethane was synthesized according to the procedure reported by Hawker et al. [42]. It was then hydrolyzed with aqueous potassium hydroxide to give tempo alcohol in quantitave yield. The asymmetric difunctional initiator, (1), was prepared from tempo alcohol and corresponding acid bromide in ca 54% yield. The obtained initiator, (1), was then characterized by ^{1}H and ^{13}C-NMR. The ^{1}H-NMR spectra of the initiator showed no signal corresponding to OH protons of the starting tempo alcohol, indicating quantitave esterification (Figure 4.1).

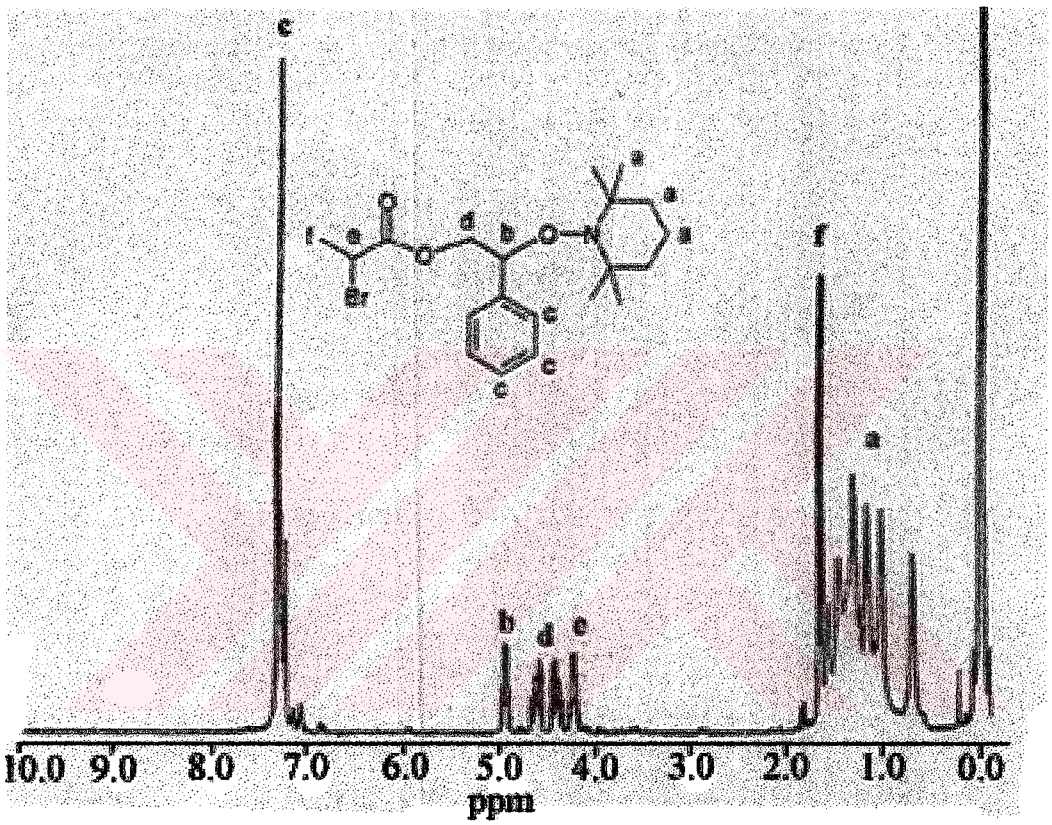
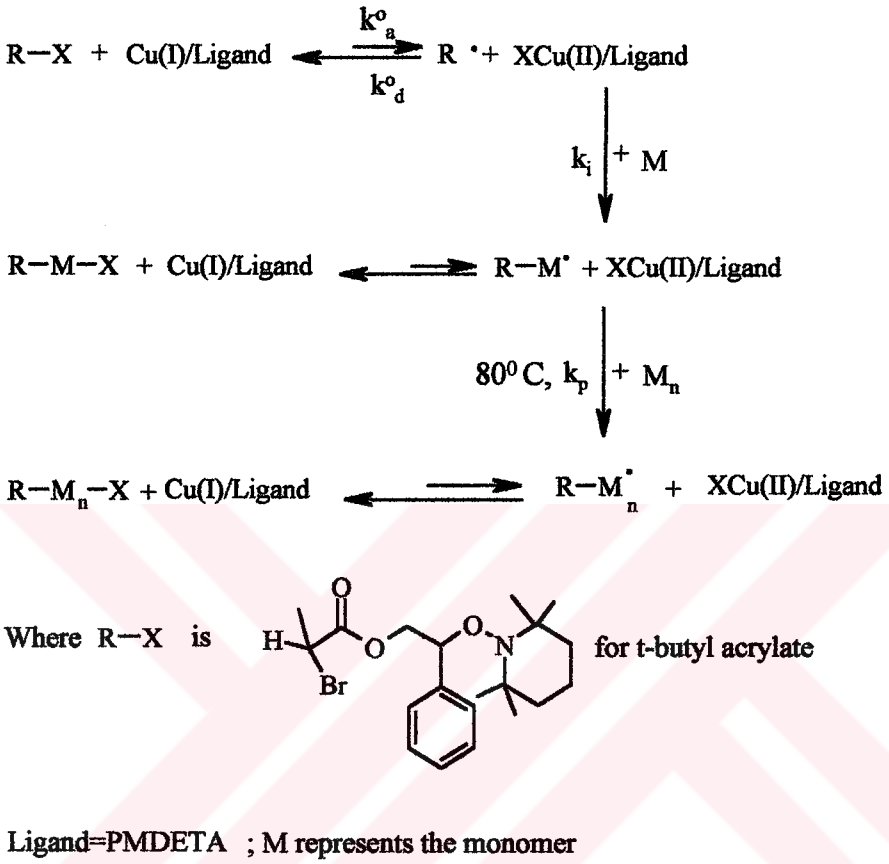


Figure 4.1 The ^{1}H-NMR spectra of the initiator, (1), 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo propanoat

4.2. Synthesis of Poly (tert-butyl acrylate, PtBA) and Polystyrene (PSt) Macroinitiators

Synthesis of PtBA was illustrated in Scheme 4.2



Scheme 4.2 Atom transfer radical polymerization (ATRP) and PtBA as a schematic representation.

2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo propanoat, **(1)** was used to perform the controlled radical polymerization of tBA and stable free radical polymerization of St. Poly(tert-butylacrylate) homopolymers with different molecular weights were synthesized via controlled radical polymerization of tBA in bulk at 80°C. The polymerization was initiated by 1 and catalyzed by the CuBr/PMDETA system. This led to formation of bromine terminated PtBA macroinitiator with narrow polydispersity. The results are tabulated in Table 4.1.

The experimental molecular weights were determined by GPC based on linear PS standards. Although the hydrodynamic volume of PtBA is not as same as those of linear PS standards, the resulting experimental molecular weights are in good agreement with theoretical molecular weights calculated from $M_{n,\,theo} = [M]_o/[I]_o x$ conv % x M_w (tBA).

