İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF STARS AND STAR COPOLYMERS VIA ATOM TRANSFER AND STABLE FREE RADICAL POLYMERIZATION

M.Sc. Thesis by
Çiğdem ÇELİK

Department : **Polymer Science and Technology**

Programme: **Polymer Science and Technology**

JANUARY 2003

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December 2002 Çiğdem ÇELİK

TABLE OF CONTENTS

TABLE OF CONTENTS

LIST OF FIGURES

Page No:

LIST OF SYMBOLS

M_n	**:** Number average molecular weight of polymers
M_w	**:** Weight average molecular weight of polymers
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

ATOM TRANSFER RADİKAL POLİMERİZASYONU VE KARARLI SERBEST RADİKAL POLİMERİZASYONU İLE STAR POLİMER VE STAR KOPOLİMERLERİN SENTEZİ

ÖZET

Son yıllarda, iyi tanımlanmış düşük molekül ağırlığı dağılımına sahip polimerlerin sentezinde kontrollü / ’yaşayan’ polimerizasyon yöntemleri kullanılmaktadır. Yaşayan polimerizasyon teknikleri, makromonomer, makrobaşlatıcı, fonksiyonel polimerler, blok ve graft kopolimerler ile yıldız tipli polimerler hazırlanmasına olanak sağlar. Son zamanlarda, yapılan çalışmalar içerisinde yıldız tipli polimerlerin sentezi büyük bir önem taşımaktadır. Bu çalışmaların neticesinde yaşayan polimerizasyon tekniklerinin uygulamada iyi sonuçlar verdiği gözlenmiştir. Bu etkinlikler içinde en etkili olanı kararlı serbest radikal polimerizasyonu (SFRP) ve M_t^n /Amin ligand kompleks kataliz sistemli atom transfer radikal polimerizasyonudur (ATRP). Her iki yöntemin avantajı ise elde edilen polimerlerin molekül ağırlığı ve uç grubu kontrolünün sağlanmasıdır.

Bu çalışmada Stiren (St), ter-butil akrilat (tBA) ve metil metakrilat (MMA) zincirleri içeren yıldız tipli triblok kopolimerlerin sentezi SFRP ve ATRP teknikleri kullanılarak yapıldı. Çalışmada ilk olarak üç fonksiyonlu başlatıcı 2-fenil-2-[(2,2, 6,6-tetrametil)-1-piperidiniloksi]etil 2,2-bis[metil(2-bromo propionat)]propionat **(1)**, sentezlenmiş ve SFRP-ATRP-ATRP polimerizasyon sıra ile iyi tanımlanmış yıldız tipli blok kopolimer sentezi gerçekleştirilmiştir.

Deneyler sonucunda, GPC ve ^{1}H-NMR cihazlarından alınan sonuçlar hedeflenen yıldız tipli polimerlerin başarıyla sentezlendiğini desteklemiştir. Teorik olarak hesaplanan molekül ağırlıklarının deney sonuçları ile uyumluluğu, dar polidispersiteye sahip kopolimerlerin elde edilmesi çalışmalarımızda kontrollü / ‘yaşayan’ polimerizasyonun yürüdüğünü göstermektedir.

SYNTHESIS OF STARS AND STAR COPOLYMERS VIA ATOM TRANSFER RADICAL POLYMERIZATION AND STABLE FREE RADICAL POLYMERIZATION

SUMMARY

Recently, the controlled \ ’living’ radical polymerizations have been utilized for the synthesis of well-defined, narrow polydispersity polymers. Macromers, macnoinitiators, functional polymers, block and graft copolymers, start-shaped polymers can be synthesized with living polymerization techniques. The field of star polymers has received considerable attention during recent years of the result of these studies, it has been observed that living polymerization techniques give favarouble results. Among this techniques stable free radical polymerization (SFRP) and M_t^n \ Ligand catalyst mediated atom transfer radical polymerization (ATRP) are effective methods for the controlled radical polymerizations. One of the advantageous of SFRP and ATRP is that the molecular weight and the chain end functionality can be controlled.

In this study, star triblock copolymer consist of styrene (St)-ter-butylacrylate (tBA)-methylmethacrylate (MMA) chains were synthesized via combination of SFRP and ATRP techniques. First, dual (trifunctional) initiator 2-phenyl-2-[(2,2,6,6-tetramethyl)-1-piperidinlyoxy]ethyl 2,2–bis[methyl (2-bromopropionato)] propionate **(4)** was synthesized. Second, well-defined star triblock copolymer were obtained via SFRP-ATRP-ATRP route.

The unimodal shapes of the traces obtained from GPC (Gel Permeation Chromatography) and ^{1}H-NMR spectrum prove that star-shaped block copolymers were successfully synthesized. The good correlation between determined molecular weight with the calculated one indicates a fully controlled \ ’living’ radical polymerizations with yielding star block copolymers with narrow polydispersity.

1. INTRODUCTION

Stars or star copolymers have attracted much attention in research over the years due to their unique three-dimensional shape and highly branched structure. In spite of that are quite different from those exhibited by linear homologues, star-shaped macromolecules have found only a few industrial applications as specialty polymers.

Among all branched structures that are known, star shaped polymers have been certainly the most investigated architectures, attracting much experimental and theoretical interest. Indeed star polymers represent the simplest model of branched structures, involving only one central branching unit per macromolecule. The best defined among them containg a precise number of arms of equal length. Such species have been useful in providing further insight into how branching affects the overall properties of polymers in solution or in melt [1].

The synthesis of star polymers by free-radical mechanism is a challenging task because of unavoidable occurence of irreversible termination reactions. Different strategies have been described that allow one to control the free-radical polymerization of miscellaneous monomers. Controlled / ’living’ radical polymerization processes have proven to be versatile for the synthesis of well-defined star polymers. Star polymers have been prepared by various controlled radical polymerization techniques including nitroxide-mediated stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP).

The strategies to generate star-shaped polymer are knowns as ’’arm first’’ and ’’core first’’. In the ’’arm first’’ approach, monofunctional, living linear macromolecules are initially synthesized. Star formation then occurs in are of two ways: a difunctional comonomer is used to provide cross-linking through propagation or a multifunctional terminating agent is added connecting a precise number of arms to a central core molecule. In the ’’core first’’ approach, 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 [2-5]. Most of the star polymers were prepared by the core first technique.

The core first approach appears more attractive provided suitable multifunctional initiators are made available. Following this route stars and star copolymers have been succesfully prepared from dual (trifunctional) initiators. For this aim, controlled radical polymerization techniques have been applied to the preparation of star homopolymers and block copolymers of styrene, methyl methacrylate and ter-butyl acrylate monomers.

2. THEORETICAL PART

2.1. Controlled/'Living' Radical Polymerization

The term controlled/'living' polymerization (C/LRP) was initially used to describe a chain polymerization in which chain breaking reactions were absent [6,7]. In such an ideal system, after initiation is completed, chains only propagate and do not undergo transfer and termination. However, transfer and termination often occur in real system. Thus, living polymerization (no chain breaking reactions) and controlled polymerization (formation of well defined polymers) are two separate terms.

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

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

-initiation is fast in comparison with propagation

-exchange between species of different reactivities is fast in comparison with propagation
-the rate of depropagation is low in comparison with propagation and the system is sufficiently homogeneous, in the sense of availability of active centers and mixing.

Well defined polymers may be formed in radical polymerization only if chains are relatively short and concentration of free radicals is low enough. There is apparent contradiction between these two requirements because usually a decrease of the concentration of radicals leads to higher molecular weights. However, the two conditions can be accommodated in systems with reversible deactivation of growing radicals. The controlled polymerization requires a low proportion of deactivated chains, which can be achieved by keeping molecular 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 bimolecular, contribution of termination becomes more significant when a large concentration of radicals [P**.**] is generated.

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

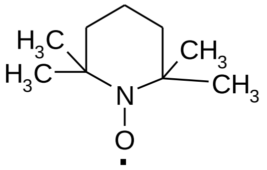
The three approaches have been used to control radical systems. The best examples of the first approach include stable free radical polymerization (SFRP), atomic transfer radical polymerization (ATRP), and photolabile iniferters. The second approach is less common and may be included some organometallic species such as $Cr^{(III)}$ or Al derivatives as well as nonpolymerizable alkenes such as stilbene or tetrathiafulvalene. The last approach can be best exemplified chemistry, via methacrylate monomers [8-11].

2.1.1 Iniferter Method

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

2.1.2 Stable Free Radical Polymerization (SFRP)

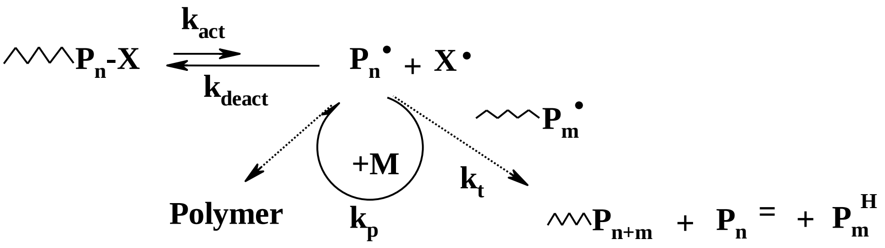
Living free radical polymerization has gained in popularity as a result of the continued expansion of the stable free radical polymeriation (SFRP) process. The use of stable nitroxide in controlled radical polymerization was first demonstrated by Solomon and Rizzardo [12]. The stable nitroxide radicals such as, 2',2',6',6'-tetramethyl-1-piperidinyloxy (TEMPO) are known to act as strong polymerization inhibitors [13-15].



TEMPO

(2',2',6',6'-tetramethyl-1-piperidinyloxy) (2.1)

The schematic representation of the mechanism of SFRP is given equation (2.2).



