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ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

**SYNTHESIS OF LINEAR AND STAR BLOCK COPOLYMERS BY
ATOM TRANSFER RADICAL POLYMERIZATION**

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**ATOM TRANSFER RADİKAL POLİMERİZASYONU İLE
LİNEER VE YILDIZ BLOK KOPOLİMERLERİN SENTEZİ**

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LIST OF SYMBOLS

M_n	: Number average molecular weight of polymer
M_w	: Weight average molecular weight of polymer
MWD	: Molecular weight distribution of polymer
MW	: Molecular weight of monomer
PtBA	: Poly (tert-butyl acrylate)
PMMA	: Poly (methyl methacrylate)
PSt	: Polystyrene
PMDETA	: N,N,N',N'',N''' -(pentamethyldiethylenetriamine)
MBP	: Methyl 2-bromopropionate
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
I, M	: Initiator and monomer respectively

SYNTHESIS OF LINEAR AND STAR BLOCK COPOLYMERS BY ATRP

SUMMARY

Star polymers have attracted much attention in research over the years due to their unique three-dimensional shape and highly branched structure. The synthesis of well-defined star polymers is a challenging task usually achieved by a “living” polymerization technique. The recent development of the controlled/ “living” radical polymerization has opened up a new and potentially wide route to well-defined macromolecules. Controlled/ “living” radical polymerization processes have proven to be versatile for the synthesis of polymers with well-defined structures and complex architectures. The most important benefit of controlled/ “living” polymerizations is that they allow to prepare new macromolecules with novel topologies, varying compositions, and functionalities placed at different parts of macromolecules or various compositions of these. Among the CRP processes, atom transfer radical polymerization (ATRP) is the most efficient method and has been successfully applied to the synthesis of special block copolymers and polymers with complex architectures such as stars because methyl 2-bromopropionate group, which is an efficient initiator of ATRP, can be easily introduced as the end group to different polymers.

In the present work, novel octa-functional initiator, 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octakis- (2-bromopropionyloxy) calix[8]arene was synthesized and used in the preparation of AB type poly(*tert*-butyl acrylate-*b*-methylmeth acrylate) and poly(*tert*-butyl acrylate-*b*-styrene) diblock copolymers. The monomodal shapes of the GPC (Gel Permeation Chromotography) traces and ¹H-NMR spectrum showed that the octa-arm and the linear diblock copolymers which were prepared to set a model for the octafunctional system were successfully synthesized by ATRP.

ATOM TRANSFER RADİKAL POLİMERİZASYONU İLE LİNEER VE YILDIZ BLOK KOPOLİMERLERİN SENTEZİ

ÖZET

Yıldız polimerler araştırmalarda üç boyutlu ve çok dallanmış yapılarından dolayı yıllardır ilgi çekmektedirler. Yıldız polimerlerin sentezi oldukça zorlu bir konu olup genellikle yaşayan polimerizasyon yöntemiyle gerçekleştirilmektedir. Kontrollü/ “Yaşayan” Radikal Polimerizasyonunun son zamanlardaki gelişimi iyi tanımlanmış ve kompleks yapılı polimerlerin sentezi için yeni ve oldukça geniş bir yol açmıştır. Kontrollü/ “Yaşayan” Polimerizasyon yöntemlerinin iyi tanımlanmış ve kompleks yapılı polimerlerin sentezinde birçok açıdan faydalar sağladığı bilinmektedir. Kontrollü/ “Yaşayan” Radikal Polimerizasyonunun en önemli faydası yeni topolojilere, farklı kısımlarında yer almış çok çeşitli fonksiyonallitelere ve kompozisyonlara sahip yeni makromoleküllerin sentezine izin vermesidir. Kontrollü/ “Yaşayan” Radikal Polimerizasyon yöntemlerinin arasında Atom Transfer Radikal Polimerizasyonu (ATRP) en etkili yöntem olup özel blok kopolimerlerin ve yıldız polimerler gibi kompleks yapılı polimerlerin sentezinde başarıyla uygulanmaktadır. Çünkü ATRP için çok etkili bir başlatıcı olan 2-bromopropanoat farklı polimerlerin uç gruplarına kolaylıkla yerleştirilebilmektedir.

Bu çalışmada, yeni sekiz fonksiyonlu bir başlatıcı olan 5,11,17,23,29,35,41,47-okta-*tert*-butil-49,50,51,52,53,54,55,56-oktakis-(2-bromopropioniloksi)kaliks[8]aren sentezlenip, AB tipli poli (*tert*-bütil akrilat-*b*- metilmetakrilat) ve poli (*tert*- bütil akrilat-*b*-stiren) diblok kopolimerlerinin hazırlanmasında başarıyla kullanılmıştır. GPC (Jel Geçirgenlik Kromatografisi) ve ¹H-NMR spektrumlarından elde edilen sonuçlar sekiz kollu diblok kopolimerlerin ve bu sekiz fonksiyonlu sisteme bir model teşkil etmesi için sentezlenen lineer diblok kopolimerlerin ATRP tekniğiyle başarıyla sentezlendiğini göstermiştir.

1.INTRODUCTION

The synthesis and characterization of star polymers has been a consistent area of exploration in the ongoing pursuit of structure property relationships in macromolecular science[1].

Star polymers are of interest because of their unique spatial shapes, different hydrodynamic properties, higher degrees of chain end functionality and lower viscosity compared to linear polymers of similar composition and molecular weights.

The synthesis of well-defined star polymers is a challenging task usually achieved following a “living” polymerization route. There are essentially two techniques for the synthesis of star polymers: In the “core-first” technique multifunctional initiators are used to grow chains from a central core resulting in macromolecules with well-defined structures in terms of both arm number and length. Most of the star polymers are synthesized by this technique. In the “arm-first” technique a few units of the divinyl coupling reagents are added to the preformed macroinitiator chain ends to form short block copolymers. The block copolymers containing the divinyl units then start to react with each other to form cross-linked cores, and this leads to the formation of star polymers. Finally star-star coupling can occur, leading to the formation of higher molecular weight stars.

By which technique star polymers are synthesized, it is essential that a controlled polymerization technique be used that maintains chain functionality. Living ionic, metathesis, and group transfer polymerizations are all adequate for the application, but all requires strenuous methods of reagent purification. Also the processes are only useful for a limited range of monomers. The use of controlled/ “living” free radical polymerizations including nitroxide-mediated stable free radical polymerization (SFRP), reversible-addition fragmentation chain transfer polymerization (RAFT), atom transfer radical polymerization (ATRP) offers the potential to overcome many of these problems. These reactions utilize a dynamic equilibrium between active and dormant species such that the concentration of free

radicals is similar to that found in conventional processes but where deactivation competes with termination, thereby limiting the irreversible reaction to low levels[2]. Specifically atom transfer radical polymerization (ATRP) provides control over chain length and functionality by successive exchanges between the halide present at the chain end of the dormant species and the transition metal compound activated by a ligand.

In this study linear and octa-arm homopolymers and diblock copolymers of tert-butyl acrylate, methylmeth acrylate and styrene monomers were synthesized via ATRP by using the core-first method.



2.THEORETICAL PART

2.1.Controlled / “Living” Radical Polymerization

Living polymerization mechanisms offer polymers of controlled architecture and molecular weight distribution. They provide a route to narrow polydispersity homopolymers, high purity block copolymers, and end functional polymers. Traditional methods of living polymerization, based on ionic, coordination or group transfer mechanisms are limited for economic reasons (due to stringent requirements on reaction conditions and monomer purity) and by the relatively small number of monomers that are amenable to these methods [3].

The use of living radical polymerization (also known as quasi- or pseudo-living radical polymerization) offers the potential to overcome many of these problems.

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 polymerizations (where the polymer chains being formed are insoluble in the reaction medium), 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 or graft copolymers.
- Systems with reversible termination but where the bond formed by primary radical termination or chain transfer is stable under the conditions of formation. Different reaction conditions are required to reinitiate polymerization. The aim of the first polymerization step is to synthesize a

macroinitiator that serves as a precursor to a block copolymer. Narrow polydispersity polymers are not available by these techniques.

- Systems with reversible termination where the bond formed by primary radical termination or chain transfer is kinetically unstable under the reaction conditions. These polymerizations should be considered as true living polymerizations. It is possible to make block copolymers and narrow polydispersity resins, since all chains grow, though not simultaneously.

In a living process the number of growing chains usually is the same as the number of initiating molecules, and it does not change during propagation until the total monomer consumption. Therefore semilogarithmic kinetic plots and molecular weight conversion dependences are linear, if the initiation is fast. If the exchange reactions between dormant and active species occur fast enough, polymers with low polydispersities can be formed. However some polymerization systems provide well-defined polymers in which chain breaking reactions cannot be totally avoided. Such systems are called controlled or “living” since they do not fulfill criteria of living polymerization because of the presence of either transfer or termination. Radical polymerization is one of them.

A typical radical polymerization includes four elementary reactions:

Formation of the initiating radicals, (slow), via the homolytic cleavage (decomposition) of a peroxide, diazo or other similar compound (**Equation 2.1**);



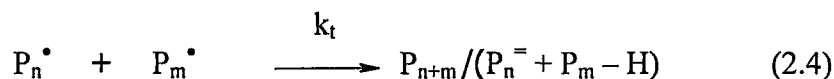
Initiation by relatively fast reaction of primary radicals with monomer to generate the first growing species. Since $k_d < k_o[\text{M}]$, the decomposition remains the rate – determining step (**Equation 2.2**):



Propagation characterized by k_p ; (**Equation 2.3**);



Termination (very fast) between growing radicals via coupling or disproportionation k_t (Equation 2.4);



Transfer reactions are usually less important unless transfer agents are present. Synthesis of high molecular weight polymers requires slow initiation to produce a low momentary concentration of growing radicals that terminate in a bimolecular process. The ratio of the rate of propagation to the rate of termination decreases with $[P^\bullet]$ since propagation is a first-order process, but termination is a second order process with respect to $[P^\bullet]$. The proportion of chains marked by termination increases with the chain length. Therefore well-defined polymers from radical polymerization may be formed only if chains are sufficiently short and concentration of free radicals is low enough.

The synthesis of well-defined polymers by controlled polymerization should occur in systems with a low momentary (stationary) concentration of growing radicals that should be reversibly deactivated to provide a relatively large number of macromolecules. There are three methods to realize these conditions:

1) Reversible homolytic cleavage of covalent species



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

This case probably is the most postulated in controlled radical polymerization. As examples of (R.); Otsu and Yoshida [4] used dithiocarbamate radicals, Georges et al. [5-6] used nitroxyl radicals and Borsing et al. [7] 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



The role of a scavenger radical may be also played by a neutral species. The persistent radical, $(P-X)\cdot$, should only cleave homolytically to form $(P\cdot)$ and the species X, but it should not react with monomer. X should be inert compound capable of reacting only with $(P\cdot)$. X may be elementoorganic or organometallic species with an even number of electrons. Some success have been reported with group XIII and XV elements such as aluminum [8] and phosphorus [9] as well as with organometallic derivatives of Co [10], Cr [11], 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.

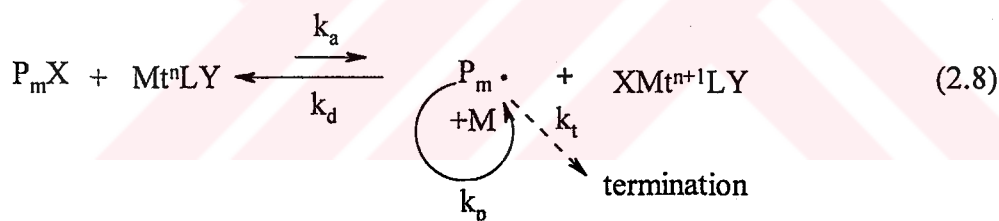
3) Degenerative transfer



In this case growing radical $(P_n\cdot)$ reacts rapidly and selectively with a transfer agent (P_1-R) to exchange the R group and form a dormant species (P_n-R) and a new radical $(P_1\cdot)$, which is capable of chain growth. $(P\cdot)$ would be generated by a classical initiator such as AIBN, BPO and redox reactions. $(P\cdot)$ can react with monomer, for propagation, with $(P-R)$, for degenerative transfer, and can also react one with another, for termination.

2.2. Atom Transfer Radical Polymerization (ATRP)

ATRP is one of the most versatile controlled radical polymerization method. This method utilizes a reversible halogen atom abstraction step in which a lower oxidation state metal (M_t^n complexed by ligands L and Y) reacts with an alkylhalide (P_m-X) to generate a radical ($P_m^\bullet$) and a higher oxidation state metal complex ($XM_t^{n+1}LY, k_a$). This radical then adds monomer to generate the polymer chain (k_p). The higher oxidation state metal can then deactivate the growing radical to generate a dormant chain and the lower oxidation state metal (k_d) as seen in (2.8). The molecular weight is controlled because both initiation and deactivation are fast, allowing for all the chains to begin growing at approximately the same time while maintaining a low concentration of active species. Termination cannot be totally avoided; however, the proportion of chains terminated compared to the number of propagating chains is small [12]. Several metal/ligand systems have been used to catalyze this process and a variety of monomers including styrene, methacrylates, and acrylonitrile have been successfully polymerized [13-15].



The rate of ATRP is internally first order in monomer, externally first order with respect to initiator and activator, Cu(I), and negative first order with respect to deactivator, XCu(II). The actual kinetics depends on many factors including the solubility of activator and deactivator, their possible interactions, and variation of their structures and reactivities with concentrations and composition of the reaction medium.

One of the most important parameters in ATRP is the dynamics of exchange, especially the relative rate of deactivation. If the deactivation process is slow in comparison with propagation, then a classic redox initiation process operates leading to conventional, and not controlled, radical polymerization. Polydispersities in ATRP

decrease with conversion, with the rate constant of deactivation, k_d , and also with the concentration of deactivator, $[XCu(II)]$. They, however, increase with the propagation rate constant, k_p , and the concentration of initiator, $[RX]_0$. This means that more uniform polymers are obtained at higher conversion, when the concentration of deactivator in solution is high and the concentration of initiator is low. Also, more uniform polymers are formed when deactivator is very reactive and monomer propagates slowly (styrene rather than acrylate) [16].

2.2.1. Monomers

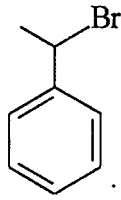
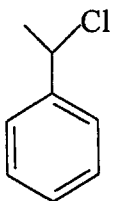
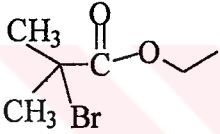
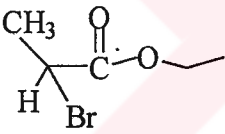
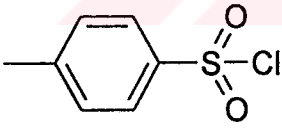
A variety of monomers have been successfully polymerized using ATRP. Typical monomers include styrenes (meth)acrylates, (meth)acrylamides, and acrylonitrile, which contain substituents that can stabilize the propagating radicals. Even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant ($K_{eq} = k_{act}/k_{deact}$) determines the polymerization rate.

2.2.2. Initiators

The main role of the initiator is to determine the number of growing polymer chains. Two parameters are important for a successful ATRP initiating system. First, initiation should be fast in comparison with propagation. Second, the probability of the side reactions should be minimized.