Table 4.1 Syntheses of PtBA macroinitiator using CuBr/PMDETA catalyst system and **1** as initiator at 80^0C, $[M]_0 = 6{,}83$ mol.l^{-1}, $[I]_0/[CuBr]/[PMDETA]=1/1/1$

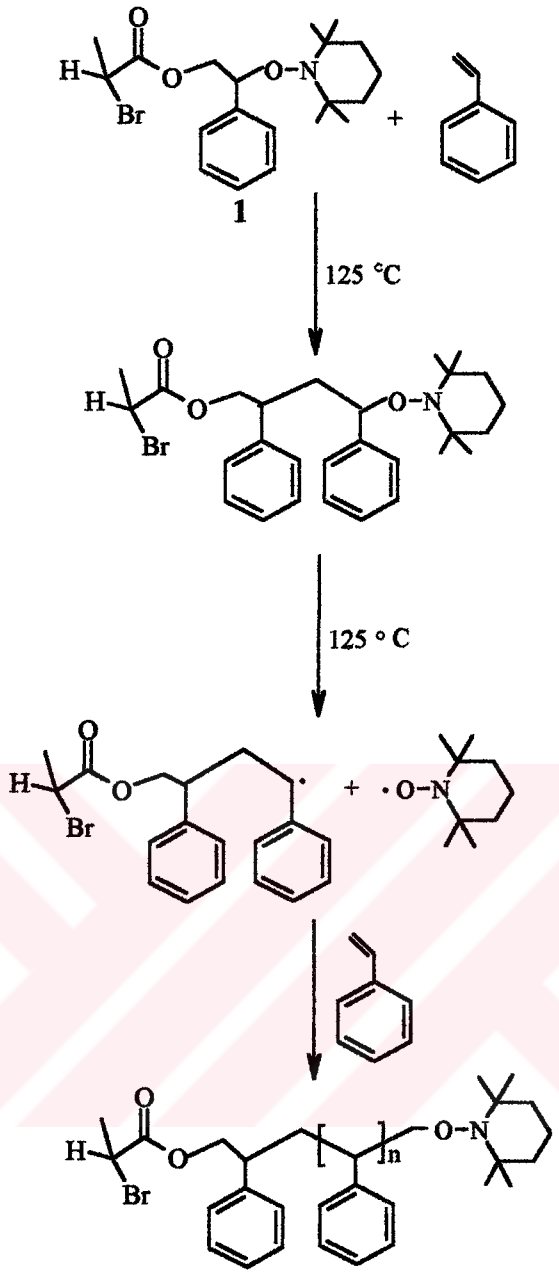
Run	$[M]_0/[I]_0$	Time (min)	Conversion(%)	Mn_{theo}	Mn_{GPC}	M_w/M_n
I	200	330	76	19400	18200	1,10
II	100	130	98	12500	12500	1,12
III	100	70	50	6400	8400	1,14

The conversions were calculated gravimetrically by the following formula;

% Conversion = (W / M) * 100

Where W represents the weight of the formed polymer and M stands for the mass of the monomer initially taken.

These results imply that polymerization of tBA proceeds in controlled manner with high initiation efficiency using 1 as initiator and CuBr/PMDETA as heterogeneous catalyst system. Synthesis of PSt was illustrated in Scheme 4.3



Scheme 4.3 Stable free radical polymerization (SFRP) of styrene as a schematic representation.

4.3. Syntheses of Block Copolymers via ATRP-ATRP-SFRP Route

The syntheses of diblock copolymers consisting of tBA and MMA segments were performed by polymerizing MMA with CuCl/PMDETA, using PtBA as macroinitiator. The polymerizations were conducted at 80°C in DPE solution (MMA/DPE=1, v/v). The other conditions and results are given in Table 4.2.

The GPC traces of macroinitiator, PII (in Table 4.2) and AB diblock copolymer, PIV (in Table 4.2) are shown in Figure 4.2. The absence of PtBA macroinitiator peak on the GPC trace of block copolymer indicates that the macroinitiator was fully converted to the block copolymer.

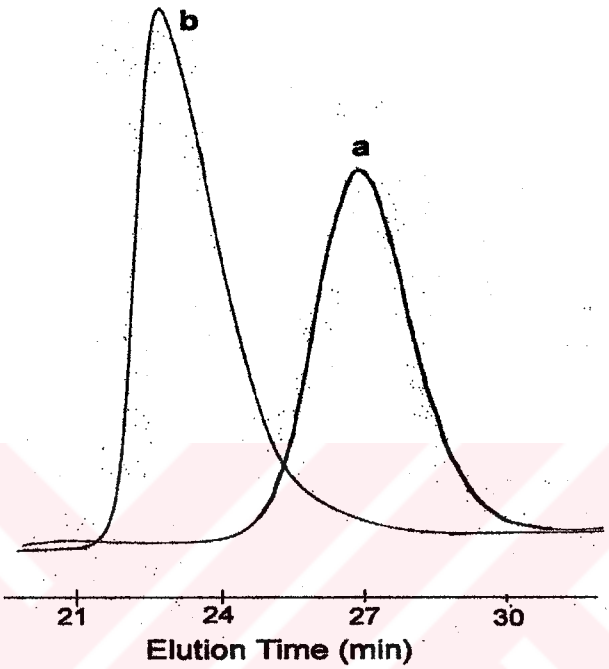


Figure4.2 GPC traces of a) PtBA homopolymer (PII) and
b) PtBA-PMMA (PIV) diblock copolymer

GPC result shows the expected increase in molecular weight through the copolymerization. The new peak at higher molecular weight is ascribed to the block copolymer. Furthermore, the absence of the PtBA macroinitiator peak on the GPC trace of resulted diblock copolymer indicates the complete conversion of the macroinitiator to the block copolymer. The composition of block copolymers was elucidated by ^{1}H NMR measurements. The ^{1}H NMR spectra of all poly (tBA-b-MMA) block copolymers exhibit the major peaks, which are characteristic of the tert-butyl acrylate and methyl methacrylate segments. The molecular weights were calculated from the integration of signals at 1.43 ppm ($C(CH)_3$) of tBA to 3.58 ppm ($-OCH_3$) of MMA (Figure 4.3). As can be seen from Table 4.2 (entry PIII-V), the experimentally obtained molecular weight is in a good agreement with theoretical molecular weight calculated from $M_{n,theo}=[M]_o/[I]_o x conv\% x M_w(MMA)+M_{n\ macroinitiator}$ for all cases. Furthermore, MWDs remained narrow for all polymerizations.

Table 4.2 Syntheses of ABC triblock copolymers via ATRP-ATRP-SFRP route.

Run	Mono-mer	$[M]_o$mol l^{-1}	$[M]_0/[I]_0$	Initiator	Time (min)	Conversion (%)	Solvent	Mn_{theo}	Mn_{GPC}	Mn_{Hnmr}	M_W/M_n	Composition ^{1}H NMR
PI[a]	tBA	6,83	200	1	330	76	-	19400	18200	-	1,10	
PII[a]	tBA	6,83	100	1	130	98	-	12500	12500	-	1,12	
PIII[b]	MMA	4,67	1000	PI	1140	54	DPE	72200	68000	72600	1,13	%73 PMMA,%27 PtBA
PIV[b]	MMA	4,67	900	PII	1080	43	DPE	51200	54700	56000	1,15	%78 PMMA, %22 PtBA
PV[b]	MMA	4,67	500	PII	1200	72	DPE	48500	50300	50500	1,07	%75 PMMA, %25 PtBA
PVI[c]	St	4,36	650	PIV	3000	30	DPE	76300	70000	79500	1,35	%54 PMMA, %30 PSt, %16 PtBA

a) $[I]_0$:$[PMDETA]_0$:$[CuBr]_0$=1:1:1, the polymerization was carried out at 80^{0}C

b) $[I]_0$:$[PMDETA]_0$:$[CuCl]_0$=1:1:1, the polymerization was carried out at 80^{0}C (MMA/DPE=1)

c) The polymerization was carried out at 125^{0}C, (St/DPE=1)

