ARCHITECTURAL AND STRUCTURAL CONTROL OF POLYMERIZATION BY NOVEL FREE RADICAL PROCEDURES

by

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ABSTRACT

Recent discovery of nitroxy mediated radical polymerization (NMRP) opens an opportunity for making new classes of materials previously inaccessible by conventional methods. The key to the successful application of NMRP technology is through the use of appropriate alkoxyamine initiators. This thesis concentrated on two areas: 1. The preparation and study of the efficiency of different functionalized alkoxyamine initiators for NMRP; 2. The use of those initiators to prepare different block copolymers.

The synthesis of various functionalized alkoxyamine initiators are described. It was found that initiators synthesized at low temperature with di-*t*-butylperoxyoxalate significantly improved the yield. The efficiencies of these initiators were studied for styrene polymerization in terms of monomer conversion, molecular weight and polydispersity of the polymer. It was demonstrated that alkoxyamines bearing acetoxy or *t*-boc groups at the *para*-position of 1-(2,2,6,6-tetramethylpiperidinyloxy)ethylbenzene behave normally as NMRP initiators while alkoxyamines having a *t*-butoxy group adjacent to the alkoxyamine group is less reactive presumably due to steric hindrance of styrene insertion into the alkoxyamine bond. In addition, a difunctional initiator with alkoxyamine groups symmetrically located at each end of a carbonate bond was synthesized to compare its efficiency to its mono-functional counterpart. Investigation of the polymerization kinetics along with molecular weight analyses revealed that polymer chain growth on both alkoxyamine sites of the difunctional initiator was equivalent.

In the second part of the thesis, the work focused on the preparation of block copolymers of polystyrene (PS) and polycarbonate (PC) using the combination of NMRP and step-growth polymerization. PS bearing *t*-boc end-groups was first prepared using *t*-boc-functionalized alkoxyamine initiators. Hydrolysis of the *t*-boc group on the PS chain-end to form reactive phenolate groups enables the functionalized PS to act as a macro chain terminator during the synthesis of bisphenol A polycarbonate, resulting in the formation of PS-*bl*-PC-*bl*-PS triblock copolymer. Two PS-*bl*-PC-*bl*-PS copolymers with different block lengths (M_n = 7,000-23,000-7,000 and 7,000-5,200-7,000) were prepared. TEM showed distinct microphase separation of PS and PC providing strong evidence of block copolymer formation. DSC analysis od the copolymer with high PC content showed two T_gs at 107 °C and 145 °C, respectively. An inward shift of the T_gs from that expected for the respective blocks indicates partial miscibility between PS and PC. The block copolymer with low PC content showed only one T_g at 107 °C implying PS and PC segments exhibits substantial miscibility. Finally, an alternative route to the preparation of PS-*bl*-PC-*bl*-PS was pursued. Alkoxyamine terminated PC was prepared and subsequently used as a macroinitiator for NMRP of styrene to form PS-*bl*-PC-*bl*-PS triblock copolymers. The use of alkoxyamine terminated PC as a macroinitiator for NMRP of styrene demonstrated that it is as effective as conventional alkoxyamine initiators for styrene polymerization and that the copolymerization was efficient.

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DEDICATION

To my husband John , my son Kevin, my daughter Michelle and my parents.

CHAPTER 1: INTRODUCTION

The control of macromolecular structure is important to obtain new materials with improved physical properties. Traditionally, the viable techniques that have offered appreciable control over polymer structure are living anionic and cationic polymerizations.[1] However, the versatility of living ionic polymerizations is practically limited due to the incompatibility of ionic chain ends with monomers containing certain functional groups.[2] In addition, ionic polymerization demands rigorous exclusion of water and oxygen along with using ultrapure reagents in the process that further reduces its general applicability for commercial purposes.

In many respects, free radical polymerizations follow much less stringent conditions compared to living ionic polymerizations. Free radical polymerization is synthetically robust and compatible with monomers containing a wide range of functional groups. Nevertheless, free radical polymerization offers little or no control over polymer structure.[3] Over the years, attempts have been made by a number of research groups around the world to combine the control of living ionic polymerization with the advantages of free radical polymerization to control macromolecular structure more simply.[4,5] In 1993, the first major success toward the goal was achieved by Georges *et al.*, using what was termed living free radical polymerization.[6] For the first time, the preparation of polystyrene with low polydispersity was reported by performing the polymerization in the presence of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and

benzoyl peroxide. The living character of the free radical polymerizations has been demonstrated by a linear increase of molecular weight of polystyrene with monomer conversion. The experiments also showed purification of the monomer was not necessary in contrast to living ionic polymerizations. Following this milestone work, living free radical polymerization has become one of the hottest topics in polymer chemistry as a new route to effectively prepare polymers with controlled architectures. [7,8,9,10]

This thesis will discuss the background that led to the discovery of living (or controlled) free radical polymerization as well as some of the initial research in the living free radical polymerization area. This section of the thesis is not meant to be exclusive, but is meant to provide some background into the field. The background will be followed by presentation of the objectives of the original research performed by the author. The subsequent chapters are divided into the sections that describe the research that was performed to fulfill the objectives.

1.1 Free Radical Chain Polymerization

The free radical polymerization process is a mainstay in the synthetic polymer industry. Robust and economical, it accounts for about fifty percent of mass-produced polymers.[11] Free radical polymerization gains its prevalence from its ability to be applied to a wide variety of vinyl and diene monomers and its relative insensitivity to solvent impurities, especially water.

In a typical free radical polymerization process, active polymer chains are initiated, propagated, and terminated in a very short period of time (typically, in a matter

of a few seconds). A typical free radical polymerization includes three elementary reactions:

- Initiation of the active monomer
- Propagation or growth of the active (free-radical) chain by sequential addition of monomers
- Termination of the active chain to give the final polymer product

Initiation in a free radical polymerization consists of two steps. The first step is the formation of radicals typically via the homolytic cleavage or decomposition of the initiator (Equation 1). This step is then followed by the reaction of these primary radicals with monomer to generate the first growing species (Equation 2).

$$I - I \xrightarrow{k_d} 2I\cdot \qquad 1$$

$$I\cdot + M \xrightarrow{k_0} P_1\cdot \qquad 2$$

In the above equations, I-I is an initiator, I· is an initiator (or primary) radical, M is a monomer, P_1 is a growing polymer chain, k_d is a dissociation rate-constant and k_0 is a propagation rate constant. Typically k_0 is much higher than k_d. The dissociation rate-constant follows an Arrhenius equation,

$$k_d = A\exp(E_a / RT) \qquad 3$$

where E_a is the activation energy for dissociation. In addition to a strong dependence on the temperature, dissociation rate-constants for different initiators vary with the nature of the system. Initiators for free-radical polymerization include many organic compounds with a labile group, such as an azo (-N=N-), disufide (-S-S-), or peroxide (-O-O-). Since initiation rate is much slower than propagation ($k_d<k_o$), the decomposition of the initiator remains the rate-determining step.

The next step, the propagation step, is characterized by Equation 4.

$$P_n\cdot + M \xrightarrow{k_p} P_{n+1}\cdot \qquad 4$$

Here, $P_n\cdot$ is a growing polymeric radical, M is mononer, and k_p is the propagation rate constant. Propagation of the radical ($P_n\cdot$) through successive additions of monomer units leads to the formation of a high molecular weight polymer.