In ATRP, alkylhalides (RX) are typically used as initiator and the rate of polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, must rapidly and selectively migrate between the growing chain and the transition metal complex. When X is either bromine or chlorine, the molecular weight control is the best. Fluorine is not used because the C-F bond is too strong to undergo homolytic cleavage.

Table 2.1. The most frequently used initiator types in ATRP systems

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 Ethyl-2-bromo isobutyrate	Methylmethacrylate
 Ethyl-2-bromo propionate	Methylacrylate and other acrylates
 p-toluene sulphonyl chloride	Methylmethacrylate

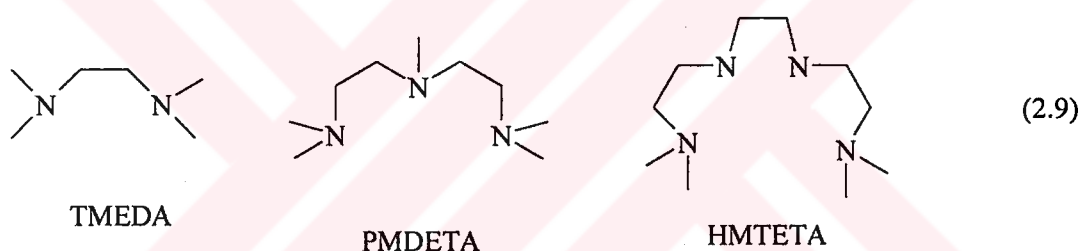
2.2.3.Ligands

The main role of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential of the metal center for the atom transfer. There are several guidelines for an efficient ATRP catalyst. First fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously. Second, the equilibrium between the alkylhalide and the transition metal is strongly shifted toward the dormant species side. This equilibrium position will render most of the growing polymer chains dormant and produce a low radical concentration. As a result, the contribution of radical termination reactions to the

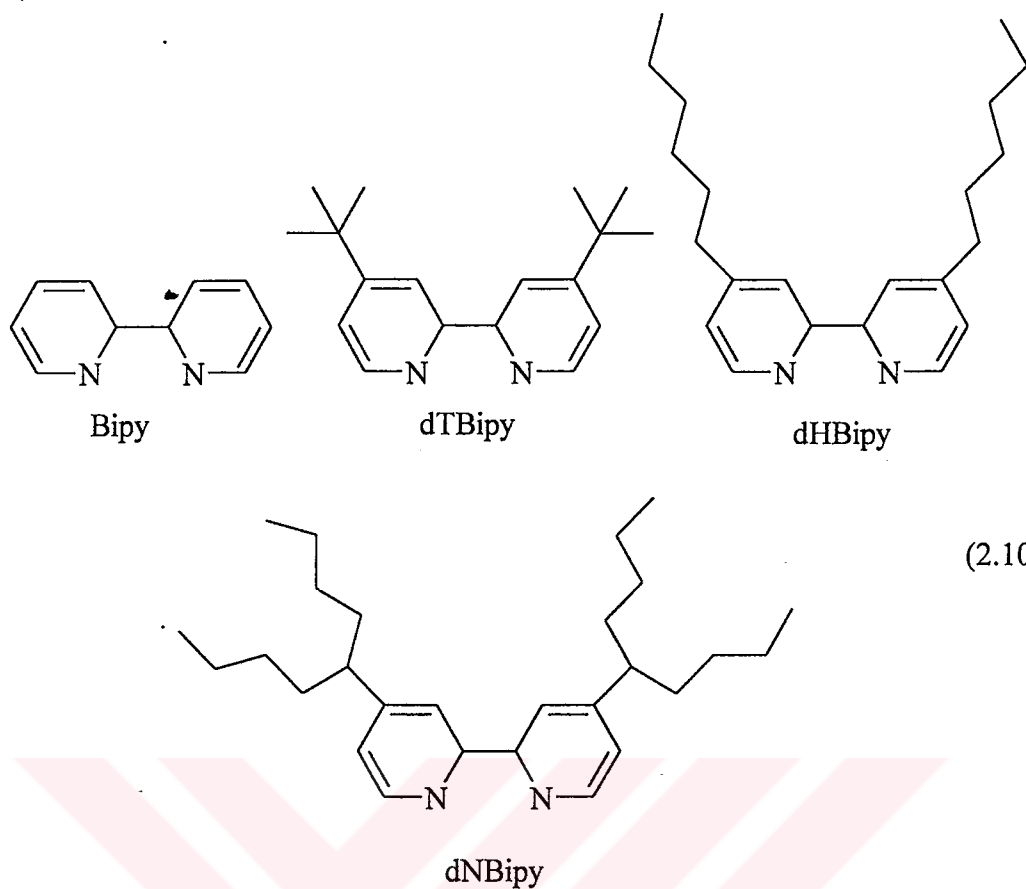
overall polymerization is minimized. Third fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the same rate, leading to a narrow molecular weight distribution. Fourth relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate. Fifth, there should be no side reactions such as β -H abstraction or reduction/oxidation of the radicals.

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-(dimethylamino)ethyl]amine (Me-TREN) and alkylpyridylmethanimines are also used.

Nitrogen based ligands:



derivatives of 2,2-bipyridine:



2.2.4. Transition Metal Complexes

Catalyst is the most important component of ATRP. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. First, the metal center must have at least two readily accessible oxidation states separated by one electron. Second the metal center should have reasonable affinity toward a halogen. Third the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo)-halogen. Fourth the ligand should complex the metal relatively strongly.

The most important catalysts used in ATRP are; Cu(I)Cl , Cu(I)Br , $\text{NiBr}_2(\text{PPh}_3)_2$, $\text{FeCl}_2(\text{PPh}_3)_2$, $\text{RuCl}_2(\text{PPh}_3)_3$, Al(OR)_3 .

2.2.5.Solvents

ATRP can be carried out either in bulk, in solution or in a heterogeneous system (e.g., emulsion, suspension). Various solvents such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide and many others have been used for different monomers. A solvent is sometimes necessary especially when the obtained polymer is insoluble in its monomer.

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

The rate equation of ATRP is formulated in discussed conditions and given in (2.11).

$$R_p = k_{\text{app}} [M] = k_p [P\cdot][M] = k_p K_{\text{eq}} [I]_0 \frac{[\text{Cu(I)}]}{[\text{Cu(II)} \text{X}]} [M] \quad (2.11)$$

Results from kinetic studies of ATRP for styrene, methyl acrylate (MA), and methyl methacrylate (MMA) under homogeneous conditions indicate that the rate of polymerization is first order with respect to monomer, initiator, and Cu(I) complex concentrations.

If the deactivation does not occur, if it is too slow ($k_p \gg k_d$), 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 (2.12).

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_d [RX]_0}{k_p [XCu^{II}]} \right) \left(\frac{2}{p} - 1 \right) \quad (2.12)$$

p = polymerization 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;

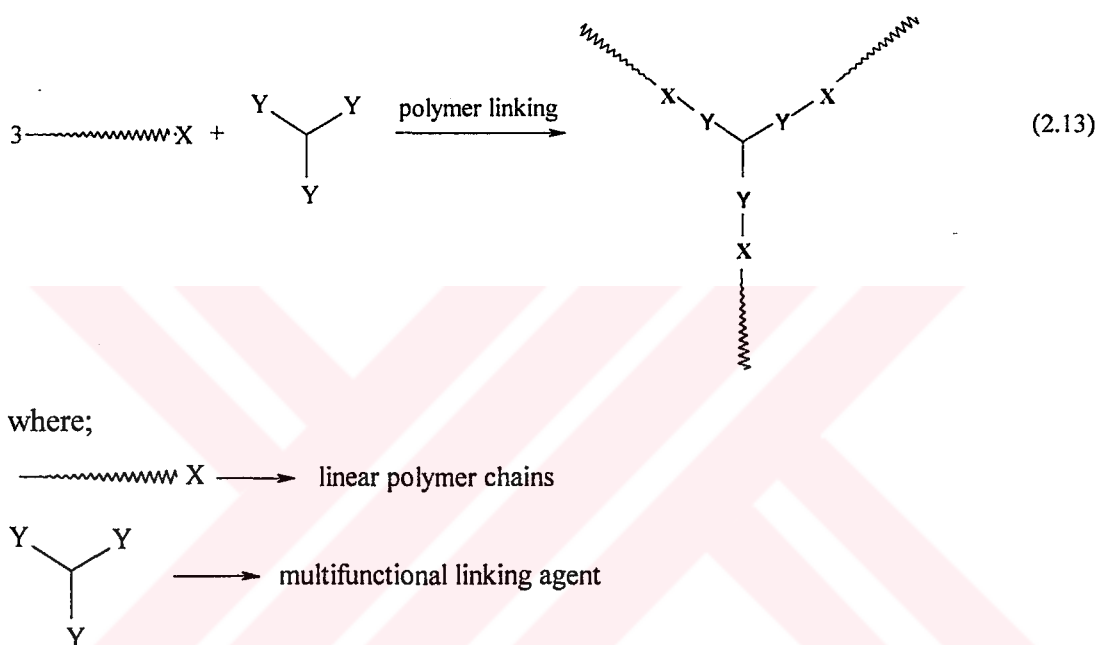
- a) For the smaller polymer chains, higher polydispersities are expected to be obtained because the smaller chains include little activation-deactivation steps resulting in little control of the polymerization.
- b) For the higher ratios of k_p / k_d , higher polydispersities (molecular weight distributions) are usually obtained.
- c) Resulting molecular weight distribution decreases as the concentration of the deactivators increases.

Star Polymers

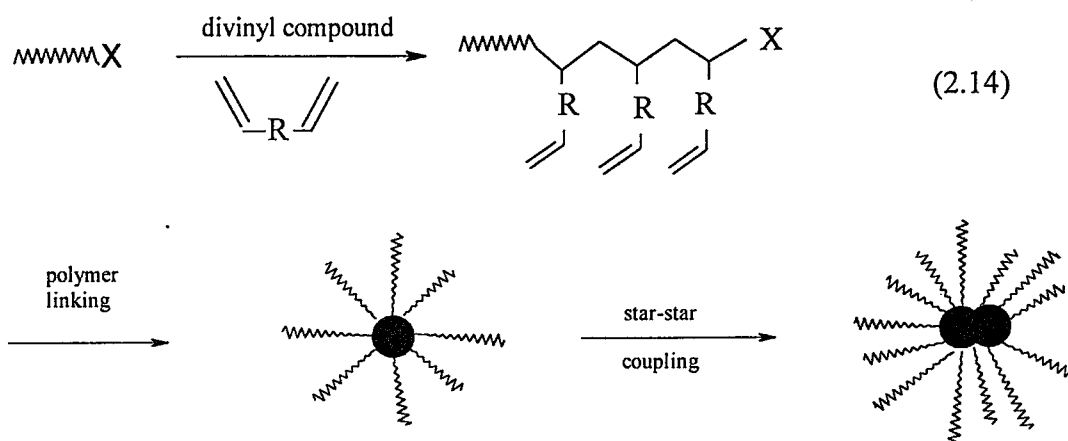
Branched polymers of controlled architecture have been designed in order to get a better understanding of the relationship between their topology and their unique solution and bulk properties, as compared to linear polymers. Among the branched structures, star polymers represent the most elementary way of arranging the subchains since each star contains only one branching point[17]. The interest in star shaped polymers stems from their unique-spatial shapes, lower viscosity compared with that of linear polymers with similar molecular weights and possible processing advantages due to their compact structure[18]. Star polymers have found applications in various areas (rheology modifiers, pressure sensitive adhesives, etc.)[19].

Stars by the Arm-First Method

This technique involves the synthesis of preformed arms ,usually through living polymerization followed by reaction with a multifunctional linking agent[20-22]. Schematic representation of star formation by the “arm-first method” is shown in (2.13).



Star formation by using the arm first technique also involves the use of divinyl coupling reagents such as DVB as a multifunctional linking agent. Initially, a few units of the divinyl coupling reagents are added to the macroinitiator chain ends to form short block copolymers. The block copolymers containing the divinyl units then start to react with each other to form cross-linked cores, and this leads to the formation of star polymers. Finally star-star coupling can occur, leading to the formation of higher molecular weight stars. The proposed mechanism for the star polymer formation in the presence of a divinyl coupling reagent is presented in (2.14) [23].



Coupling of monofunctional living chains with a difunctional reagent was first applied to living anionic polymerization. A similar approach has also been successful with ATRP. There are several parameters in an ATRP that should be controlled carefully in order to maximize the yield of stars and prevent star-star coupling reactions. Some detailed studies have been carried out on the coupling of monofunctional polystyrenes and polyacrylates with divinylbenzene (DVB) and di(meth)acrylates to prepare star polymers and the following guidelines have been developed:

- The ratio of difunctional reagent to growing chains seems to be optimal in the range of 10-20
- Monomer conversion (or reaction time) has to be carefully controlled and stopped before star-star coupling occurs.
- Higher yields of stars are observed for polyacrylates than for polystyrenes. This may be attributed to a higher proportion of terminated chains in styrene polymerization.
- The choice of the difunctional reagent is important and reactivity should be similar to, or lower than that of the arm-building monomers.
- Halogen exchange slightly improves efficiency of star formation.
- Solvent, temperature, catalyst concentration should be also optimized [24].

Some of the recent studies on star synthesis by the arm-first method are described below:

An original study based on the arm-first approach was reported by Fraser and colleagues [25], who synthesized 2,2-bipyridil- carrying PS and PMMA chains by

ATRP, which they managed to chelate onto a hexadendate Fe(II)- based complex to form corresponding star-like polymers, thus containing a metallic core.

To derive their PS stars, Matyjaszewski and colleagues[23] used a preformed PS macroinitiator obtained by ATRP that was allowed to react with various divinyl monomers, in the presence of Cu/Br dipyridyl in anisole at 110 °C. A ratio of 5:15 between divinylbenzene and PS macroinitiator was found to be optimal for the star formation. Other experimental parameters such as the choice of solvent, the addition of Cu(II), and the reaction time were found to be crucial for the formation efficient star formation.

Stars by the Core-First Method

The core-first approach has come to maturity after it was shown in the 1990s that stars of precise functionality could be obtained from multifunctional initiators.

The core-first method involves the use of a multifunctional initiator, and the number of arms in the star polymer can be determined by the number of initiating sites on the initiator[18-26-27]. In this technique multifunctional initiators are used to grow chains from a central core resulting in macromolecules with well-defined structures in terms of both arm number and length. Furthermore the reaction consists solely of stars in the absence of linear polymers[2]. Most of the star polymers were prepared by this technique.

The first report of the core-first technique described the hexakis(bromomethyl)benzene-initiated ATRP of styrene, methyl acrylate, and methylmethacrylate [28], but its use was rather limited due to poor solubility in the reaction media.

Pugh et. al. used a trifunctional initiator for the synthesis of three-arm polyacrylates for investigations of liquid crystalline polymers [29].

Sawamoto [30] and Gnanou [17] also discussed the use of modified calixarenes as initiators for ATRP. Sawamoto studied the synthesis of homo and block-star copolymers from dichloroacetate functionalized calixarenes with four, six and eight initiating sites per molecule[30]. Similarly Gnanou used an octafunctional calixarene composed of 2-bromopropionate moieties in the copper bromide/bipyridyl promoted ATRP of styrene[17].