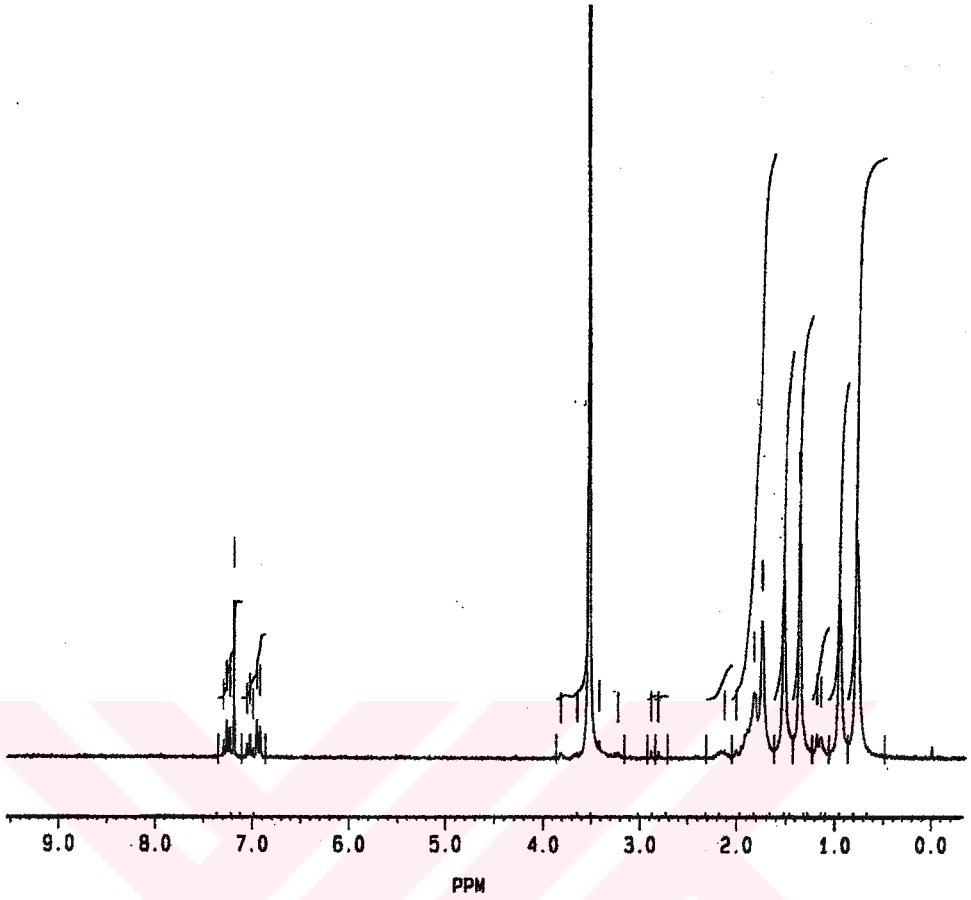
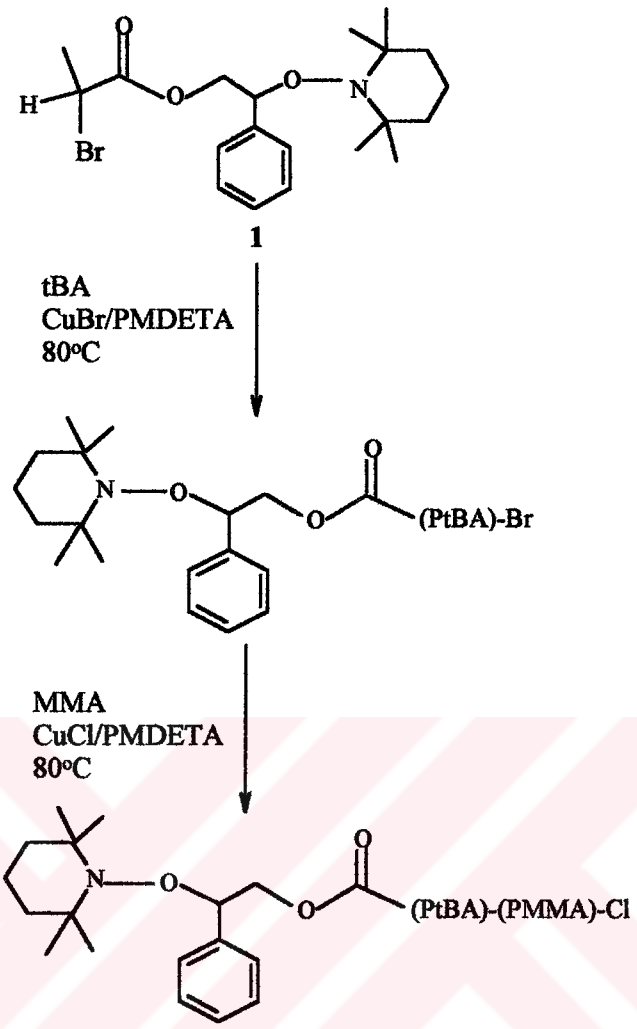


Figure 4.3 The ^{1}H NMR spectra of PtBA-PMMA diblock copolymer (PIII)

These observations suggest that high blocking efficiency was achieved by the halogen exchange utilized in these experiments. As it was previously demonstrated that bromine terminal group of acrylate can be converted to chlorine soon after the polymerization of MMA started where CuCl was used as Cu(I) species. Thus, the halogen exchange enhances the rate of initiation over the rate of propagation. As a consequence, the blocking efficiency was increased. It is also interesting to note that the high end functionality was maintained for the PtBA macroinitiator, PII (Table 4.2), even though the polymerization proceeded up to 98% conversion. Synthesis of poly(tBA-b-MMA) diblock copolymer was illustrated in Scheme 4.4.



Scheme 4.4 Synthesis of poly(tBA-b-MMA) diblock copolymer using ptBA as macroinitiator as a schematic representation.

The alkoxyamine ended diblock copolymers were used as a macroinitiator for SFRP of styrene to afford ABC type tiblock copolymers. The SFRP of styrene was carried out at 125^{0}C in DPE solution (St/DPE= 1; v/v) and the results were given in Table 4.2. The GPC trace of triblock copolymer is shown in Figure 4.4 together with the diblock copolymer and homopolymer. Although the GPC trace of triblock copolymer was unimodal, the small amount of tailing was observed in the molecular weight range of precursor diblock copolymer. Moreover, the polydispersity of the resulting triblock copolymer PVI (in Table 4.2) is slightly higher than those of corresponding macroinitiators.

