ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF ASYMMETRIC DIFUNCTIONAL INITIATORS AND THEIR USE IN THE PREPARATION OF HOMO AND BLOCK COPOLYMERS VIA ATOM TRANSFER AND STABLE FREE RADICAL POLYMERIZATION SEQUENCE

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

İKİ FONKSİYONLU ASİMETRİK BAŞLATICILAR SENTEZİ, ATOM TRANSFER VE KARARLI SERBEST RADİKAL POLİMERİZASYONLARI İLE HOMO VE BLOK KOPOLİMER ELDESİNDE KULLANIMLARI

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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
Є	: Molar absorption coefficient
I, M	: Initiator and monomer respectively
Ph	: Phenyl

SUMMARY

SYNTHESIS OF ASYMMETRIC DIFUNCTIONAL INITIATORS AND THEIR USE IN THE PREPARATION OF HOMO AND BLOCK COPOLYMERS VIA ATOM TRANSFER AND STABLE FREE RADICAL POLYMERIZATION SEQUENCE

The ability to synthesize macromolecules with complex and controlled architectures is becoming an increasingly important aspect of polymer science. Traditionally, control of macromolecular architecture has been achieved by using living polymerization techniques such as anionic, cationic procedures. Specifically, controlled architecture possesses some characteristics, which are molecular weight control, end group control, ability to form block copolymers, and a living nature. In 1993, Georges et al. have reported that low polydispersity polystyrene can be prepared by free radical chemistry using a system that can be considered to be a living polymerization. This pioneering report was 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 in tern leads to control of the polymerization, which is called as stable free radical polymerization (SFRP). In 1995, Matyjaszevski et al. developed an alternative living free radical polymerization process using a copper (I)- catalyzed atom transfer process, atom transfer radical polymerization (ATRP). ATRP can be applied to polymerize both styrenic and acrylic type monomers.

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 initiators, 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino) oxy] ethyl 2-bromopropanoate, 9-antryl methyl 2-bromo propanoate, and 9-antryl methyl 2-bromo-2-methyl propanoate, were synthesized and used in ATRP of methyl metacrylate or tert-butyl acrylate leading to corresponding polymer TEMPO or anthracene moiety as chain end, according to the order mentioned above. The TEMPO headed polymers were found to be efficient

initiators for stable free radical polymerization (SFRP) of styrene. ^{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

İKİ FONKSİYONLU ASİMETRİK BAŞLATICILAR SENTEZİ, ATOM TRANSFER RADİKAL POLİMERİZASYONU VE KARARLI SERBEST RADİKAL POLİMERİZASYONLARI İLE HOMO VE BLOK KOPOLİMER ELDESİNDE KULLANIMLARI

Kompleks ve kontrollü mimariye sahip makro moleküllerin sentezi üzerine yapılan çalışmalar,son yıllarda polimer biliminde gittikçe artan bir öneme sahiptir. Klasik olarak, makro moleküler mimarinin kontrolü yalnızca yaşayan anyonik ve katyonik polimerizasyon teknikleri ile başarılabilmektedir. Kontrollü mimari denilince, molekül ağırlık kontrolü, uç grup kontrolü, blok kopolimer oluşturabilme ve yaşayan karakter akla gelmektedir. 1993 yılında Georges ve çalışma grubu, yaşayan polimerizasyon özelliği gösteren serbest radikal polimerizasyon ile düşük molekül ağırlığı dağılımına sahip polistiren elde ettiler. Bu çalışma kararlı serbest nitroksit radikalinin, 2,2,6,6-tetrametilpiperidinil-1-oksi (TEMPO), kullanımına dayanmaktadır ve serbest radikal polimerizasyonu (SFRP) olarak bilinen bu sistemde TEMPO büyüyen zincirin sonunda ısısal olarak kopabilen bir uç grup olarak kontrollü polimerizasyona neden olmaktadır. Diğer taraftan Matyjaszwski ve grubu 1995 yılında atom transfer radikal polimerizasyonunu (ATRP) gerçekleştirmişlerdir. ATRP, Cu(I) / ligand sistemi ile katalizlenen yaşayan serbest radikal polimerizasyon sistemidir. Bakır kompleksli ATRP sistemleri başlıca stiren, akrilat vb monomerlerin polimerizasyonlarında başarıyla kullanılmaktadır.

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 başlatıcılar, 2-fenil-2-[(2,2,6,6-tetrametilpiperidinil)oksi]etil 2-bromo propanoat, 9-antril metil 2-bromo propanoat ve 9-antril metil 2-bromo-2-metil propanoat, sentezlenip metil metakrilat ve ter-butil akrilat polimerlerinin ATRP metodu ile eldesinde başlatıcı olarak kullanılmışlardır ki elde edilen polimerlerden TEMPO sonlu başlatıcıdan sentezlenin stirenin SFRP tekniği ile polimerleştirilebilmesi için uygun birer başlatıcı olduğu anlaşılmıştır. ^{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.

PART 1

INTRODUCTION

The development of new polymeric materials having improved and/or new mechanical and physical properties has recently become a vital facet for polymer science from both an academic and industrial viewpoint.

Almost half of the plastics are produced by free radical polymerization. Although the free radical polymerization is the most widely used commercial technique for preparing variety of vinyl polymers it has still some disadvantageous. 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. Ability of getting polymers with controlled molecular weight and well-defined architecture is one of the main goals in modern synthetic polymer chemistry because 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.

There are number of methods that can be utilized to gain such control. These include living ionic polymerization, nitroxide-mediated polymerization of styrene, ruthenium (II)/aluminum based polymerization of methacrylates, cobalt (II)-mediated polymerization of acrylates, and of course atom transfer radical polymerization (ATRP) of a variety of monomers. However, since the synthetically demanding experimental requirements of ionic polymerization such as rigorous exclusion of

water and oxygen and the use of ultra pure reagents and solvents further reduce its general applicability ATRP seems to be the most versatile technique among all these methods.

In many respects, free radical procedures are the opposite of living ionic polymerization since they are synthetically robust, compatible with a wide range of functional groups. The development of a living free radical procedure, which combines the desirable attributes of traditional free radical systems with desirable attributes of living polymerization, would be a significant development in not only polymer synthesis but also polymer science in general.

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

In this study, emphasis is placed on the synthesis of asymmetrical difunctional initiators and their use as initiator of the controlled homo and block polymerizations of tert-butyl acrylate, methyl methacrylate and styrene monomers.

PART 2

THEORITICAL PART

2.1 FREE RADICAL POLYMERIZATION

Free radical polymerization is the most important commercial process for the preparation of the high molecular weight polymers. A wide variety of monomers can be polymerized or co-polymerized under relatively simple experimental conditions [1]. 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 [2]. Why free radical polymerization is of importance 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.
- Although a few types of monomers limit the ionic polymerization techniques, a variety of monomers can be polymerized via free radical polymerization route.

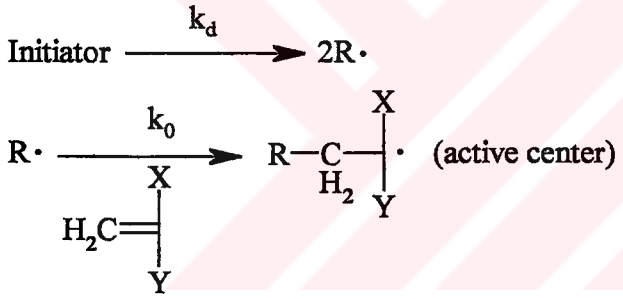
Free radical polymerization is initiated by radicals and propagated by macro radicals. These radicals exhibit an unpaired electron. Initiating radicals are rarely formed by

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

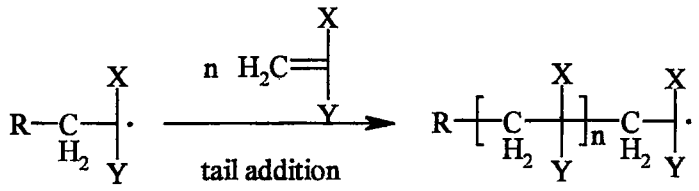
Initiation occurs from the reaction of an initiator-derived radical center with a monomer molecule. Firstly a couple of radical occurs by a homolytic cleavage of the initiator. If the radicals are formed in the presence of vinyl monomers, these radicals react with the double bond and generate a new radical. The first one is known as the dissociation and the second is the association step in the initiation of free radical polymerization. Since $k_d < k_o[M]$, the decomposition is the rate determining step in the initiation process [3].



(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 [4].



(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.

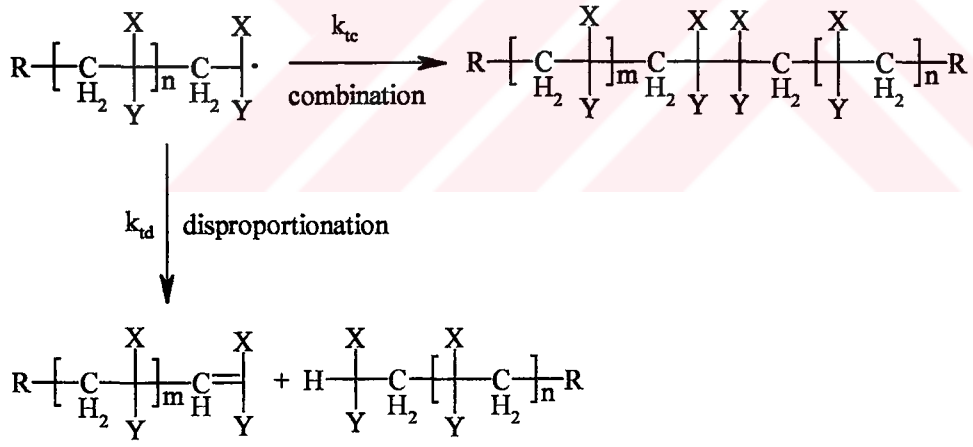
1) The Self Reaction of Carbon-Centered Radicals

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.

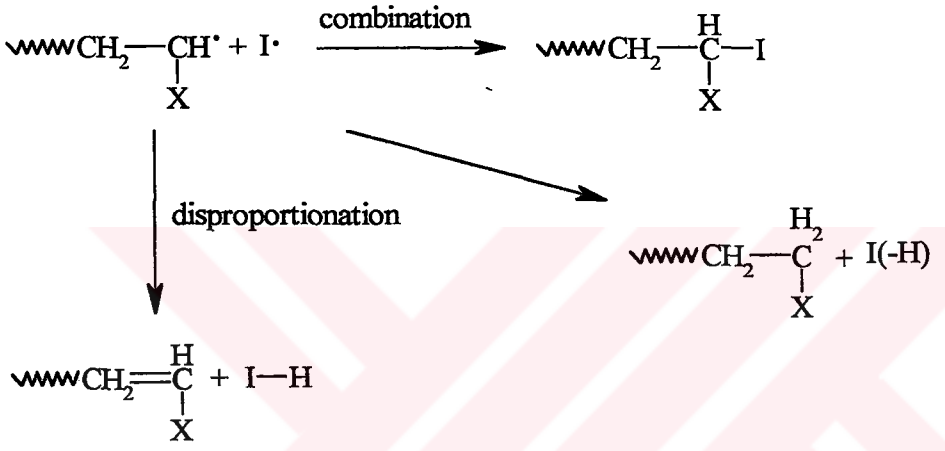


(2.3)

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).



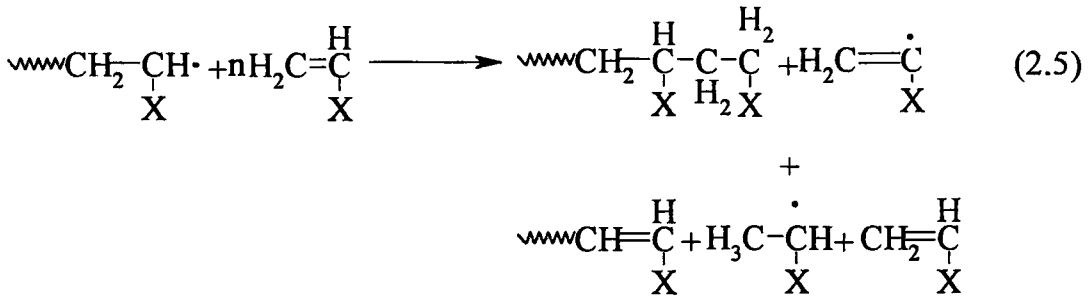
(2.4)

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

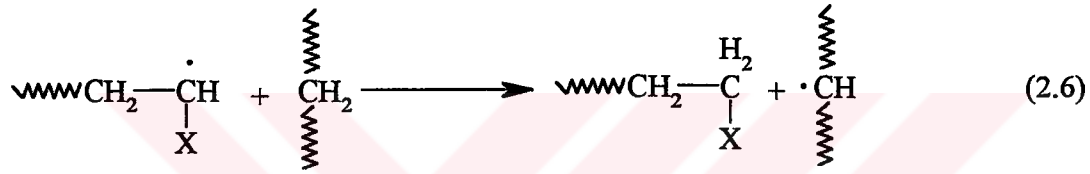
If the generated monomer radicals become stable via resonance structure they do not initiate polymerization of a new chain. An example is given in (2.5)



(2.5)

b) Transfer to Polymer Chain

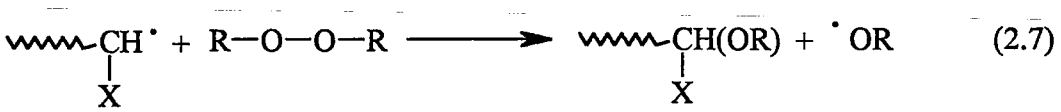
The transfer of an active center exist on a growing chain radical to the another polymer chain results in branching but it does not influence the length of the chain.