Propagation will continue until the termination step occurs. One obvious termination mechanism occurs when two propagating radicals of arbitrary molecular weight $P_n\cdot$ and $P_m\cdot$ are combined by forming a covalent bond between the two radical chains, as illustrated in Equation 5.

$$P_n\cdot + P_m\cdot \xrightarrow{k_t} P_{n+m} \qquad 5$$

Termination can also occur by a disproportionation reaction to result in two terminated chains, as illustrated in Equation 6. In this case, one terminated chain will have an unsaturated carbon-carbon bond while the other terminated end is fully saturated.

$$P_n\cdot + P_m\cdot \xrightarrow{k_{td}} (P_n+1)+(P_m-1) \qquad 6$$

In addition to termination by combination and disproportionation, another mechanism of termination is chain transfer by hydrogen atom abstraction from an initiator, monomer, polymer, or solvent, represented as SH in Equation 7. In general terms, this process may be represented as

$$P_n\cdot + SH \xrightarrow{k_{tr}} P_nH + S\cdot \qquad 7$$

As illustrated, the radical site is transferred to the chain-transfer agent SH, which can then add monomer units to continue the polymerization process. The terminated chain resulting from chain transfer then will have one or two chain-transfer moieties at the polymer ends. Chain transfer along with premature chain termination often yields polymers with a broad polydispersity.

The existence of high free radical concentrations and multiple pathways for chain termination, does not allow control of the polymer structure. The free radical polymerization method, while suitable for making homopolymer due to its favorable reaction rate and insensitivity to impurities, is generally not applicable for preparing polymers with specific structures, e.g. block copolymers.

1.2 Living Polymerization

Living polymerization has been demonstrated as a viable technology to gain good control over the molecular structure of polymers.[2] Ziegler was the first to discover

aspects of living polymerization as early as the late 1920's.[12] In the study of butadiene polymerization initiated by lithium alkyls, the reinitiation of the already "inactive" polybutadiene was observed. It was found that the molecular weight of the "inactive" polymer started to grow again as more monomer was added to the system. Unfortunately, the observation did not arouse interest because the phenomenon was considered as a result of incompletion of the polymerization and thus was not appreciated at the time.

Szwarc later demonstrated that in a batch styrene polymerization in the presence of lithum alkyls, polymerization resumed upon the addition of fresh styrene monomer.[13] The molecular weight of the newly formed polymer was higher than that of the previous one proving that active macromolecules were still capable of further chain growth. Further work based on that concept also led to the formation of polystyrene-*bl*-polyisoprene copolymers.[14]

Living polymerization systems as defined by Webster,[15] have three primary characteristics. First, assuming that the initiator is 100% efficient, the ultimate molecular weight is given by Equation 8, where DP is the degree of polymerization, $\Delta[M]$ is the concentration of monomer that has participated in the polymerization, and $[I_0]$ is the initial concentration of initiator in the system.

$$DP_n = \frac{\Delta[M]}{[I_0]} \qquad 8$$

Furthermore, the molecular weight distribution (DP_w/DP_n) is narrow and is given by Equation 9 in the ideal case.

$$\frac{DP_w}{DP_n} = 1 + \frac{1}{DP_n} \qquad 9$$

The polydispersity therefore decreases towards a value of unity as molecular weight increases. Finally, in contrast to conventional free radical polymerization reactions, where high molecular weight material is formed early in the reaction and molecular weight remains relatively constant as a function of conversion, in a living polymerization the molecular weight increase linearly with conversion.

In practice, all living polymerizations deviate to some degree from this ideal case.[15,16] For example, initiation may not occur at precisely the same time for all chains leading to a broadening of polydispersity from the ideal living case. Experimentally, the best way to evaluate whether a system is truly living can be done by studying the following characteristics:

a) linear kinetics plots in semilogarithmic coordinates ($\ln[M]_o/[M]$ vs. time), if the reaction is first order in monomer concentration; acceleration on such plots may indicate slow initiation whereas deceleration may indicate termination or deactivation of the catalyst (initiator).

b) linear evolution of molecular weights with conversion; molecular weights lower than predicted $\Delta[M]/[I_o]$ ratios indicate transfer, molecular weight higher than predicated by $\Delta[M]/[I_o]$ indicate inefficient initiation or chain coupling.

c) polydispersity should decrease with conversion for systems with slow initiation and slow exchange; polydispersity increases with conversion when the contribution of chain breaking reactions become significant.

d) end functionalities are not affected by slow initiation and exchange but they are reduced when chain breaking reactions become important.

Typical dependencies for living systems and the corresponding deviations are illustrated in Figures 1. 1. and 1.2.[17]

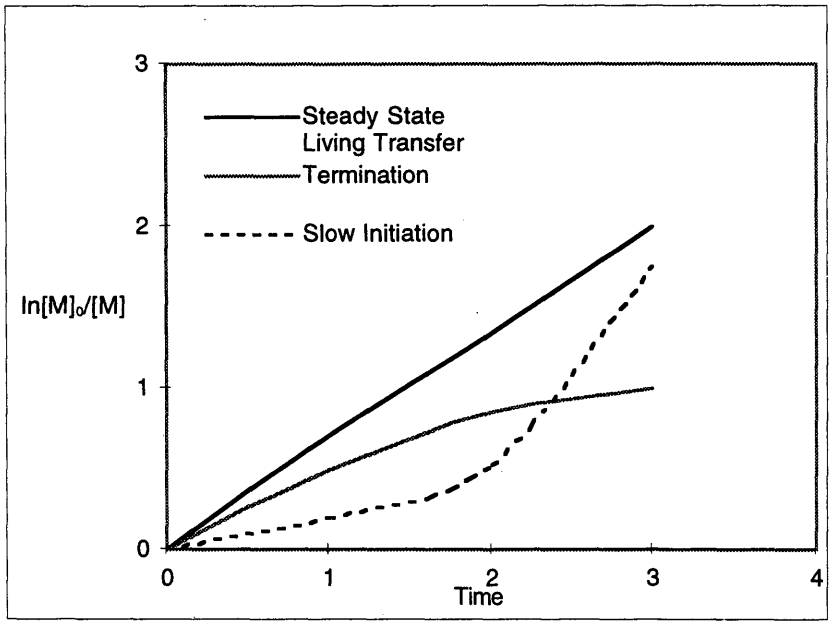


Figure 1.1. Schematic Effect of Slow Initiation, Transfer, Termination and Exchange on Kinetics