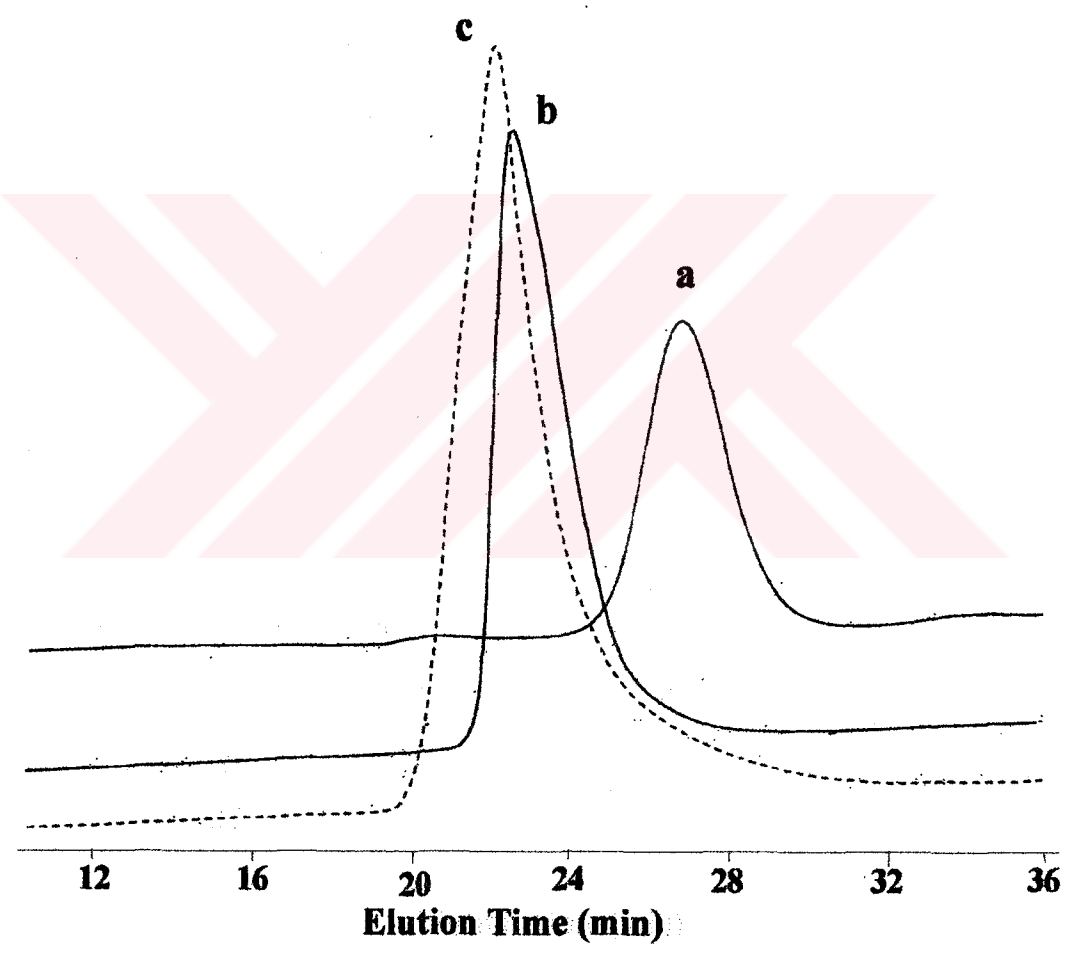


Figure 4.4 The GPC traces of a) PtBA homopolymer b) PtBA-PMMA diblock copolymer and c) PSt-PtBA-PMMA triblock copolymer (PVI)

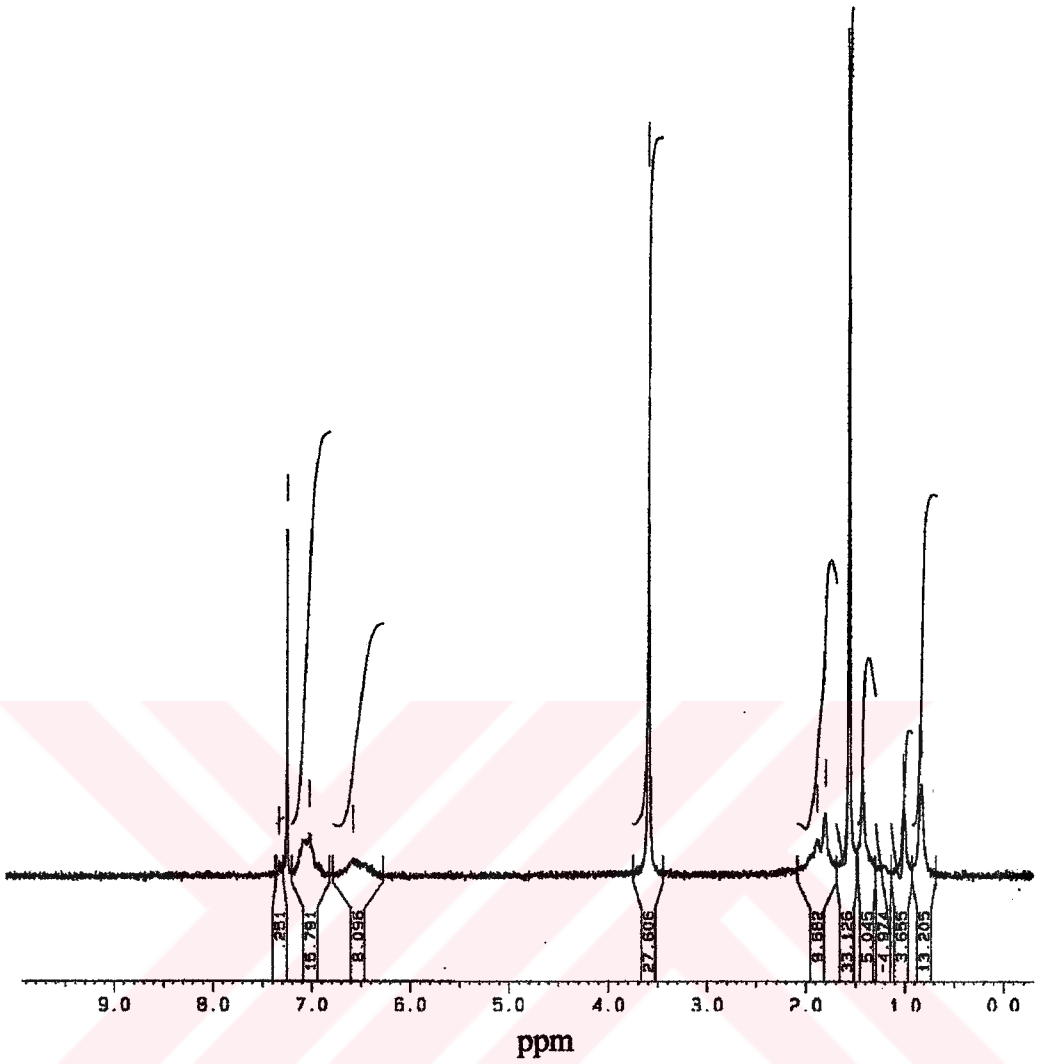
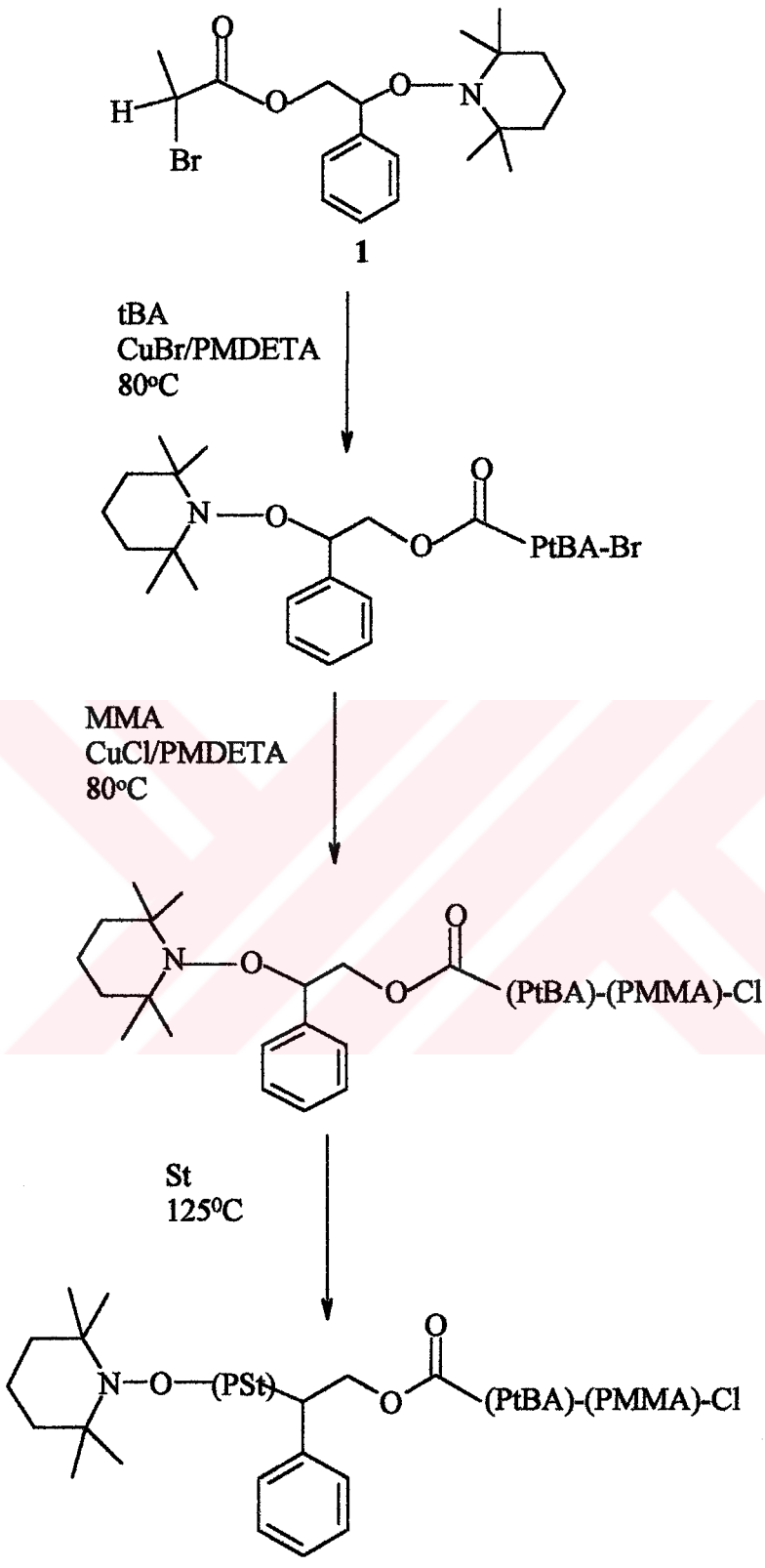