(2.2)

P_n-X : Alkyl halides (Dormant Species)

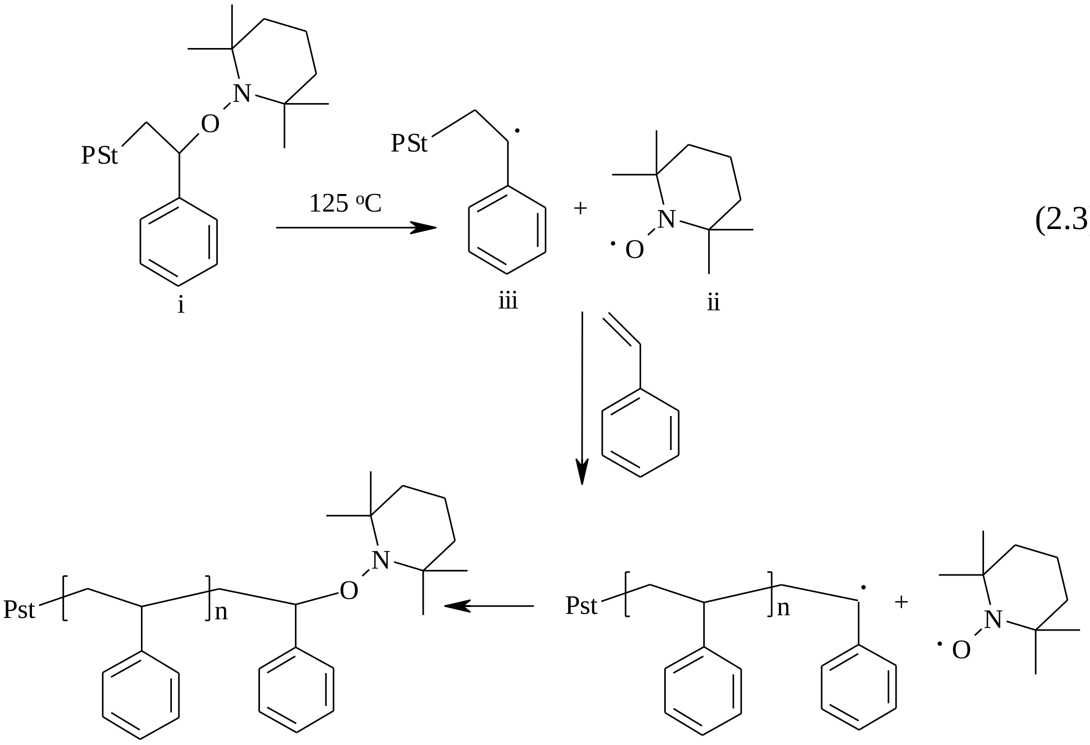
M : Monomer

k_a, k_d : Rate constants of activation and deactivation

k_p, k_t : Rate constants of propagation and termination

The dormant species decomposes homolytically into a transient (active species, $P_n^{\bullet}$) and a persistent species ($X^{\bullet}$). The free radical can add monomer and thus polymerize. The persistent species is generally a nitroxide stable free radical that it does not initiate polymerization. The concentration of active species is kept low because the equilibrium is pushed toward the dormant species.

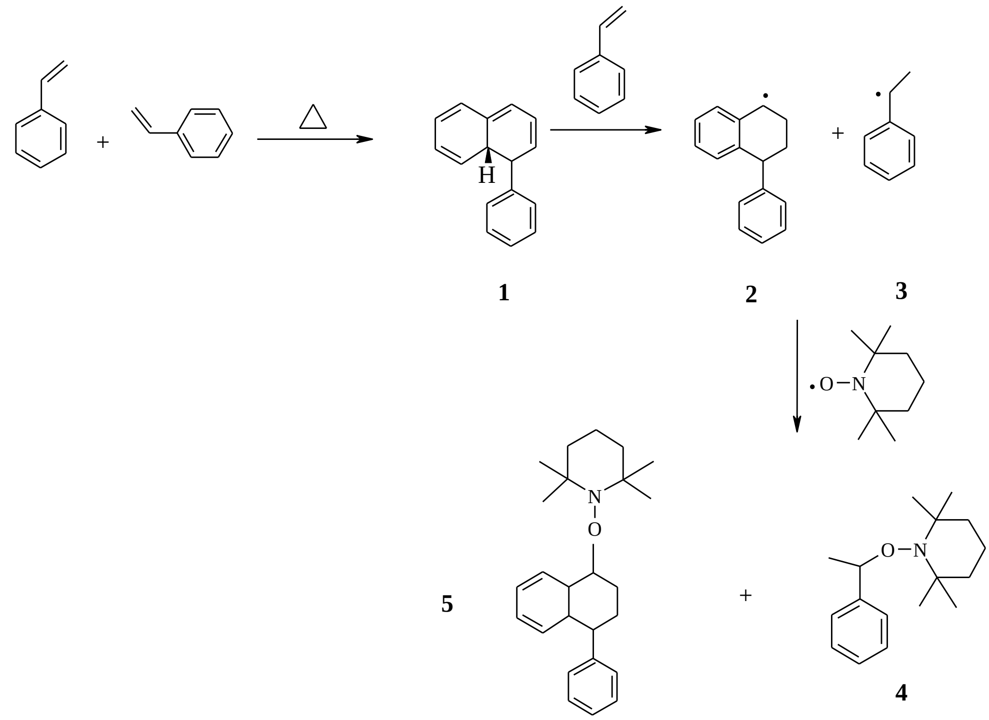
The origin of the unprecedented control in niroxide mediated living free radical polymerizations is believed to be the reversible termination of the growing polymeric radical to give a dormant, or inactive, species in which the nitroxide moiety is covalently bound to the polymer chain end. At lower temperatures, 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 (2.3) 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 (2.3).



(2.3)

The C/LRP started with Georges [16] SFRP of bulk styrene at 120-130 ^{0}C, initiated by benzoyl peroxide (BPO) in the presence of 1.3 equiv of TEMPO. Good control was observed for moderate molecular weights $Mn<10^5$ for styrene and styrene copolymers. However, it was difficult to homopolymerize other monomers.

Thermal initiation (or autopolymerization) in styrene has been known for some time. Mayo compound (1) proposed that the generation of radicals proceeded through a Diels-Alder reaction involving two styrene molecules (2.4). The product then undergoes a molecular assisted homolysis reaction with another molecule of styrene, producing a styryl radical and an aromatized radical. Both radical can initiate polymerization, or in the presence of nitroxide, be trapped to form an alkoxyamine.



(2.4)

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.

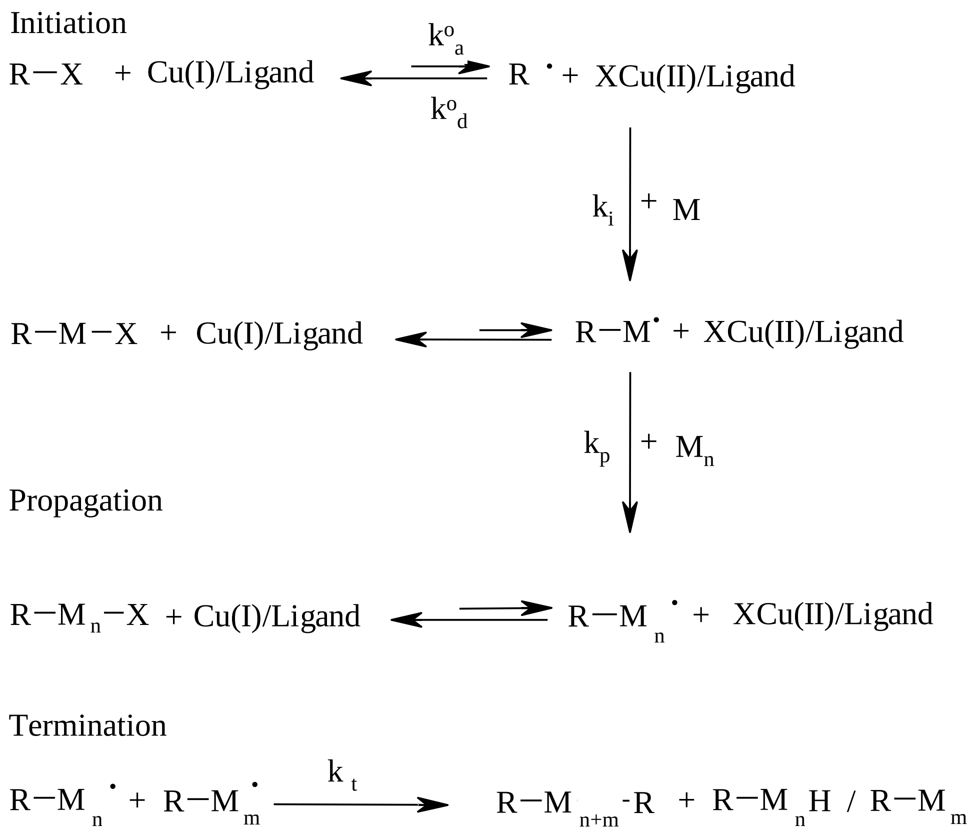
Advantages of SFRP over other controlled polymerization methods include that no (metal) catalyst is required and no further purification is needed.

2.1.3 Atom Transfer Radical Polymerization (ATRP)

The name of atom transfer radical polymerization (ATRP) comes from the atom transfer step, which is the key elemantary reaction responsible for the uniform growth of the polymeric chains. ATRP 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 [17-20].

As a multicomponent system, ATRP includes the monomer, an initiator with a transferable halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Both activating and deactivating components of the catalytic system must be simultaneously present. Sometimes an additive is used. For a successful ATRP, other factors, such as solvent, temperature, concentrations and solubility of all components, and sometimes the order of their addition must be also taken into consideration.

The schematic representation of the mechanism of ATRP is given in equation (2.5).



(2.5)

2.1.3.1 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 formulated in discussed conditions and given in (2.6).

$$R_p = k_{app}[M] = k_P[P.][M] = k_p K_{eq}[I]_0 \frac{[\,Cu(I)\,]}{[\,Cu(II)\,X\,]}[M] \qquad (2.6)$$

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 ($k_p >> k_d$), 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 (2.7).

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_d [RX]_0}{k_p [XCu^{II}]} \right) \left(\frac{2}{p} - 1 \right) \tag{2.7}$$

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

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 weight distributions) are usually obtained.