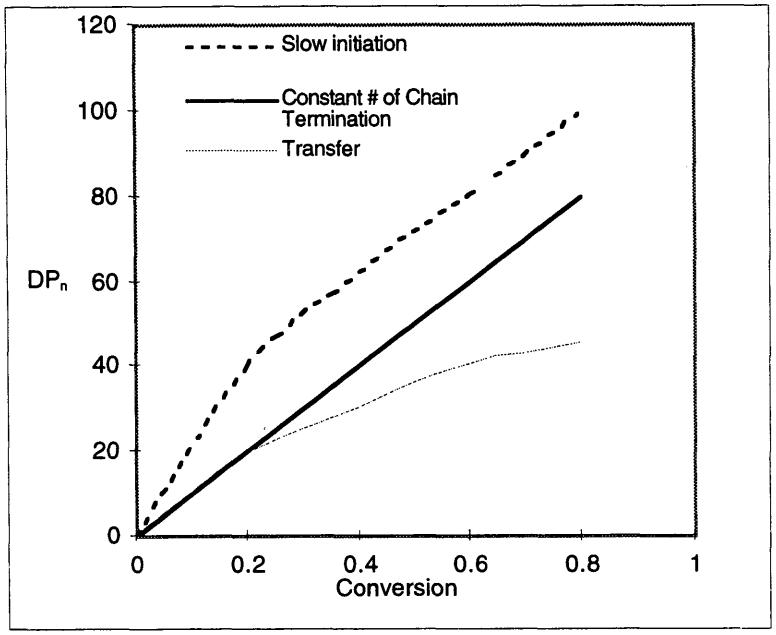


Figure 1.2. Schematic Effect of Slow Initiation, Transfer, Termination and Exchange on Molecular Weight

1.3 Living cationic polymerization

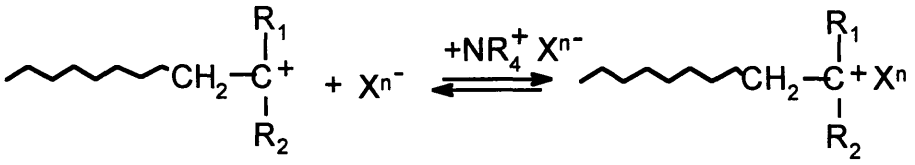
Since the discovery of living anionic polymerization in 1956 by Swarc, efforts were made to develop living cationic polymerization.[18] However success remained elusive in this field due to extremely unstable cationic species during the polymerization.[19]

Kennedy introduced the concept of *inifer*, a dual functional species that worked simultaneously as initiator and transfer agent for the living cationic polymerization.[20] This new technology allowed the control of the formation and reactivity of cationic intermediates in the initiation and propagation steps. Reversible interactions between

carbocations and nucleophiles were promoted, thus lowering the available positive charge on the reactive centers.[21,22]

These stabilizing interactions can be obtained by one, or the combination of, the following approaches:

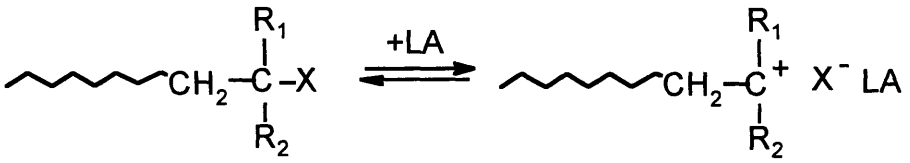
- The use of nonpolar or weakly polar solvents of the addition of a common ion salt in order to reduce the ionic dissociation of active species and suppress the contribution of free carbocations to the polymerization:



highly reactive,
uncontrolled polymerization

moderate reactive,
controlled polymerization

- The use of a suitably nucleophilic counterion able to strongly interact with the carbocation. In this case, the only ionic species formed are paired ions, which coexist in dynamic equilibrium with a large proportion of covalent species; the fast and reversible ionization of the latter polymer ends, generally obtained through a transient complexation with a weak Lewis acid (LA) used as catalyst, allows all the chains to grow at the same rate. This mechanism applies to both living and *inifer* polymerization systems.



inactive moderately active

An important feature of this *inifer* technology is its very low instantaneous concentration of propagating species that minimizes a premature chain transfer and termination. Therefore, overall polymerization rates are drastically lowered in comparison with anionic systems. The propagation rate in cationic polymerization is much slower than initiation rate, making control of molecular structure possible.

More recent research efforts have been focused on the *inifer* technique to develop well-defined telechelic polyisobutylenes,[23] polyvinylethers[24] and polystyrenes.[25] The fundamental principles of living cationic polymerization have also been applied to various alkenyl monomers. However the electrophilic/nucleophilic balance between the carbocationic species and its associated counterion has to be adjusted case by case. It is only valid for a given polymerization system and will vary with the nature of the monomer, the solvent, and the process temperature.

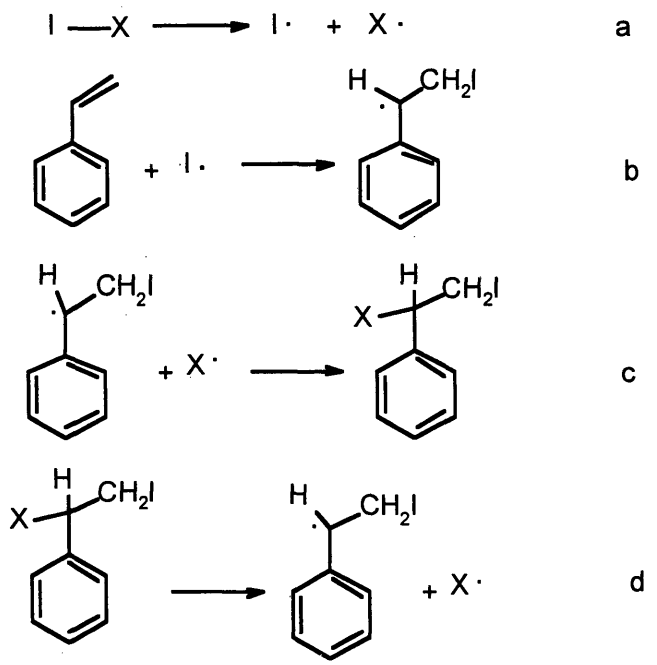
It is worth mentioning that while ionic polymerizations are a good technique to control polymer structure, the process conditions associated with the technique are quite stringent. Typically reagents need to be purified before the reaction and cryogenically obtained reaction temperatures are required. Water and air should be excluded from the polymerization to prevent quenching of the polymerization. The high cost of the process therefore limits its commercial application.

1.4 Living Free Radical Polymerization

The first evidence of controlling polymer structure using free radical polymerization was reported by Borsi, who used diaryl and triaryl protected groups in the polymerization of methyl methacrylate. It was observed that molecular weight increased with conversion. He also tried using the concept to make block copolymers.[4] The study was further extended by Braun to other systems.[26] However, Braun in many cases could not get low polydispersities and found that the molecular weights did not increase linearly with conversion. A possible reason for such deviation from living characteristics was a slow but continuous initiation by the bulky organic radicals.

In 1982 Otsu, for the first time, used the term living radical polymerization to describe a polymerization in the presence of dithiocarbamates as illustrated in Scheme 1.1.[27] In analogy to the *inifers* used in carbocationic systems by Kennedy,[28] he proposed that dithiocarbamates act as an *iniferter*, an agent functioning as *ini*tiator, trans*fer* agent, and *ter*minator. In the polymerization, which relies on preliminary photochemical initiation, the dithiocarbamate radical serves both as an initiator of new chains (reaction b) and a reversible trapping agent (reactions c and d). The bond between the terminal monomer unit of the polymer and X breaks, and another monomer or a number of monomer units add before the chain is terminated again with X. X is generally a relatively stable radical that can complex reversibly with the end of the growing chain. Chain growth starts with the breaking of a polymer-dithiocarbamate bond. Addition of monomer occurs and is then followed by termination of the thiocarbamate radical

recapping with the polymer chain. This cycle repeats itself until either 1) an irreversible termination reaction occurs (coupling, disproportionation or chain transfer); 2) the reaction stops because no monomer remains; or 3) the heat or light source is removed.