EXPERIMENTAL PART

3.1. Chemicals used

a) Monomers

Tert-butyl acrylate (*t*BA, 99% Aldrich), methyl methacrylate (MMA, 99% Aldrich), and styrene (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.

3.2. Synthesis of Octafunctional Initiator 5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-Octakis- (2-bromopropionyloxy) calix[8]arene,(1)

In a 250 ml two-neck flask, equipped with a magnetic stirrer, 2 g (1.53×10^{-3} mol) of TBC-8 was suspended in 20 mL of dry THF. Then 5.1 mL of triethylamine (3.67×10^{-2} mol) was added and the mixture became homogenous upon stirring. The solution was cooled to 0°C and 3.84 mL (3.67×10^{-2} mol) of 2-bromopropionyl bromide dissolved in 20 ml of THF were added dropwise over a period of 1h. And then the reaction mixture was stirred at room temperature for 24 h. The solution was concentrated and precipitated in ice cold water. The crude solid compound thus obtained was dissolved in diethylether and washed successively with dilute K_2CO_3 water solution and dried over anhydrous Na_2SO_4 . Ether was removed and the concentrate precipitated from a mixture of methanol/water (90/10 v/v). The precipitation was repeated two more times to obtain a white powder of **1** in 78% yield.

3.3.Synthesis of Linear Poly(*tert*-butyl acrylate) (PtBA) Homopolymers

PtBA homopolymers were synthesized by ATRP of *tert*-butylacrylate in bulk at 100⁰C using CuBr/*N,N,N',N'',N'''*- pentamethyldiethylenetriamine (PMDETA) as a catalyst system and methyl 2-bromopropionate (MBP) as initiator.

Into a Schlenk tube, equipped with a magnetic stirring bar *t*BA (5mL, 3,4x10⁻² mol), PMDETA (71,2 μL, 3,4x10⁻⁴ mol), CuBr (49mg, 3,4x10⁻⁴ mol) and the initiator (38 μL, 3,4x10⁻⁴ mol) were added in the order mentioned. The reaction mixture was degassed by three freeze-pump-thaw cycles and left in vacuo. The tube was then placed in an oil bath thermostated at 100⁰C. After it was stirred for given times, the tube was cooled to room temperature and the contents were dissolved in THF and passed through a column of neutral alumina to remove the copper catalyst from the polymer. The excess of THF was evaporated under reduced pressure. The polymer was precipitated into excess of methanol/water (80/20 v/v). After decanting off methanol/water, the polymer was dissolved in dichloromethane and dried over anhydrous Na₂SO₄. CH₂Cl₂ was removed by evaporation and the polymer was dried under vacuum.

3.4.Synthesis of Linear (PtBA-*b*-PMMA) and (PtBA-*b*-PSt) diblock copolymers

(PtBA-*b*-PMMA) diblock copolymers were synthesized by ATRP of MMA in solvent (DPE) at 90⁰C using CuCl/PMDETA catalyst system and PtBA as macroinitiator.

Into a Schlenk tube, equipped with a magnetic stirring bar, MMA(2,2 mL, 2,05x10⁻² mol), CuCl(2 mg , 2x10⁻⁵ mol), PMDETA (4,2 μL , 2x10⁻⁵ mol) , diphenylether (DPE) (MMA/DPE =1/2 ; v/v) and PtBA (M_n= 19700; 0,4g) as macroinitiator were added in the order mentioned. The reaction mixture was degassed by three freeze-pump- thaw cycles and left in vacuo. Then the tube was placed in an oil- bath thermostated at 90⁰C. After it was stirred for given times, the tube was cooled to room temperature and the contents were dissolved in THF then the solution was filtered through neutral alumina for removal of copper salts. THF was removed by evaporation then the polymer was precipitated into methanol/water (80/10; v/v) and then isolated by vacuum filtration. The polymer was dried overnight in a vacuum oven.

(*PtBA-b-PSt*) diblock copolymer was synthesized by ATRP of styrene in bulk at 100 °C using CuBr/PMDETA catalyst system and *PtBA* as macroinitiator.

Into a Schlenk tube, equipped with a magnetic stirring bar, St (1.25 mL, $1,09 \times 10^{-2}$ mol), PMDETA (11,3 μ L, $5,4 \times 10^{-5}$ mol), CuBr (7,7 mg, $5,4 \times 10^{-5}$ mol), and *PtBA* (M_n = 9300; 0,5g) as macroinitiator were added in the order mentioned. The reaction mixture was degassed by three freeze-pump-thaw cycles and left in vacuo. Then the tube was placed in an oil-bath thermostated at 100 °C. After it was stirred for 130 min., the tube was cooled to room temperature and the reaction mixture was diluted with THF then the solution was filtered through neutral alumina for removal of copper salt. THF was removed by evaporation then the polymer was precipitated into methanol/water (80/11; v/v) and then isolated by vacuum filtration. The polymer was dried overnight in a vacuum oven.

3.5. Synthesis of Octa-arm *PtBA* stars

Octa-arm *PtBA* star polymers were prepared by ATRP in bulk at 100 °C. CuBr/PMDETA was used as a catalyst system and (1), as an octafunctional initiator. *tBA* (10 mL, 0,068 mol), PMDETA (38 μ L, $1,82 \times 10^{-4}$ mol), CuBr (0,026 g, $1,82 \times 10^{-4}$ mol), and the octa-functional initiator (1), (0,054 g, $2,27 \times 10^{-5}$ mol) were added into a 100 mL two-neck flask equipped with magnetic stirring bar. The reaction mixture was degassed by three freeze-pump-thaw cycles three times to remove dissolved gases and left in vacuo. Then the tube was placed in an oil-bath thermostated at 100 °C. After it was stirred for 65 min., the tube was cooled to room temperature and the reaction mixture was diluted with THF. Then the purification procedure described for linear *PtBA* was applied in the same way.

3.6. Synthesis of Octa-arm *PtBA-b-PMMA* and *PtBA-b-PSt* Star Diblock Copolymers

Octa-arm *PtBA-b-PMMA* stars were prepared by ATRP of MMA in solvent (DPE) at 90 °C using CuCl/PMDETA catalyst system and octa-arm *PtBA* star as macroinitiator.

MMA (11,2 mL, 0,105 mol), CuCl (4 mg, 4×10^{-5} mol), PMDETA (8,5 μ L, 4×10^{-5} mol), diphenylether (DPE) (MMA/DPE = 1/1; v/v) and *PtBA* (M_n = 59700; 0,3 g) as macroinitiator were added into a Schlenk tube equipped with a magnetic stirring bar

in the order mentioned. The reaction mixture was degassed by three freeze-pump-thaw cycles and left in vacuo. Then the tube was placed in an oil-bath thermostated at 90 °C. After it was stirred for 65 min., the tube was cooled to room temperature and the contents were dissolved in THF then the solution was filtered through neutral alumina for removal of copper salts. THF was removed by evaporation then the polymer was precipitated into methanol/water (80/5 ; v/v) and then isolated by vacuum filtration. The polymer was dried 24 hours in a vacuum oven.

Octa-arm *PtBA-*b**-PSt stars were prepared by ATRP of styrene in bulk at 100 °C . CuBr/PMDETA was used as a catalyst system and octa-arm *PtBA* star as a macroinitiator.

St (2,5 mL , $2,2 \times 10^{-2}$ mol), PMDETA (6 μ L , $2,89 \times 10^{-5}$ mol) , CuBr (4,14 mg, $2,89 \times 10^{-5}$ mol) , and *PtBA* as a macroinitiator (M_n = 16600 ; 0,06 g) were added into a Schlenk tube equipped with magnetic stirring bar. After it was stirred for 65 min, the tube was cooled to room temperature and the reaction mixture was diluted with THF. Then the solution was filtered through neutral alumina for removal of copper salts. THF was removed by evaporation then the polymer was precipitated into methanol/water (80/12 ; v/v) and then isolated by vacuum filtration. The polymer was dried overnight in a vacuum oven.

3.7.Characterization

The ^1H -NMR spectra was recorded on a Bruker spectrometer (250 MHz for proton) in CDCl_3 solution using tetramethylsilane as an internal standart. Gel Permeation Chromatography (GPC) measurements were carried out with an Agilent Model 1100 instrument consists of pump, refractive index dedector, UV dedectors and four Waters Styragel columns (HR 5E, HR 4E, HR 3 and HR 2). THF was used as eluent at flow rate of 0.3 mL/min. at 30 °C. The molecular weights of the polymers were calculated with the aid of polystyrene standarts (polymer laboratories). All polymers obtained were dried overnight under vacuum and the conversions were determined by gravimetrically.

RESULTS AND DISCUSSION

4.1.Synthesis of Initiator

4.1.1.Synthesis of Octafunctional Initiator 5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-Octakis-(2 bromopropionyloxy)calix[8]arene (1)

5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-Octakis-(2 bromopropionyloxy)calix[8]arene,(1), was synthesized according to the procedure reported by Angot et. al.[17]. The octafunctional initiator ,(1), was prepared from 4-*tert*-butylcalix[8]arene (TBC-8) and 2-bromopropionylbromide in ca 78 % yield. The obtained initiator ,(1), was then characterized by ¹H-NMR. ¹H-NMR spectra of the initiator showed no signal corresponding to –OH protons of the starting TBC-8, indicating quantitative esterification (Figure 4.1).

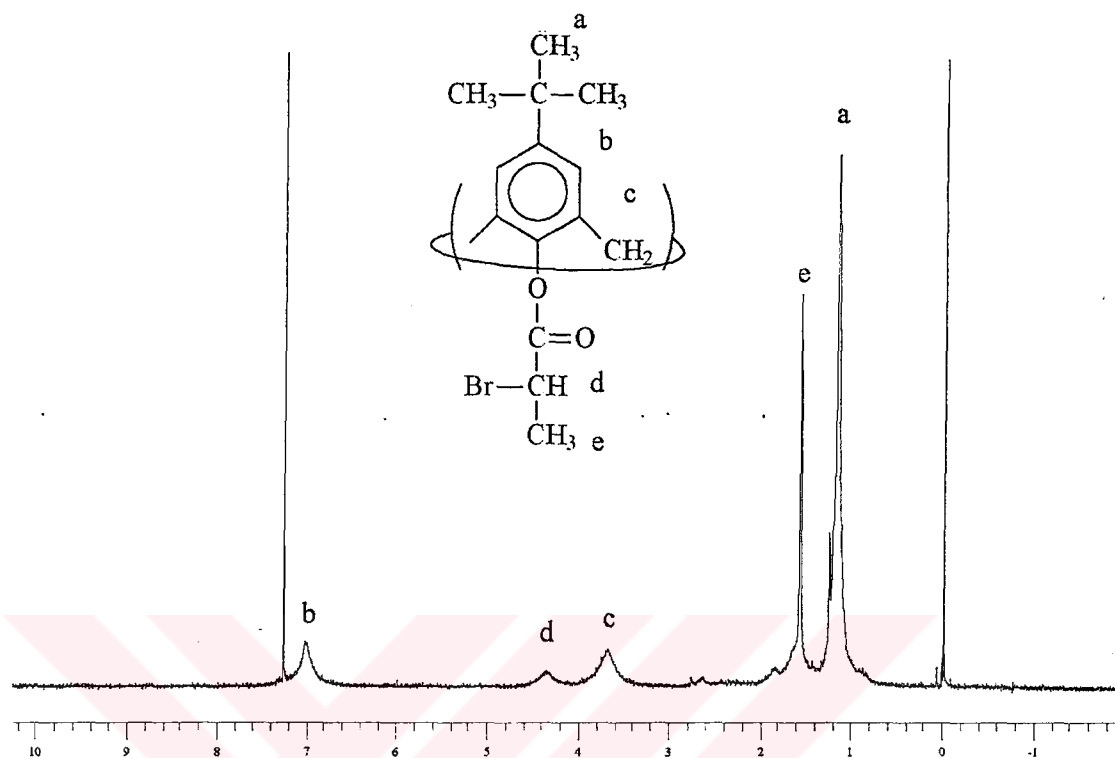
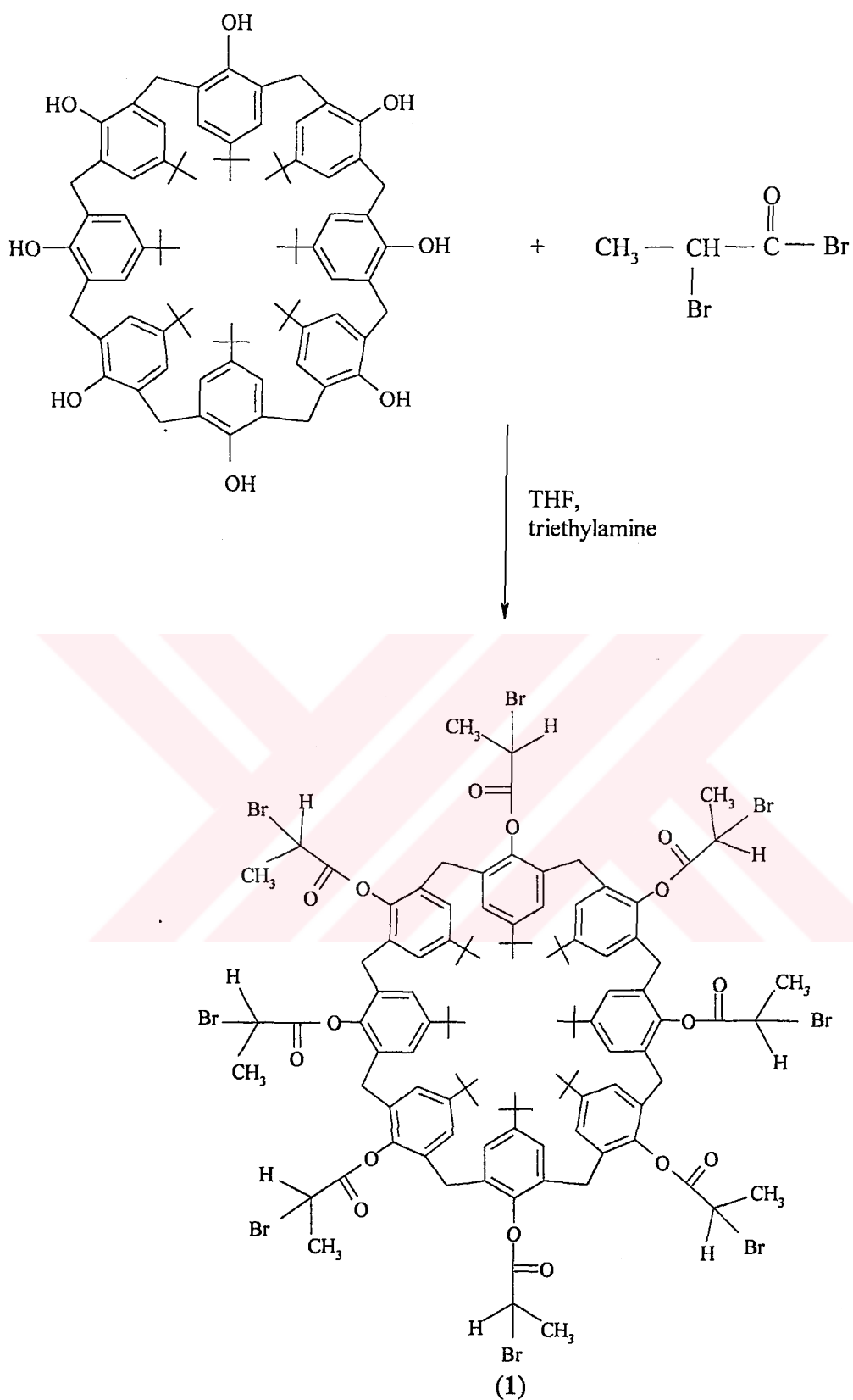


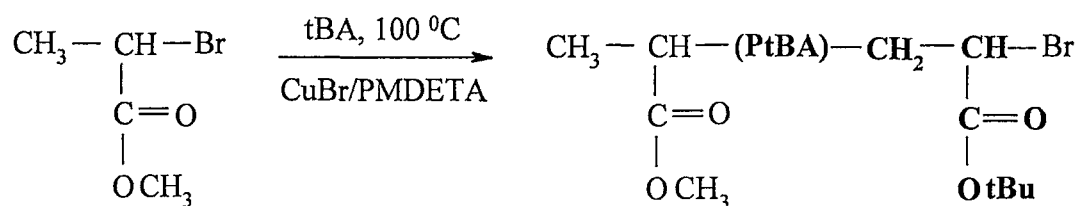
Figure 4.1. The ^1H -NMR spectra of the initiator,(1), 5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-Octakis-(2 bromopropionyloxy)calix[8]arene



Scheme 4.1. Synthesis of 5,11,17,23,29,35,41,47-Octa-*tert*-butyl-49,50,51,52,53,54,55,56-Octakis-(2 bromopropionyloxy)calix[8]arene (1)

4.2. Synthesis of Linear PtBA Macroinitiators by ATRP

Synthesis of Linear PtBA was illustrated in Scheme 4.2



Scheme 4.2. Synthesis of linear ptBA homopolymer

PtBA homopolymers with different molecular weights were synthesized via ATRP of *t*BA in bulk at 100⁰C using CuBr complexed by PMDETA as the catalyst and methyl 2-bromopropionate (MBP) as the initiator. The results of the polymerization reactions are summarized in Table 4.1.