(2.6)

c) Transfer to Initiator

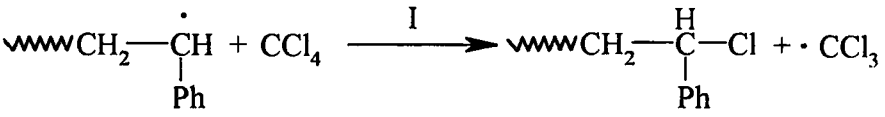
Transfer to initiator involves the termination of a propagating radical by reaction of a molecule of initiator. The resulting polymer possesses two initiator-derived end groups, and in the process, a new primary radical is formed, which may initiate a new chain.



(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.



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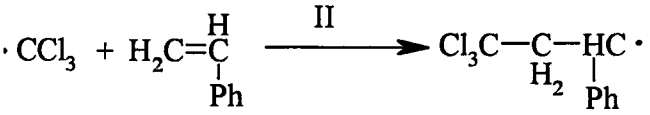
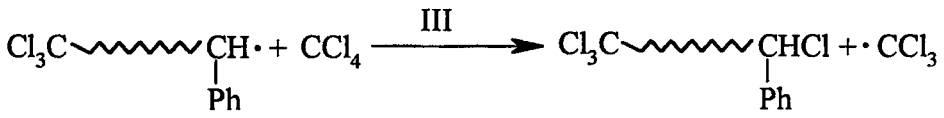
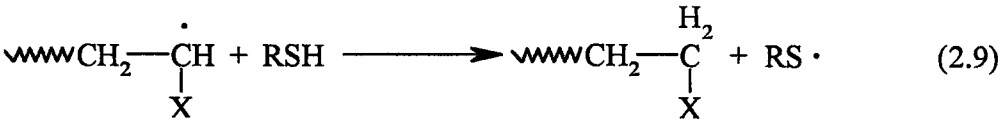




e) Transfer to Modifier



(2.9)

4) Termination by Impurities

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

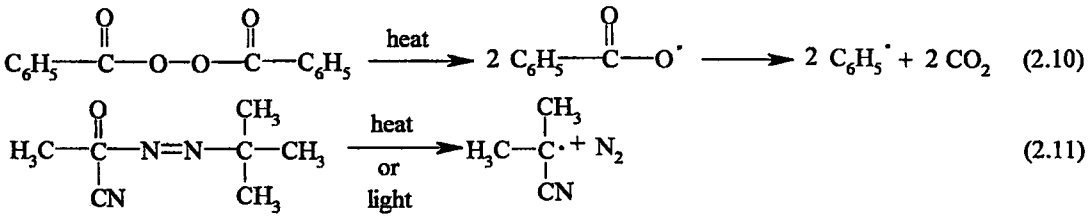
2.1.1 Free Radical Initiators

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.

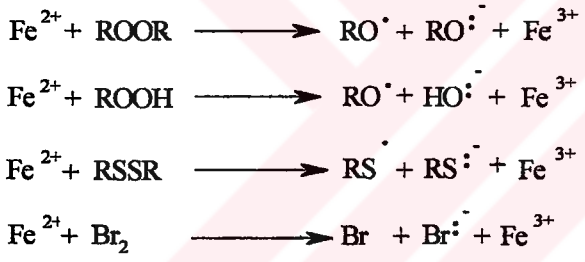


(2.10)

(2.11)

2.1.1.2 Initiators Giving Radicals by Electron Transfer

The most important one is the redox reactions.

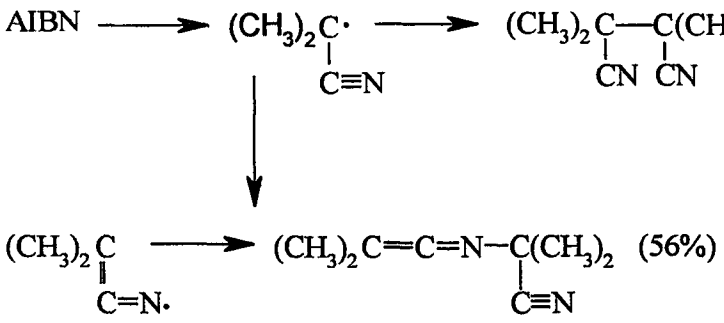


(2.12)

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

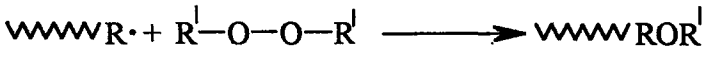
2.1.2 Initiator Efficiency

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).



(2.13)

Eefficiency 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.



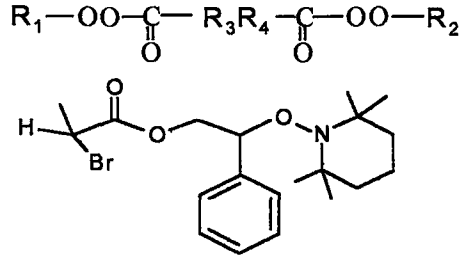
(2.14)

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 [5].

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)

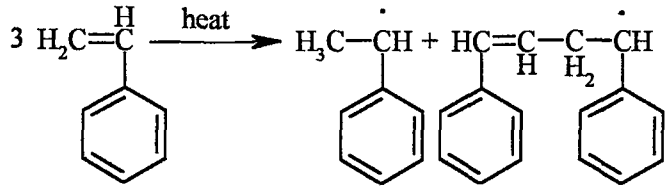
In free radical polymerization process, homo-polymers are unavoidably produced together with block copolymers, two radicals are created by the scission of peroxide and only one will be connected to the active polymer chain. Separation procedures are, therefore, necessary to isolate the block copolymer [2].

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 [6-7].

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 some styrene derivatives such as 2-vinyl tiyofen, 2-vinyl furan [8-9].

Although the exact mechanism is not known, the works done on this subject [10-11] 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 OR LIVING RADICAL POLYMERIZATIONS

The control of macromolecular structure has recently become one of the most important subjects for polymer science from both an academic and an industrial viewpoint, because ability to control macromolecular architecture can lead to development of the new polymeric materials with better mechanical and physical properties [12].

The classical techniques offering appreciable control over macromolecular structure, such as anionic and cationic polymerizations, cannot find a wide application area due to stringent requirements on reaction conditions and monomer purity. On the other hand, it is well known that free radical polymerization is the most important process to prepare high molecular weight polymers. A variety of monomers can be polymerized or co-polymerized under relatively simple conditions. Therefore, the development of a living free radical procedure, which combines the desirable attributes of traditional free radical systems with desirable attributes of living polymerizations, would be a significant development in polymer science in general.

In living process, number of growing chains is usually the same with the number of initiating molecules and it does not change during propagation until the total monomer consumption. Hence semi-logarithmic kinetic plots and molecular weights conversion dependences are linear, of course if the initiation is fast. Also low polydispersities can be achieved via the living process. However some polymerization systems provide well-defined polymers in which chain-breaking reactions cannot be avoided completely. These are called controlled or pseudo-living since they do not fulfill the criteria of living polymerization because of the presence of either transfer or termination. Radical polymerization is one the pseudo-living polymerization techniques.

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

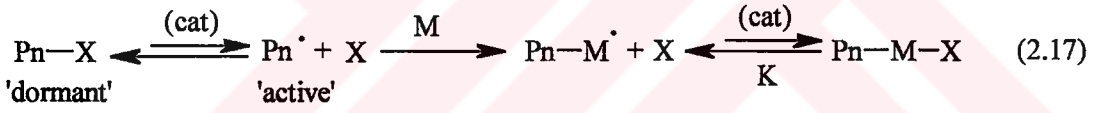
in inclusion complexes. Unfortunately these systems have little generality and do not have application in the synthesis of high purity block copolymers.

- 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).



$$\underset{\text{'dormant'}}{Pn{-}X} \overset{(cat)}{\rightleftharpoons} \underset{\text{'active'}}{Pn^{\bullet} + X} \xrightarrow{M} Pn{-}M^{\bullet} + X \overset{(cat)}{\underset{K}{\rightleftharpoons}} Pn{-}M{-}X \qquad (2.17)$$

cat=Nu^-, Lewis acids, hv, heat
X=protective group
Pn=polymer chain
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 $[I]_0$,

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

$$P{-}R \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P\cdot + R\cdot \qquad (2.18)$$

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 [13] used dithiocarbamate radicals, Georges et al. [14-15] used nitroxyl radicals and Borsing et al. [16] 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

$$P\cdot + X \rightleftharpoons (P{-}X)\cdot \qquad (2.19)$$

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 [17] and phosphorus [18] as well as with organometalic derivatives of Co [19], Cr [20], 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

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

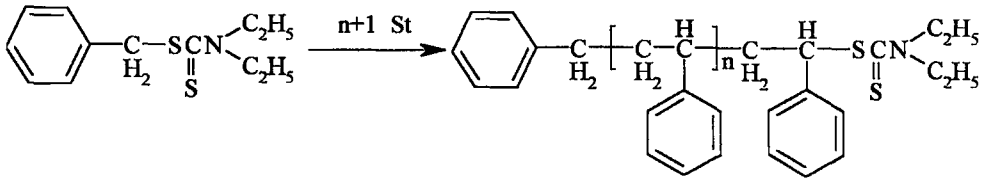
In this case growing radical (Pn.) reacts rapidly and selectively with a transfer agent (P1-R) to exchange the R group and form a dormant species (Pn-R) and a new radical (P1.), which is capable of chain growth. (P.) would be generated by a classical initiator such as AIBN, BPO and redox reactions. (P.)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

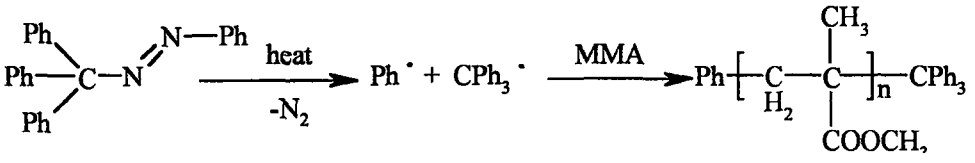
As discussed previously, the potential of organosulfides as initiators of living radical polymerization was first recognized by Otsu and Yoshida [13]. Living polymerization initiated by these species involves monomer insretion to C-S bond. BDC (Benxyl N,N-diethyl dithiocarbamate) and XDC (xylene bis (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 [21]. 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 [22] 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.