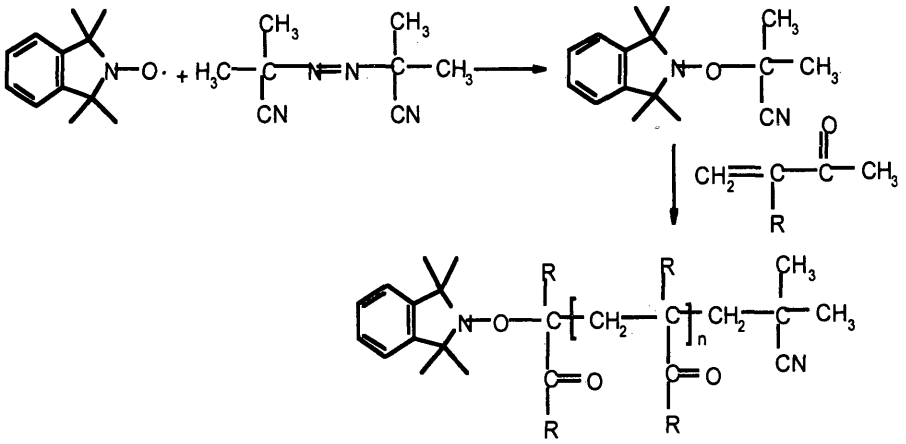


Scheme 1.1 The Mechanism of Styrene Polymerization in the Presence of Iniferter (I=X=MeNCS2)

The iniferter technology is an important milestone in the development of living free radical polymerization. It has been used quite extensively to generate end-functionalized polymers,[29] as well as functional iniferters[30] and polymeric iniferters,[31] which are used as precursors for diblock and multiblock copolymer synthesis.

A new system for controlling radical polymerizations based on nitroxide as a stable radical appeared in the patent literature in 1985.[32] Polymer molecular weight was shown to increase with monomer conversion suggesting a living free radical system. Unfortunately, the work of Rizzardo and Solomon was not sufficiently recognized at that time.[32]

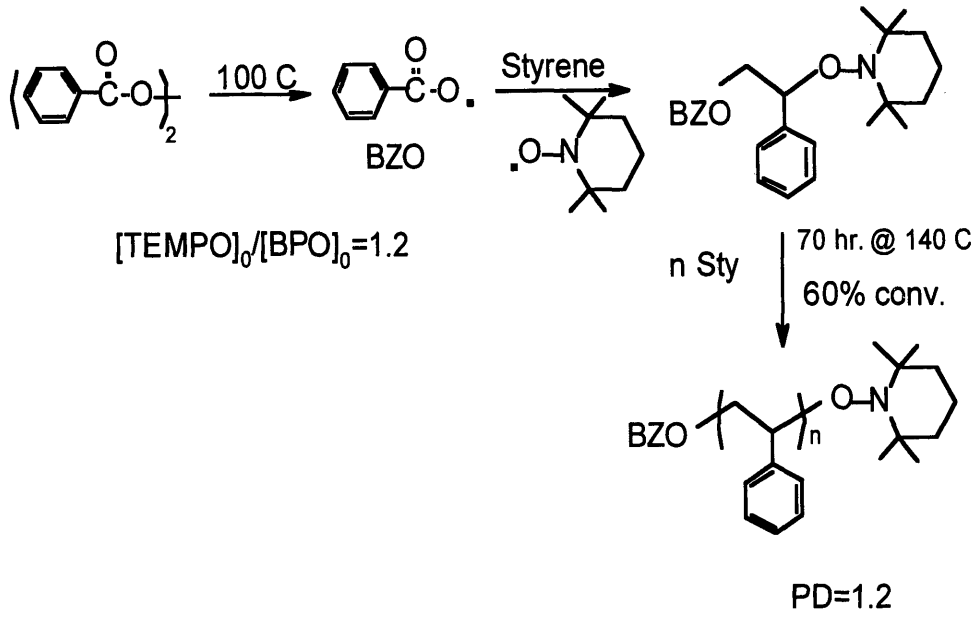
In the early 1990's, the use of long-lived acrylazoxyl radicals to moderate the polymerization of acrylates and methacrylate had been described.[33] The acrylazoxyl radicals are generated either by electron transfer between active carbon-halogen reagents with arenediazoate anions or by one-electron oxidation of arenediazoate, hyponitrite, or cyanate anion with arenediazonium ions. In the former case, the polymerization initiation species may be a succinimide radical while in the latter case it is an aryl radical. It was further reported that this method could be used for the synthesis of block copolymers of acrylates with methacrylates as shown in Scheme 1.2.



R=H or alkyl

Scheme 1.2. Living Polymerization of Acrylates and Methacrylates

In 1993, Georges reported the preparation of polystyrene with polydispersity well below the theoretical limit of 1.5 for conventional free radical polymerization in the presence of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and benzoyl peroxide.[34] Stable TEMPO free radicals were expected to moderate the polymerization by its reversible reaction with the chain end (Scheme 1.3). Reactions were conducted at a temperature at which the half-life of initiator, in this case benzoyl peroxide (BPO), was less than three minutes. Alkoxyamines were generated *in situ* from benzoyl peroxide with a small excess of TEMPO ($[TEMPO]_0/[BPO]_0=1.2$). It was anticipated that at the high temperatures (110-140 °C), carbon radicals initiated by BPO were coupled with nitroxide stable free radicals so that all active chains would be initiated at the same time.[35] It was found that the molecular weight of the polymer was proportional to the reciprocal of the concentration of alkoxyamines and molecular weights increased linearly with conversion. The observation fits well with the typical characteristics for living polymerization. Furthermore the polymers obtained had narrow molecular weight distribution of 1.1-1.3.

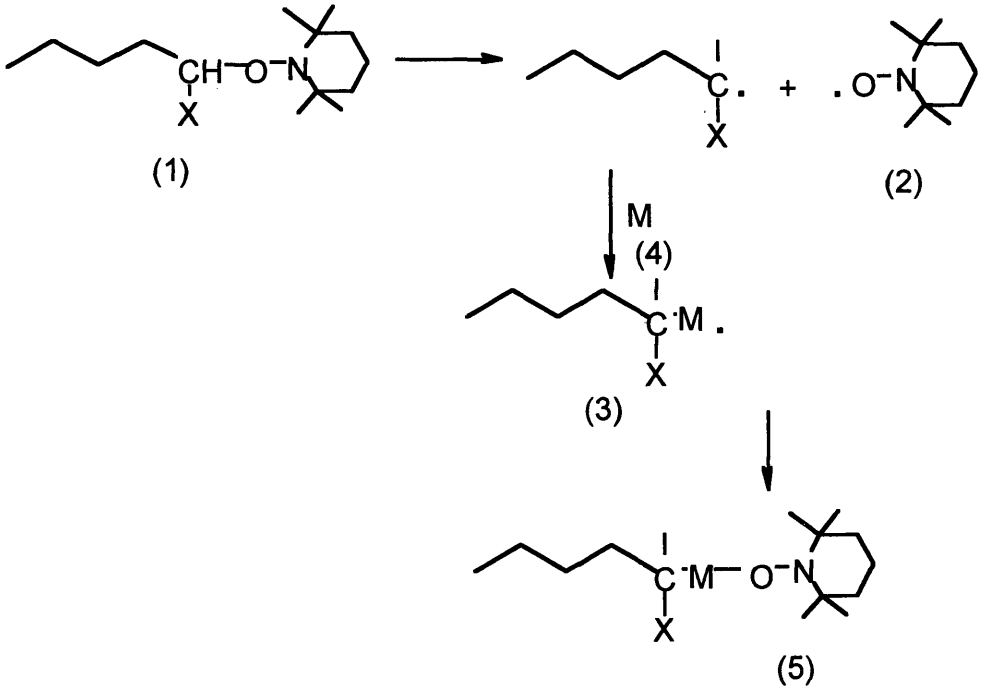


Scheme 1.3. Living Free Radical Polymerization of Styrene Initiated by Benzoyl Peroxide-TEMPO