Under typical reaction conditions, a linear semilogarithmic plot of monomer conversion vs time was observed indicating that the apparent propagation rate constant is first-order in the monomer concentration; this implies that the concentration of the growing radicals stays constant during the polymerization regardless of the initial concentration of the initiator (Figure 4.2). The number average molecular weights of PtBA homopolymers, increased linearly with monomer conversion and agreed well with the theoretical ones assuming that each initiator molecule produced one polymer chain (Figure 4.3).

Table 4.1. ATRP of *t*BA Using the CuBr/PMDETA Catalyst system, Initiated by Monofunctional Initiator (Methyl 2-Bromopropionate) at 100°C in bulk

Run	$[M]_0$ (mol l ⁻¹)	$[M]_0/[I]_0$	Time (min.)	Conversion (%)	$M_{n,theo}^b$	$M_{n,GPC}^c$	M_w/M_n	f^d
PI ^a	6.8	100	10	32	4200	5100	1.18	0.82
PII ^a	6.8	100	15	44	5700	6500	1.16	0.88
PIII ^a	6.8	100	20	68	8700	10300	1.12	0.84
PIV ^a	6.8	100	30	74	9500	11200	1.13	0.85
PV ^a	6.8	100	45	87	11200	12300	1.13	0.91

^a $[I]_0$: [PMDETA]₀: [CuBr]₀ = 1:1:1

^b $M_{n,theo} = ([M]_0/[I]_0 \times \text{conversion} \times MW_{\text{monomer}})$

^cMolecular weights were calculated with linear PSt standards

^d f (initiator efficiency) = $(M_{n,theo} / M_{n,exp})$

The experimental number average molecular weights were determined by GPC based on linear PS standards and the theoretical ones were calculated as follows;

$$M_{n,theo} = ([M]_0/[I]_0 \times \text{conversion \%} \times MW_{\text{monomer}})$$

The conversions were calculated gravimetrically by the following formula:

$$\text{Conversion\%} = (W/M) \times 100 \quad \text{where;}$$

W: weight of the formed polymer

M: weight of the monomer initially taken

Size exclusion chromatography (SEC) traces of the obtained polymers displayed narrow and monomodal molecular weight distribution (M_w/M_n).

These results show that the polymerization of *t*BA proceeded in a controlled manner with high initiation efficiency using methyl 2-bromopropionate as initiator and CuBr/PMDETA as catalyst system.

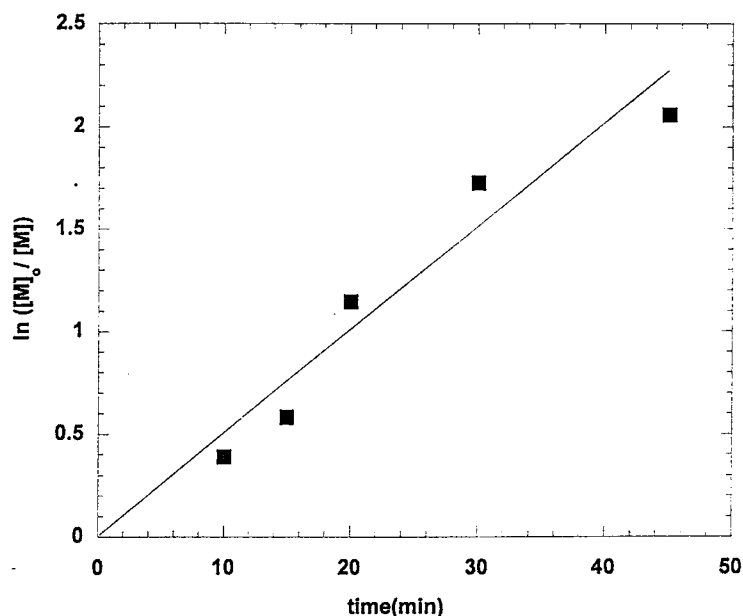


Figure 4.2. Plot of $\ln([M]_0/[M])$ vs. time for ATRP of *t*BA with monofunctional initiator at 100 °C in bulk. $[tBA]_0/[I]_0/[CuBr]_0/[PMDTA]_0$: 100 / 1 / 1 / 1 ; $[tBA]_0=6.8M$; $[MBP]_0=68mM$; $[CuBr]_0=68mM$; $[PMDTA]_0=68mM$.

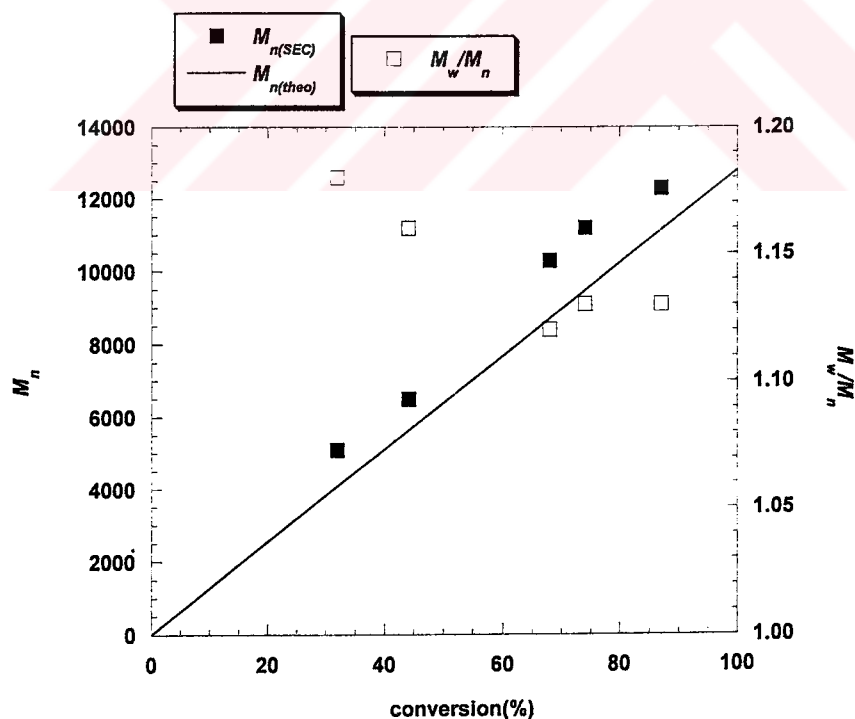
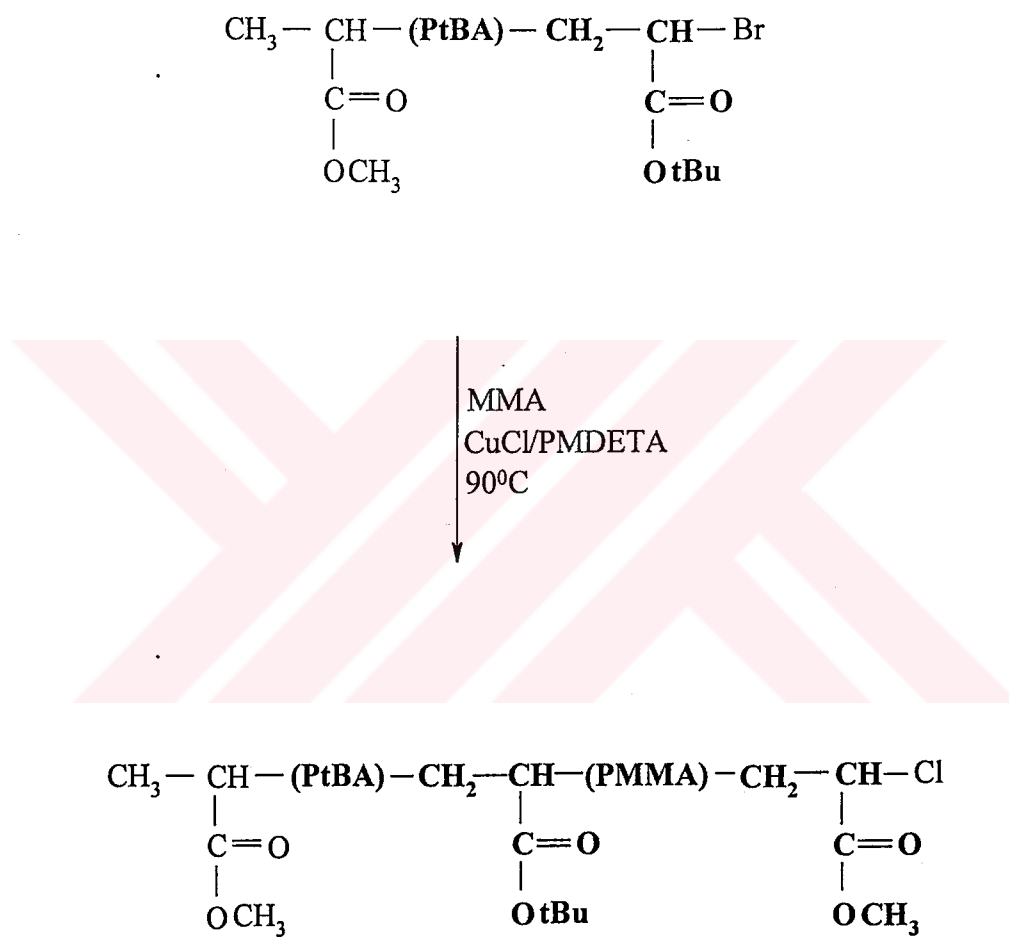


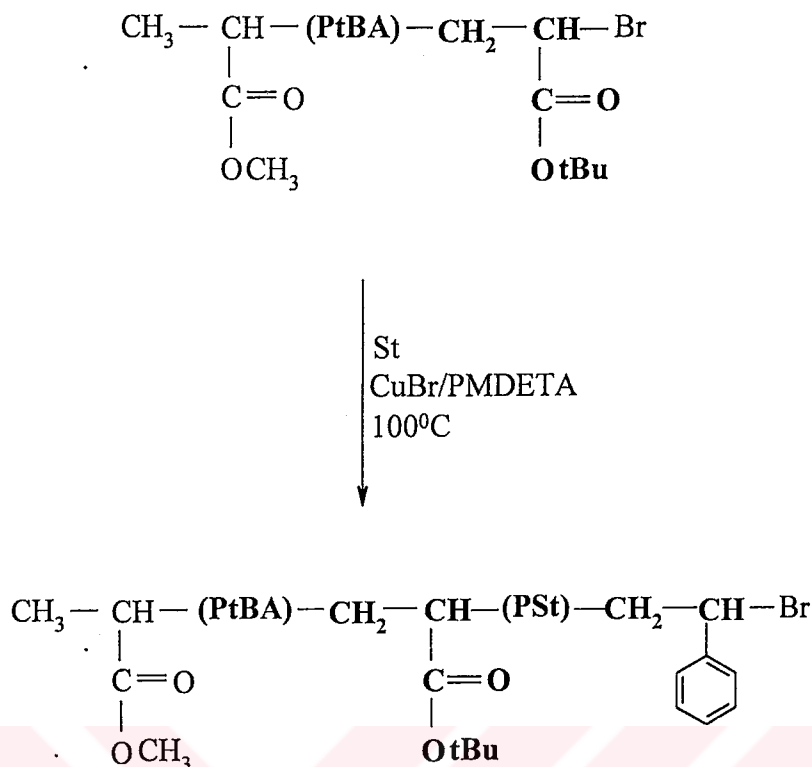
Figure 4.3. Evolution of experimental molecular weights and polydispersities with monomer conversion for ATRP of *t*BA with monofunctional initiator at 100°C in bulk: $[tBA]_0/[I]_0/[CuBr]_0/[PMDTA]_0$: 100 / 1 / 1 / 1 ; $[tBA]_0=6.8M$; $[MBP]_0=68mM$; $[CuBr]_0=68mM$; $[PMDTA]_0=68mM$.

4.3. Synthesis of Linear *PtBA-b*-PMMA and *PtBA-b*-PSt Diblock Copolymers via ATRP

The synthesis of (*PtBA-b*-PMMA) and (*PtBA-b*-PSt) diblock copolymer were given in Scheme 4.3 and Scheme 4.4.



Scheme 4.3. Synthesis of Linear (*PtBA-b*-PMMA) diblock copolymer



Scheme 4.4. Synthesis of (PtBA-*b*-PSt) diblock copolymer

The synthesis of linear diblock copolymers consisting of *t*BA and MMA segments was achieved with bromine ended PtBA precursors as macroinitiators via ATRP of MMA using CuCl/PMDETA catalyst system. The polymerizations were performed at 90⁰ C in DPE solution (MMA/DPE: 1/2 ; v/v) (Table 4.2).

The synthesis of linear (PtBA-*b*-PSt) diblock copolymer was also performed with bromine ended PtBA homopolymer as macroinitiator via ATRP of St using CuBr/PMDETA catalyst system at 100⁰ C in bulk (Table 4.2).

Plot of $\ln[M]_0/[M]$ versus time for (PtBA-*b*-PMMA) diblock copolymers was linear indicating that the apparent propagation rate constant is first order in the monomer concentration(Figure 4.4). The experimental number average molecular weights of PtBA-*b*-PMMA blocks determined by GPC based on PMMA standarts increased linearly with monomer conversion which were in good agreement with theoretical M_n values (Figure 4.5).

The experimental M_n value of the linear (PtBA-*b*-PSt) diblock copolymer was determined by GPC based on PSt standards and was also agreed well with the theoretical one.