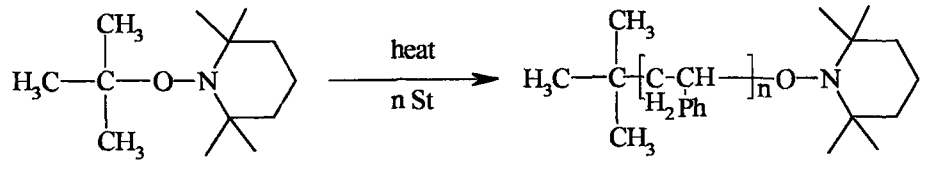


(2.22)

Living radical polymerization of methyl merthacrylate 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 [23] also used this initiator to prepare methacrylate block co-polymers.

c) Alkoxyamines

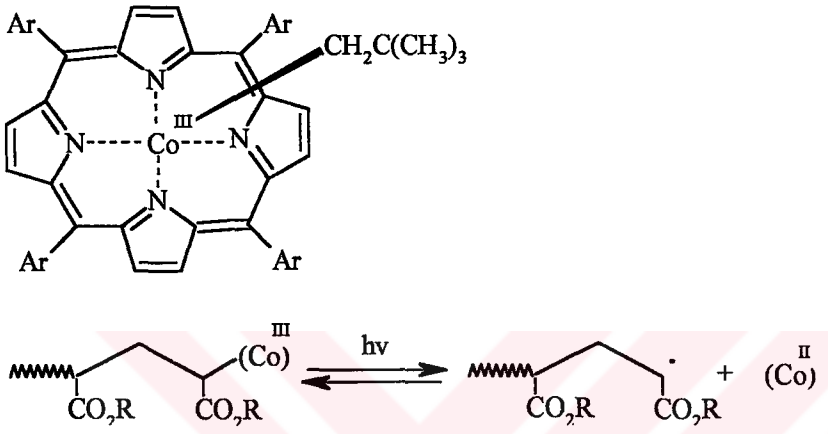
Rizzardo et al. [24] pioneered the use of alkoxyamines as initiators in living free radical polymerizations. The C-O bond is relatively weak and undergoes homolysis on heating to yield a reactive carbon-centered radical and a stable nitroxide. The carbon-centered radical initiates the polymerization 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. [20] 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 Stable Free Radical Polymerization (SFRP)

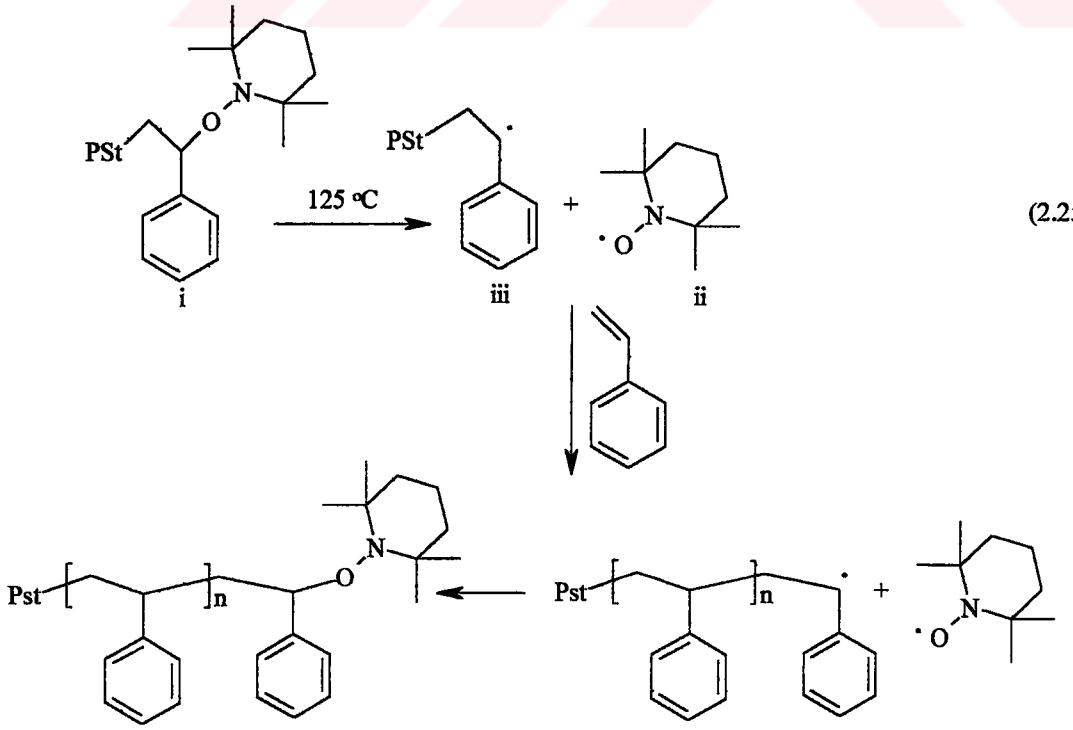
Early attempts to realize a living free radical procedure involved the concept of reversible termination of growing polymer chains by interferters, as discussed previously. Unfortunately, this strategy suffered from high polydispersities, because the stable radicals formed in iniferter case can further initiate chain polymerization and so reduce the control over the molecular weight and chain ends. 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

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 (2.25) 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 (2.25).



(2.25)

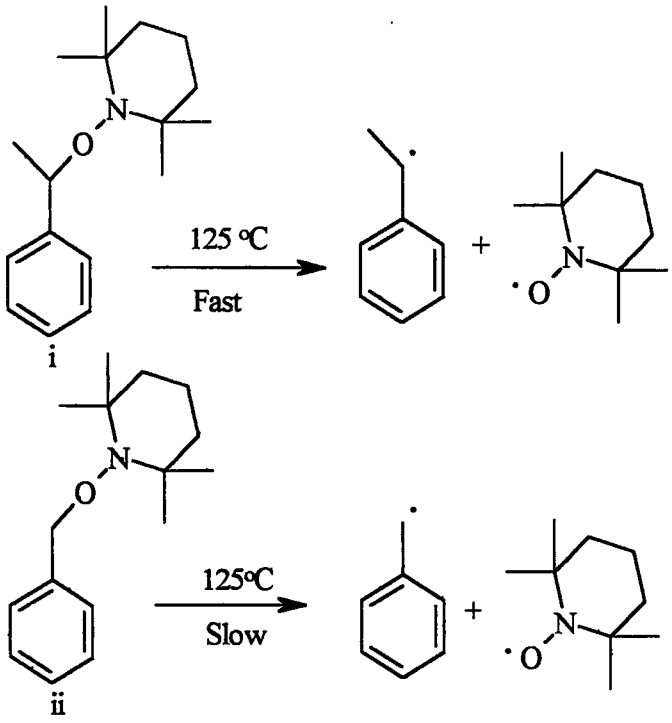
as termination, disproportionation, or combination, which enables the polymer chain to grow in a controlled process. However it should be pointed out that the occurrence of these side reactions is not eliminated, in the strictest sense, the polymerizations are not truly living. The possible side reactions 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.

2.2.2.1 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 (2.26) 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.

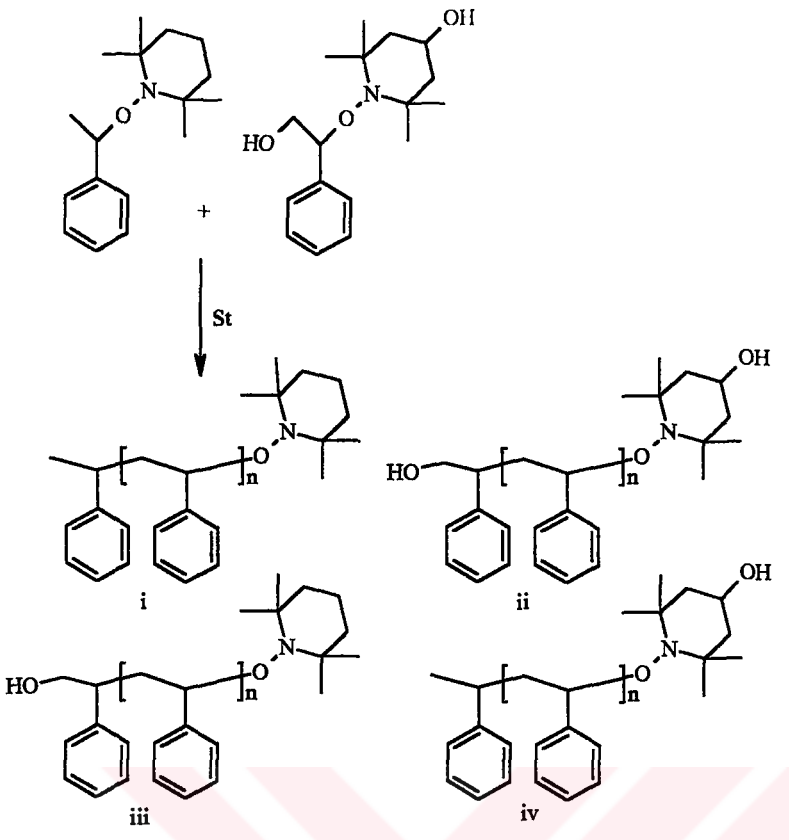


(2.26)

The steric or electronic nature of nitroxide can significantly increase the rate of polymerization [26]. For example Puts and Sogah [27] have shown that by replacement of two methyl groups with pheny 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 hydroxy groups. Theoretically if an insertion type occurs only two products should be formed, seen in (2.27) 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.



(2.27)

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.

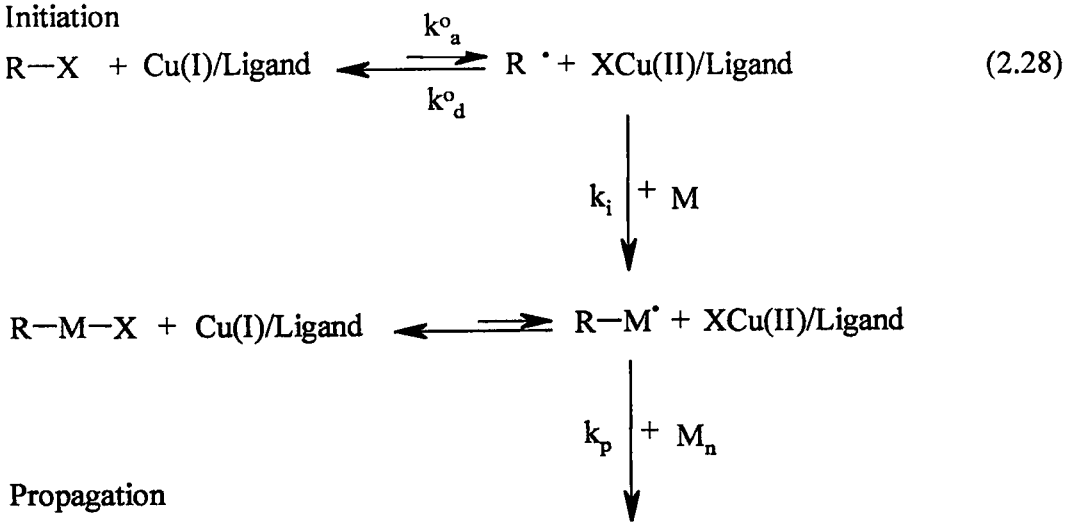
c) Polydispersities of smaller than 1,5 can be achieved.

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

2.2.3 Atom Transfer Radical Polymerization (ATRP)

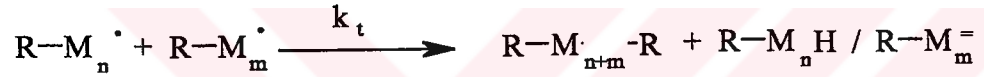
Atom transfer radical polymerization is one of the most widely used living free radical polymerization techniques and seems to be the most versatile one. This technique can successfully be applied to the living radical polymerization of methyl methacrylate, acrylate and styrene monomers with well-controlled molecular weights and well-defined structures [28-31]. 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 (2.28).

Initiation



Propagation

Termination



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.

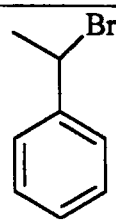
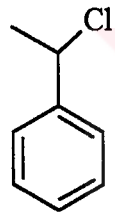
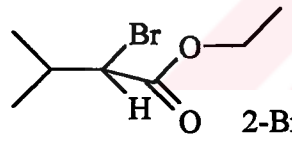
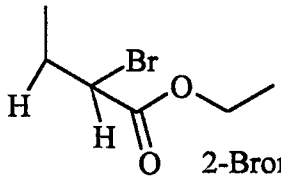
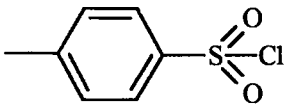
2.2.3.1 Initiators

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

2.2.3.2 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) / $3PR_3$.

2.2.3.3 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_6-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

2.2.3.4 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.

2.2.3.5 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 kp / kt 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.

When ATRP is conducted in a solvent, the rate of polymerization has been found to be slower with compared to solvent-free atom transfer radical polymerizations. This was also the case in our experiments. In our experiments, although ATRP of t-butyl acrylate in ethylene carbonate cannot even reach to 20% conversion within 4 hours, the solvent-free polymerization of the same t-butyl acrylate at the same conditions reached to 87% conversion in just 1,5 hours. As a result it can be said that using solvent in ATRP reduces the rate of the polymerization.

2.2.3.6 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 (2.29).

$$R_p = k_{app}[M] = k_p[P.][M] = k_p K_{eq}[I]_O \frac{[Cu(I)]}{[Cu(II)X]}[M] \qquad (2.29)$$

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 (2.30).

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_d[RX]_0}{k_p[XCu^{II}]}\right)\left(\frac{2}{p} - 1\right) \qquad (2.30)$$

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

PART 3

EXPERIMENTAL PART

3.1 Chemicals Used

a) Monomers

Methyl methacrylate (MMA, 99% Fluka) was passed through basic alumina column to remove inhibitors and then used without further purification.

Tert-butyl acrylate (tBA, 99% Aldrich), and styrene (St, 99% Aldrich) were passed through basic alumina column to remove inhibitors and then dried over CaH_2 and then distilled under reduced pressure 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 reagent were purchased from Aldrich and used as received.