1.4.1 The mechanism of nitroxide-mediated living free radical polymerization

The control in nitroxide mediated "living" free radical polymerization is believed to be the reversible termination of the growing polymer radical by the stable nitroxide free radical to give a dormant species in which the nitroxide moiety is covalently bonded to the polymer chain end. At lower temperatures, this trapping mechanism results in termination of the polymerization reaction as nitroxides are good inhibitors for the polymerization of vinyl monomers. However, at high temperatures, typically 100°C or greater, the C-ON bond of the alkoxyamine is homolytically unstable and undergoes

fragmentation to regenerate the stable nitroxide free radical (2) and the polymeric radical. The polymeric radical can then undergo chain extension with monomer to yield a similar polymeric radical (3), in which the degree of polymerization has increased. Recombination of a polymeric radical with the nitroxide then gives a dormant species (5) with a similar structure as (1). The cycle of homolysis/monomer addition/recombination can be repeated as illustrated in Scheme 1.4.



Scheme 1.4. The Mechanism of Nitroxide Mediated Living Polymerization

Unlike the early iniferter work, the mediating nitroxide free radical does not initiate the polymerization of vinyl monomers; therefore, no additional propagating centers are

created. The nitroxide free radical (2) does however react with the carbon centered free radical on the propagating chain (3) leading to efficient capping of the chains.[3] A favorable consequence of the presence of significant amounts of covalent, or inactive, chain ends is that the overall concentration of reactive chain ends is decreased substantially. This lowers the occurrence of unwanted side reactions such as termination (by disproportionation or combination) and enables the polymer chains to grow in a controlled fashion. It should be pointed out that the occurrence of these side reactions is not totally eliminated and it has been observed that the polydispersity increases linearly with increasing M_n.[36] Unwanted termination seems to be inevitable for radical reactions. Two growing polymer radicals readily recombine or disproportionate, in contrast to two cationic or two anionic chain ends in ionic polymerization. Since it is probably impossible to ensure total suppression of chain transfer and termination, it is essential that these processes be kept to a minimum. So in the strictest sense, the polymerizations are not truly living. For this reason, the reaction is usually termed living/controlled or "living".

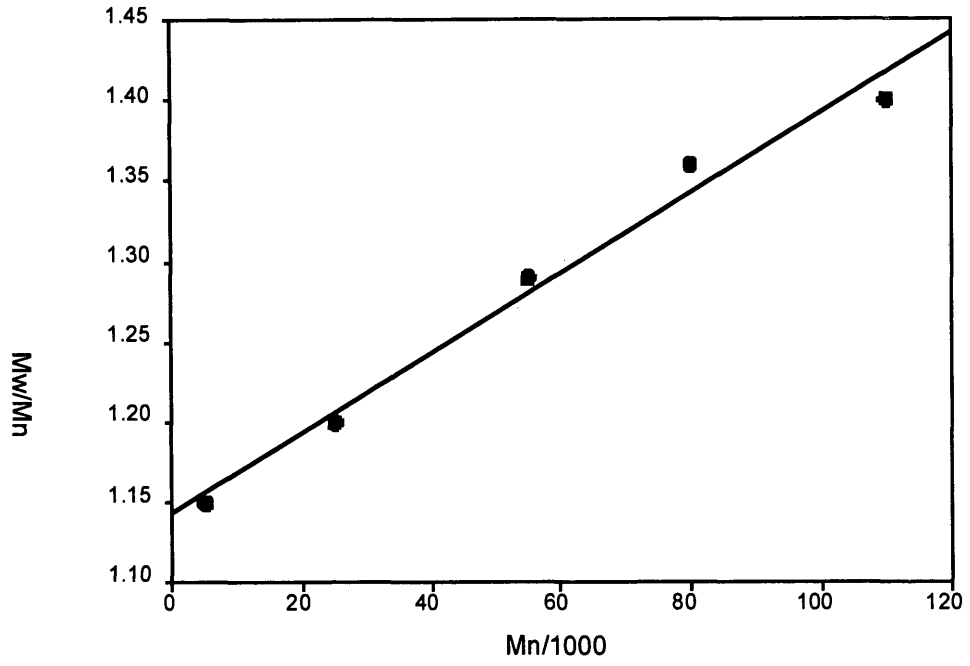


Figure 1.3. Linear Increase of Polydispersity as a Function of Increasing Number Average Molecular Weight

1.4.2 Kinetics of nitroxide-mediated living free radical polymerization

The general mechanism of living/controlled free radical polymerization is based on the reversible termination of growing radicals with a mediating group, X (for example, an alkoxyamine such as TEMPO). The reversibility allows for a large total number of chains P-X with only a small, stationary concentration of growing macromolecular radicals P· ,

$$P\cdot + X \rightleftharpoons P\text{-}X \qquad 10$$

In the ideal case, this results in the continuous growth of all chains but at a rate much slower than a "normal" radical polymerization. Propagation in this system is the reaction between growing radicals P· and monomer M (equation 11), and true termination results from a bimolecular reaction between growing radicals (P·) via coupling or disproportionation (equation 12).

$$P_n\cdot + M \rightarrow P_{n+1}\cdot \qquad 11$$

$$P_n\cdot + P_m\cdot \rightarrow P_{n+m}\ or\ (P_n^{=} + P_m - H) \qquad 12$$

The reversible reaction of Equation 10 is not considered as termination because it only temporarily deactivates growing chains. The rate of termination increases with the second power of the concentration of radicals, but the rate of propagation increases proportionally to the first power of the radical concentration.[35] Thus, the contribution of termination and the proportion of terminated chains increases with the concentration of free radicals:

$$\cdot\ R_t / R_p = k_t[P\cdot]^2 / k_p[P\cdot][M] \approx [P\cdot] \qquad 13$$

where R_t is the termination rate, k_t is the rate constant of termination, R_p is the propagation rate, and k_p is a propagation rate constant. The control of macromolecular structure requires low ratios of R_t/R_p and low [P·]. Molecular weight usually increases with a decrease in the concentration of growing species. However, this includes the

concentration of not only the active but the dormant, temporarily deactivated species as well:

$$DP \approx \Delta[M]/([P\cdot]+[P-X]) \qquad 14$$

The above equation is accurate provided that exchange between both species is fast and the contributions of termination and transfer are negligible.