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

2.1.3.2 Monomers

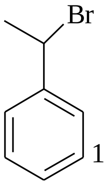
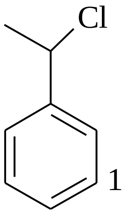
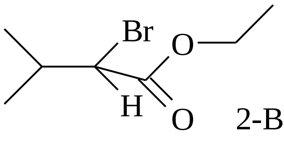
A variety of monomers have been successfully polymerized using ATRP; styrenes, (meth)acrylates, (meth)acrylamides, acrylonitrile, N-vinylpyridine, and diens, which contain substituents that can stabilize the propagating radicals. The polydispersities of the polymers obtained via ATRP techniques should be between 1.05 and 1.5.

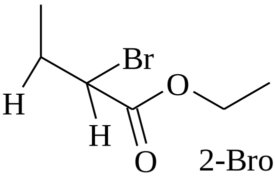
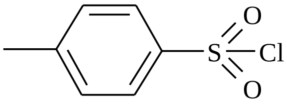
2.1.3.3 Initiators

The main role of the initiator is to determine the number of growing polymer chains. In ATRP, alkyl halides (RX) are typically used as initiators. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, should 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 best.

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

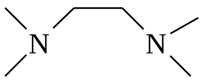
Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 2-Bromo ethyl isobutyrate	Methylmethacrylate

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

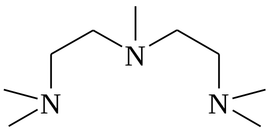
2.1.3.4 Ligands

The main role of ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal. The most widely used ligands for ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as N,N,N',N",N" pentamethyldiethylenetriamine (PMDETA), Tetramethylethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetraamine (HMTETA), tris [2-(dimetylamino) ethyl]amine (Me-TREN) and alkylpyrdylmethanimines are also used.

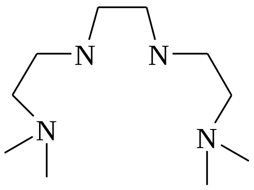
Nitrogen based ligands:



TMEDA



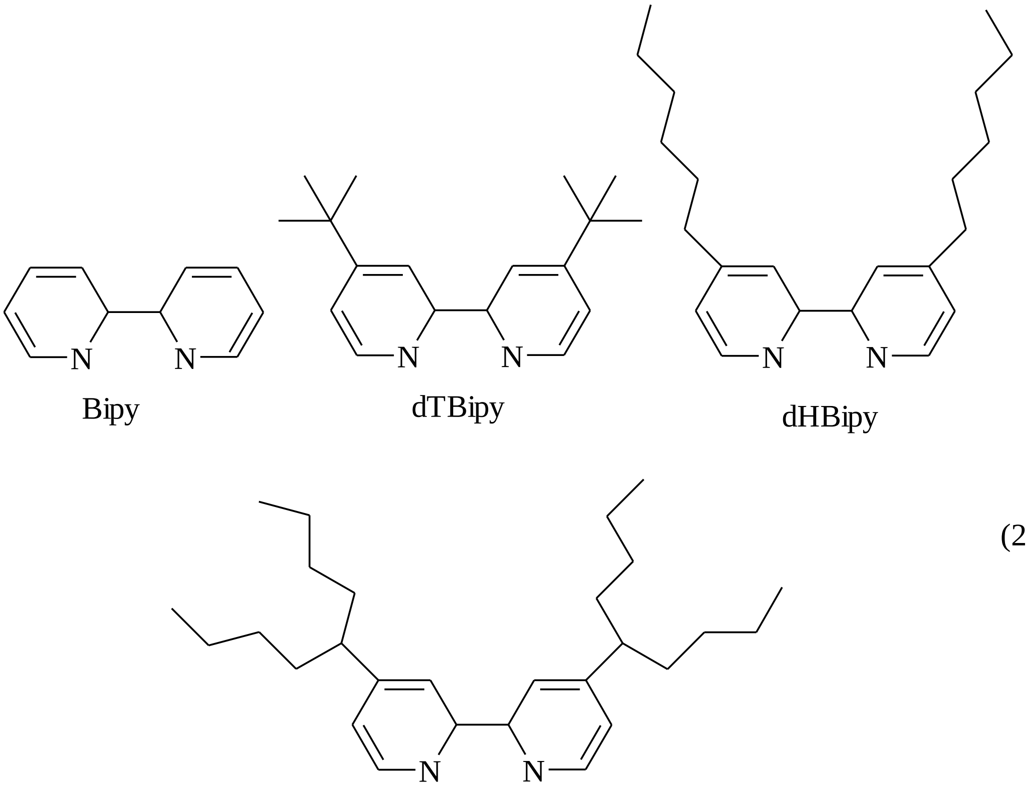
PMDETA



HMTETA

(2.8)

derivatives of 2,2-bipyridine:



(2.9)

2.1.3.5 Transition Metals Complexes

The most important component of ATRP is the catalyst. 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 upon oxidation to accommodate a halogen. Fourth, the ligand should complex the metal relatively strongly. The most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, $NiBr_2(PPh_3)_2$, $FeCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3$ / $Al(OiPr)_3$.

2.1.3.6 Solvents

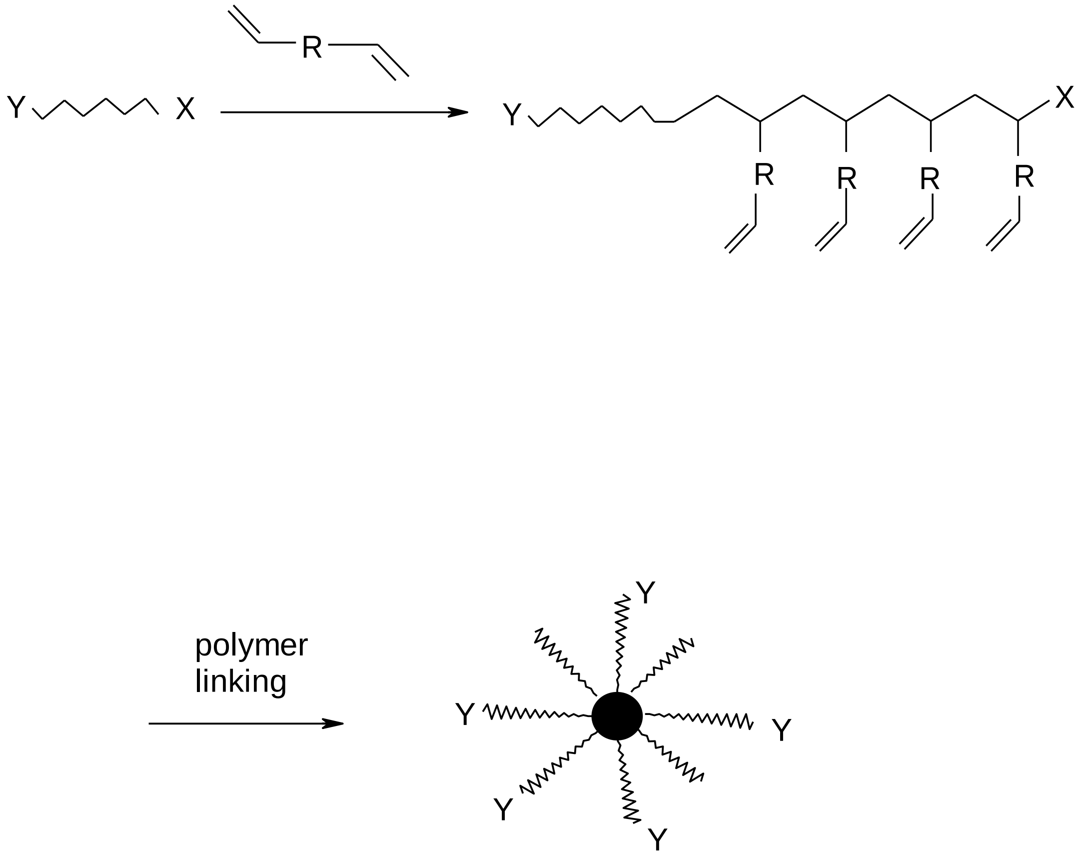
ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethylformamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used in the polymerization of diffferent monomers.

2.1.4 Stars and Star Block Copolymers

There are essentially two strategies to engineer star-branched polymers: one can either resort to the ’’arm first’’ method or turn to the ’’core-first’’ route; the two approaches are complementary with their respective merits and drawbacks. Among all branched architectures, star polymers correspond to the simplest possible arrangement of macromolecular chains in a branched structure since they involve only one central branching point per macromolecule [21].

2.1.4.1 Stars by the Convergent Approach

Although being known since the 1950s and developed in the context of anionic polymerization, it is only relatively recently that the approach resting on the participation of a divinylic compound in the star formation was applied to C / LRP. The divinylic compound actually plays the role of a coupling agent. On its addition onto a solution containing a ’’living’’ polymer, one can trigger its polymerization and grow a short block-carrying pendant double bonds. Starlike polymers are formed in a second step through intermolecular reactions between the remaining ’’living’’ precursos and the pendant double bonds. Concomitantly to this mechanism of core formation, stars can also be built through intermolecular reactions involving the divinylic blocks themselves. Under these conditions, the number of chains attached to the core depends on several parameters such as the molar ratio (*r*) of the divinylic compound to the precursor, the molar mass of the latter, and the temperature. These features, which were established a long time ago for anionically derived star polymers also apply to stars derived by C / LRP (Scheme 2.1). The most recent studies on star synthesis by this convergent approach are described below.



Scheme 2.1 Star polymer synthesis through the use of a divinylic compound.

To derive their PS stars, Matyjaszewski and colleagues [22] used a performed PS macroinitiator obtained by ATRP that was allowed to react with various divinylic monomers, in the presence of CuBr / dipyridyl in anisole at 110 ^{o}C. A ratio of 5:15 between divinyl benzene 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 efficient star formation.

The synthesis of star polymers by SFRP through a convergent approach was also described in two reports. Long and colleagues [23] observed that a ratio of 67 between divinylbenzene and their PS –TEMPO precursor is needed for obtaining PS stars. In contrast, Hadjichristidis et al [24]. Employed much smaller ratios (between 3 and 13) to obtain their PS stars. As such stars contained many TEMPO-based alkoxyamines at their core, a large number of arms (up to 600) could be grown outward by SFRP, affording to stars with PDIs in the range of 1.55-1.56.