The theoretical number average molecular weights of PtBA-*b*-PMMA and PtBA-*b*-PSt diblock copolymers were calculated by the following formula:

$$M_{n,theo}: ([M]_0/[I]_0 \times \text{conversion\%} \times MW_{\text{monomer}}) + M_n(\text{macroinitiator (PtBA)})$$



Table 4.2. Synthesis of Linear P*t*BA-*b*-PMMA and P*t*BA-*b*-PSt diblock copolymers via ATRP

Run	Monomer	Initiator	[M] ₀ (mol l ⁻¹)	[M] ₀ /[I] ₀	Time (min)	Conv (%)	M _{n,theo}	M _{n,GPC} ^g	M _{n,Hnmr}	M _w /M _n	<i>f</i>	Composition ¹ H NMR
PVI ^a	tBA	MBP ^d	6.8	100	30	76	9800 ^e	9300	-	1.13		
PVII ^a	tBA	MBP	6.8	300	90	63	24000 ^e	19700	-	1.14		
PVIII ^b	MMA	PVII	3.1	1000	70	12	31700 ^f	41900	32800	1.17	0,76	46%PMMA, 54%P <i>t</i> BA
PIX ^b	MMA	PVII	3.1	1000	300	30	49800 ^f	75700	57940	1.15	0,66	71%PMMA, 29%P <i>t</i> BA
PX ^b	MMA	PVII	3.1	1000	495	61	80800 ^f	89300	69500	1.18	0,90	76%PMMA, 24%P <i>t</i> BA
PXI ^b	MMA	PVII	3.1	1000	960	87	106800 ^f	114300	87180	1.18	0,93	81%PMMA, 19%P <i>t</i> BA
PXII ^c	St	PVI	8.7	200	130	8	11000 ^f	16900	13800	1.14	0,65	63 %P <i>t</i> BA, 37%PSt

^a [I]₀: [PMDETA]₀: [CuBr]₀= 1:1:1 ; Temp: 100°C ; ^b [I]₀: [PMDETA]₀: [CuCl]₀= 1:1:1 ; (MMA/DPE:1/2) ; Temp: 90°C;

^c [I]₀: [PMDETA]₀: [CuBr]₀= 1:1:1 ; Temp: 100°C

^d MBP=methyl 2-bromopropionate ;

^e M_{n,theo}: ([M]₀/[I]₀ x conversion % x MW_{monomer})

^f M_{n,theo}: ([M]₀/[I]₀ x conversion % x MW_{monomer}) + M_n (macroinitiator) (PBA)

^g Molecular weights were calculated with linear PSt and PMMA standards

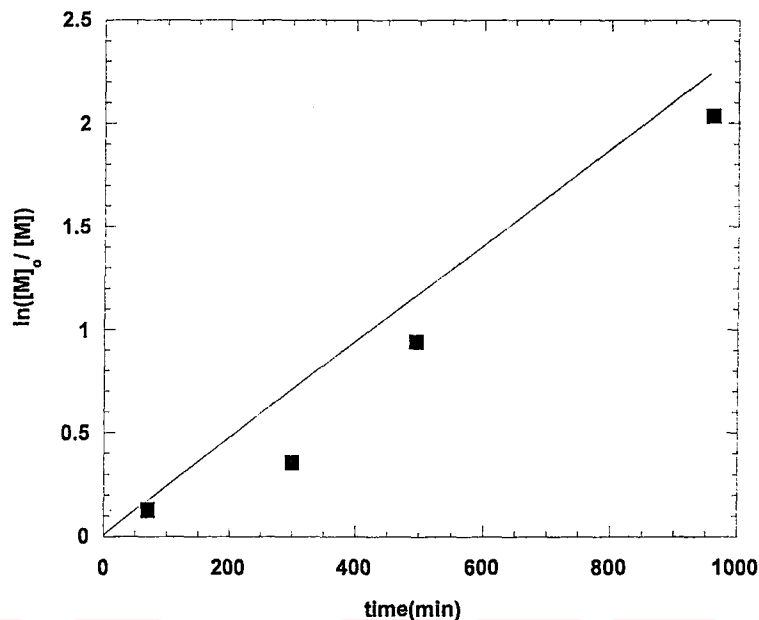


Figure 4.4. Plot of $\ln ([M]_0/[M])$ vs time for ATRP of MMA with linear PtBA macroinitiator at 90 °C in DPE (MMA/DPE:1/2) ; $[MMA]_0/[I]_0$ $[CuCl]_0/[PMDETA]_0$:1000/ 1 / 1 / 1 ; $[MMA]_0=3.1M$; $[PtBA]_0=3mM$; $[CuCl]_0=3mM$; $[PMDETA]_0=3mM$.

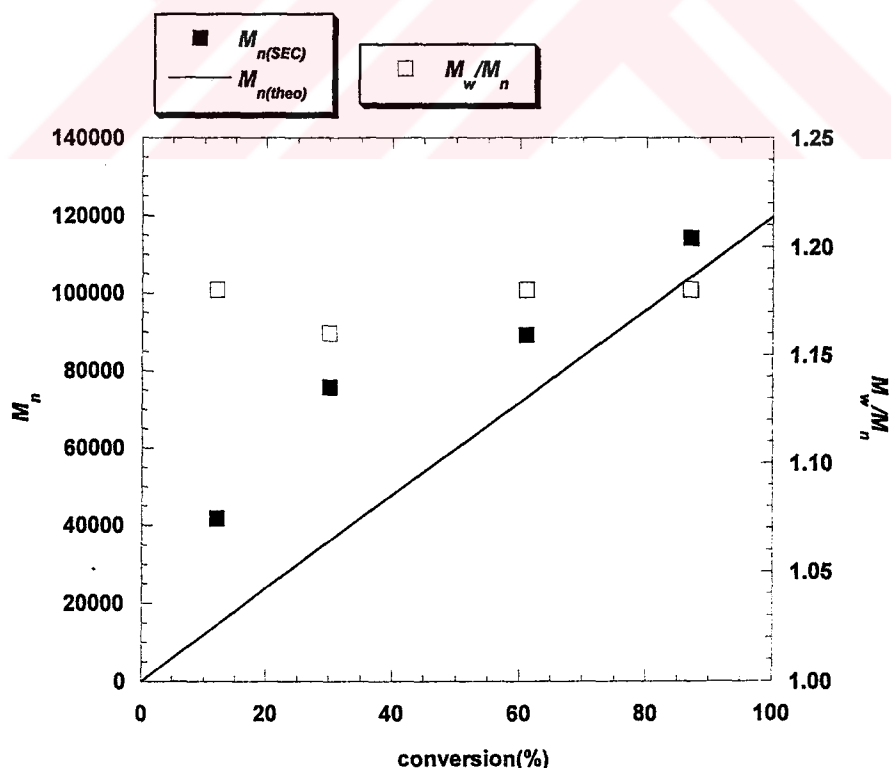


Figure 4.5. Evolution of experimental molecular weights and polydispersities with monomer conversion for ATRP of MMA with linear PtBA macroinitiator at 90°C in DPE (MMA/DPE:1/2) ; $[MMA]_0/[I]_0$ $[CuCl]_0/[PMDETA]_0$:1000 / 1 / 1 / 1 ; $[MMA]_0=3.1M$; $[PtBA]_0=3mM$; $[CuCl]_0=3mM$; $[PMDETA]_0=3mM$.

The GPC traces of macroinitiators (*PtBA*) and (*PtBA-b-PMMA*) and (*PtBA-b-PSt*) diblock copolymers were shown in Figure 4.6 and Figure 4.7.

GPC results both for *PtBA-b-PMMA* and *PtBA-b-PSt* blocks showed the expected increase in molecular weight through the copolymerizations. The absence of *PtBA* macroinitiator peaks on the GPC traces of block copolymers indicate that the macroinitiators was fully converted to block copolymers. Peaks corresponding to *PtBA-b-PMMA* and *PtBA-b-PSt* clearly shifted to higher molecular weight region of the chromatogram indicating that both the chain end functionality of the macroinitiators and the blocking efficiency were high and the polymers obtained were of low polydispersity and the GPC traces were monomodal.



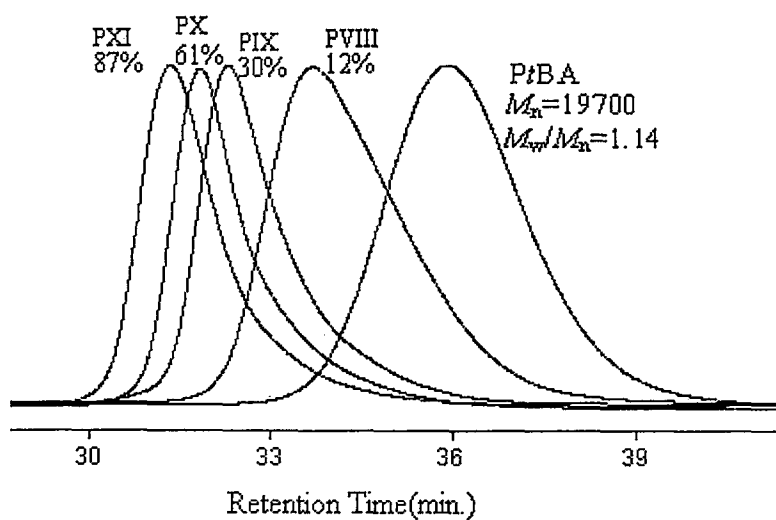


Figure 4.6. GPC traces of the linear pBA precursor (PVII), and linear pBA-*b*-PMMA (PVIII, PIX, PX, PXI) diblock copolymers.

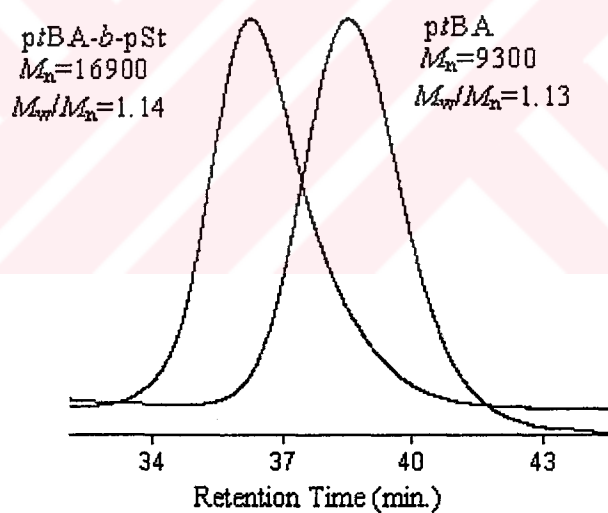


Figure 4.7. GPC traces of linear pBA precursor (PVI) and linear pBA-*b*-pSt (PXII) diblock copolymer

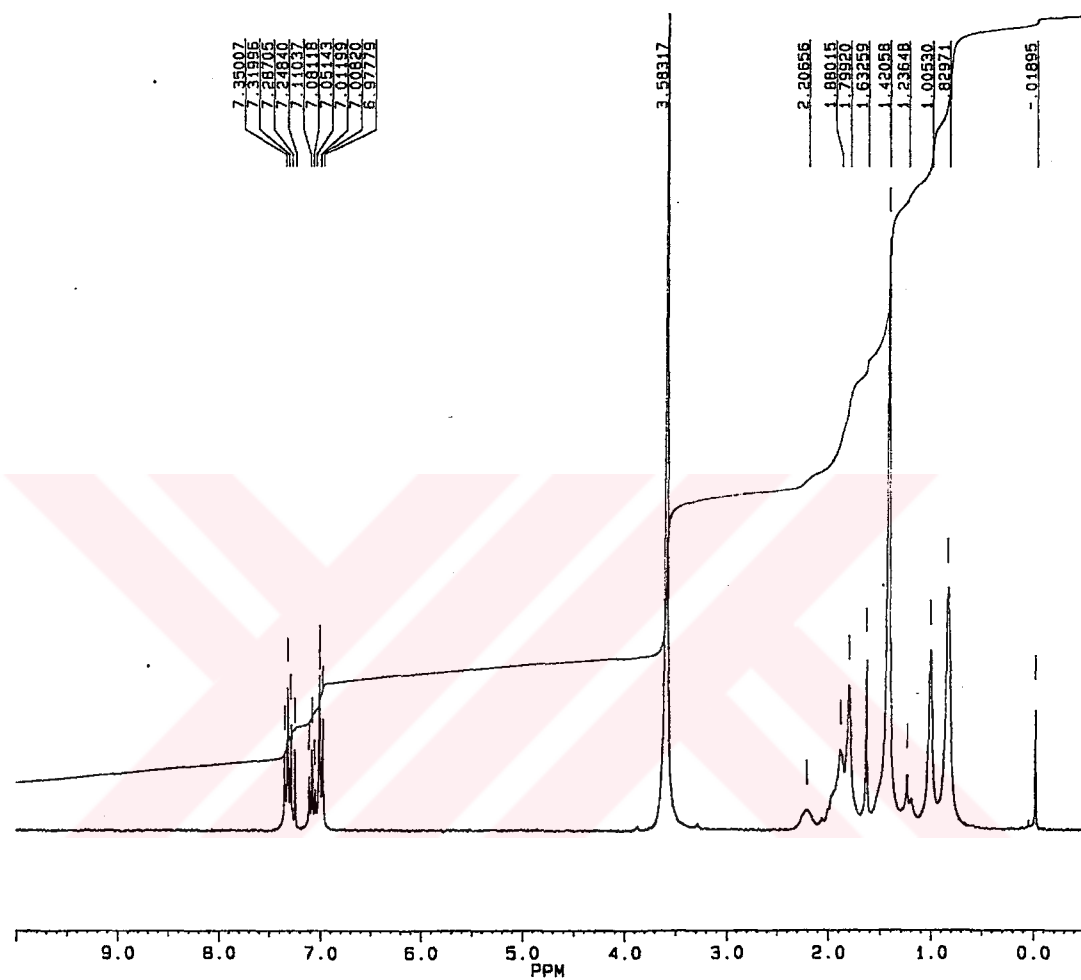


Figure 4.8. ^1H -NMR spectra of linear $\text{PtBA-}b\text{-PMMA (PX)}$ diblock copolymer

The composition of block copolymers was elucidated by ^1H -NMR measurements. The ^1H -NMR spectra of poly (*t*BA-*b*-MMA) block copolymers exhibited the major peaks which are characteristic of tert-butylacrylate and MMA segments. The molecular weights were calculated from the integration of signals at 1.42 ppm. (-C(CH₃)₃) of *t*BA to 3.58 ppm.(-OCH₃) of MMA for P*t*BA-*b*-PMMA diblock copolymers(Figure 4.8).