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

It was synthesized according to the procedure of Hawker [33]. (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,(2)

To a round bottom flask were added 1 (0.85 g, 3.06 mmol), triethylamine (Et_3N) (0.7 ml, 5 mmol), and 20 ml of dry tetrahydrofuran (THF). To the reaction mixture, stirred at 0°C under nitrogen was added drop wise 2-bromopropanoyl bromide (0.53 ml, 5mmol) 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, crude product was dissolved in dichloromethane (CH_2Cl_2) and washed successfully with dilute Na_2CO_3 (sodium carbonate) aqueous solution and dried over anhydrous sodium sulfate (Na_2SO_4). CH_2Cl_2 was removed and the crude ester was purified by reparative TLC (Thin Layer Chromatography) (8:2 hexane / ethyl acetate) to give **(2)** as a pale yellow oil (0.52 g, 41%).

3.3 Synthesis of 9-antryl methyl 2-bromo propanoate, (3)

To a round bottom flask were added 9-anthracene methanol (2 g, 9.6 mmol), triethylamine(1.4 ml, 10 mmol), and 20 ml of dry THF. To the reaction mixture, stirred at 0°C under nitrogen was added dropwise 2-bromopropanoyl bromide (1.1ml, 10.4 mmol) in 10 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, crude product was dissolved in dichloromethane and washed successfully with water and dried over anhydrous sodium sulfate (Na_2SO_4). CH_2Cl_2 was removed and the yellow residue was crystallized over 2:1 ratio of hexane / trichloromethane ($CHCl_3$).

3.4 Synthesis of 9-antryl methyl 2-bromo-2-methyl propanoate, (4)

To a round bottom flask were added 9-anthracene methanol (1 g, 4.8 mmol), triethylamine(0.98 ml, 7 mmol), and 20 ml of dry THF. To the reaction mixture, stirred at 0°C under nitrogen was added dropwise 2-bromopropanoyl bromide (0.87

ml, 7 mmol) in 10 ml of dry THF over a period of 45 minutes. The reaction mixture was stirred at room temperature overnight. The salt was removed by filtration and after THF evaporation, crude product was dissolved in dichloromethane and washed successfully with dilute Na_2CO_3 (sodium carbonate) aqueous solution for three times and dried over anhydrous sodium sulfate (Na_2SO_4). CH_2Cl_2 was removed and the yellow residue was self-crystallized. Since its NMR result showed that it included 20% of anthracene methanol, it was also crystallized over hexane for two times more, and finally light-yellow crystals with 60% of yield were obtained.

3.5 Synthesis of Poly (methyl methacrylate) and Poly (tert-butyl acrylate)

The general procedure for atom transfer radical polymerization (ATRP) was as follows; to a schlenk tube equipped with magnetic stirring bar, ligand, catalyst, degassed monomer, solvent and initiator were added in the order mentioned. Tube was degassed by three freeze-pump-thaw cycles, left under vacuum and placed in thermostated oil bath at given temperature, 90°C for the ATRP studies in this work. 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. Poly (methyl methacrylate), PMMA, sample was dissolved in THF and precipitated in methanol, filtered and dried in vacuum oven at 50°C for overnight. The conversions were determined by gravimetrically. PMMA was prepared in 50 vol% diphenylether (DPE) solution at 90°C using CuCl / N,N,N',N",N"-pentamethyldiethylenetriamine (PMDETA) as the catalyst and **(3)** and **(4)** as the initiators.

The formed PMMA have anthracene functionality at their chain ends, which enable the co-polymerization with another monomer like cyclohexane oxide [34]. Anthracene molecule absorbs the light at 350 nm and there will be an electron transfer mechanism between the photosensitized anthracene and an onium salt, like N-etoxy-2-methyl pyridinium hexaflorophosphate ($EMP^+PF^-_6$) and a cation occurs on the anthracene molecule which can further initiate a cationic polymerization, for example of cyclohaxane oxide. So, the obtained PMMA can further be used as a

macro-initiator for another polymerization, as a result of a natural characteristic of multi-functionality.

Poly (tert-butylacrylate), (PtBA), was prepared in bulk and in ethylene carbonate at 90°C using CuBr / PMDETA as the catalyst and (**2**) as initiator.

3.6 Synthesis of block copolymers

The block copolymer was prepared by the stable free radical (SFRP) of styrene using PtBA as macro-initiator. The reaction mixture containing styrene and the macro-initiator was degassed and polymerized at 125°C for the given time.

3.7 Characterization

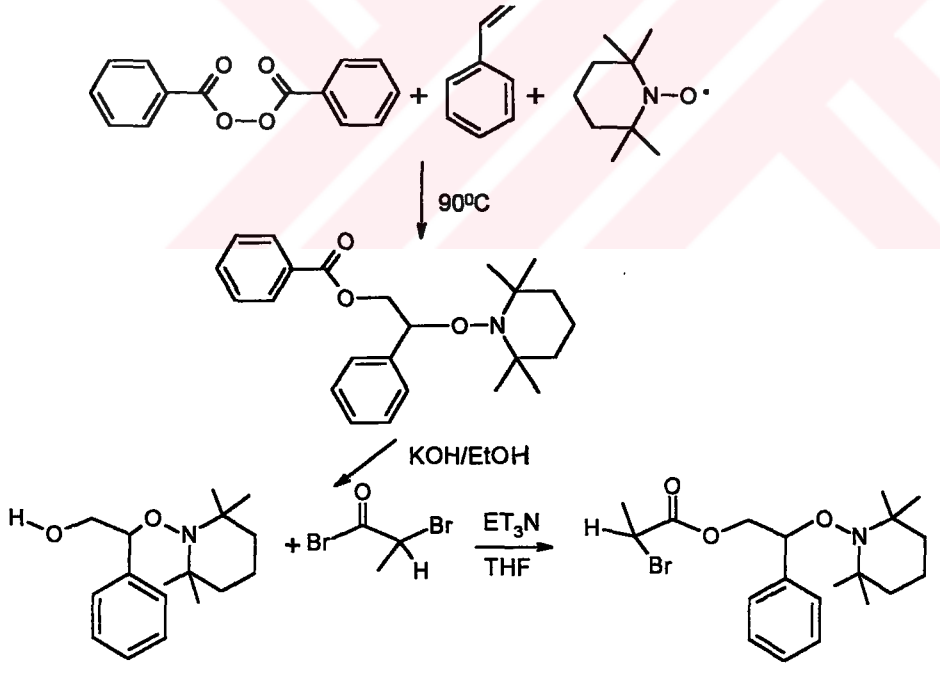
Size exclusion analyses, or in other words gel permeation chromatograms (GPC), were performed with a set up consisting of Waters pump (model 600E) and three Waters styragel HR3, HR4, HR4E columns. THF was used as the eluent at a flow rate of 1mL / min and the detection was achieved with a Waters differential refractometer (model 410). Molecular weights were calculated using polystyrene standards. ^{1} H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AC 250 (250 MHz for proton and 62.90 MHz for carbon) in $CDCL_3$. UV-Visible spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer in dichloromethane.

PART 4

RESULTS AND DISCUSSIONS

4.1 Synthesis of Initiators

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



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

1(benzyloxy)-2-phenyl-2-(2',2',6',6'-tetramethyl-1-piperidinooxy)ethane was synthesized according to the procedure reported by Hawker et al. [33]. It was then hydrolyzed with aqueous potassium hydroxide to give tempo alcohol in quantitave yield. The asymmetric difunctional initiator, (**2**), was prepared from tempo alcohol and corresponding acid bromide in ca 45% yield after purification. The obtained initiator, (**2**), 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).

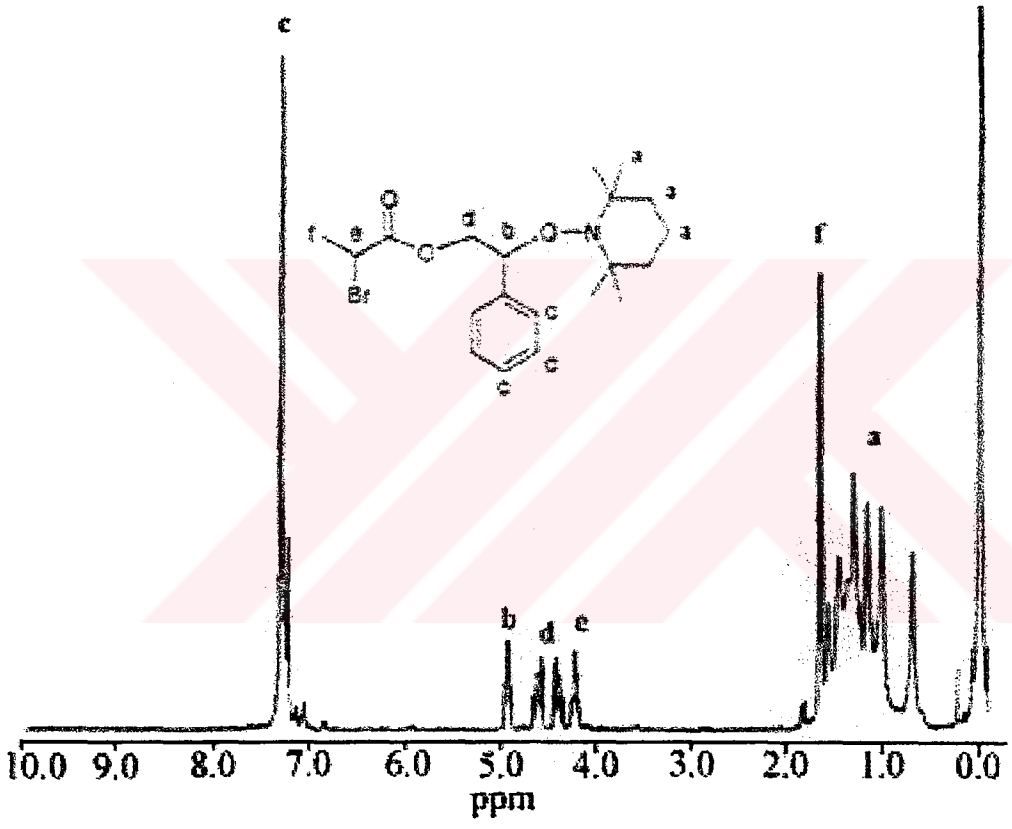
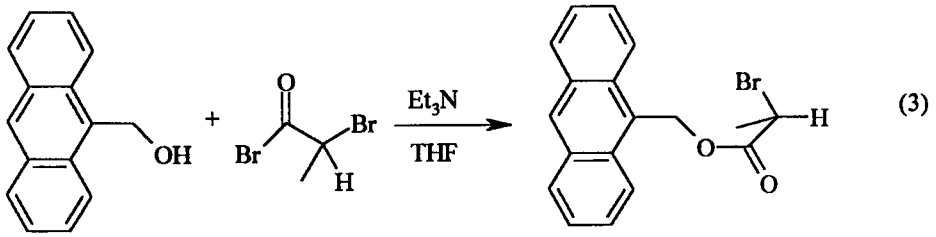
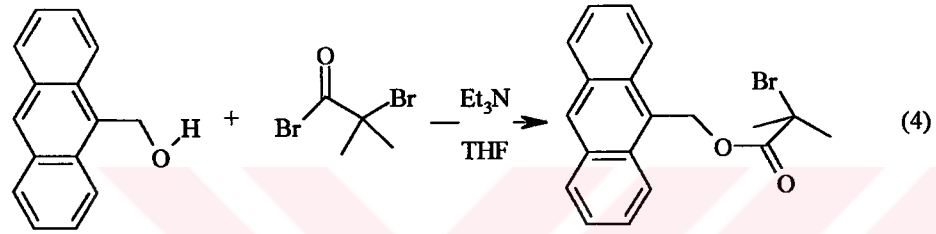


Figure 4.1 The ^{1}H-NMR spectra of the initiator, (**2**), 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo propanoat

4.1.2 Synthesis of 9-antryl methyl 2-bromo propanoat, (3), and 9-antryl methyl 2-bromo-2-methyl propanoat, (4)

The synthetic approach for the preparation of (3) and (4) is given in Scheme 4.2





Scheme 4.2 Synthesis of 9-antrylmethyl 2-bromo propanoat, (3), and 9-antryl methyl 2-bromo-2-methyl propanoat, (4)

The ^{1}H-NMR spectra of both initiators showed no signal corresponding to OH bond and this is an evidence for good esterification reactions (Fig. 4.2 and Fig. 4.3).

According to the integration of ^{1}H-NMR ($CDCl_3$) spectrum of 9-antrylmethyl 2-bromo propanoat; δ 7.47-8.53 ppm (m, 9 ArH of anthracene), 6.23 ppm (q, $C\underline{H}_2$-O), 4.36 ppm (q, J=6.9Hz, 1H, CH_3-$C\underline{H}$-Br), 1.79 ppm (d, J=6.9Hz, 3H, $C\underline{H}_3$-CH-Br).

According to the integration of ^{1}H-NMR ($CDCl_3$) spectrum of 9-antrylmethyl 2-bromo –2-methyl propanoat; δ 7.43-8.52 ppm (m, 9 ArH of anthracene), 6.21 ppm (s, 2 H, CH2-O), 1.87 ppm (s, $(C\underline{H}_3)_2$-C-Br).