It is worth pointing out that in most of the studies cited above, gel formation was observed above a critical value of the ratio between the divinyl monomer and the linear precursor.

An original study also based on the arm-first approach was reported by Fraser and colleagues [25], who synthesized 2,2'-dipyridiyl-carring PS and PMMA chains by ATRP, which they managed to chelate onto a hexadendate Fe(II)-based complex to form corresponding starlike polymers, thus containing a metallic core. However, and as described below, the core-first method is certainly better suited to the synthesis of well-defined starlike polymers, particularly those of precise functionality.

2.1.4.2 Stars by the Divergent Approach : Use of Multifunctional Initiators

The core-first approach has come to maturity after it was shown in the 1990s that stars of precise functionality could be obtained from multiionic initiators. Such well-defined stars of precise functionality are quite useful in providing acute insight into how branching affects the overall properties of polymers in solution or in the melt. However, the main limitation of the core-first method is the development of suitable multifunctional initiators.

Hawker [26] was the first to demonstrate the possibility of obtaining well-defined PS stars by the core-first methodology. This author prepared a TEMPO-based trialkoxyamine that was designed to initiate the SFRP of styrene in there directions and produce a triarm PS star (M_n = 20,000 g/mol; PDI = 1.2). The latter was characterized by comparing its molar mass with that of its hydrolyzed arms isolated after cleavage of the central core. Gnanou and co-workers [27] also resorted to SFRP to prepare triarmed PS and Pn-BuA stars of rather high molar mass; they used to this end an original trifunctional alkoxyamine on the basis of the β-hydrogen-containing nitroxide of Atochem.

Many other groups have also resorted to ATRP to derive star polymers by the core-first method, using various families of multifunctional initiators: the latter include inorganic heterochelics such as cyclotetrasiloxanes or cyclophosphaneze, activated phenol derivatives, glucose, or calixarene derivatives with four to eight ATRP-initiating sites, tetrakis(bromomethyl benzene), hexa and dodecafunctional carbosilane-based dendritic cores or other dendritic moities, and various multifunctional aromatic sulfony chlorides that were used in conjunction with various activators based on either copper, ruthenium or nickel halides, and miscellaneous ligands. Stars carrying polystyrene, polymethacrylate, or polycrylate arms whose number ranged from 3 to 21were synthesized via this route.

The scope and limitations of the CuBr / dipyridyl catalytic system, which is also the most commonly used one in ATRP, have been investigated by the Gnanou group in the context of star synthesis [28,29]. PS stars with predictable molar masses and polydispersity index close to unity, constituted of precisely four, six, and eight arms were synthesized, starting from calixarene-derived initiators. For instance, octafunctional PS stars exhibiting molar masses as high as 600.000 g/mol^{-1} could be prepared by polymerizing styrene in bulk, discontinuing the polymerization to low conversion, typically below 15-20 %, to prevent stars from mutually coupling. In the case of hexa- and tetrafunctional PS stars, well-defined samples could be obtained within a alerger range of conversion because of the lower probability of such hexa- and tetraarmed species to get coupled, as compared to the case of the octafunctional system. Therefore, the lower the functionality of the stars prepared, the higher the conversion above which star-star coupling became detectable.

2.1.4.3 Star-Shaped Block Copolymers by the Core-First Approach

The possibility of derivatizing the arm tips and therefore deriving reactive stars is another reason for the attractiveness of the core-fist method. Taking advantage of the presence of reactive end groups in core-first stars, different groups synthesized star-shaped block copolymers (PS, PMMA, PTHF, PEO, PCL, etc.), either by sequential C / LRP or by switching from one mechanism to C / LRP as was done for the block copolymer synthesis [30,31].

To obtain star block copolymers, the simplest method is, however, to sequentially polymerize two monomers by C / LRP; the restrictions mentioned in the section devoted to block copolymers also apply here. Few star block copolymers were derived in this way; for instance, hexaarmed poly(methyl acrylate-*b*-isobornyl acrylate), octaarmed poly(methyl methacrylate-*b*-*n*-butyl methacrylate) stars, potentially useful as thermoplastic elastomers, or multiarmed poly(methyl methacylate-*b*-*ter*-butyl acrylate) and poly(*ter*-butyl acrylate-*b*-methyl methacylate) stars were reported. In the case of the two latter structures, the *ter*-butyl groups of the P*t*-BuA blocks were selectively hydrolyzed, affording dodecaarm starblock poly(acrylic acid)$_{12}$-*b*-PMA$_{12}$ and PMMA$_{12}$-*b*-poly(acrylic acid)$_{12}$ copolymers. Investigations by ^{1}H-NMR showed that they responded to changes of the polarity of the solvent in which they were placed; these systems formed so-called stable unimolecular miscelles owing to the precise topological arrangement of the chain units [32,33].

3. EXPERIMENTAL PART

3.1. Chemicals used

a) Monomers

Styrene (St, 99% Aldrich), ter-butyl acrylate (tBA, 99% Aldrich), and methylmethacrylate (MMA, 99% Aldrich) were passed through basic alumina column to remove inhibitors and then distilled over CaH_2 and 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. Hexane was purchased from Aldrich and distilled over P_2O_5 prior to use. All other reagents were purchased from commercial sources and used as received.

3.2. Synthesis of 2-phenyl-2-[(2,2,6,6-tetramethyl)piperidinyloxy]-1-ethanol

To a round-bottom flask were added BPO (4.7 g) 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 3 g) in St (300 mL) at 90-95 ^{0}C under nitrogen for 30 min and then removing excess St. It was purified. The compound (**1**), obtained as a solid (2.6 g). The ^{1}H-NMR spectrum of the product was similar to that reported by Hawker et al [34].

To a solution of the compound (**1**), (2.4 g) in ethanol (35 mL) was added aqueous KOH (8.5 mL of a 1 N solution), and the solution was heated at reflux under nitrogen for 5 h. After ethanol was removed by evaporation. The crude product was dissolved in dichloromethane and washed water, and then extracted. The extract was dried over anhydrous Na_2SO_4 and dichloromethane evaporated under vacuum to dryness. The crude product was passed through a column of silica gel using 1:4 hexane / dichloromethane, gradually increasing to 1:9 hexane / dichloromethane mixture to give hydroxy derivative. The compound (**2)** was obtained as a pale yelow oil (1.51 g) [35].

3.3. Synthesis of 2,2-bis[methyl (2-bromopropionato)] propionyl chloride

In a three-neck flask equipped with magnetic stirrer, 2,2-bis [methyl (2-bromo propionato] propionic acid (5 g, $1.2x10^{-2}$ mol) was dissolved in benzene (50 mL). Phosphoruspenta chloride (3 g, $1.4x10^{-2}$ mol) was then added. The solution was kept under stirring at room temparature overnight. The salts were filtred off and benzene was removed by evaporation. Hexane was added in order to remove the excess of PCl_5. The organic phase was recorved and the solvent evaporated under vacuum. A brown liquid compound (**3**) was obtained (2,74 g) [36].

3.4. Synthesis of 2-phenyl-2-[(2,2,6,6-tetramethyl)-1-piperidinyloxy]ethyl 2,2-bis[methyl(2-bromopropionato)] propionate, (4)

To a round-bottom flask were added 2-phenyl-2-[(2,2,6,6-tetramethylpiperidinyloxy]-1-ethanol (**2**) (1.2 g, 4.32 mmol), triethylamine (Et_3N) (1 mL, 7.16 mmol), and 20 mL of dry tetrahydrofuran (THF). To the reaction mixture, stirred at 0-5 ^{0}C was added drop wise 2,2-bis [methyl (2-bromopropionato)] propionyl chloride (**3**) (2.7 g, 6.39 mmol) in 10 mL of dry THF over a period of a half hour. The reaction mixture was stirred at room temperature overnight. The salt was removed by filtration and after THF evaporation, the crude product was dissolved in dichloromethane and washed with excess Na_2CO_3 aqueous solution (5 %) and water. Then dried over anhydrous Na_2SO_4, dichloromethane was removed and the crude ester was passed through a silica gel column prepared with 1:1 hexane / dichloromethane. The resulting material was obtained as a pale yelow oil (2.41 g, 62 %).

3.5 Synthesis of star Polystyrene macroinitiators

Polystyrene (PSt) macroinitiator was prepared by SFRP of styrene and **4** as an dual (trifunctional) initiator at 125 ^{0}C. The reaction mixture in a Schlenk tube was degassed by three freeze-pump-thaw cycles, left under vacuum and placed in a thermostated oil bath at given temperature. After the polymerization, the reaction mixture was diluted with THF and precipitated in methanol and then isolated by vacuum filtration.

3.6. Synthesis of star diblock copolymers

Poly(St-b-tBA) diblock copolymer was prepared by ATRP of tBA using CuBr / N,N,N’,N’’,N’’,-pentamethyldiethylenetriamine (PMDETA) as catalyst and polystyrene as macroinitiator at 80 ^{o}C. To a Schlenk tube equipped with magnetic stirring bar, the degassed monomer, ligand, catalyst, initiator were added in the order mentioned. Tube was degassed by three freeze-pump-thaw cycles, left under vacuum and placed in a thermostated oil bath at given temperature. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and unreacted monomer was evaporated under reduced pressure. The resulting polymer was dissolved in THF, precipitated from excess of methanol / water (80/20; v/v) and then isolated by vacuum filtration.

3.7 Synthesis of star triblock copolymers

Star-shaped triblock copolymer synthesized by SFRP-ATRP-ATRP route. Triblock copolymer was prepared by ATRP of MMA using CuCl / PMDETA as catalyst, diphenylether (DPE) (MMA/DPE=1,v/v) and poly(St-*b*-tBA) diblock copolymer as macroinitiator. The reaction mixture was degassed and polymerized at 80 ^{0}C for given times. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and unreacted monomer was evaporated under reduced pressure. The resulting polymer was dissolved in THF, precipitated from excess of methanol / water (80/20; v/v) and then isolated by vacuum filtration.