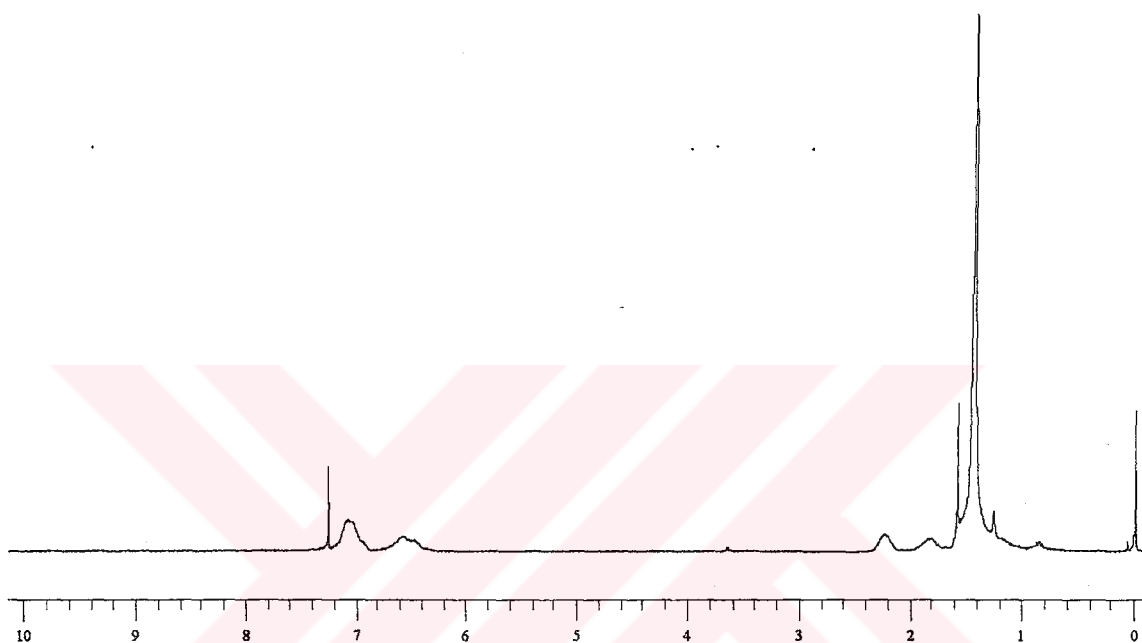


Figure 4.9. ¹H-NMR spectra of linear PtBA-*b*-PSt (PXII) diblock copolymer

Integrating the signal between 6.5-7.0 ppm of PSt (aromatic protons) and 1.42 ppm of *t*BA ($-\text{C}(\text{CH}_3)_3$) allowed us to evaluate the composition and the molecular weight of PtBA-*b*-PSt diblock copolymer (Figure 4.9).

4.4.Synthesis of Octa-arm PtBA Stars

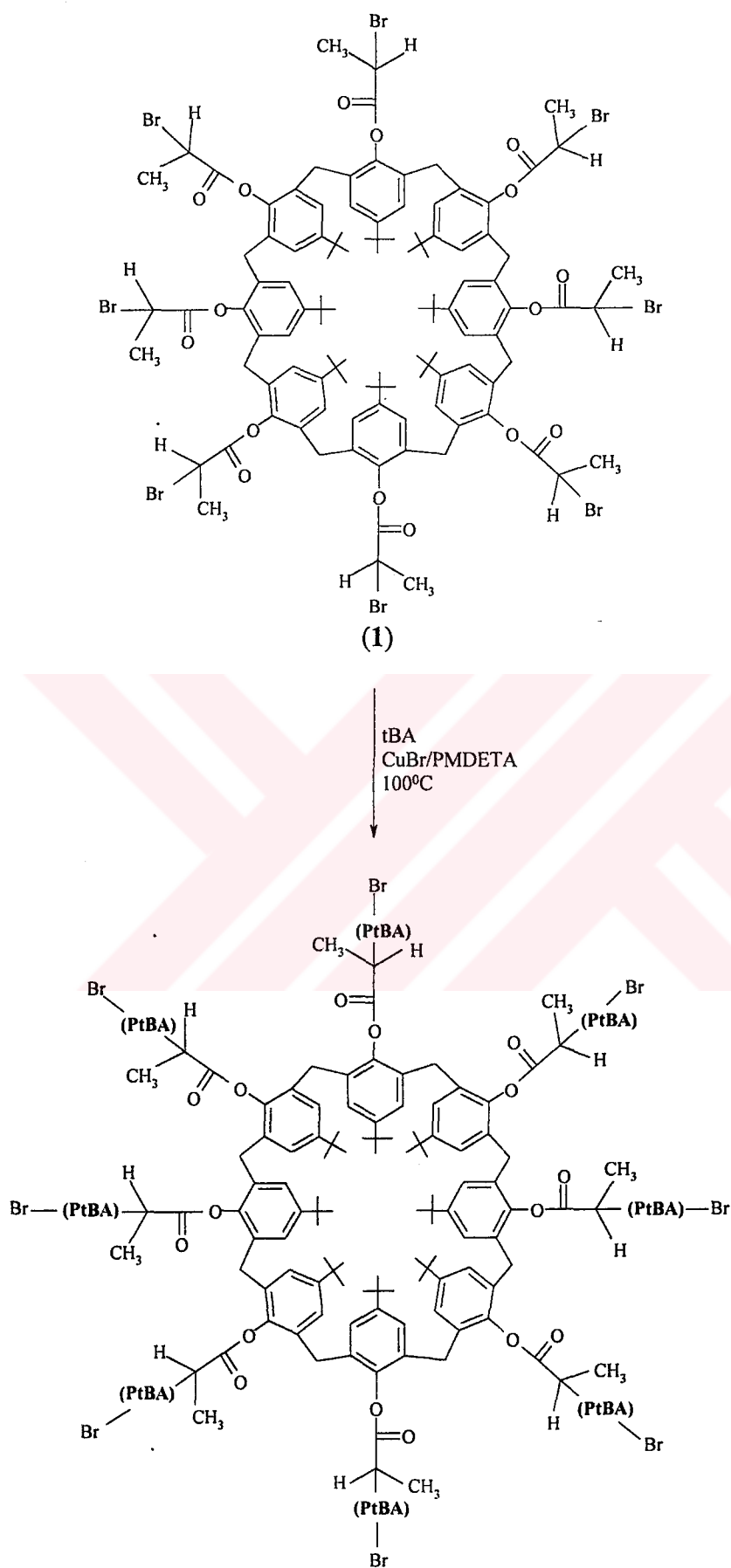
Octa-arm PtBA stars were prepared by ATRP of *t*BA using CuBr/PMDETA as a catalyst system and (1) as multifunctional initiator at 100⁰ C in bulk. The results of the bulk polymerization are listed in Table 4.3 and the synthesis of octafunctional PtBA stars is illustrated in Scheme 4.5.

The experimental M_n values of the obtained polymers agreed well with the theoretical values only below 25% conversion for the octafunctional system. Beyond 25% monomer conversion, experimental values of molar masses strongly departed from expected ones, which can be attributed to the irreversible coupling of the growing radicals between different stars. These coupling reactions between two different growing stars which is termed as “intermolecular termination” causes an increase in the molar mass and after one intermolecular termination between two growing stars the resulting polymer constitutes of 14 branches instead of the expected octa-arm star.

The molecular weight distributions of the obtained polymers remained very low below 25% monomer conversion. The GPC traces based on PSt standarts were unimodal and the experimental number average molecular weights were in good agreement with the theoretical ones. However, the M_n values based on GPC were slightly lower than the calculated M_n values which can be attributed to the difference in hydrodynamic volume between star and linear polymers.

The theoretical number average molecular weights were calculated by the following formula:

$$M_{n,theo}: ([M]_0/[I]_0 \times \text{conversion \%} \times MW_{(tBA)}) + MW_{(1)}$$



Scheme 4.5. Synthesis of octa-arm *ptBA* homopolymer

Table 4.3. Synthesis of Octa-arm P*t*BA Homopolymers by ATRP at 100 °C in bulk.

Run	Monomer	Initiator	[M] ₀ (mol l ⁻¹)	[M] ₀ /[I] ₀	Temp (°C)	Time (min)	Conv (%)	M _{n,theo} ^b	M _{n,GPC} ^c	PDI
PXIII ^a	tBA	1	6.8	3000	100	22	4	17800	16600	1.15
PXIV ^a	tBA	1	6.8	3000	100	30	9	37000	33500	1.11
PXV ^a	tBA	1	6.8	3000	100	50	11	44700	38400	1.11
PXVI ^a	tBA	1	6.8	3000	100	65	15	60100	59700	1.11
PXVII ^a	tBA	1	6.8	3000	100	150	25	98500	89400	1.08
PXVIII ^a	tBA	1	6.8	3000	100	220	29	113900	91600	1.11

^a [I]₀: [PMDETA]₀: [CuBr]₀= 1:8:8

^b M_{n,theo}: ([M]₀/[I]₀ x conversion % x MW_{tBA}) + MW₍₁₎

^c Molecular weights were calculated with linear PSt standards.

The plot of $\ln[M]_0/[M]$ versus time for octa-arm pBA homopolymers was linear indicating that the consumption of monomer increases linearly with time (Figure 4.10). Figure 4.11 shows the molecular weight and polydispersity as a function of conversion for the same reactions. The experimental molecular weights increased linearly up to $M_n=91600$ and the molecular weight distributions remained very low. ($M_w/M_n=1.11$).



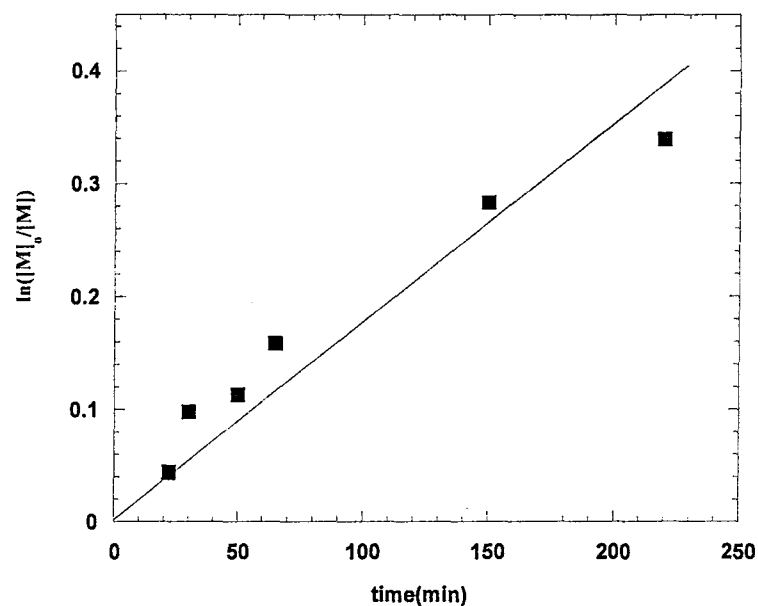


Figure 4.10. Plot of $\ln([M]_0/[M])$ vs time for ATRP of *t*BA with octafunctional initiator (1) at 100°C in bulk: $[tBA]_0/[I]_0$ $[CuBr]_0/[PMDETA]_0$:3000/1/8/8 ; $[tBA]_0=6.83M$; $[PMDETA]_0=18mM$; $[CuBr]_0=18mM$; $[I]_0=2.27mM$.

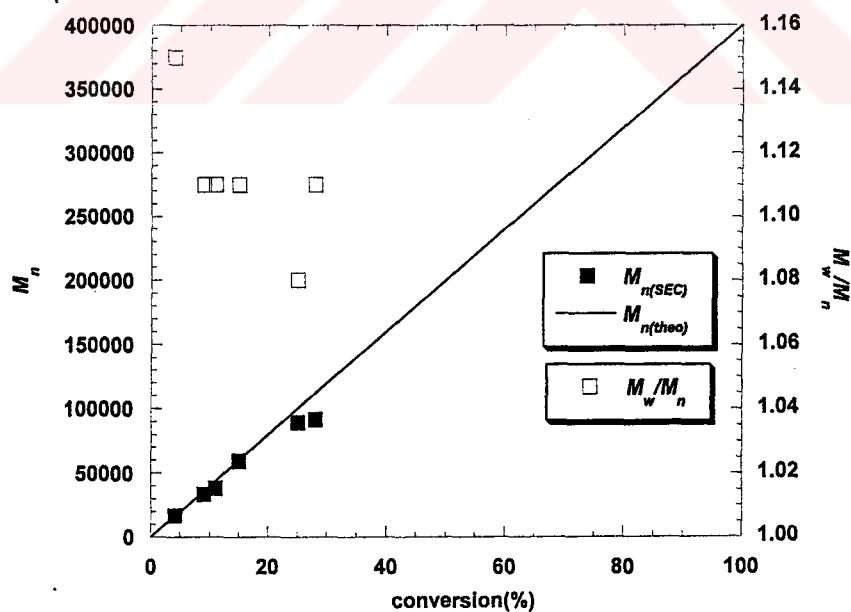


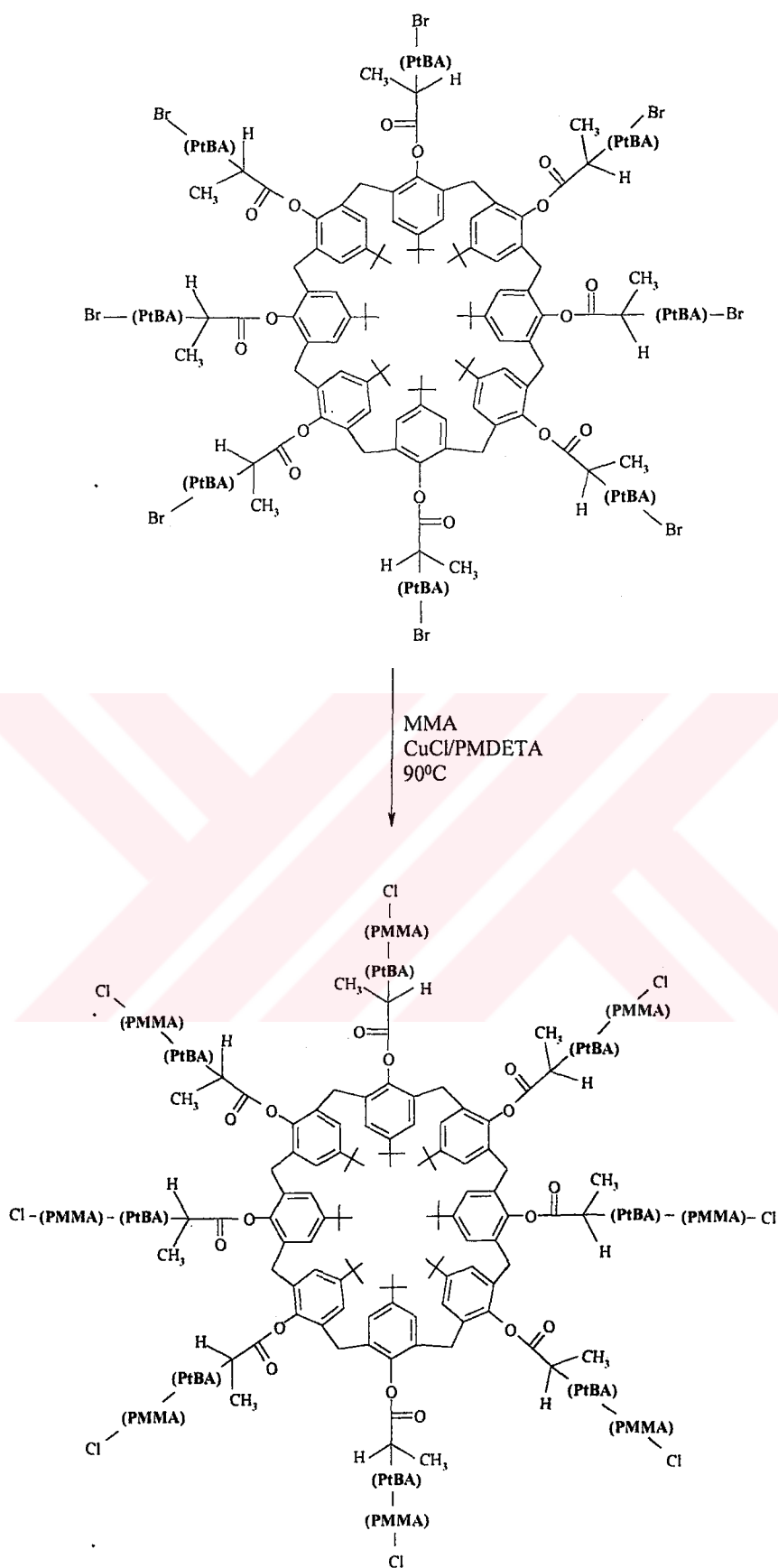
Figure 4.11. Evolution of experimental molecular weights and polydispersities with monomer conversion for ATRP of *t*BA with octafunctional initiator (1) at 100°C in bulk. $[tBA]_0/[I]_0$ $[CuBr]_0/[PMDETA]_0$:3000/1/8/8 ; $[tBA]_0=6.83 M$; $[PMDETA]_0=18mM$; $[CuBr]_0=18mM$; $[I]_0=2.27mM$.