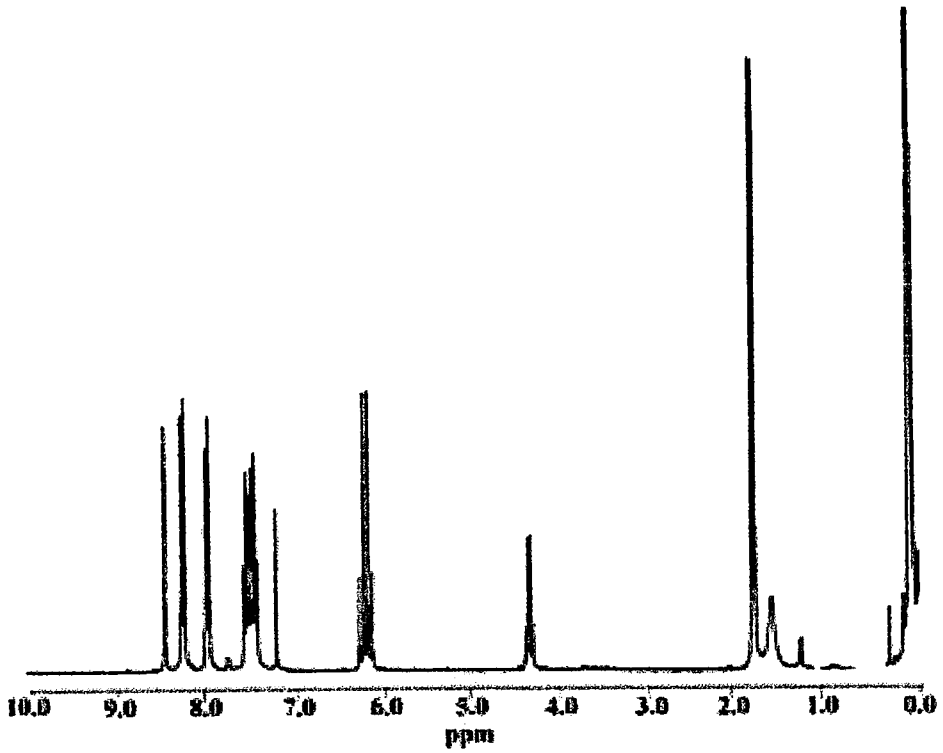


Figure 4.2 The ^{1}H-NMR spectra of the initiator, 9-antryl methyl 2-bromo propanoat, (**3**).

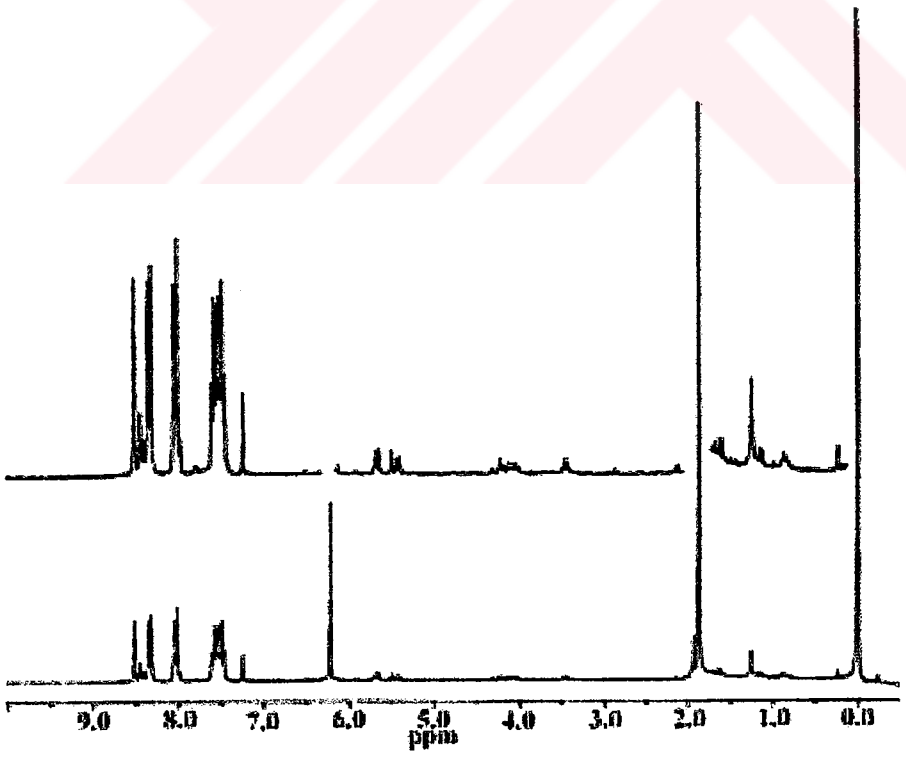


Figure 4.3 The ^{1}H-NMR spectra of the initiator, 9-antryl methyl 2-bromo-2-methyl propanoat, (**4**).

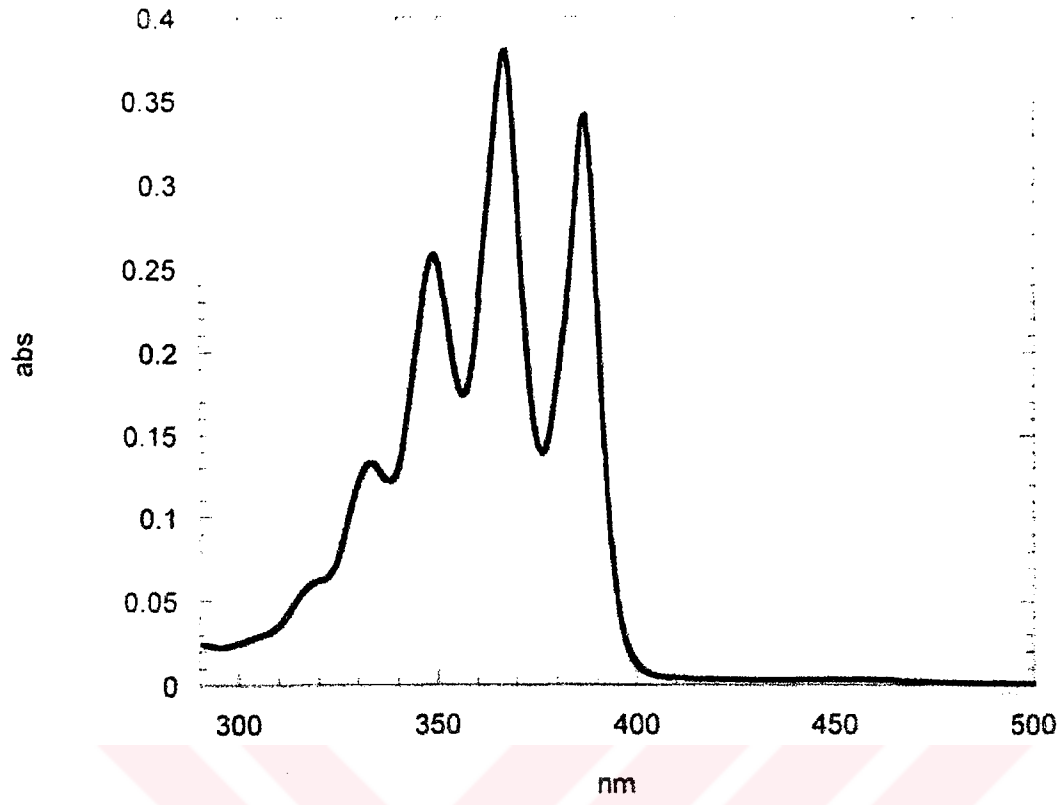


Figure 4.4 UV spectra of 9-antryl methyl 2-bromo propanoat, (**3**)

Both of the initiators (**3**) and (**4**) have the same UV spectra as the anthracene itself. The relationship between the absorbance and the wavelength of the anthracene-labeled initiators, (**3**) and (**4**), given in Figure 4.4 and Figure 4.5 respectively, provides an evidence that the anthracene molecule was surely incorporated into the initiators.

Absorbance values of the anthracane-labeled initiators, (**3**) and (**4**), also change linearly with respect to concentration, as it should be. The relationship between the absorbance and the concentration values of the (**3**) and (**4**), which is seen in Figure 4.7 and 4.8 respectively, is of importance in the calculation of their molar absorption coefficients, ϵ, which then was used to determine their number average molecular weights (Mn) from their UV spectra. In this report, only the Mn values of PMMA initiated by (**4**) were calculated by the aid of its UV spectra. The UV-based molecular weights were calculated using Lambert Beer Law that dictates the equation given in Scheme 4.3.

$A = \epsilon * C * L$

A = Absorbance

C = Concentration [mol / L]

L = The distance [cm], through which the light passes, in our experiments L = 1 cm

Scheme 4.3. Lambert Beer Law

Molar absorption coefficient, ϵ, could easily be found from the slope of the above equation as 8291 for (**3**) 7278 for (**4**) respectively. The next step in the calculation of Mn from UV spectra is now to measure the absorbance value of the polymer obtained by using one of the initiators (**3**) and (**4**) at a certain concentration by the aid of the previously determined ϵ value of that initiator. In this report absorbance values were all measured at 366 nm where the anthracane molecule gives its maximum response under UV light. Then the concentration, [mol / L], corresponding to that absorbance value can be determined by the Lambert Beer Law given in Scheme 4.3. Since the concentration of the polymer in terms of [mass / volume] is already known, Mn value of the polymer can be calculated dividing these two concentrations to each other;

Mn = Concentration taken [mass / volume] / Concentration, calculated [mol / L]

The relationship between the absorbance and the wavelength of the poly (methyl methacrylate) synthesized in the presence of 9-antryl methyl 2-bromo propanoat, (**3**), is seen in Figure 4.6. To be able to calculate its molecular weight, Mn, from UV its absorbance value at 366 nm was used.

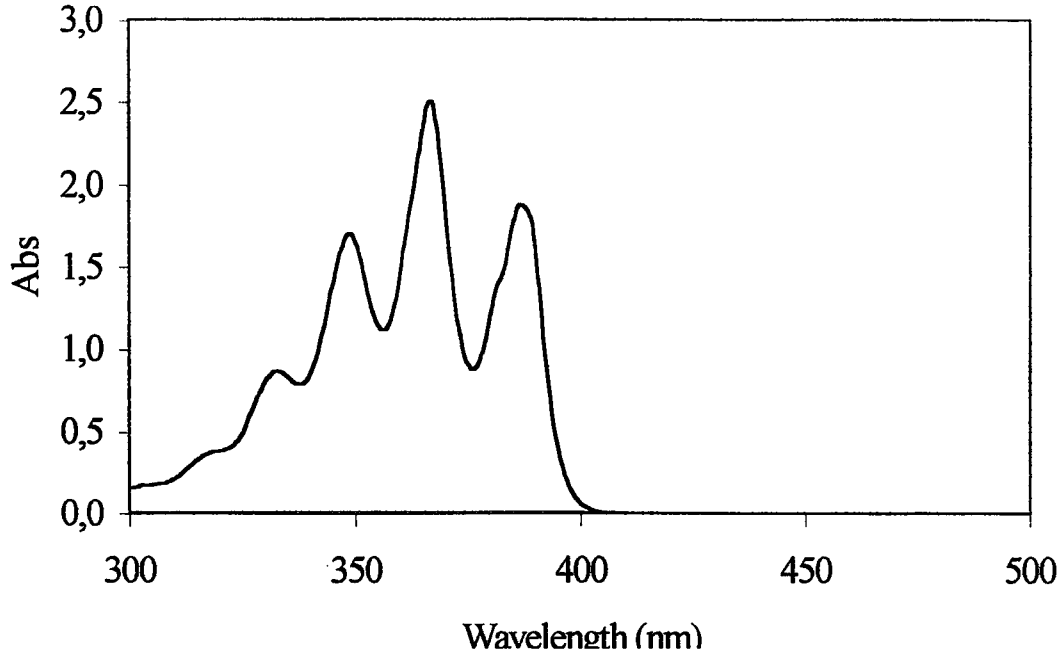


Figure 4.5 UV spectra of 9-antryl methyl 2-bromo-2-methyl propanoat, (**4**)

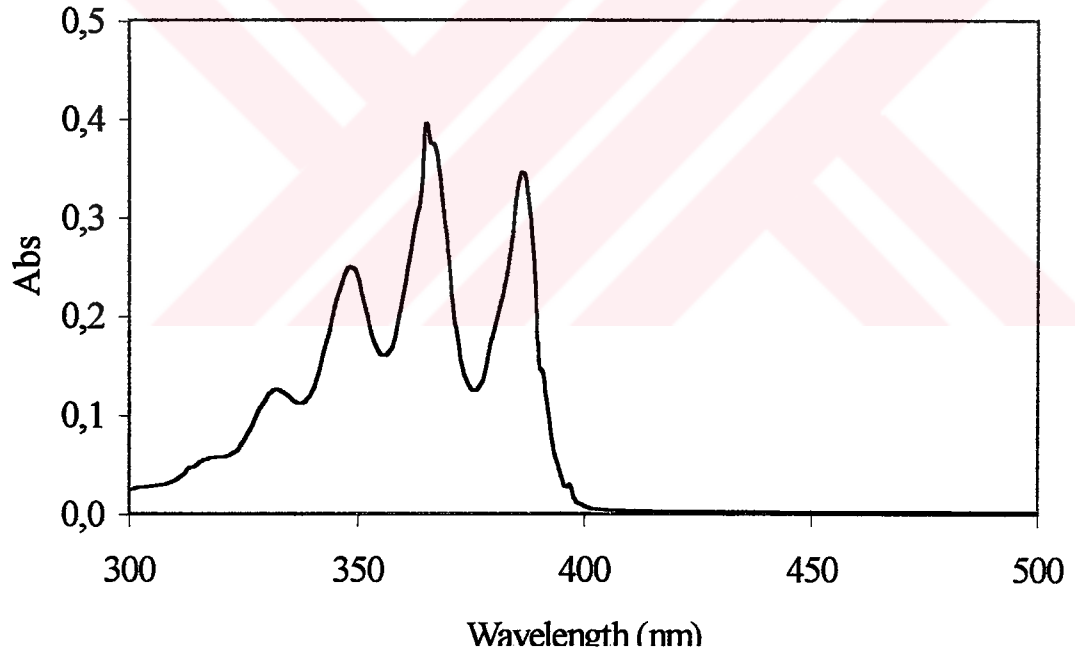


Figure 4.6 UV spectra of poly (methyl methacrylate), (PMMA) sample with the code of TPMMA 3 in Table 4.1

Figure 4.5 and Figure 4.6 provide evidence that the anthracene molecule is surely incorporated into the polymer chains.