Figure 4.5 The ^{1}H NMR spectra of PSt-PtBA-PMMA triblock copolymer (PVI)

These results indicate that the initiation efficiency of diblock copolymer diminished, presumably due to partially loss of alkoxyamine functionality, during its previous two-step synthesis. Synthesis of ABC type triblock copolymer via ATRP-ATRP-SFRP route was illustrated in Scheme 4.5. Integrating the signal between 6,5-7,0 ppm of PSt (aromatic protons) and 3,58 ppm of PMMA (OCH_3) allowed us to evaulate the composition of triblock copolymer (Figure 4.5).It is worth to mention that there is a discrepancy between the molecular weights of triblock copolymers obtained from GPC and the theoretical value that is however close to the molecular weight determined by ^{1}H NMR.



Scheme 4.5 Synthesis of poly(St-b-tBA-b-MMA) triblock copolymer as a schematic representation.

4.4. Syntheses of Block Copolymers via SFRP-ATRP-ATRP Route

SFRP of styrene was carried out in bulk at 125^{0}C. Three PSt macroinitiators were prepared by applying different initial monomer/initiator ratio. The results and conditions are tabulated in Table 4.3. As can be seen in Table 4.3, there is a good agreement between the molecular weights determined by GPC and theoretical molecular weights. These results indicate that high initiation efficiency was obtained in our experimental condition using **1** as an initiator.

The syntheses of diblock copolymers consisting of St and tBA segments were performed by ATRP of tBA using CuBr/PMDETA as catalyst and bromine ended PSt macroinitiators. The polymerizations were conducted at 80°C in bulk. The other conditions and results are given in Table 4.3. The composition and molecular weight of diblock copolymers were determined via ^{1}H NMR measurements (Figure 4.5). As was seen in Table 4.3, a good agreement was observed between the theoretical molecular weights and calculated ones from ^{1}H NMR, where GPC values deviated from each. This is likely due to the solution property of block copolymers consisting of PSt and PtBA segments shows different behaviour than of linear PSt standards where high molecular weight of PtBA is a second segment.

Table 4.3 Syntheses of ABC triblock copolymers via SFRP-ATRP-ATRP route.

Run	Monomer	$[M]_o$mol l^{-1}	$[M]_0/[I]_0$	Initiator	Time (min)	Conversion (%)	Solvent	Mn_{theo}	Mn_{GPC}	Mn_{Hnmr}	M_W/M_n	Composition ^{1}H NMR
PVII[a]	St	8,73	300	1	1140	55	-	17200	20000	-	1,14	
PVIII[a]	St	8,73	100	1	1200	46	-	14400	14200	-	1,17	
PIX[a]	St	8,73	100	1	1080	40	-	4200	4500	-	1,21	
PX[b]	tBA	6,83	550	PVII	330	25	-	37600	33000	36300	1,15	%47 PSt, %53 PtBA
PXI[b]	tBA	6,83	550	PVII	345	25	-	37600	32000	36300	1,12	%47 PSt, %53 PtBA
PXII[b]	tBA	6,83	900	PVIII	3900	61	-	70400	64000	68000	1,25	%21 PSt, %79 PtBA
PXIII[b]	tBA	6,83	300	PIX	220	68	-	30400	27200	32000	1,15	%13 PSt, %87 PtBA
PXIV[c]	MMA	4,67	570	PX	420	14	DPE	44300	40000	46400	1,16	%37 PSt, %41 PtBA, %22 PMMA
PXV[c]	MMA	4,67	1150	PXI	1200	54	DPE	98500	50000	106000	1,22	%16 PSt, %18 PtBA, %66 PMMA
PXVI[c]	MMA	4,67	500	PXIII	50	17	DPE	40500	40000	41500	1,15	%10 PSt, %67PtBA, %23 PMMA
PXVII[c]	MMA	3,12	1200	PXIII	240	23	DPE	59600	50000	61000	1,12	%7 PSt, %46PtBA, %47 PMMA

a) The polymerization was carried out at 125^{0}C b) $[I]_0$:$[PMDETA]_0$:$[CuBr]_0$=1:1:1, the polymerization was carried out at 80^{0}C

c) $[I]_0$:$[PMDETA]_0$:$[CuCl]_0$=1:1:1, the polymerization was carried out at 80^{0}C (MMA/DPE=1)