4.5.Synthesis of Octa-arm PtBA-*b*-PMMA and PtBA-*b*-PSt star diblock copolymers

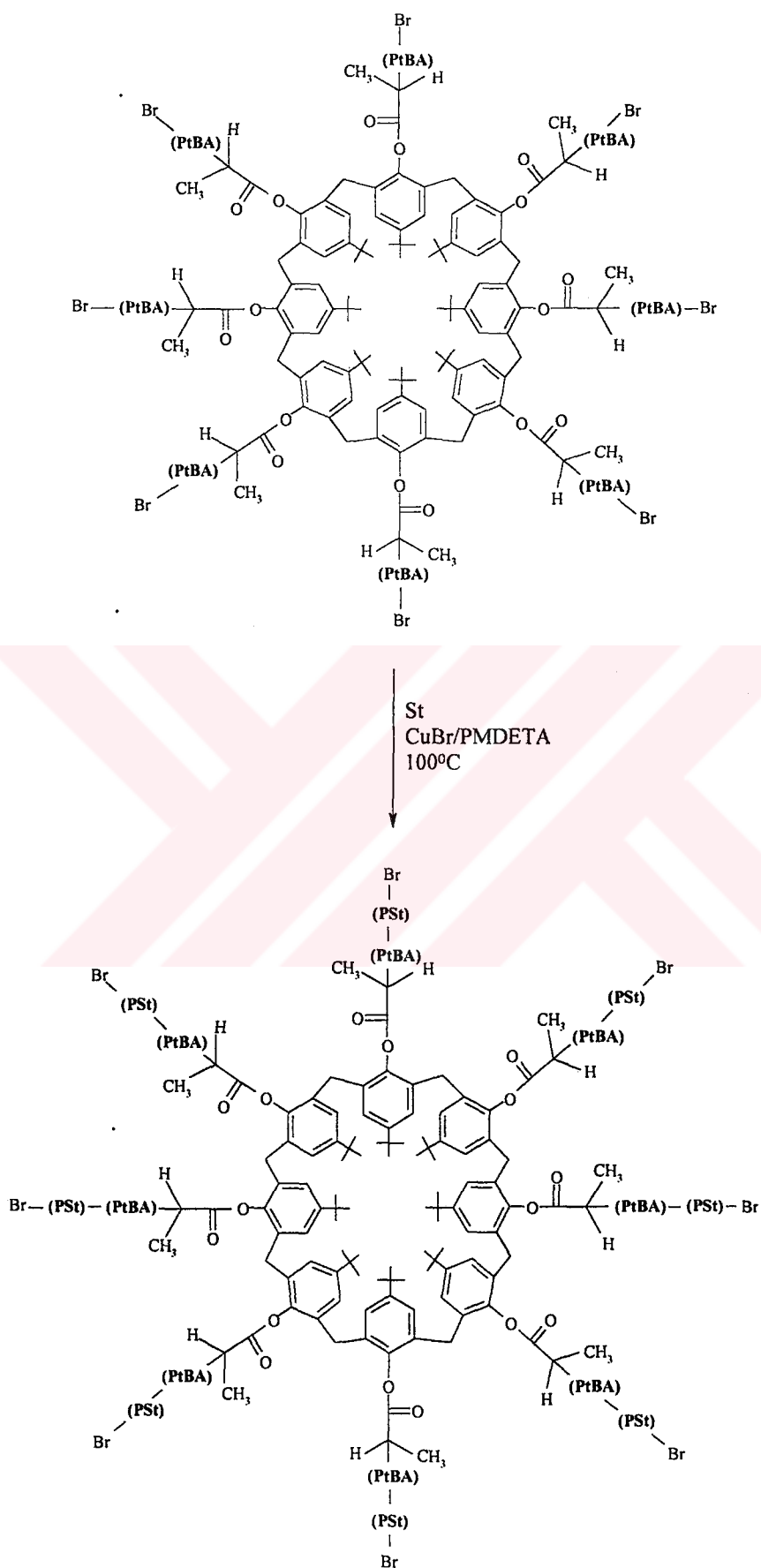
Synthesis of PtBA-*b*-PMMA and PtBA-*b*-PSt star diblock copolymers was illustrated in Scheme 4.6 and Scheme 4.7.

Synthesis of star diblock copolymers consisting of *t*BA/MMA segments were performed by ATRP of MMA using CuCl/ PMDETA catalyst system and bromine-ended octa-arm PtBA macroinitiator. The polymerizations were conducted at 90 °C in DPE solution . Similarly PtBA-*b*-PSt star diblock copolymers were prepared by ATRP of styrene using CuBr/PMDETA catalyst system and bromine-ended octa-arm PtBA macroinitiator at 100 °C in bulk (Table 4.3).

PtBA-*b*-PMMA stars with narrow molecular weight distributions could be synthesized by maintaining the monomer conversion below 15 % . To obtain well-defined stars of high molar mass (up to M_n of 232400 g mol⁻¹) it was found to use high [M]₀/[I]₀ ratios (up to 21000) to grow the star arms slowly.



Scheme 4.6. Synthesis of octa-arm *PtBA-b-pMMA* diblock copolymer



Scheme 4.7. Synthesis of Octa-arm *pBA-b-pSt* diblock copolymer

PtBA macroinitiator with a number average molecular weight of 16600 was used in the preparation of PtBA-*b*-PSt diblock copolymer with $[M]_0/[I]_0$ ratio of 6000 and 1% monomer conversion. To obtain a well-defined PtBA-*b*-PSt diblock copolymer at higher $[M]_0/[I]_0$ ratio (=8000) with higher monomer conversion, a small amount of CuBr₂ was used in order to lower the propagating radical concentration by deactivation process.

The polymers prepared under these conditions were of low polydispersity and the GPC traces were monomodal. Also GPC traces showed the expected increase in molecular weight through the copolymerization both for PtBA-*b*-PMMA and PtBA-*b*-PSt diblock copolymers.



Table 4.4. Synthesis of Octa-arm PtBA-b-PMMA and PtBA-b-PSt diblock copolymers via ATRP.

Run	Monomer	Initiator	$[M]_0$ (mol l ⁻¹)	$[M]_0/[I]_0$	Temp (°C)	Time (min)	Conv (%)	$M_{n,theo}$	$M_{n,GPC}^g$	$M_{n,Hnmr}$	M_w/M_n	Composition ¹ H NMR
PXIII ^a	tBA	1	6.8	3000	100	22	4	17800 ^e	16600	-	1.15	-
PXIV ^a	tBA	1	6.8	3000	100	30	9	37000 ^e	33500	-	1.11	-
PXVI ^a	tBA	1	6.8	3000	100	65	15	60100 ^e	59700	-	1.11	-
PXIX ^b	MMA	PXVI	4.7	16000	90	35	7	172000 ^f	135000	147700	1.30	65%PMMA, 35%PtBA
PXX ^b	MMA	PXVI	4.68	21000	90	65	12	312000 ^f	232400	199600	1.36	75%PMMA, 25%PtBA
PXXI ^c	St	PXIV	8.48	8000	100	210	3	58500 ^f	56200	58100	1.09	53%PtBA, 47%PSt
PXXII ^d	St	PXIII	8.64	6000	100	65	1	22800 ^f	33900	32700	1.25	45%PtBA, 55%PSt

^a $[I]_0$: [PMDETA]₀: [CuBr]₀ = 1:8:8 ; ^b $[I]_0$: [PMDETA]₀: [CuCl]₀ = 1:8:8 ; (MMA/DPE : 1/1) ; ^c $[I]_0$: [PMDETA]₀: [CuBr]₀ = 1:11:8:3 ;

^d $[I]_0$: [PMDETA]₀: [CuBr]₀ = 1:8:8

^e $M_{n,theo}$: ($[M]_0/[I]_0$ x conversion % x MW_{monomer})

^f $M_{n,theo}$: ($[M]_0/[I]_0$ x conversion % x MW_{monomer}) + M_n (macroinitiator)

^g Molecular weights were calculated with linear PSt and PMMA standards.

Figure 4.12 and Figure 4.13 indicates the comparison of GPC traces of two different *PtBA-b-PMMA* diblock copolymers prepared by using the same *PtBA* macroinitiator at different initial monomer/initiator ratios. The absence of *PtBA* macroinitiator peaks on the GPC traces of block copolymers indicates that the macroinitiator was fully converted to block copolymers. Peaks corresponding to *PtBA-b-PMMA* clearly shifted to higher molecular weight region of the chromatogram indicating that both the chain end functionality of the macroinitiators and the blocking efficiency were high.

Similarly Figure 4.14 and Figure 4.15 show the GPC traces of octa-arm *PtBA* macroinitiator and *PtBA-b-PSt* diblock copolymers. The peaks corresponding to diblock copolymers clearly shifted to higher molecular weight region of the chromatogram and the absence of the *PtBA* macroinitiator peaks on the resulted block copolymer indicates the complete conversion of the macroinitiators to the block copolymers.

The experimental number average molecular weights of *PtBA-b-PMMA* diblock copolymers were determined by GPC based on PMMA standards. The deviation of the experimental M_n values of star diblock copolymers from theoretical M_n values can be attributed to the different hydrodynamic volumes of star polymers relative to linear analogues of the same molecular weight.

The experimental number average molecular weights of *PtBA-b-PSt* diblock copolymers were determined by GPC based on PSt standards and were in good agreement with the theoretical ones.

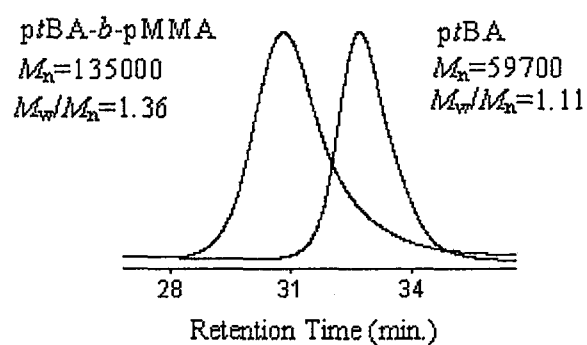


Figure 4.12. GPC traces of octa-arm *ptBA* precursor(PXVI) and *ptBA-b-pMMA* (PXIX) diblock copolymer

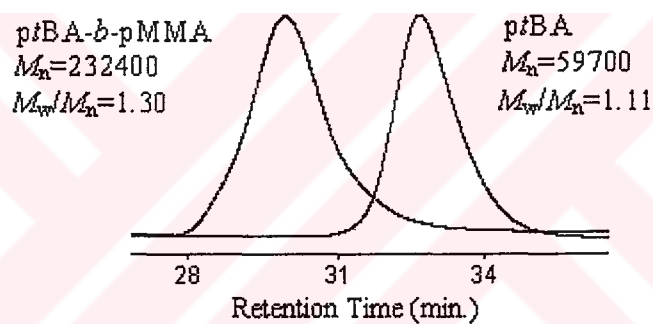


Figure 4.13. GPC traces of octa-arm *ptBA* precursor(PXVI) and *ptBA-b-pMMA* (PXX) diblock copolymer

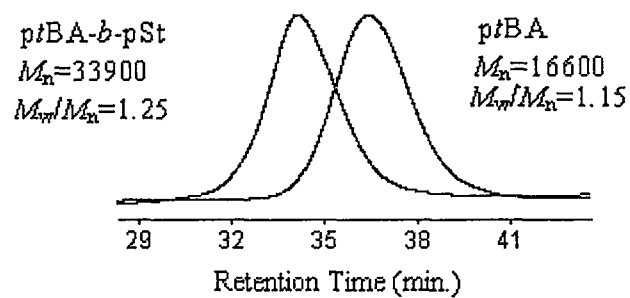


Figure 4.14. GPC traces of octa-arm *ptBA* precursor(PXIII) and octa-arm *ptBA-b-pSt* (PXXII) diblock copolymer

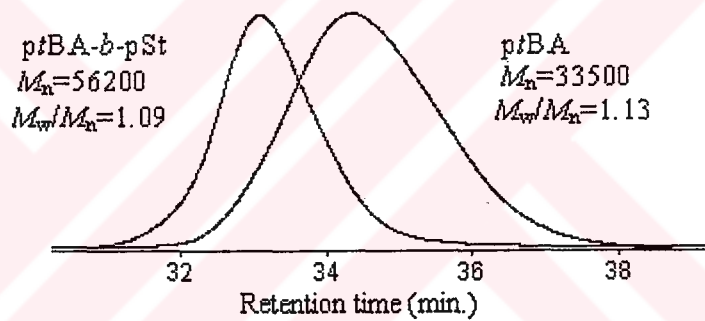


Figure 4.15. GPC traces of octa-arm *ptBA* precursor(PXIV) and octa-arm *ptBA-b-pSt* (PXXI) diblock copolymer

The composition of block copolymers was elucidated by ^1H -NMR measurements. The ^1H -NMR spectra of poly (*t*BA-*b*-MMA) block copolymers exhibited the major peaks which are characteristic of tert-butylacrylate and MMA segments. The molecular weights were calculated from the integration of signals at 1.43 ppm. (-C(CH₃)₃) of *t*BA to 3.58 ppm.(-OCH₃) of MMA for PtBA-*b*-PMMA diblock copolymers(Figure 4.16).