3.8 Characterization of star homopolymers and block copolymers

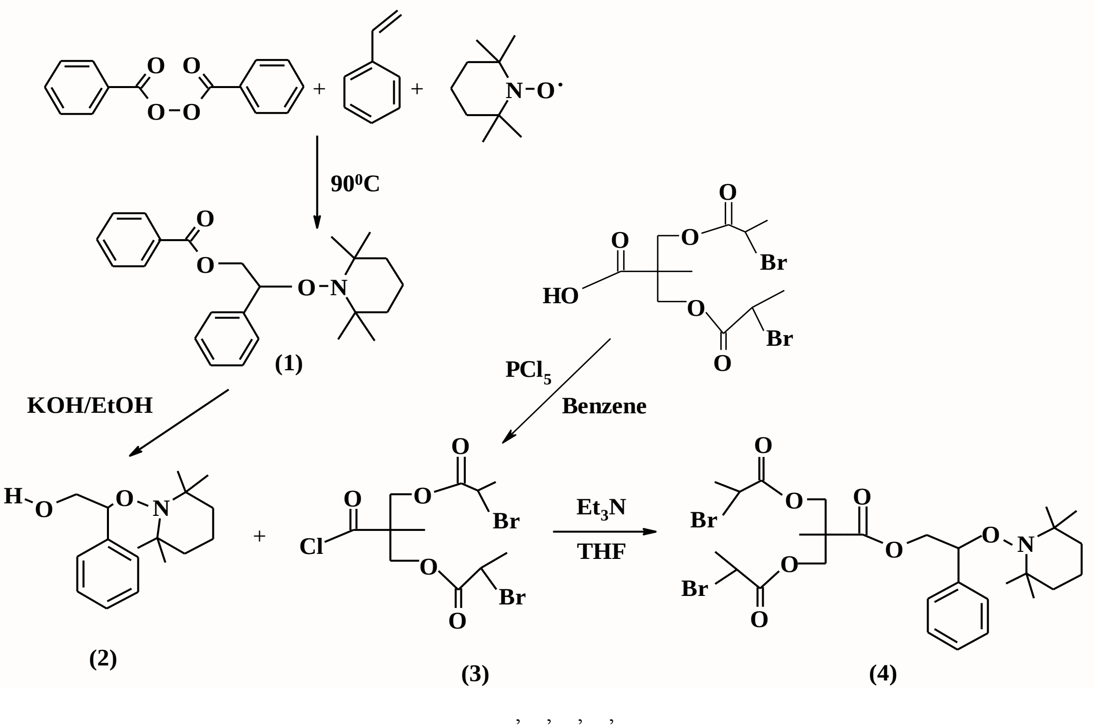
The ^{1}H-NMR spectra were recorded on a Bruker spectrometer (250 MHz for proton) in $CDCl_3$ solution using tetramethylsilane as an internal standart. The number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) were determined by Gel Permeation Chromatography (GPC). GPC analyses were performed with an Agilent Model 1100 instrument consist of pump and refractive-index detector and four Waters Styragel Columns (HR 5E, HR4E, HR 3, and HR 2). THF was used as eluent at a flow rate of 0.3 mL / min at 30 ^{0}C. The molecular weight of the polymers was calculated with the aid polystyrene standards. All polymers obtained were dried under vacuum for 24 h and the conversions were determined by gravimetrically.

4. RESULTS AND DISCUSSIONS

4.1 Synthesis of Initiator

4.1.1 Synthesis of 2-phenyl-2-[(2,2,6,6tetramethyl)-1-piperidinlyoxy] ethyl 2,2–bis[methyl(2-bromopropionato)] propionate, (4)

The dual (trifunctional) initiator (**4**) was synthesized from TEMPO alcohol and corresponding acid chloride in ca 62% yield. The synthesis of initiator is shown scheme 4.1.



Scheme 4.1 Synthesis of 2-phenyl-2-[(2',2',6',6'tetramethyl)-1-piperidinlyoxy] ethyl 2,2–bis[methyl(2-bromopropionato)] propionate, (**4**)

First, 2-phenyl-2-(2,2,6,6-tetramethylpiperidinyloxy)-1-ethanol (**2**) was synthesized from the reaction of BPO (benzoyl peroxide) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), in styrene at 90-95 ^{0}C [36]. It was then hydrolyzed with aqueous potassium hydroxide to give TEMPO alcohol in quantitative yield. Second, 2,2–bis[methyl (2-bromopropionato] propionyl chloride (**3**) was prepared from 2,2–bis[methyl(2-bromopropionato)] propionic acid and PCl_5 in benzene. Third, the initiator (**4**) was synthesized. The obtained initiator (**4**) was characterized by ^{1}H- NMR. The ^{1}H-NMR spectra of the initiator showed no signal corresponding to OH protons of the starting TEMPO alcohol (Figure 4.1). According to the spectra, a peak was seen at 1.3-1.5 ppm (6H, CH_2), b peak was seen at 4.92 ppm (1H, C*H*H), c peak was seen at 7.26-7.32 ppm (5H, ArH), d,e,f peaks were seen at 4.07-4.54 ppm (1H C*H*H, 2H CH_2), g peak was seen at 1.72-1.82 ppm [3H, $CH(CH_3)$].

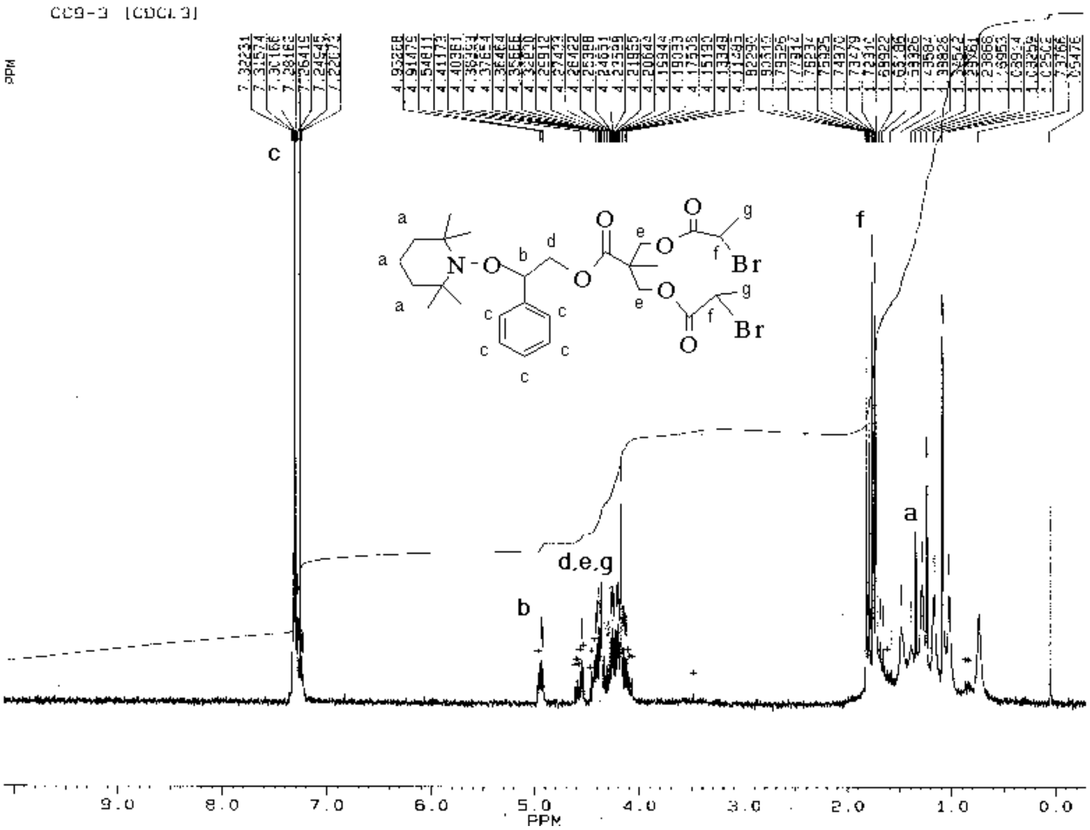
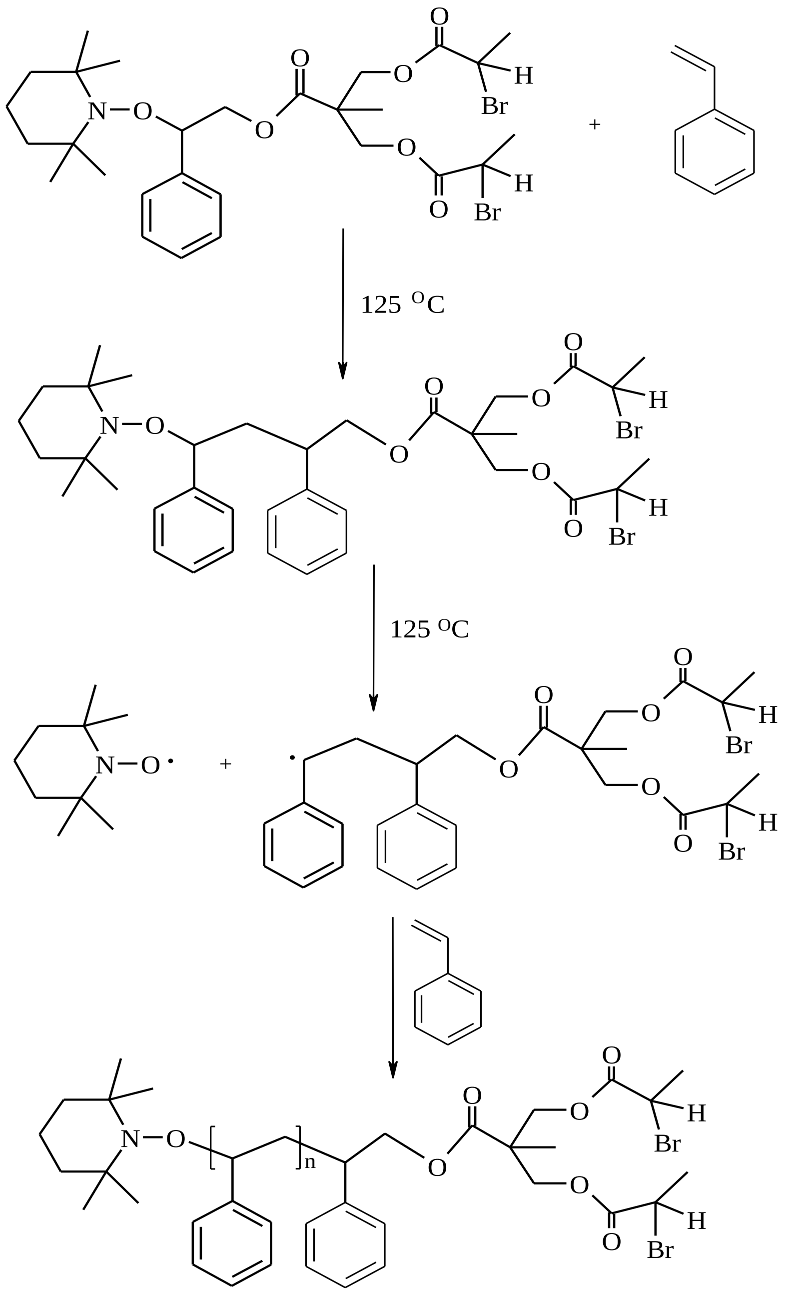


Figure 4.1 The ^{1}H-NMR spectra of the initiator (**4**), 2-phenyl-2-[(2,2,6,6tetramethyl)-1-piperidinlyoxy] ethyl 2,2–bis[methyl(2-bromopropionato)] propionate.