1.5 Atom transfer radical polymerization

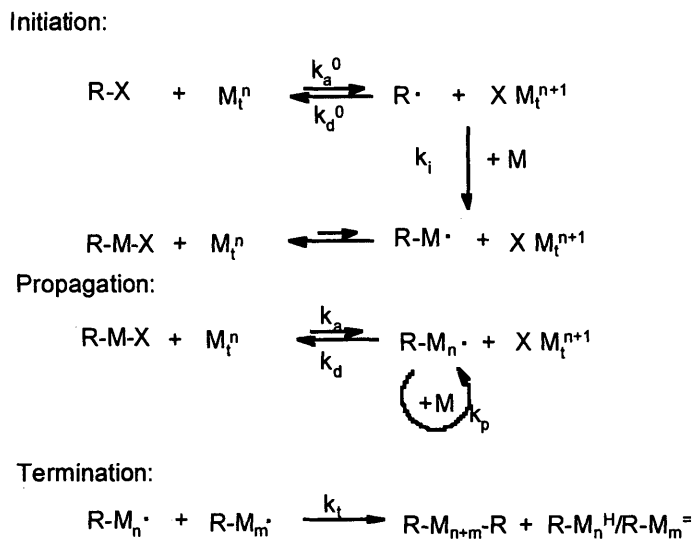
Atom transfer radical polymerization (ATRP) is emerging as an effective method for the controlled polymerization of styrene, methacrylates and other vinylic monomers.[37, 38, 39] The reaction has been developed from the Kharasch reaction used for carbon-carbon bond formation in organic synthesis. Two research groups independently reported the use of this reaction for living polymerization of vinyl monomers. Sawamoto described the use of $Ru(PPh_3)_3Br_2$ in conjunction with an alkyl chloride and an aluminum phenoxide/alkoxide activator for the living polymerization of methyl methacrylate in toluene at 60°C.[50] Matyjaszewski utilized copper (I) halides in conjunction with 2,2'-bipyridine as a complexing ligand for the controlled polymerization of styrene, methyl and butyl acrylates and methyl methacrylate.[48, 40] The reaction is approximately first order with respect to copper for 1-phenylethyl bromide and 1-phenylethyl chloride initiated styrene polymerization. The molecular weight increases with monomer conversion and polydispersity of 1.1 has been obtained with number average molecular weights up to 10,000.[45] This system has been used for preparing many end-functional polymers and macromolecules.[41] In addition, statistical, gradient, alternating, block and

graft copolymers have also been prepared by the method.[42] Control of topology has also been obtained to produce star, comb, hyperbranched, and branched copolymers.[43,44]

In ATRP a metal catalyst, usually a complex of copper (I) halide and and a complexing ligand such as 2,2'bipyridyl, undergoes a one electron oxidation with simultaneous abstraction of a halogen atom from a substrate. This inner-sphere electron transfer process reversibly generates an organic radical and a copper (II) complex. The experimental evidence is not conclusive whether the intermediate radicals are free-radicals, in a solvent cage, or coordinated to the metal center, but the most plausible mechanism based upon experimental evidence involves free-radicals.[17] After the back transfer, the copper(I) complex is formed, completing the catalytic cycle. If the radical species, before and after addition of unsaturated substrate, possess comparable stabilization, then the activation-addition-deactivation cycle will repeat until all of the unsaturated substrate is consumed. This process results in a chain-growth polymerization. Scheme 1.5 shows the mechanism of ATRP, which consists of phenomenologically related initiation and propagation processes. These sequences are comprised of an atom-transfer equilibrium along with radical addition to the monomer. Termination by radical coupling and disproportionation are included in the mechanism because of the magnitude of the associated rate constants; however, only a few percent of polymer chains in ATRP undergo bimolecular termination. Additionally some other side reactions may limit the attainable molecular weight.[45,46] The net propagation sequence can be considered as an "insertion" process proceeding via radical intermediates.

The proper choice of the initiator, R-X, is very important for efficient ATRP. Important parameters include correct values of the rate constant of activation,

deactivation and addition at the initiation stage in comparison with those at the propagation stage (k_a^0, k_d^0, k_i versus k_a, k_d, k_p).



Scheme 1.5 The mechanism of Atom Transfer Radical Polymerization

The rate law for ATRP can be derived from Scheme 1.5 by neglecting the contribution of termination, assuming that initiation is complete and using the fast equilibrium approximation – a necessary condition for achieving low polydispersity.[47] Under these conditions the concentration of propagating radicals, [P·] is equal to (k_a/k_d) [R-M_n-X]([M_t^n]/[XM_t^{n+1}])

$$R_p = k_{app}[M] = k_p[P\cdot][M] = k_p k_a / k_d [M][RX]_0 (M_t^n]/[XM_t^{n+1}] \qquad 15$$

In Equation 15 $[RX]_0$ refers to the initial concentration of initiator which corresponds to the concentration of dormant chains ([R-M_n-X]). Results from the kinetics of

polymerization using soluble catalyst systems indicate that the rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and catalyst complex concentration.[48] It is recognized that in ATRP and in all other controlled radical polymerizations, termination is not entirely eliminated. Therefore, chains will continuously terminate resulting in a change in the radical concentration that may lead to some deviation from the first order kinetics with respect to monomer.

Polymerization systems utilizing this concept have been developed using Cu (I),[48] Ni (II), [49,50] Ru (II)/$Al(OR)_3$[51], Fe(II)[52] , Cr(II)[53] and Co(II)[54] complexes to catalyze the radical-forming equilibrium. Copper (I) is the most extensively studied catalyst of ATRP process. ATRP can be used for many vinyl monomers including styrene and substituted styrenes, acrylates, methyacrylates, acrylonitrile and dienes. The current catalyst systems are not sufficient to polymerize less reactive monomers such as ethylene, α-olefins, vinyl chloride and vinyl acetate.

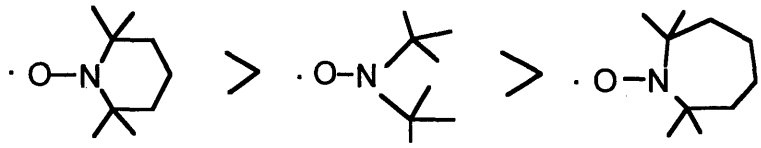
Although ATRP is more versatile in term of monomer choices, it is unfortunate that this mechanism requires a rather large amount of transition metal compound. Therefore, the final polymer contains high concentrations of residual metal that is undesirable for commercial production.