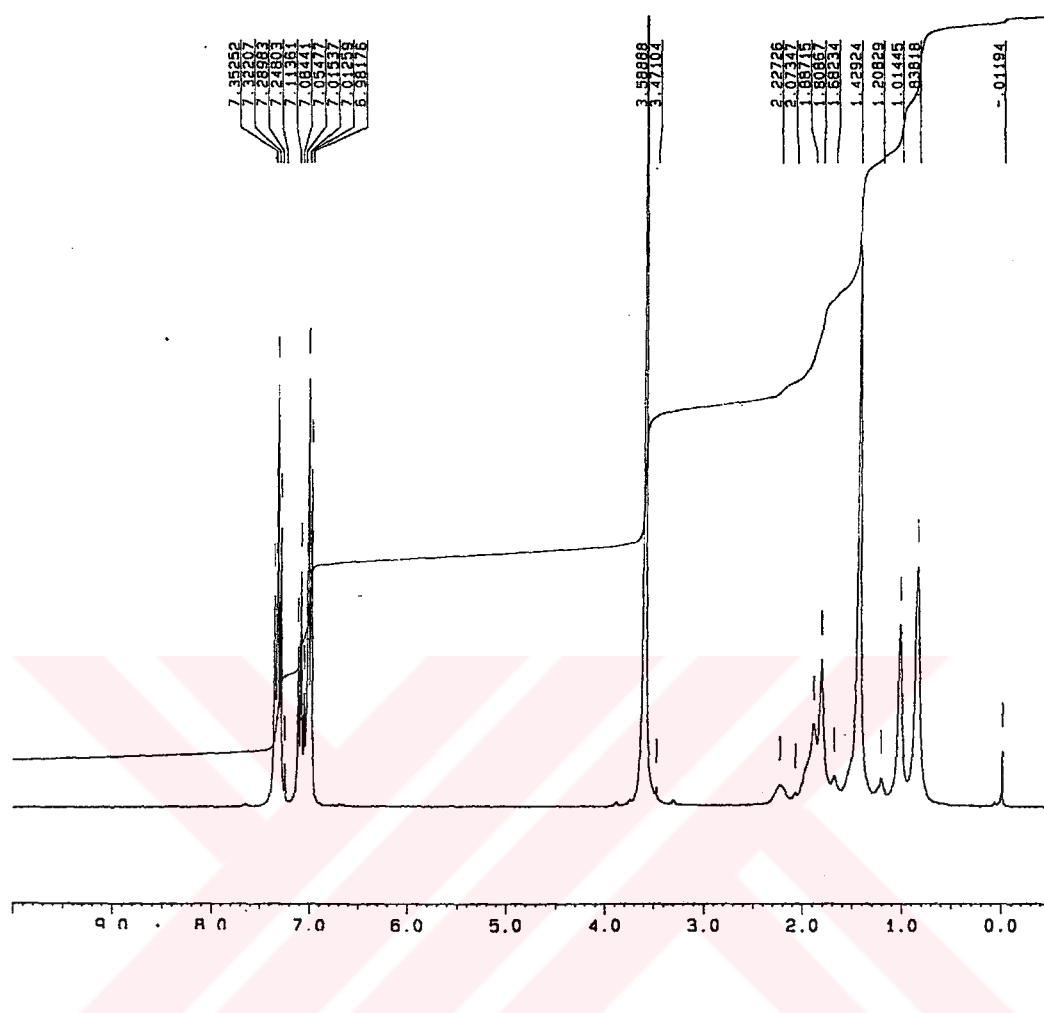


Figure 4.16. ^1H -NMR spectra of octa-arm PtBA-*b*-PMMA (PXX) diblock copolymer

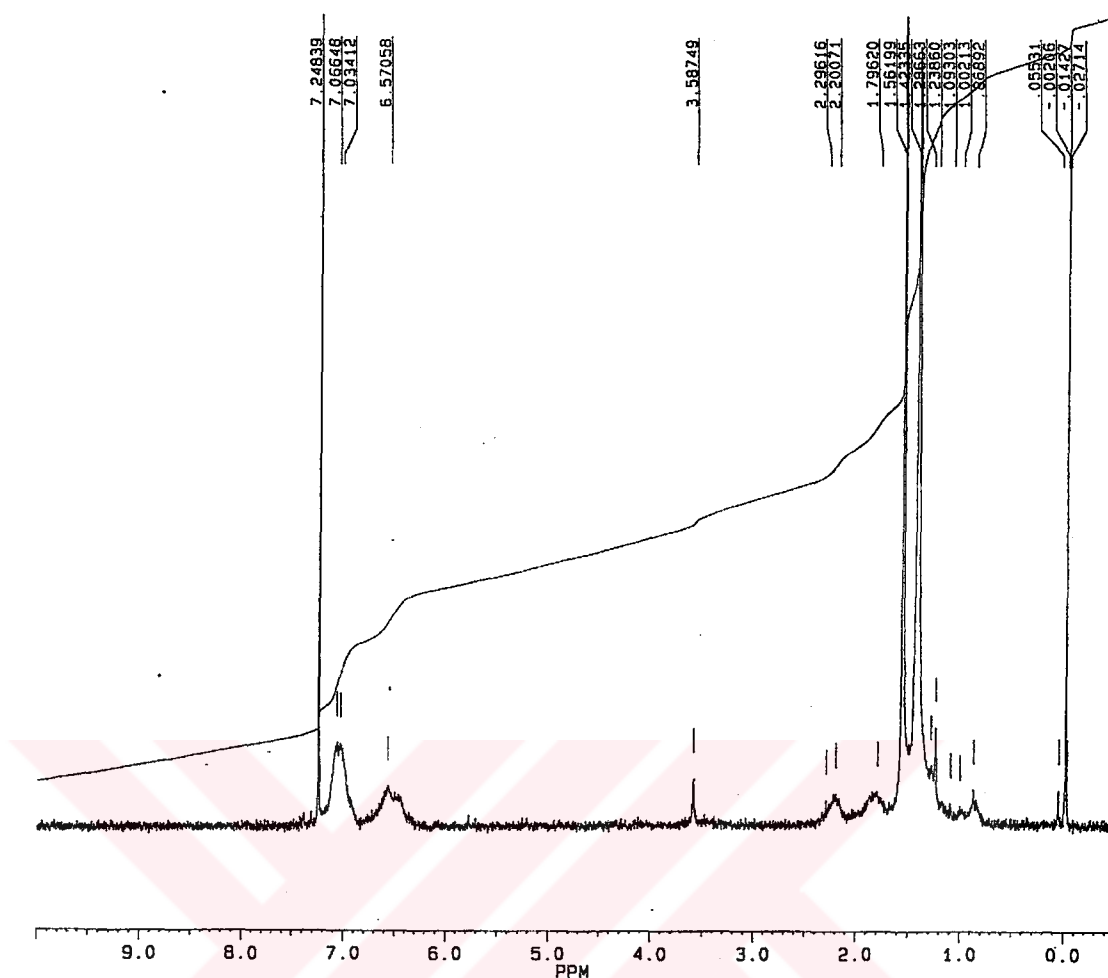


Figure 4.17. ^1H -NMR spectra of octa-arm $\text{PtBA-}b\text{-PSt}$ (PXXII) diblock copolymer

Integrating the signal between 6.5-7.0 ppm of PSt (aromatic protons) and 1.43 ppm of $t\text{BA}$ ($\text{C}(\text{CH}_3)_3$) allowed us to evaluate the composition and the molecular weight of $\text{PtBA-}b\text{-PSt}$ diblock copolymer (Figure 4.17 and Figure 4.18).

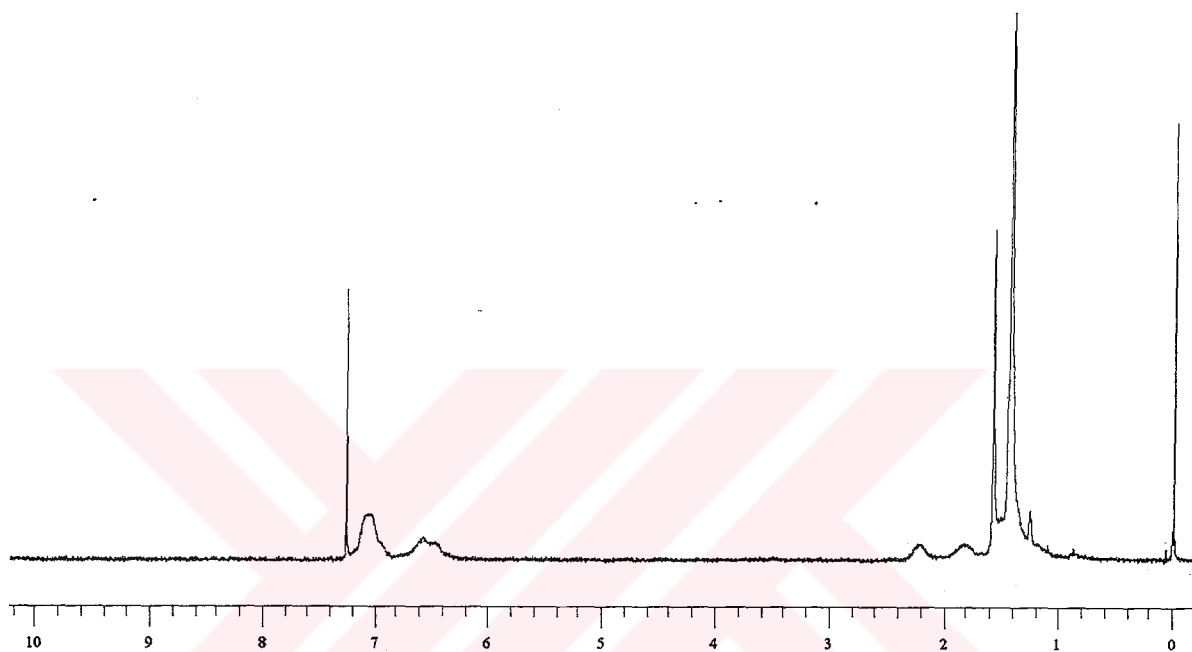


Figure 4.18. ^1H -NMR spectra of octa-arm PtBA-*b*-PSt (PXXI) diblock copolymer

5.CONCLUSION AND RECOMMENDATIONS

A novel calixarene-based octafunctional initiator , (1) , was synthesized by an esterification reaction between *p-tert*-butyl-calix[8]arene and 2-bromopropionylbromide in one step and successfully used in the preparation of octa-arm star block copolymers. To set a model for the octafunctional system linear homo and diblock copolymers of the same monomers were also prepared with a monofunctional initiator by using the same reaction components.

Linear and octa-arm *Pt*BA-*b*-PMMA and *Pt*BA-*b*-PSt diblock copolymers were synthesized with *Pt*BA macroinitiators prepared by using methyl 2-bromopropionate as a monofunctional initiator and (1) as an octafunctional initiator respectively. *t*BA and St polymerizations were conducted at 100 °C in bulk using CuBr/PMDETA catalyst system and MMA polymerizations were carried out at 90 °C in DPE using CuCl/PMDETA catalyst system.. Both for the linear and the octafunctional systems $\ln([M]_0/[M])$ vs. time plots exhibited the linear relation between the monomer consumption and time. Furthermore, number average molecular weights also increased linearly with conversion throughout the polymerizations. The experimental molecular weights of the obtained polymers were determined by GPC (Gel Permeation Chromatography) and were in good agreement with the theoretical ones. However, the observed molecular weights of the star polymers were lower than the calculated ones which can be attributed to the difference in hydrodynamic volumes of star and the linear polymers. The block compositions of the copolymers were determined by ¹H-NMR measurements.

In this study, by applying one of the most efficient CRP technique, ATRP, well-defined linear and star diblock copolymers with various molecular weights, narrow molecular weight distributions and predetermined block lengths could be successfully synthesized with high blocking efficiency by using mono and octafunctional alkyl halide initiators.

REFERENCES

- [1] Simms, J.; Spinelli, H. J. In *Macromolecular Design of Polymeric Materials*; Hatada, K., Kitayama, T., Vogl, O., Eds.; Marcel Dekker: 1997. New York , p 379
- [2] Matyjaszewski, K. ; Miller, P.J.; Pyun, J.; Kickelbick, G.; Diamanti, S., 1999. *Macromolecules* , **32**, 6526-6535
- [3] Webster, O. 1991. *Science*, , **251**, 887
- [4] Otsu, T.; Yoshida, M.; 1982. *Macromol. Chem. Rapid. Commun.*, **3**, 127
- [5] Georges, M.K.; Veregin, R.P.N.; Kozmaier, P.M.; Hamer, G.K., 1993. *Macromolecules*, **26**, 2987
- [6] Georges, M.K.; Veregin, R.P.N.; Kozmaier, P.M.; Hamer, G.K., 1993. *Macromolecules*, **26**, 5316
- [7] Borsig, E.; Lazar, M.; Capla, M.; Fildrian, S., 1969. *Angew. Macromol. Chem.*, **9**, 89
- [8] Mardare, D., Matyjaszewski, K., 1994. *Am. Chem. Soc. Polym. Preprints*, **27**, 645
- [9] Gresia, D.; Mardare, D.; Matyjaszewski, K., 1994. *Am. Chem. Soc. Polym. Preprints*, **35** (1), 466
- [10] Harwood, J.H.; Arvanitopoulos, L.D.; Gravel, M.P., 1994. *Am. Chem. Soc. Polym. Preprints*, **35**(2), 549
- [11] Wayland, B.B.; Pismik, G.; Mukerjee, S.L.; Fryd, M., 1994. *J. Am. Chem. Soc.*, **116**, 7943
- [12] Davis, K.A.; Matyjaszewski, K., 2000. *Macromolecules*, **33**, 4039
- [13] Patten, T.E.; Matyjaszewski, K., 1998. *Adv. Mater.*, **10**, 901
- [14] Matyjaszewski, K., 1999. *Chem. Eur. J.*, **5**, 3095
- [15] Patten, T.E.; Matyjaszewski, K., 1999. *Acc. Chem. Res.*, **32**, 895
- [16] Matyjaszewski, K.; 2003. *Macromol. Symp.* **195**, 25-31

- [17] Angot, S.; Murthy, K.S.; Taton, D.; Gnanou, Y., 1998. *Macromolecules*, , 31, 7218-7225
- [18] Clouet, E.; Fillaut, J.L.; Gnanou, Y.; Astruc, D. In *Macromolecular Engineering Recent Advances*; Mishra, M.K., Nuyken, O., Kobayashi, S., Yagci, Y., Sar, B., Eds.; 1995. Plenum Press: New York,; p 47
- [19] Simms, J.A. 1991. *Rubber Chem. Technol.*, 64, 139
- [20] Morton, M.; Helminiak, T.D.; Gadkary, S.D.; Bueche, F. 1962. *J. Polym. Sci.* 57, 471.
- [21] Hsieh, H.L.; Quirk, R.P.; *Anionic Polymerization*; Marcel Dekker: 1996. New York,; pp 333-368
- [22] Hadjichristidis, N. 1999. *J. Polym. Sci., Part A: Polym. Chem.*, 37, 857.
- [23] Xia, J.; Zhang, X.; Matyjaszewski, K.; 1999. *Macromolecules*, 32, 4482-4484
- [24] Matyjaszewski, K.; 2003. *Polym Int* 52: 1559-1565
- [25] Wu, X., and Fraser, C. L., 2000. *Macromolecules*, 33, 4053
- [26] Sawamoto, M. In *Cationic Polymerizations*; Matyjaszewski, K. , Ed.; Marcel Dekker: 1996. New York, p 381
- [27] Kennedy, J.P.; Jacob, S. 1998. *Acc. Chem. Res.*, 31, 835
- [28] Wang, J. -S.; Greszta, D.; Matyjaszewski, K. 1995. *Polym. Mater. Sci. Eng.*, 416
- [29] Kasko, A. M.; Heintz, A.M.; Pugh, C. 1998. *Macromolecules*, 31, 256
- [30] Ueda, J.; Kamigaito, M.; Sawamoto, M.; 1998. *Macromolecules*, 31, 6762

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