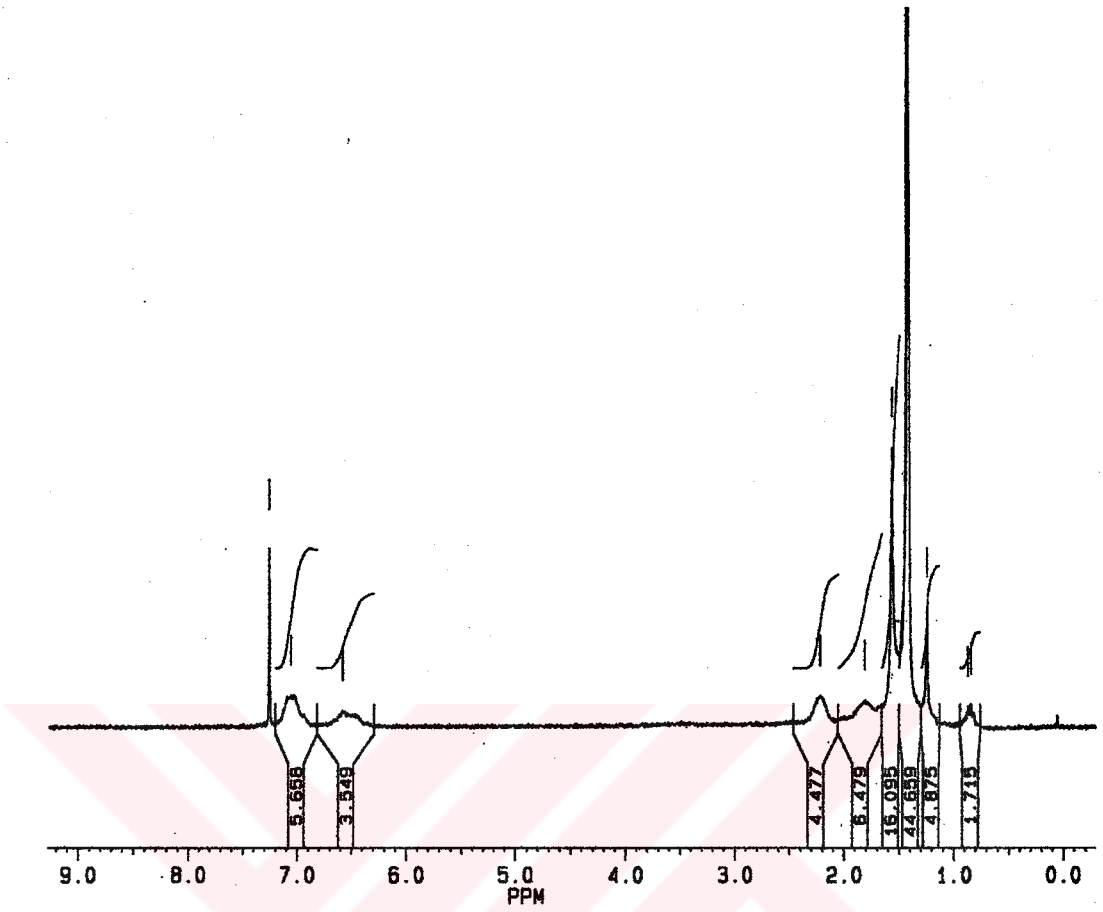


Figure 4.6 The ^{1}H NMR spectra of PSt-PtBA diblock copolymer (PXII)

Figure 4.7 shows GPC traces of macroinitiator and diblock copolymer. The peak corresponding to diblock copolymer clearly shifted to higher molecular weight region chromotogram indicated that both the chain end functionality of macroinitiator and the blocking efficiency were high.

Figure 4.7 indicates that comparison of GPC traces of two different PSt macroinitiators and PSt-PtBA diblock copolymer prepared by different initial monomer/initiator ratios. The new peak at higher molecular weight is ascribed to the block copolymer. Furthermore the absence of the PSt macroinitiator peak on the resulted block copolymer indicates the complete conversion of the macroinitiator to the block copolymer.

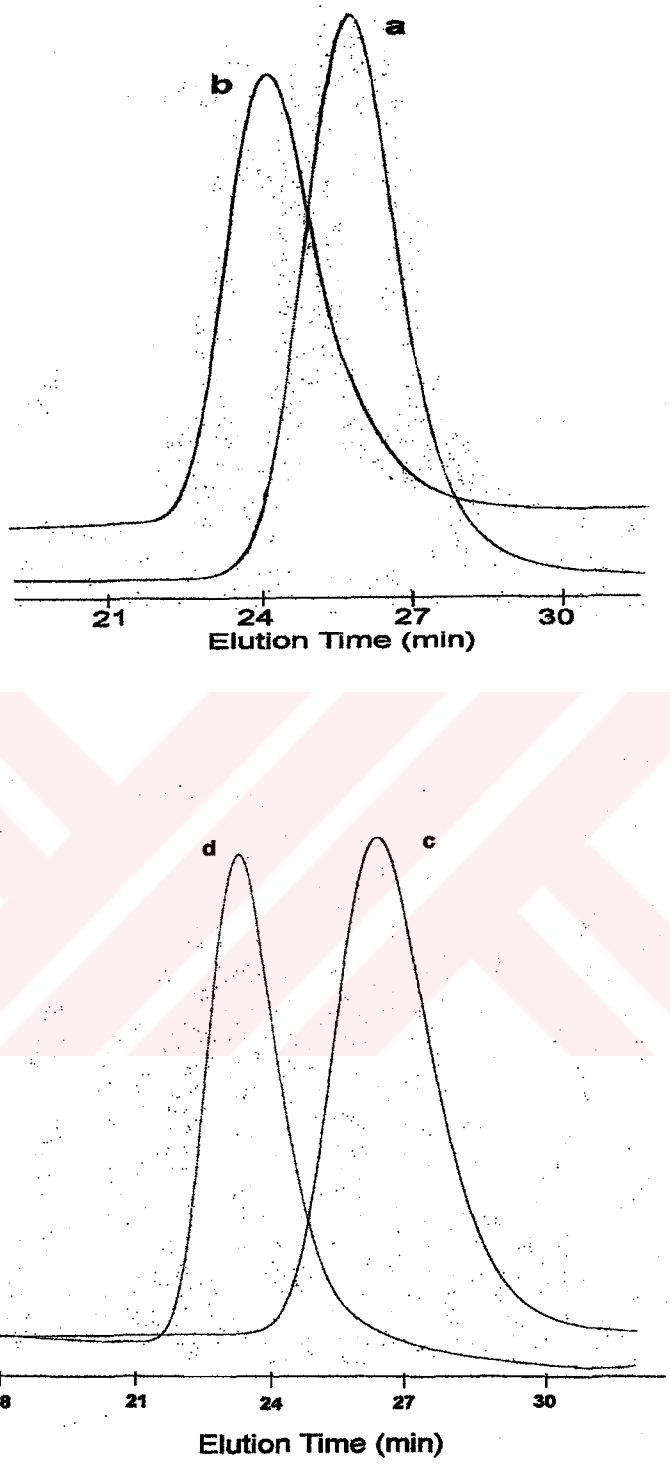
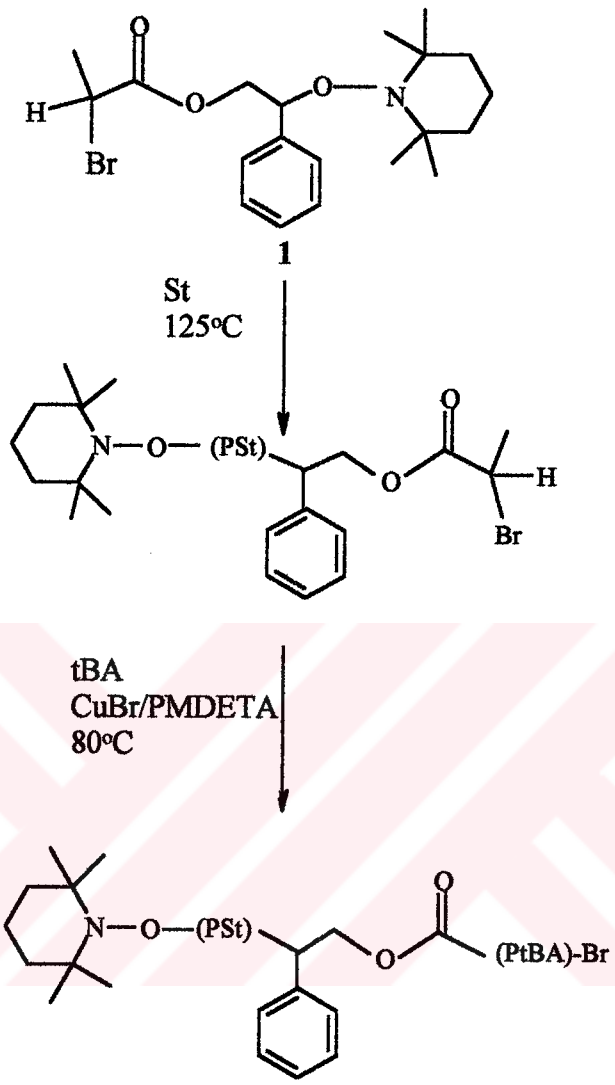


Figure 4.7 The comparison between the GPC traces of a,c) PSt homopolymer and b,d) PSt-PtBA diblock copolymer

Synthesis of poly(St-b-tBA) diblock copolymer was illustrated in Scheme 4.5



Scheme 4.5 Synthesis of poly(St-b-tBA) diblock copolymer using polystyrene as macroinitiator

Thus obtained diblock copolymers were further extended via ATRP of MMA using CuCl/PMDETA as a catalyst at 80^0C to afford ABC triblock copolymers. The experimental conditions and the properties of triblock copolymers were given in Table 4.3. The GPC values deviate from theoretically calculated molecular weights and those determined by ^{1}H NMR (Figure 4.8) both of which however are in good agreement. The GPC traces of triblock copolymers were given in Figure 4.9 and Figure 4.10.