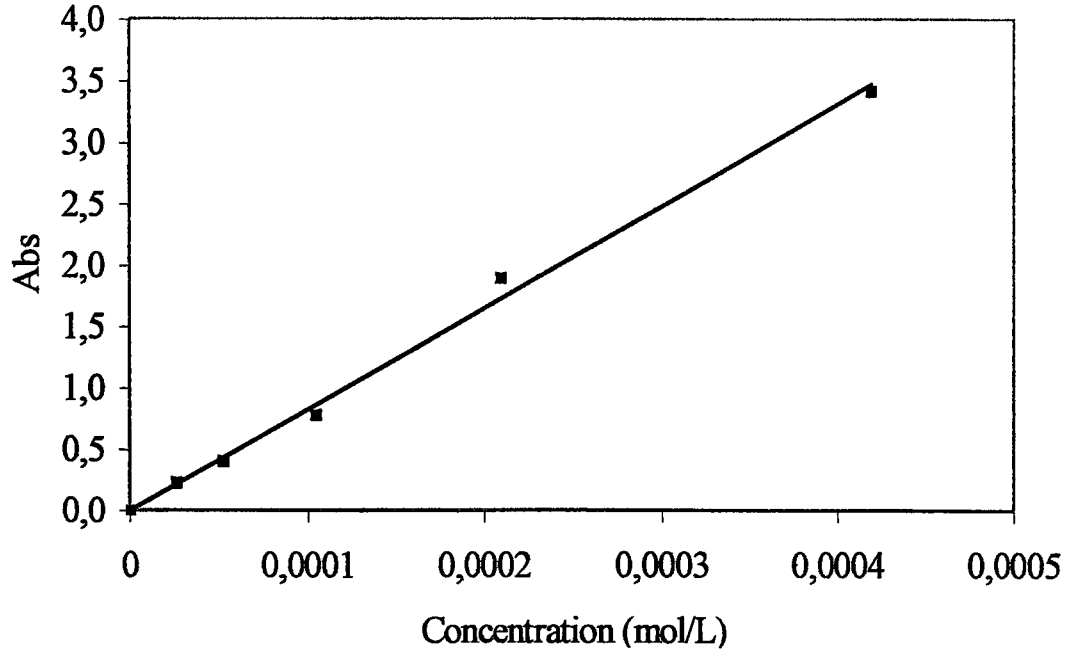


Figure 4.7 The relationship between absorbance and the concentration of 9-antryl methyl 2-bromo propanoat, (**3**)

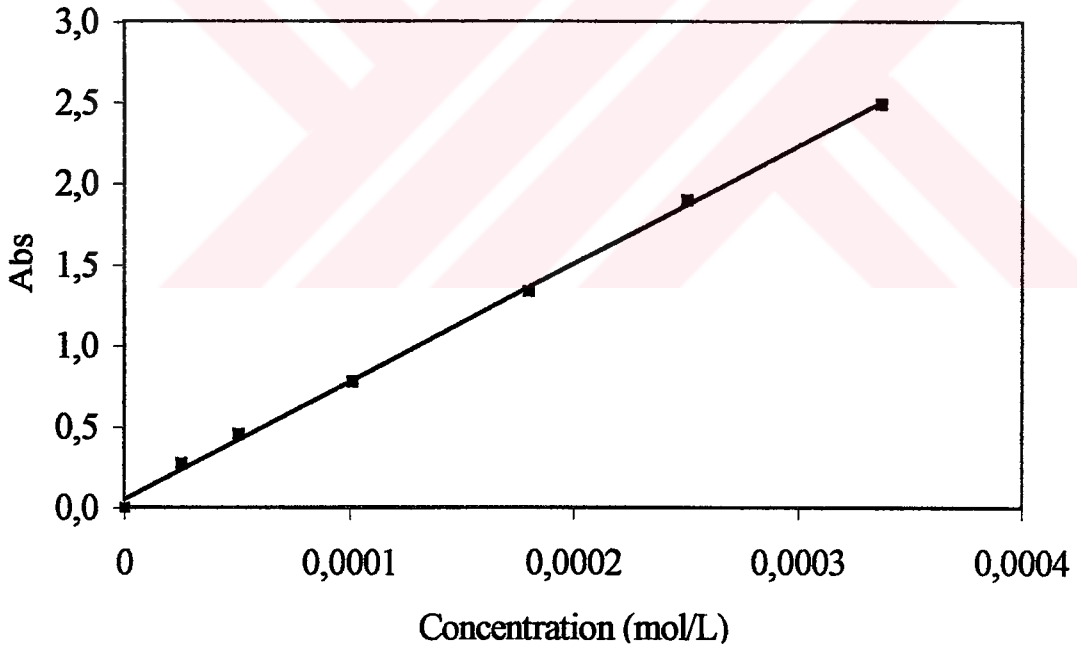
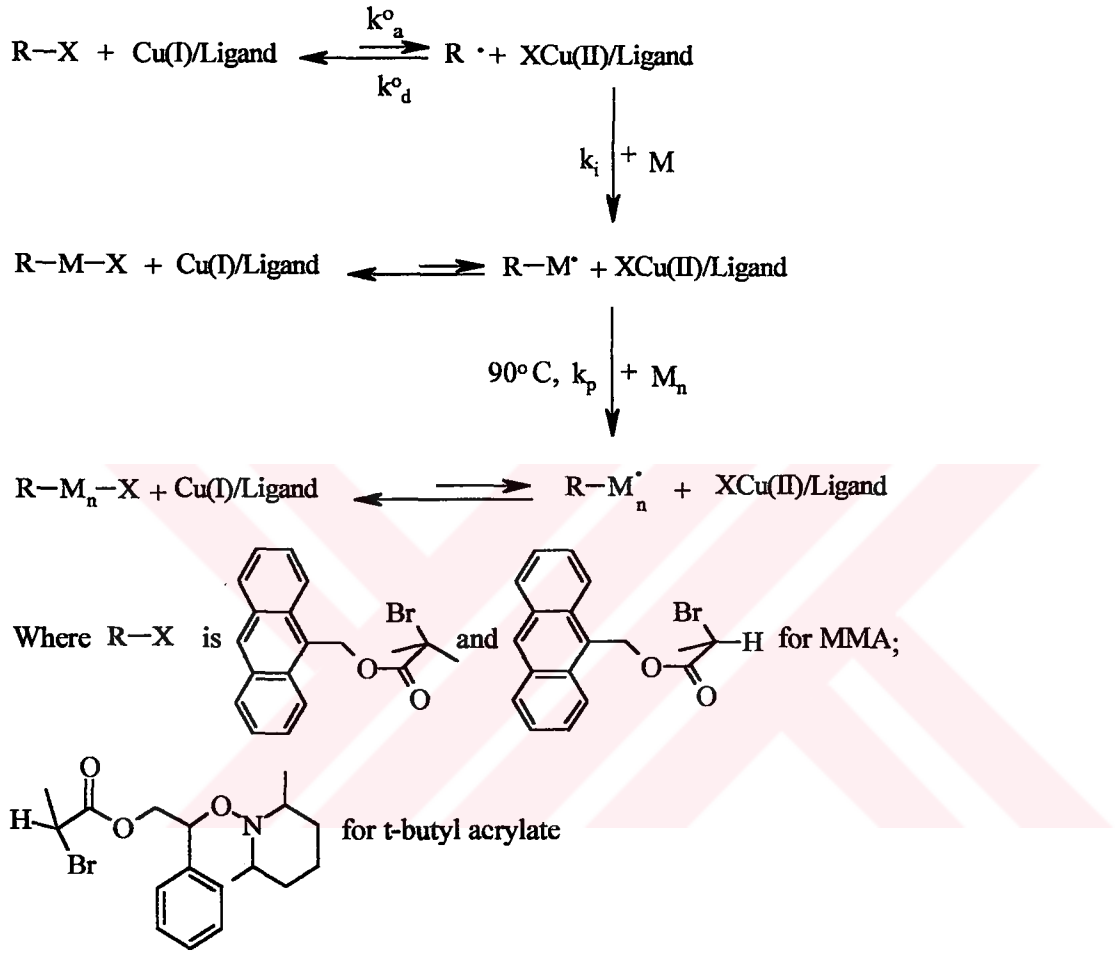


Figure 4.8 The relationship between absorbance and the concentration of 9-antryl methyl 2-bromo-2-methyl propanoat, (**4**)

4.2 Synthesis of poly (methyl methacrylate, PMMA) and poly (tert-butyl acrylate, PtBA)

Synthesis of PMMA and PtPA were illustrated in Scheme 4.4



Ligand=PMDETA ; M represents the monomer

Scheme 4.4 Atom transfer radical polymerization (ATRP) of PMMA and PtBA as a schematic representation.

9-antryl methyl 2-bromo propanoat, (**3**), and 9-antryl methyl 2-bromo-2-methyl propanoat, (**4**), were used to perform the controlled polymerization of PMMA and 2-phenyl-2-[(2,2,6,6- tetramethylpiperidino)oxy]ethyl 2-bromo propanoat, (**2**), for that of PtBA. In the case of ATRP of PMMA, CuCl complexed by PMDETA used as catalyst at 90°C in 50 vol. % diphenyether. This led to formation of PMMA with anthracane moiety at the chain end. As shown in Table 4.1, the molecular weights of

resulted PMMA, synthesized in the presence of (**4**) as the initiator, found experimentally are in agreement in a general tendency, with the theoretically calculated ones, although some deviations are observed for small conversions. Its molecular weight distribution (MWD) is low enough.

Table 4.1 Atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) in diphenylether (DPE) at 90°C with (**4**), as the initiator, $[M]_0$=4,67M, $[M]_0/[I]_0$ 200, $[I]_0/[Cu(I)]/[Ligand]$=1/1/1

POLYMER	TIME(MIN)	% CONV	Mn Theoritical	Mn GPC	Mn UV	MWD
TPMMA1	15	9	2200	8300	8100	1,145
TPMMA2	25	21	4600	10600	10300	1,147
TPMMA3	30	36	7600	10500	10300	1,125
TPMMA4	60	46	9600	15900	14900	1,150
TPMMA5	90	54	11200	14100	16800	1,169
TPMMA6	120	67	13800	20800	17600	1,158
TPMMA7	150	78	16200	24000	20600	1,117

TPMMA represents the poly (methyl methacrylate) synthesized in 9-antryl methyl 2-bromo-2-methyl propanoat, (**4**), as the tertiary initiator and MWD means the molecular weight distributions of the polymers

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.

As listed in Table 4.1, the molecular weights calculated by gel permeation chromatography (GPC) are very closed to those obtained from UV spectra. This also includes an evidence of that one anthracene molecule is incorporated in each polymer chain, which was assumed in the calculation of the number average molecular weights (Mn) of the polymer from UV method via Lambert Beer Law as mentioned previously. In additionally, the conversions increase with time proportionally, and the polymers have low molecular weight distribution as seen in Table 4.1, indicating the polymerization really follows the ATRP route.