4.2 Synthesis of Star PSt macroinitiators

2-phenyl-2-[(2,2,6,6tetramethyl)-1-piperidinlyoxy] ethyl 2,2–bis [methyl (2-bromo propionato)] propionate (**4**) was used to perform the SFRP of styrene. SFRP of styrene was carried out in bulk at 125 ^{0}C.

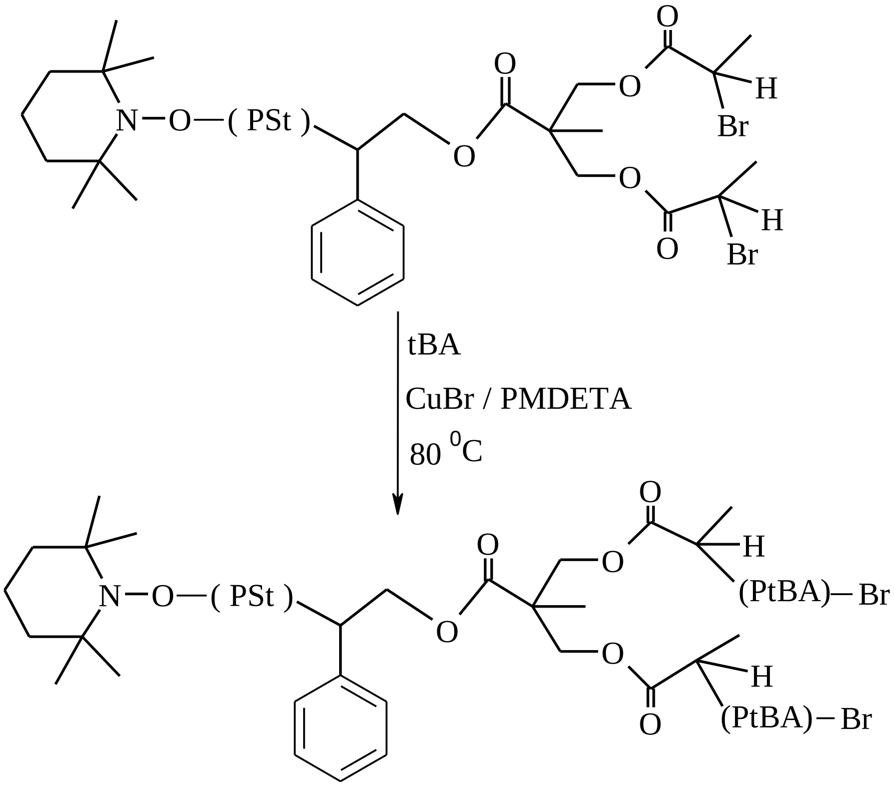


Scheme 4.2 SFRP of styrene as a schematic representation.

PSt macroinitiators with different molecular weights were prepared by various initial monomer / initiator ratio. The results and conditions are tabulated in Table 4.1. The experimental molecular weights were determined by GPC. The experimental molecular weights are in good agreement with theoretical molecular weights calculated from $M_{n,theo} = [M]_0 / [I]_0 \times \text{conv} \% \times M_w(\text{St})$.

4.3. Syntheses of star block copolymers via SFRP-ATRP-ATRP route.

The syntheses of star diblock copolymers consisting of St and tBA segments were prepared by ATRP of tBA using CuBr / PMDETA as a catalyst and bromine-ended PSt as macroinitiators. The polymerization were conducted at 80 ^{0}C. Synthesis of star PS-PtBA diblock copolymers were shown in scheme 4.3.



Scheme 4.3 Synthesis of star poly(St-*b*-tBA) diblock copolymer using polystyrene as macroinitiator.

The results and other conditions are given in Table 4.2. As can be seen from Table 4.2, the experimentally obtained molecular weight is in a good agreement with theoretical molecular weight calculated from $M_{n,\ theo} = [M]_0 / [I]_0 \times conv\ \% \times M_w (tBA) + M_{w\ macroinitiator}$ for all cases. A good agrement was observed between the theoretical molecular weights and calculated ones from ^{1}H-NMR, where GPC values deviated from each.

Figure 4.2 and Figure 4.3 shows GPC traces of macroinitiator and diblock copolymer. The peak corresponding to diblock copolymer clearly shifted to higher molecular weight region of the chromatogram indicating that both the chain-end functionality of macroinitiator and the blocking efficiency were high. The absence of the PSt macroinitiator peak on the resulted block copolymer indicates the complete conversion of the macroinitiator to the block copolymer.

Table 4.1 Syntheses of PSt Macroinitiators via SFRP.

Run	Monomer	$[M]_o$mol l^{-1}	$[M]_0/[I]_0$	Initiator	Time (min)	Conversion (%)	Solvent	Mn_{theo}	Mn_{GPC}	Mn_{Hnmr}	M_W/M_n
PI[a]	St	8.73	300	**1**	1800	61	-	19100	20400	-	1,28
PII[a]	St	8.73	300	**1**	1680	39	-	12300	12600	-	1,20
PIII[a]	St	8.73	300	**1**	1680	39	-	12200	13200	-	1,13
PIV[a]	St	8.73	100	**1**	1260	32	-	3400	4200	-	1,18

a) The polymerization was carried out at 125^0C.

Table 4.2 Syntheses of star diblock copolymers via ATRP.

Run	Monomer	$[M]_o$mol l^{-1}	$[M]_0/[I]_0$	Initiator	Time (min)	Conversion (%)	Solvent	Mn_{theo}	Mn_{GPC}	Mn_{Hnmr}	M_W/M_n	Composition ^{1}H NMR
PV[b]	tBA	6.83	500	PI	360	40	-	45500	47700	56300	1,23	%34 PSt, %66 PtBA
PVI[b]	tBA	6.83	200	PI	300	51	-	33600	35900	40500	1,33	%41 PSt, %59 PtBA
PVII[b]	tBA	6.83	300	PII	300	50	-	32000	59700	48000	1,16	%21 PSt, %79 PtBA
PVIII[b]	tBA	6.83	550	PIII	330	24	-	30600	45400	36200	1,18	%26 PSt, %74 PtBA

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

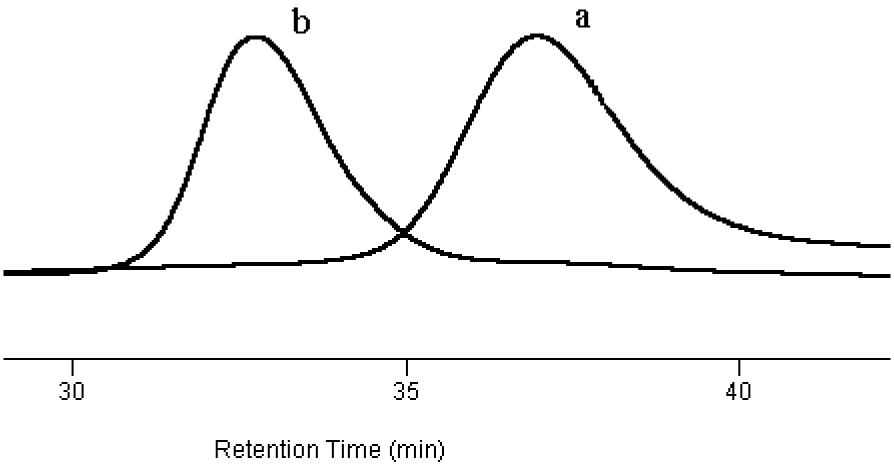


Figure 4.2 GPC traces of Star PSt homopolymer (P II) (a), Star PSt-PtBA diblock copolymer (P VII) (b).