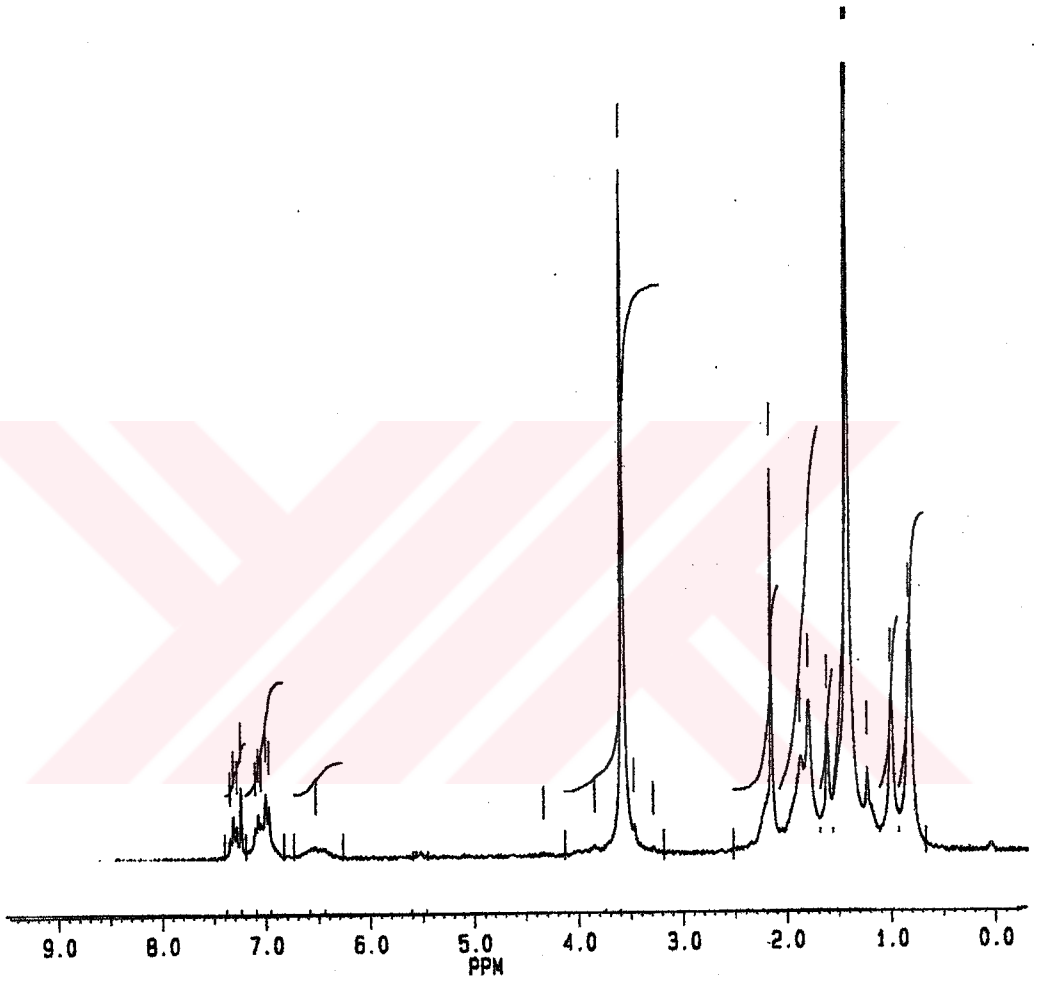


Figure 4.8 The ^{1}H NMR spectra of PSt-PtBA-PMMA triblock copolymer (PXVII)

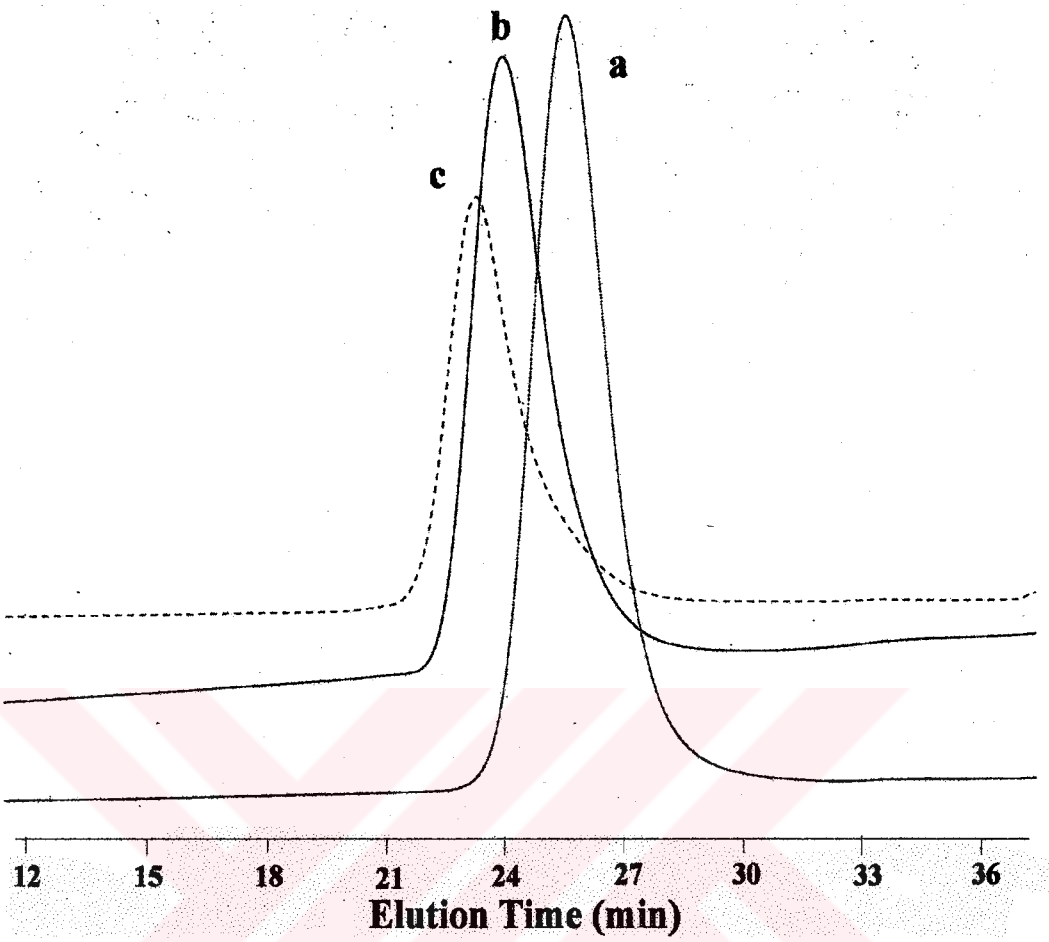


Figure 4.9 The comparison between the GPC traces of a) PSt homopolymer (PVII), b) PSt-PtBA diblock copolymer (PX) and c) PSt-PtBA-PMMA triblock copolymer (PXIV).

Figure 4.9 and Figure 4.10 indicates that the comparison of triblock copolymers prepared by different monomer/initiator ratio. The clear shift was observed from GPC traces of triblock copolymers implying that successive formation of triblock copolymer. The absence of the PSt-PtBA diblock peak on the GPC trace of resulted block copolymer indicates that the complete conversion of the diblock copolymer to the triblock copolymer. These results concludes that initiation effiiency of diblock copolymer was high and bromine end functionality remains intact during previous its two-step synthesis described above.