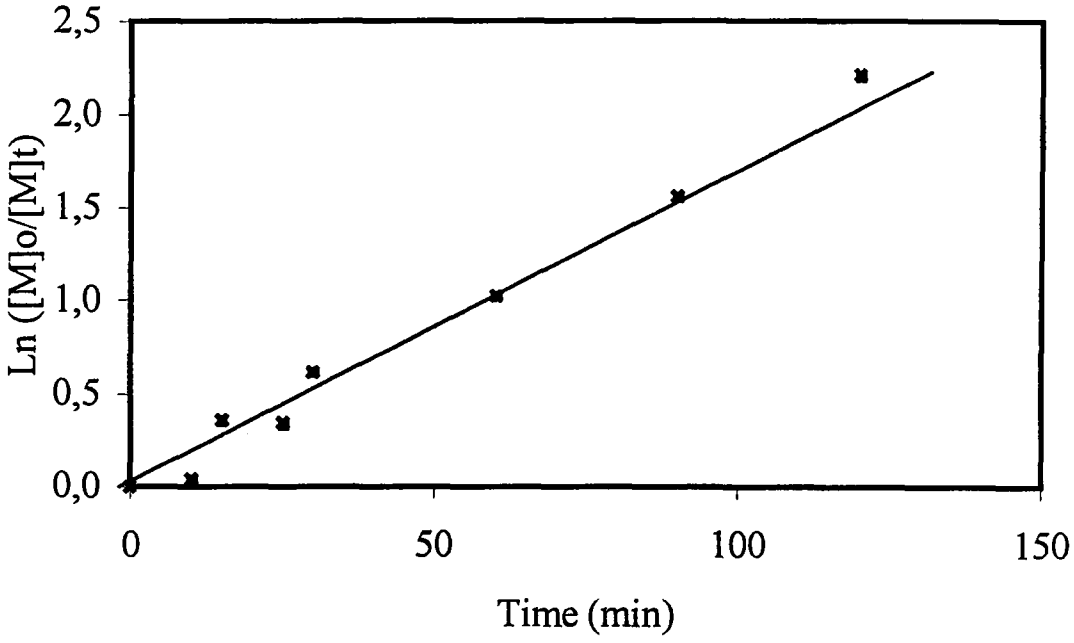


Figure 9. Semi-logarithmic kinetic plot of atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) in diphenyl ether (DPE) at 90°C with 9-antrylmethyl 2-bromo propanoat, (**3**), as the initiator, $[M]_0$=4,67M, $[M]_0/[I]_0$=200, $[I]_0/[Cu(I)]/[Ligand]$=1/1/1

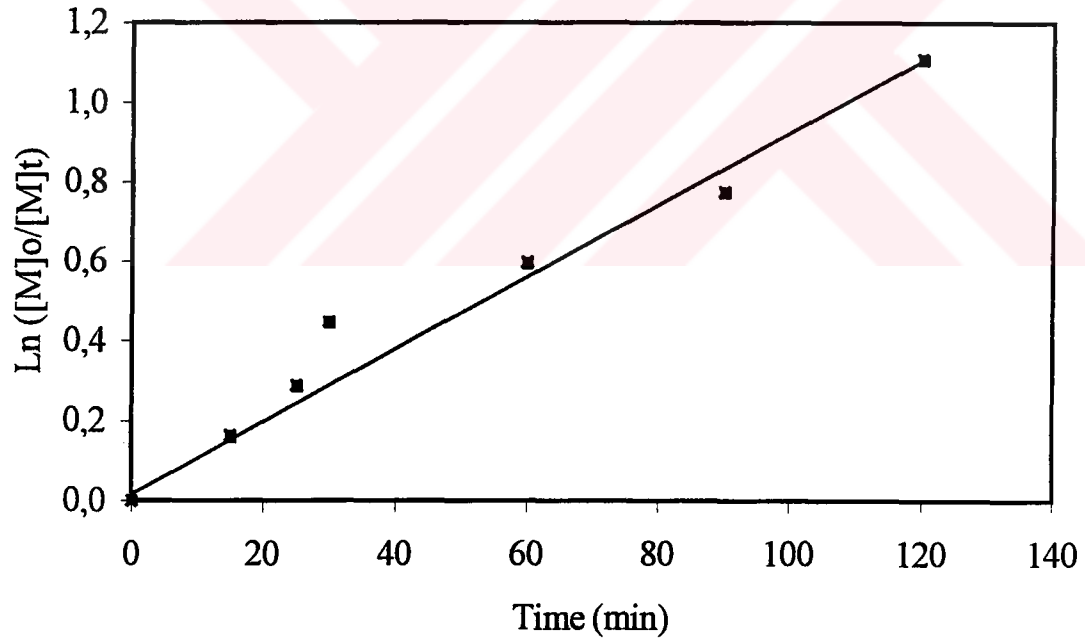


Figure 10. Semi-logarithmic kinetic plot of atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) in diphenyl ether (DPE) at 90°C with 9-antrylmethyl 2-bromo-2-methyl propanoat, (**4**), as the initiator, $[M]_0$=4,67M, $[M]_0/[I]_0$=200, $[I]_0$ /[Cu(I)]/[Ligand]=1/1/1

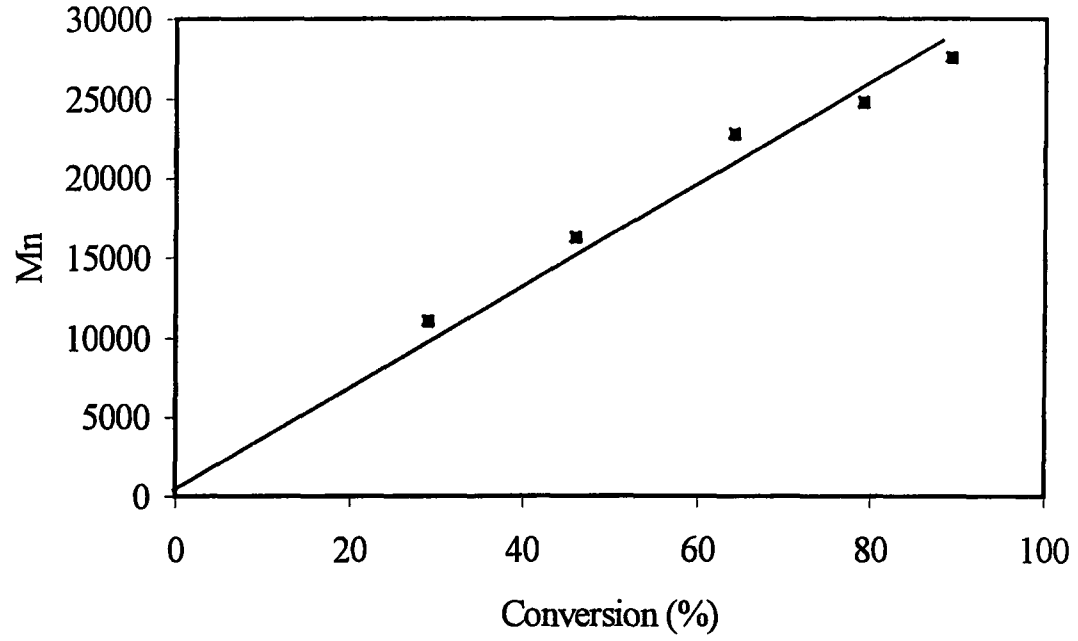


Figure 11. Dependence of number average (Mn) molecular weight calculated from gel permeation chromatography (GPC) on conversion in atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) in diphenylether (DPE) at 90°C with 9-antrylmethyl 2-bromo propanoat, (**3**), as the initiator. $[M]_0$=4,67M, $[M]_0/[I]_0$=200, $[I]_0/[Cu(I)]/[Ligand]$=1/1/1

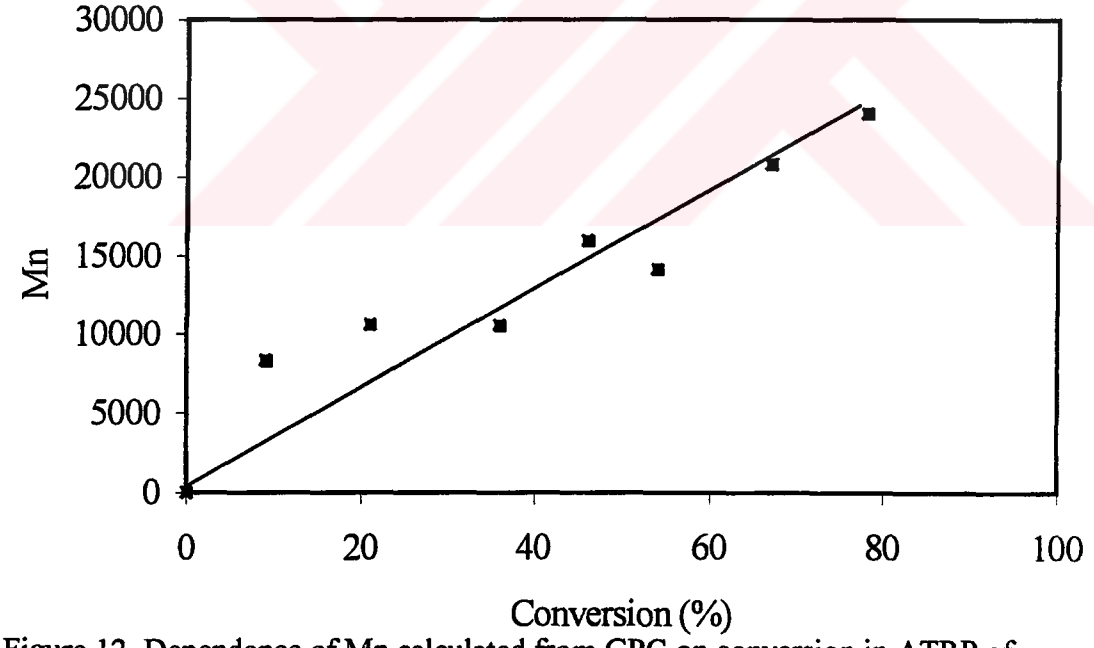


Figure 12. Dependence of Mn calculated from GPC on conversion in ATRP of MMA in DPE at 90°C with 9-antrylmethyl 2-bromo-2methyl propanoat, (**4**), as the initiator. $[M]_0$=4,67M, $[M]_0/[I]_0$=200, $[I]_0/[Cu(I)]/[Ligand]$=1/1/1