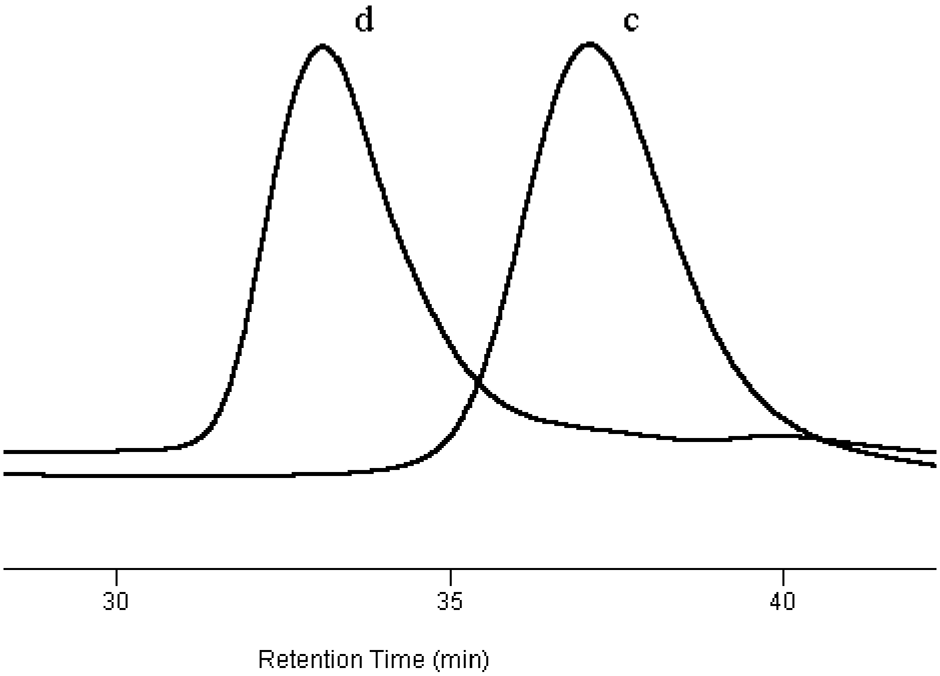


Figure 4.3 GPC traces of Star PSt homopolymer (P III) (c), Star PSt-PtBA diblock copolymer (P VIII) (d).

The composition and molecular weight of diblock copolymers were determined via ^{1}H-NMR measurement (Figure 4.4). ^{1}H-NMR spectra of all poly(St-*b*-tBA) block copolymers exhibit major peaks that are characteristic of the PSt and PtBA segments. Integrating the signal between 6.5 and 7.0 ppm PSt (aromatic protons) and 1.43 ppm of PtBA [$C(CH_3)_3$] allowed us to evaluate the composition of diblock copolymer.

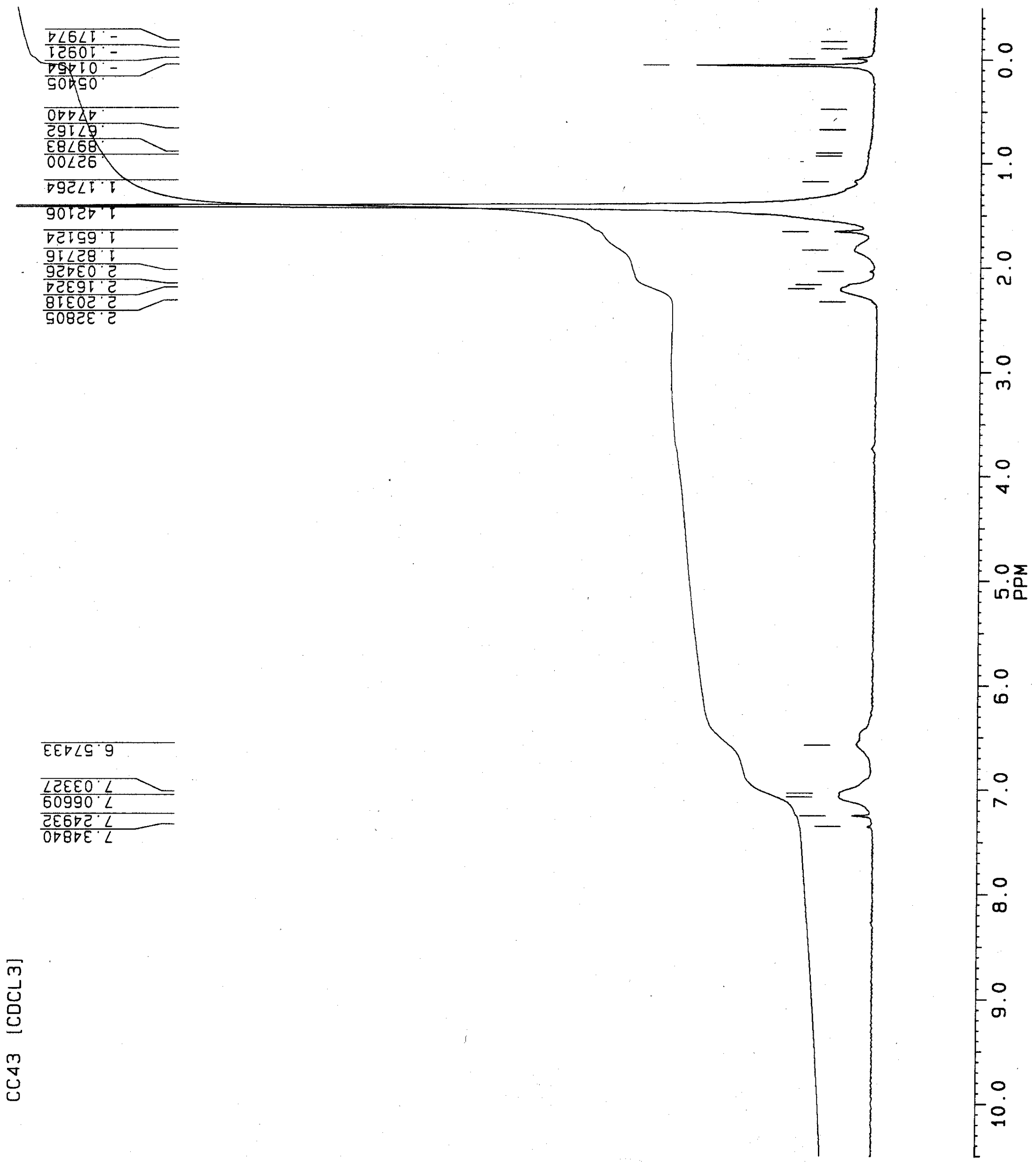
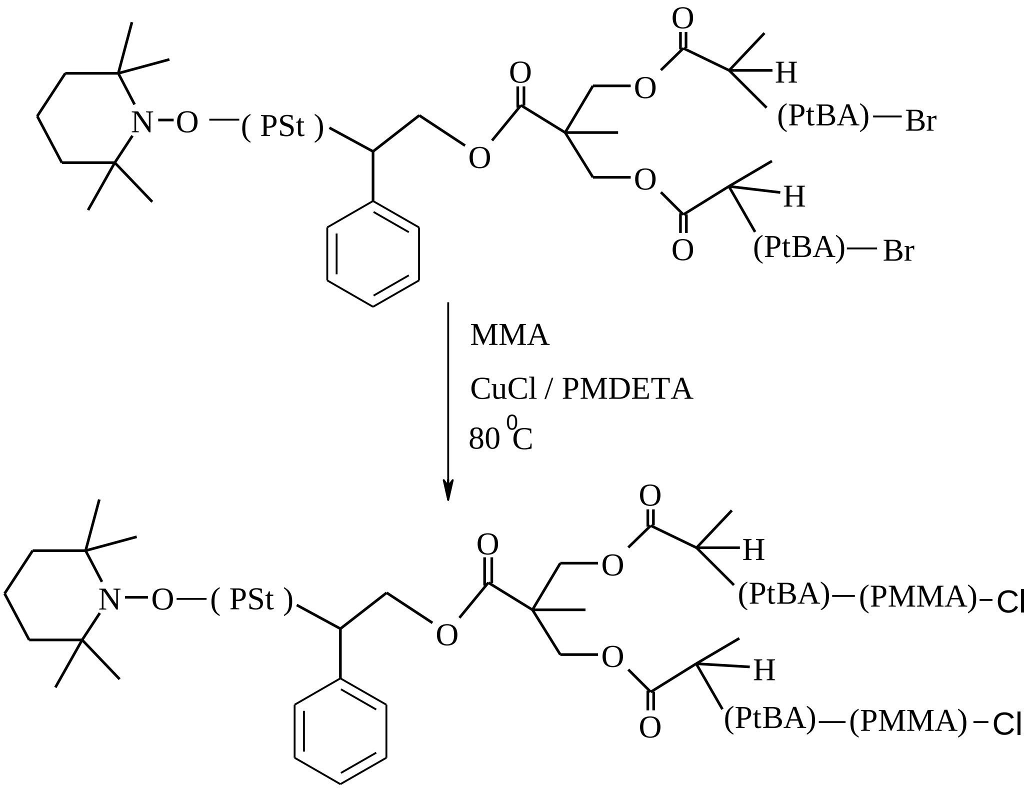


Figure 4.4 The ^{1}H-NMR spectra of star PSt-PtBA diblock copolymer.

The obtained diblock copolymers were extended via ATRP of MMA using CuCl / PMDETA as a catalyst to afford star triblock copolymers. The ATRP of MMA was carried out at 80 ^{0}C in DPE solution (MMA / DPE = 1; v/v). Synthesis of star triblock copolymer via SFRP-ATRP-ATRP route was illustrated in Scheme 4.4.



Scheme 4.4 Synthesis of star triblock copolymer via SFRP-ATRP-ATRP route.

The experimental conditions and properties of star triblock copolymers were given in Table 4.3. Again, the GPC values deviate from the theoretically calculated molecular weights and those determined by ^{1}H-NMR.

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

Run	Monomer	$[M]_o$mol l^{-1}	$[M]_0/[I]_0$	Initiator	Time (min)	Conversion (%)	Solvent	Mn_{theo}	Mn_{GPC}	Mn_{Hnmr}	M_W/M_n	Composition ^1H NMR
PIX[c]	MMA	9.34	1200	PV	240	61	DPE	121000	100900	103400	1,29	%12 PSt, %24 PtBA, %64 PMMA
PX[c]	MMA	9.34	500	PVI	300	37	DPE	54500	60500	74000	1,38	%18 PSt, %26 PtBA, %56 PMMA
PXI[c]	MMA	9.34	300	PVII	240	57	DPE	77000	85000	70000	1,16	%9 PSt, %32 PtBA, %59 PMMA
PXII[c]	MMA	9.34	300	PVIII	240	68	DPE	66000	79000	68500	1,29	%10 PSt, %28 PtBA, %62 PMMA

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

The GPC trace of triblock copolymer is shown in Figure 4.5 and Figure 4.6 together with the diblock copolymer and homopolymer. The clear shift was observed from GPC traces of triblock copolymers implying that successive formation of triblock copolymer.