1.5 Recent developments in living free radical polymerization

In the original nitroxide-mediated polymerization, Georges used a bimolecular initiating system consisting of a traditional radical initiator (such as benzoyl peroxide) in conjunction with excess TEMPO.[6] The excess TEMPO was required to ensure that all of

the newly generated polymer chains were terminated by nitroxide.[55] However, the excess TEMPO results in a decrease in polymerization rate. Reducing the nitroxide level, and thereby increasing the rate of polymerization, has been accomplished by the use of initiator-nitroxide adducts (unimolecular initiators) such as 2,2,6,6-tetramethyl-1-(1-phenethyloxyl)piperidine.[56] The unimolecular initiator can be obtained by coupling TEMPO with carbon radicals prepared by hydrogen abstraction from ethylbenzene. This nitroxyl-containing (or alkoxyamine) initiator has been shown to function as a living/controlled free radical polymerization initiator for styrene polymerization and resulted in the production of low polydispersity polymer.[57]

In recent years, much attention has been focused upon synthesis of initiator model compounds to understand the mechanism and kinetic details of the living free radical process.[58,59,60,61,62,63,64] These studies have shown that, at elevated temperatures, the carbon alkoxyamine bond joining the benzyl unit is reversibly labile.[7, 8] This reversible capping mechanism dramatically reduces the concentration of active free radicals in the polymerization and prevents unwanted termination and side reactions. Typically for TEMPO containing initiators, the high dissociation energy of the carbon alkoxyamine bond requires the living polymerization be conducted at a high temperature, typically >110 °C. Lower polymerization temperatures are preferred to suppress both thermal initiation and degradation of the alkoxyamine. Concerning the cleavage of the C-O bonds in alkoxyamines, Moad and Rizzardo had established the following increasing order of bond strength for the C-O bonds from the measurement of dissociation rates of various alkoxyamines obtained from cyclic and acyclic nitroxide.[65]



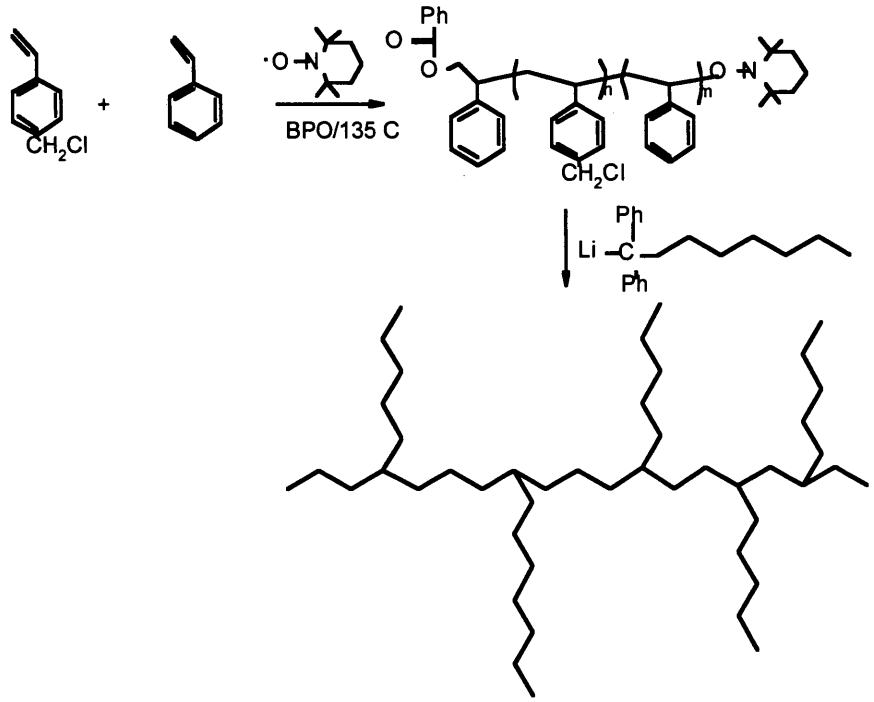
Using di-*tert*-butyl nitroxide rather than TEMPO, Hammouch *et al.* demonstrated that living polymerization could be controlled at the rather low temperature of 90 °C, instead of a more typical 120 °C. It was found that replacement of a six-member ring by two *t*-butyl groups makes homolysis of the C-O bond kinetically more favorable resulting in faster polymerization. Puts and Sogah also reported that the asymmetric nitroxide, 2,5-dimethyl-2,5-diphenylpyrrolidin-1-oxyl (DDPO) effectively mediates the free-radical polymerization of styrene.[66] The polymerization showed faster kinetics and better molecular weight control compared to TEMPO-mediated polymerization. Yamada studied the structure effect of nitroxide on living free radical polymerization and indicated that all cyclic nitroxide, except oxazolidinyloxyl were critical to control the molecular weight and polydispersity of polystyrene.[67] 2,2,3,3,5-pentamethyl-5-phenylpyrrolidinyloxyl and 2,3,3,5-tetramethyl-2,5-diphenylpyrrolidinyloxyl yielded polystyrene samples with number average molecular weight of 100,000 and polydispersity less than 1.5, whereas 2,2,6,6-tetramethylpiperidinyloxyl resulted in polymers with considerably lower M_n and slightly lower polydispersity under similar reaction conditions. The polymerization in the presence of oxazolidinyloxyl radicals was found to proceed almost without any influence from nitroxide.

Hawker *et al.* synthesized a variety of unimolecular alkoxyamine initiators containing reactive functional groups.[68] The efficiency of these initiators was evaluated in terms of conversion, molecular weight control, and polydispersity. They found that, for

the benzylic derivatives, the presence of an α-methyl group was essential for the free radical polymerization to proceed with living character. However, a variety of functional groups could be substituted at the β-carbon position, or on the phenyl ring, without affecting the polymerization rate or the polydispersity of the polymers. It was also demonstrated that molecular weight control was more attainable for the unimolecular alkoxyamine initiators than for the bimolecular systems.

The main benefit of nitroxyl mediated radical polymerization (NMRP) is to use the technology for preparing various block copolymers with controlled architecture. Georges demonstrated that NMRP worked well for the preparation of alkyl acrylate homo- and block copolymers.[69] Furthermore, to prepare polystyrene-*bl*-polybutadiene copolymer, Georges[70] first made a polystyrene block using the bimolecular initiator system of TEMPO and benozyl peroxide. Then polystyrene-*bl*-polybutadiene copolymers were prepared in a subsequent step by dissolving the TEMPO-terminated polystyrene and a small amount of benzoic acid in a solution of ethyl acetate and dimethyl sulfoxide. 1,3-Butadiene was added to this solution to obtain the di- or triblock copolymer.