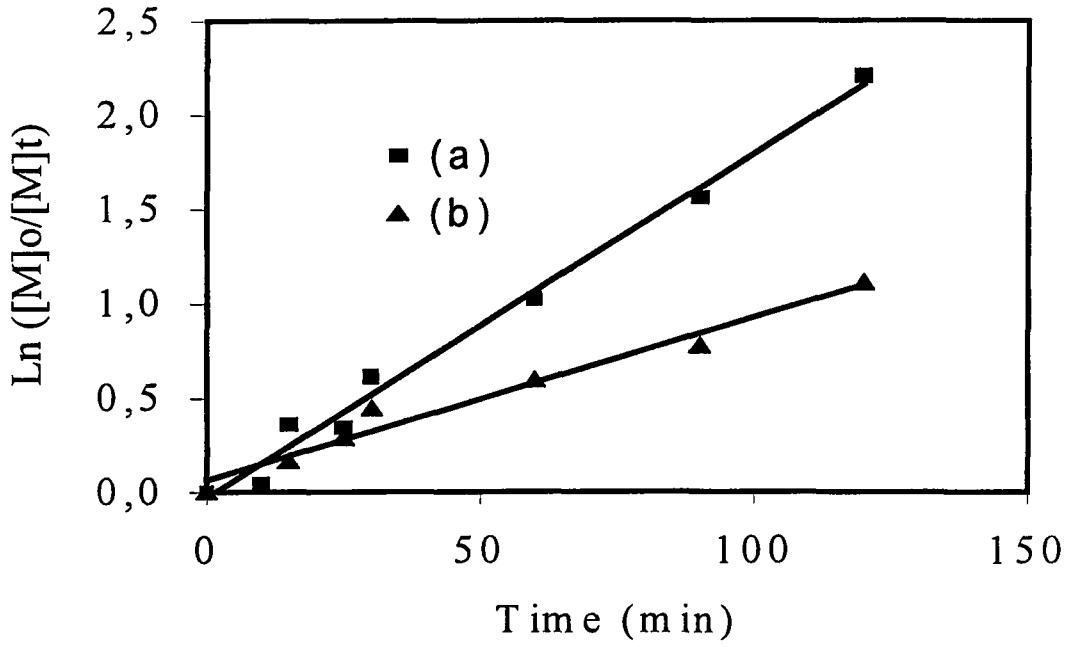


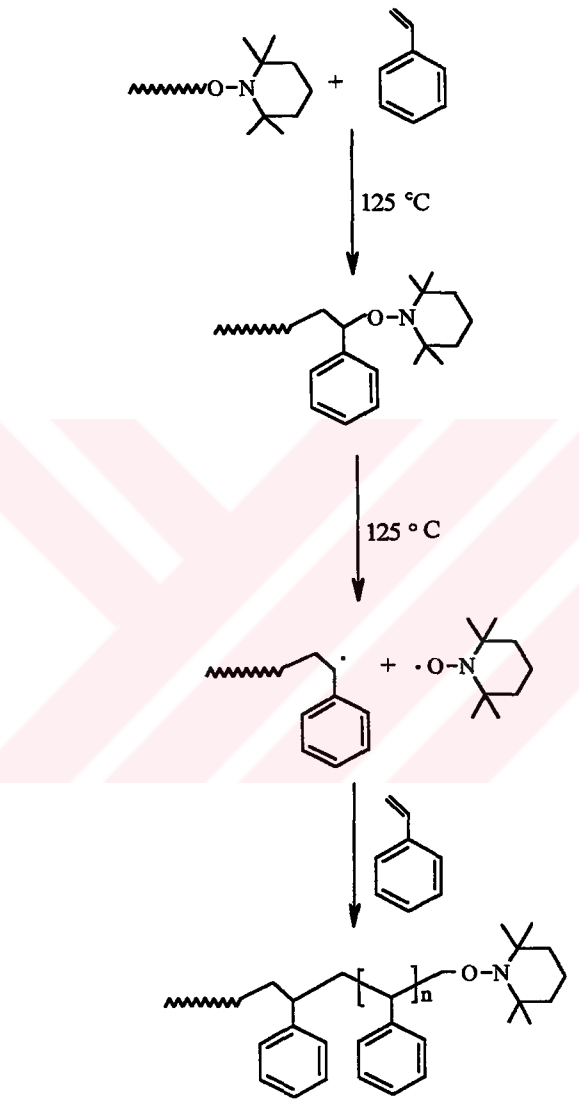
Figure 4.13 Comparison of the semi-logarithmic kinetic plots of PMMA's obtained by ATRP with 9-antrylmethyl 2-bromo propanoat, (**3**), illustrated with (a) and 9-antrylmethyl 2-bromo-2methyl propanoat, (**4**), illustrated with (b)

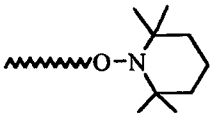
As shown in Figure 4.13, the polymerization of MMA proceeds through approximately first-order kinetics with respect to monomer concentration for both secondary and tertiary initiation systems. The number average molecular weights (Mn) that were evaluated by Gel Permeation Chromatography (GPC) increase with the monomer conversion (Figures 4.11-12), which indicates a constant concentration of growing chain radicals throughout the reaction.

The method used for the preparation of PMMA has been applied to obtain PtBA in the presence of 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo propanoat, (2), as the initiator and CuBr complexed by PMDETA as the catalyst both in bulk and in ethylene carbonate for the given times, as shown in Table 4.2. As can be seen in Table 4.2, using solvent in ATRP reduced the rate of the polymerization and the control over the polymerization, which can be understood from the deviation in the agreement of the theoretically calculated molecular weights with the experimentally calculated ones. On the other hand, in solvent-free ATRP of tert-butyl acrylate, experiment 2, the system has the molecular weight agreement and high enough polymerization rates.

4.3 Synthesis of tert-butyl acrylate (tBA) – styrene (St) block copolymer

The schematic representation of the synthetic approach is given in Scheme 4.5. PtBA prepared in ATRP system in bulk was used as macro-initiator for the stable free radical polymerization (SFRP) of styrene in bulk at 125°C.




represents the TEMPO headed PtBA

Scheme 4.5 Schematic representation of the block co-polymerization of tert-butylacrylate with styrene via stable free radical polymerization (SFRP) route.

As seen in Table 4.3, the experimentally calculated, both via gel permeation chromatography (GPC) and the nuclear magnetic resonance spectrospin (NMR), molecular weights (Mn) of the resulted block copolymer are in good agreement with the theoretically calculated one. The final block copolymer has also low molecular weight distribution (MWD).

Table 4.2 Atom transfer radical polymerization (ATRP) of tert-butyl acrylate (tBA) at 90°C with (**2**), as the initiator, $[M]_0$=6,83M, $[M]_0/[I]_0$= 100, $[I]_0/[Cu(I)]/[Ligand]$=1/1/1

Polymer Code	Reaction Time (min)	Conversion (%)	Solvent	Mn GPC	Mn Theoretical	MWD
HPTBA 1	240	17	Ethylene Carbonate	4600	2600	1,22
HPTBA 2	90	84	-	13900	11300	1,32

HPTBA represents the homo polymer of tBA in the presence of 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo propanoat, (**2**), as the initiator

Tablo 4.3 Synthesis of tert-butylacrylate (tBA)-styrene (St) block copolymer using PtBA as the macro-initiator, $[M]_0 / [I]_0 = 200$, $[M]_0$=8,73 M, Temperature=125°C

Polymer Code	Initiator	Monomer	Time (hr)	Conversion (%)	Mn GPC	Mn Theoretical	Mn NMR	MWD
CPTBAS	HPTBA 2	Styrene	16	60	30748	26408	28000	1,40

CPTBAS means the copolymer of styrene and tert-butyl acrylate synthesized in the presence of PtBA, polymerized in bulk-second experiment.

The theoretical molecular weights were calculated by the formula of $Mn_{theo} = ([M]_0 /[I]_0 * \text{conversion} * MW_{monomer}) + MW_{initiator}$,where $MW_{monomer}$ and $MW_{initiator}$ are the molecular weights of the monomer and the initiator used.

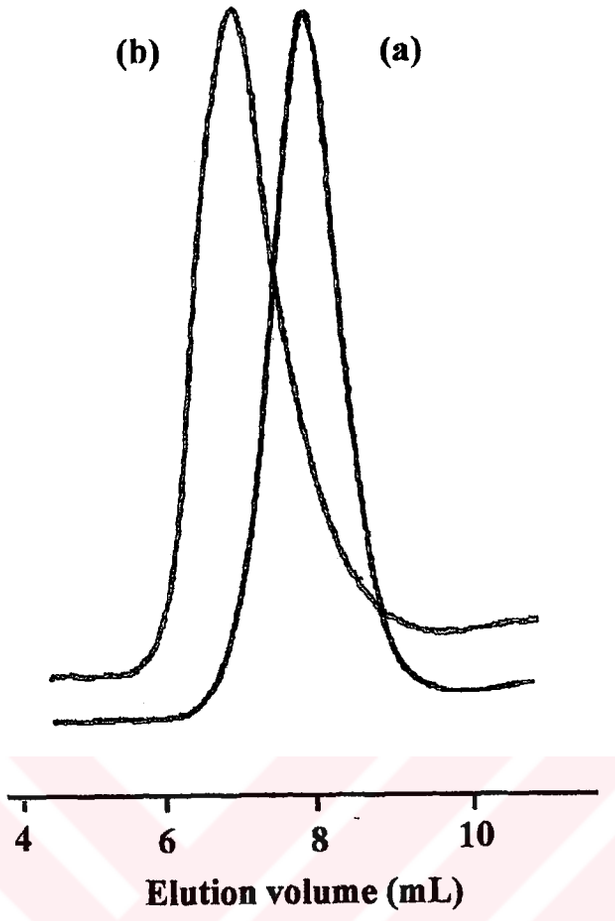


Figure 4.14 Comparison of Gel Permission Chromatography (GPC) traces for (a) homo poly (tert-butyl acrylate), (PtBA), and (b) block co-polymer of PtBA and styrene, (PtBA-b-styrene)

This GPC result shows the expected increase in molecular weight through the co-polymerization. The new peak at higher molecular weight is ascribed to the block copolymer. Furthermore, the absence of the PtBA macro-initiator peak on the GPC trace of resulted block copolymer indicates the complete conversion of the macro-initiator to the block copolymer.

^{1}H-NMR spectrum of PtBA-b-styrene (Figure 4.15) exhibits the major peaks characteristics of the styrene and tert-butylacrylate segments in block copolymer. From the integration ratio of the signals at 1.43 ($C(CH_3)_3$) (of PtBA) to 6.3-7.2 ppm (ArH of PSt), the molecular weight was calculated (28000). This value is in agreement with theoretical molecular weight calculated from $Mn_{theo} = ([M]_0 / [I]_0 * \text{conversion} * 104) + 13900$ where 104 and 13900 are the molecular weight of styrene and PtBA macro-initiator respectively.

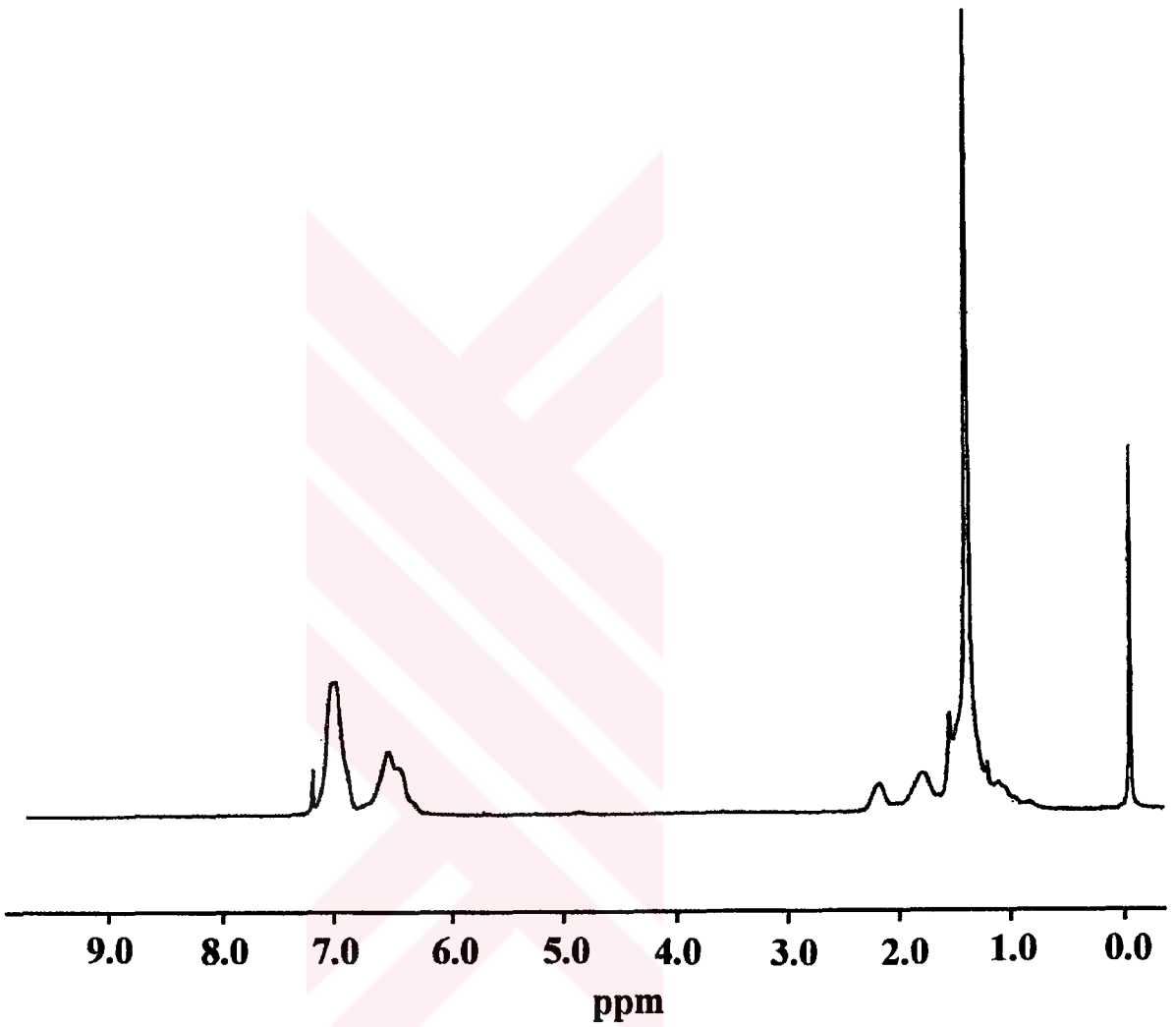


Figure 4.15 ^{1}H NMR spectrum of the copolymer of t-butyl acrylate and styrene

CONCLUSIONS AND RECOMMENDATIONS

In conclusion, novel asymmetric difunctional initiators, 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo propanoat, (2), 9-antryl methyl 2-bromo propanoat, (3), and 9-antryl methyl 2-bromo-2-methyl propanoat, (4), were synthesized and successfully used in the preparation of homo and block copolymers via atom transfer radical polymerization (ATRP) and stable free radical polymerization (SFRP) techniques. Besides the preparation of poly (methyl methacrylate, PMMA) using ATRP route, a versatile approach leading to tert-butyl acrylate-styrene block copolymer obtained by the combination of ATRP and SFRP have been demonstrated in the present work.

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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