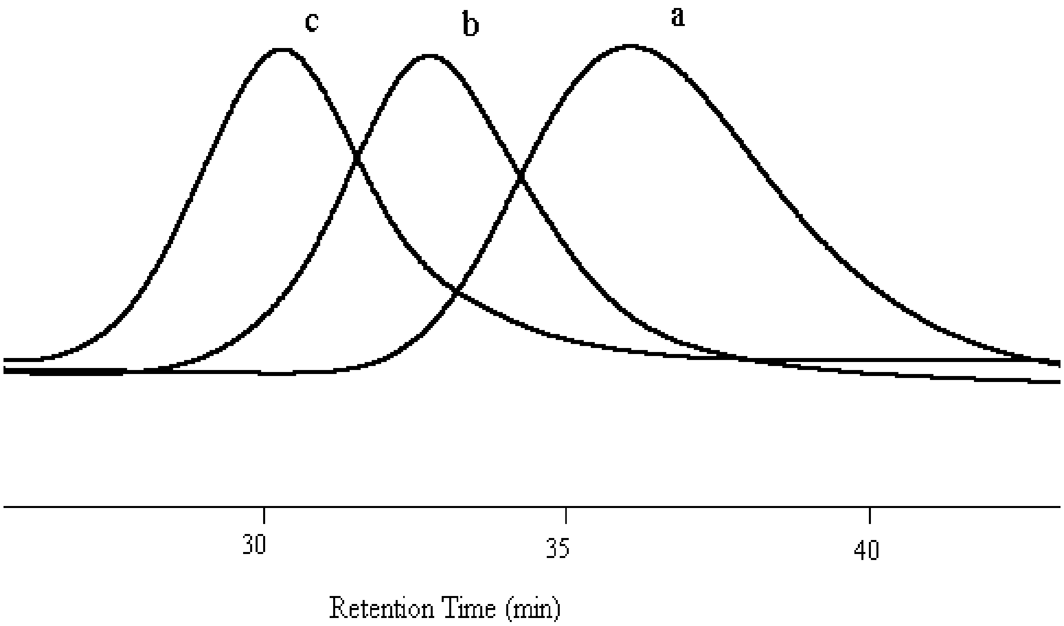


Figure 4.5 The comparison between the GPC traces of Star PSt homopolymer (P I) (a), Star PSt-PtBA diblock copolymer (P VI) (b), and Star PSt-PtBA-PMMA triblock copolymer (P X) (c).

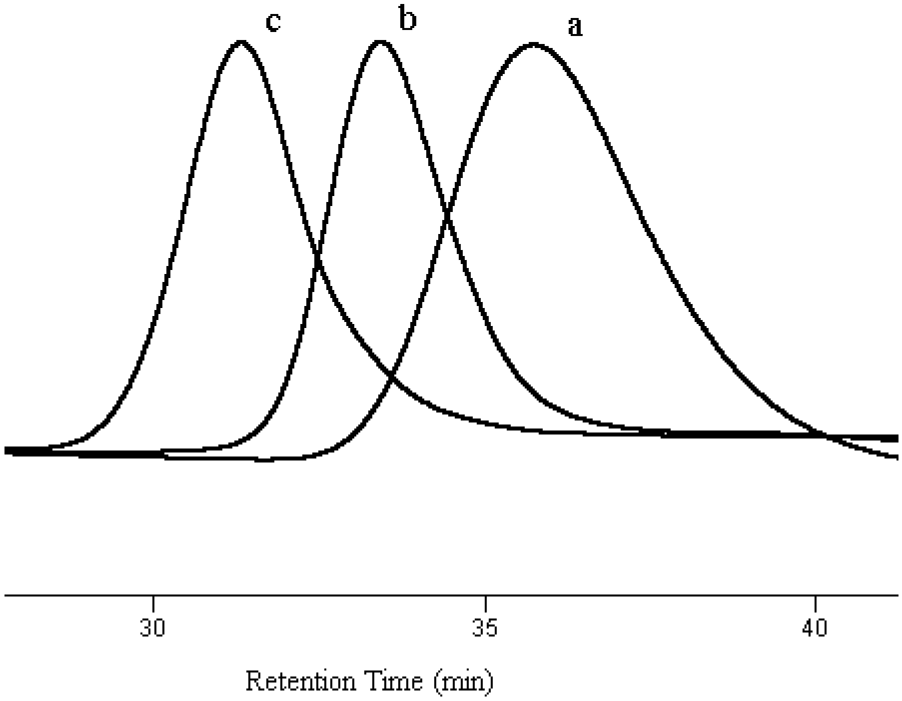


Figure 4.6 The GPC traces of Star PSt homopolymer (P I) (a), Star PSt-PtBA diblock copolymer (P V) (b), and Star PSt-PtBA-PMMA triblock copolymer (P IX) (c).

The GPC values deviate from theoretically calculated molecular weights and those determined by ^{1}H-NMR (Figure 4.7) both of which however are in good agreement. Integrating the signal 1.43 ppm PtBA [$C(CH_3)_3$] and 3.58 ppm of PMMA ($-OCH_3$) allowed us to evaluate the composition of triblock copolymer.

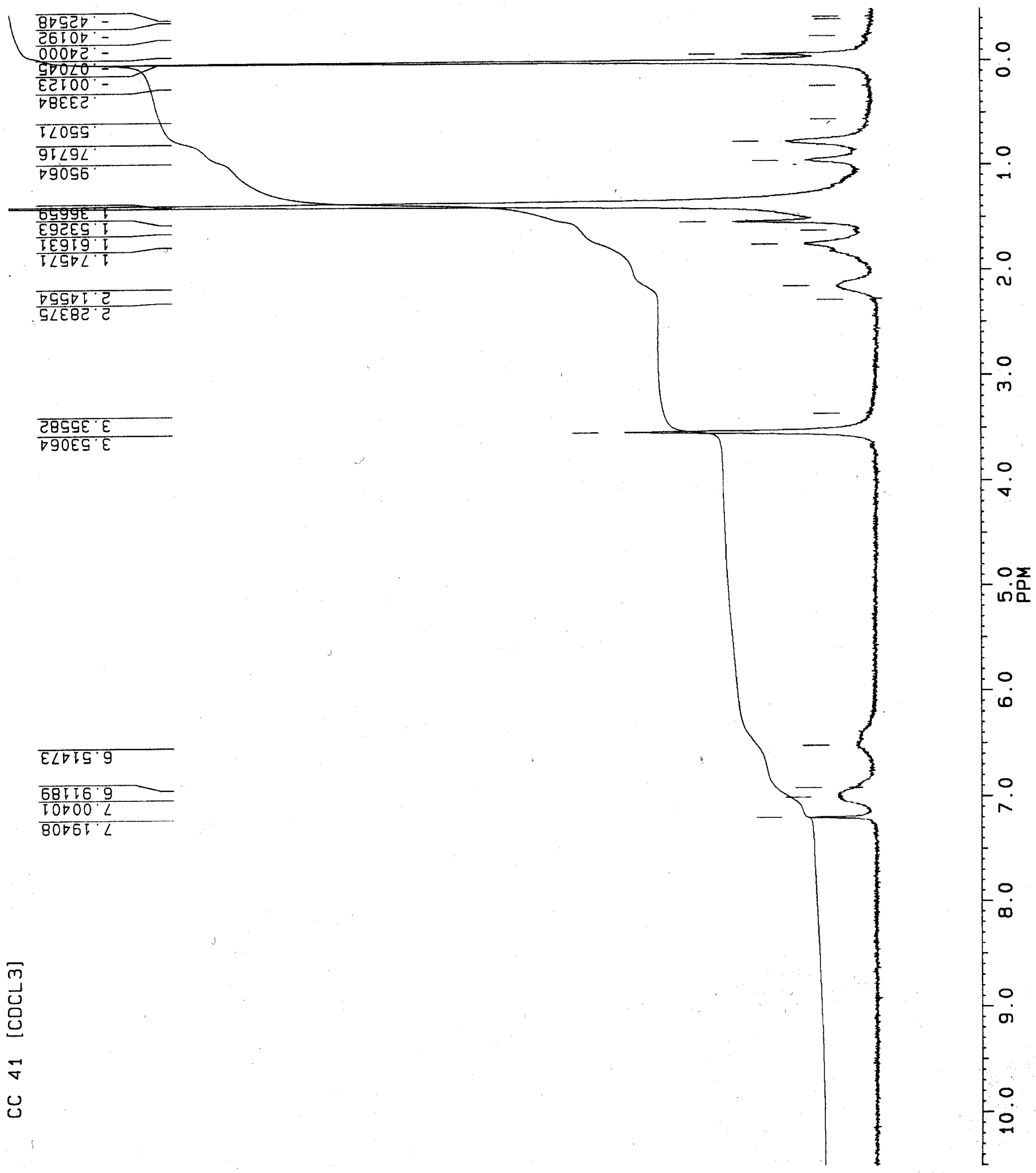


Figure 4.7 The ^{1}H-NMR spectra of star PSt-PtBA-PMMA triblock copolymer.

5. CONCLUSIONS AND RECOMMENDATIONS

In conclusion, dual (trifunctional) initiator 2-phenyl-2- [(2,2,6,6-tetramethyl)-1-piperidinyloxy] ethyl 2,2-bis [methyl(2-bromopropionato] propinate (**4**) was synthesized and successfully used in the preparation of stars and star block copolymers having PSt-PtBA-PMMA segments via SFRP-ATRP-ATRP route.

In this route, the CuCl / PMDETA catalyst was used to enhance the rate of cross-propagation where bromine-ended PtBA was used as macroinitiator for MMA polymerization. Therefore, high blocking efficiency was achieved during the synthesis of star block copolymers.

In our study, ATRP-ATRP-SFRP route was not utilized in the preparation of star block copolymers. This route was less efficient in the preparation of star triblock copolymer because some TEMPO-end functionality might be lost during the first two ATRP sequences.

According to the analysis, the observed molecular weights of stars and star block copolymers measured by GPC were in reasonably agreement with the theoretical molecular weight and calculated from those of ^{1}H-NMR. Stars and star block copolymers of well defined structure with predetermined block lengths and low polydispersity were obtained.

These studies are showed that controlled / ’living’ polymerization techniques are useful methods in order to prepare stars and star block copolymers.

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