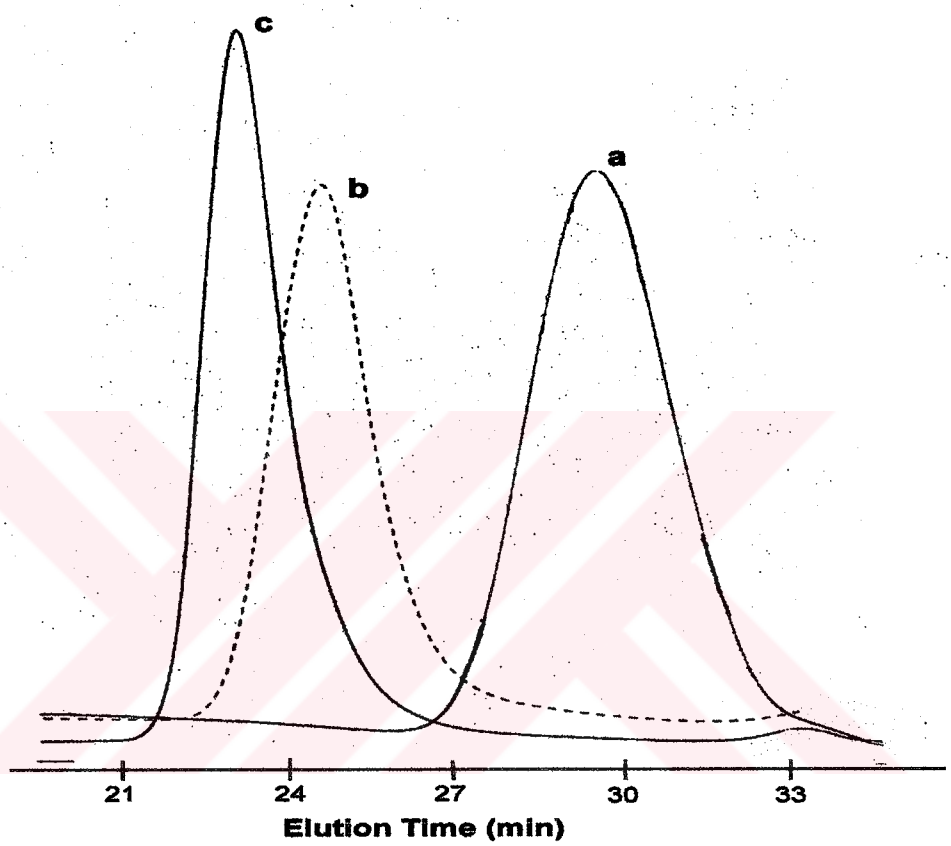
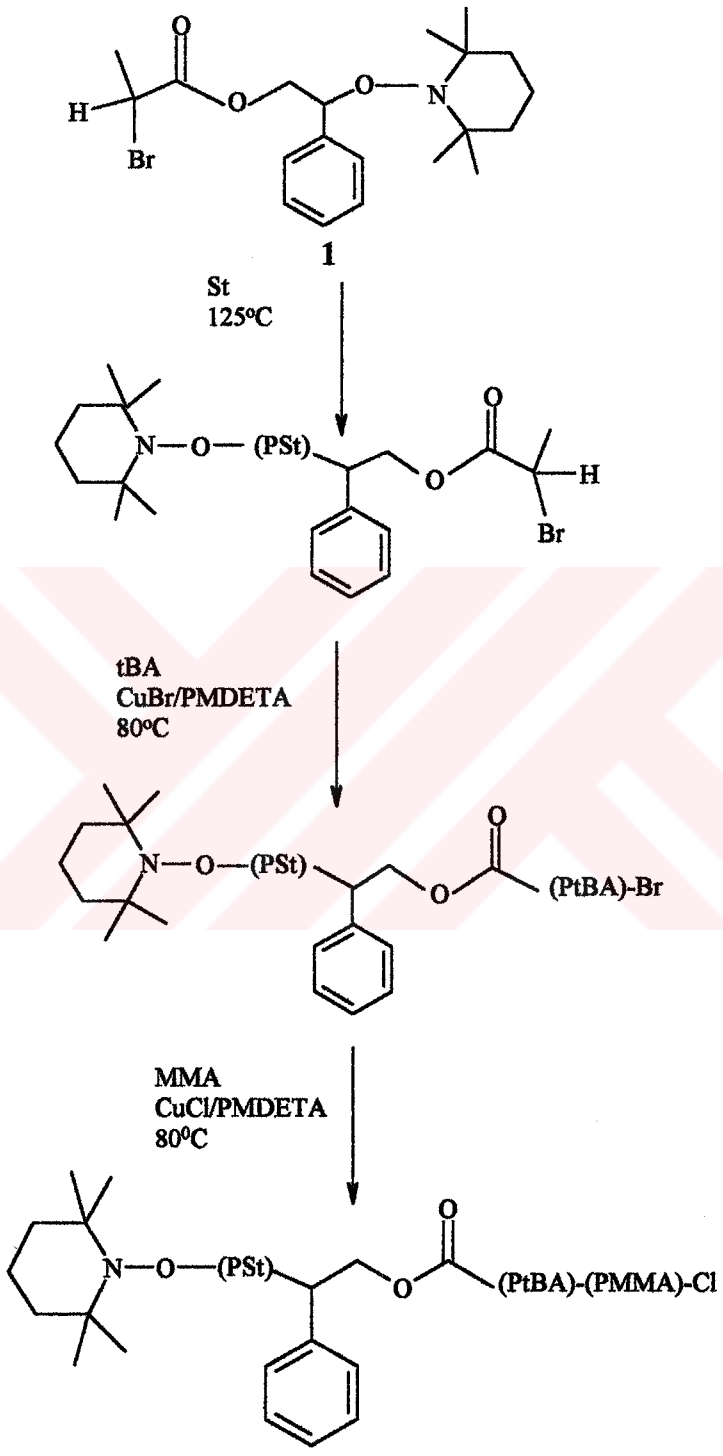


Figure 4.10 The GPC traces of a) PSt homopolymer (PIX), b) PSt-PtBA diblock copolymer (PXIII) and c) PSt-PtBA-PMMA triblock copolymer (PXVII).

Synthesis of ABC type triblock copolymer via SFRP-ATRP-ATRP route was illustrated in Scheme 4.6.



Scheme 4.6 Synthesis of ABC triblock copolymer via SFRP-ATRP-ATRP route.

5. CONCLUSIONS AND RECOMMENDATIONS

In conclusion asymmetric difunctional initiator 2-phenyl-[2,2,6,6-tetramethylpiperidinooxy]ethyl 2-bromo propionate, (1) was synthesized and successfully used in the preparation of two triblock copolymers containing same monomer segments via ATRP-ATRP-SFRP or SFRP-ATRP-ATRP route.

In both route, halogen exchange was employed to enhance the rate of cross propagating where bromine ended PtBA was used as macroinitiator for methylmethacrylate polymerization. Therefore, high blocking efficiency was achieved during the synthesis of di or triblock copolymer. The observed molecular weights of homopolymers and block polymers measured by GPC (Gel permeation chromatography) were in reasonably agreement with the theoretical molecular weight and calculated from those of ^{1}HNMR. Block copolymers with various molecular weights and narrow molecular weight distributions were prepared. Furthermore, high end functionality is maintained, making block copolymerization efficient. Well-defined homopolymers, di and triblock copolymers with predetermined block lengths and low polydispersities were synthesized.

These studies are expected to contribute the development of the controlled radical polymerization techniques in a positive way and then enable the manufacturing of the advanced technologic materials with better mechanical and physical properties.

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