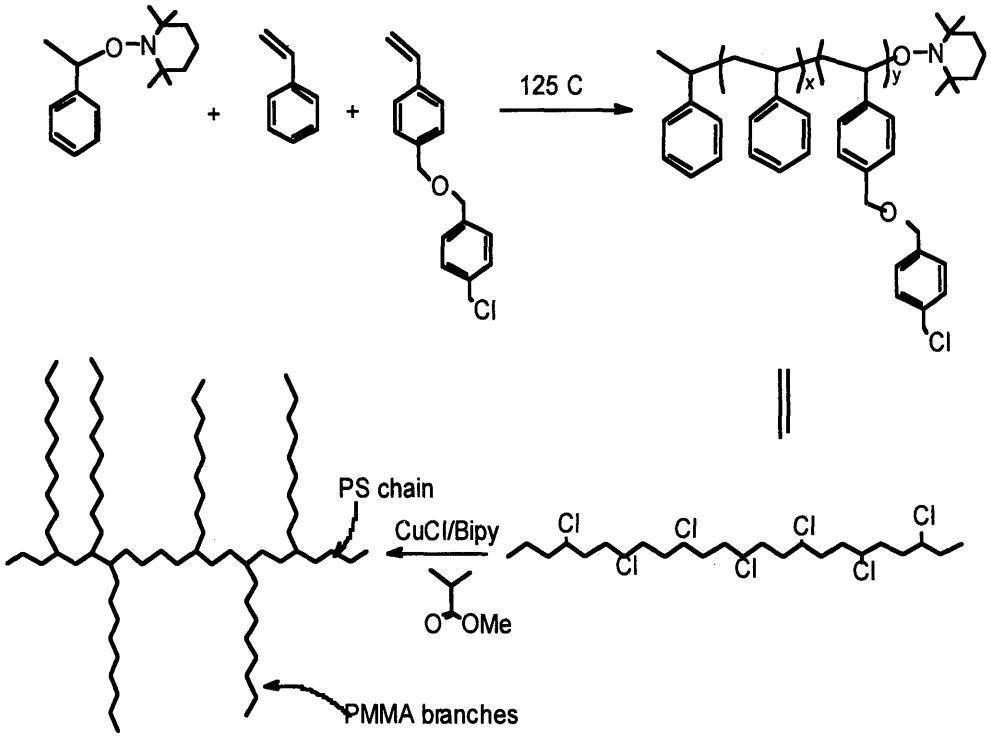
Besides the block and random copolymers, NMRP has been explored in preparation of grafted and arborescent polymers.[71] NMRP can be used for the polymerization of 4-(chloromethyl)styrene with living fashion and resulted in low polydispersity polymer. The polymerization rate for 4-(chloromethyl)styrene is substantially faster than styrene polymerization in a comparable nitroxide concentration. Substituent effects clearly play a major role in this process. NMRP leaves the chloromethyl groups intact and permits flexibility to form various arborescent copolymers.



Scheme 1.6 Preparation of Grafted Copolymers

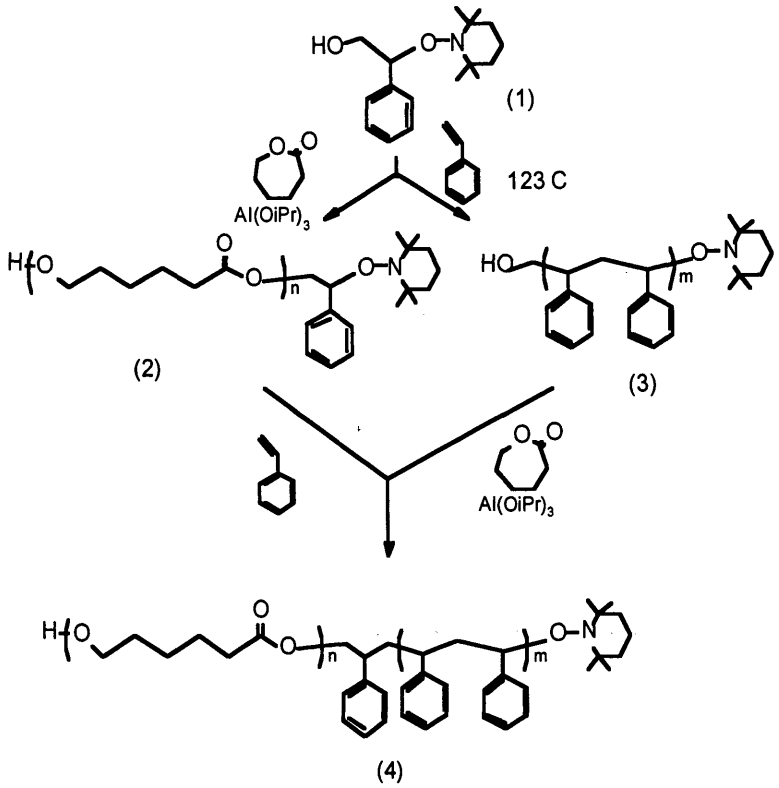
To expand the ranges of monomers for copolymerization, a new approach was utilized by Hawker.[72] The synthesis was based on a sequential two-step free radical approach in which an initial nitroxide-mediated radical polymerization was followed by a "living" atom transfer radical polymerization (ATRP) to yield graft and dendrigraft products. These two processes could be combined owing to their inherent chemical dissimilarity. While NMRP is thermally activated at 125° C and needs no added reagents for chain growth, the ATRP procedure requires the addition of $Cu^{I}Cl$/2,2'-bipyridine complex to the reaction mixture in order for polymerization to proceed. Therefore, a linear backbone incorporating latent ATRP-initiating sites might be grown by NMRP.

Subsequently, without further chemical modification, the growth of grafted chains may be initiated by the addition of $Cu^{I}Cl$/2,2'-bipyridine complex. Such a tandem approach allowed the synthesis of a variety of branched macromolecular architectures with a broad range of chemical compositions in only two steps. Polystyrene grafted poly(methyl methacrylate) and polystyrene grafted poly(butyl methacrylate) have been prepared by this method. The molecular weight of grafted chains was controlled by the amount of monomer added. Low polydispersity was maintained in both graft copolymers.



Scheme. 1.7 Preparation of Grafted Copolymer by the Combination of NMRP and ATRP

While NMRP is successful to make various vinyl copolymers, it does not address the issue of dissimilar monomer systems that are polymerized by fundamentally different chemistry, such as ring opening and free radical procedures. To solve this difficultly a number of works have examined the polymerization of dissimilar monomers.[73] Hawker demonstrated that one of the major advantages of NMRP was the stability of its initiating or propagating center.[66] This has enabled the development of a wide variety of functionalized unimolecular initiators which may be used for combining NMRP with other living polymerizations. An advantage of such initiator systems is that the novel block copolymers can be prepared under mild conditions in the minimum number of steps to eliminate intermediate functionalization reactions. Hawker reported the successful preparation of a block copolymer of polystyrene-*bl*-polycaprolactone using functionalized alkoxyamine initiator.[74] The double head initiator contains one primary alcohol initiating a living ring opening polymerization of cyclic lactone and a benzylic group for the NMRP of styrene.



Scheme 1.7 The Preparation of Block Copolymer Using the Combination of Ring Opening Polymerization and NMRP.

Yoshida used a different approach to combine the two different polymerization procedures. He reported the formation of block copolymer of polystyrene-*bl*-polycaprolactone by combining a living ring opening polymerization with NMRP.[75] Poly(ε-caprolactone) with TEMPO at the chain end was first attained through the anionic polymerization of ε-caprolactone by an aluminum tri(4-oxy-TEMPO), which was prepared by the reaction of triethylaluminum and 4-hydroxy-TEMPO. Then the TEMPO supported poly(ε-caprolactone) behaved as a polymeric counter radical for the radical polymerization of styrene to form the block copolymer.

1.6. Thesis Objectives

This thesis focuses on two objectives: 1. the synthesis of initiators with different functional groups to understand the effects on the control of the living free radical polymerization process, and 2. the use of the functional initiators to combine living free radical polymerization with step growth polymerization to prepare polystyrene-*bl*-polycarbonate-*bl*-polystyrene (PS-*bl*-PC-*bl*-PS) triblock copolymers.

Selection of the right initiator is key in achieving living free radical polymerization since the effectiveness of an initiator depends strongly on its chemical structure. Chapter 2 discusses the synthesis and characterization of various unimolecular TEMPO initiators containing other functional groups such as acetoxy, *t*-boc, or arylcarbonate. Polymerizations of styrene in the presence of the functionalized unimolecular initiators were evaluated in terms of monomer conversion, polymer molecular weight, and polydispersity. Chapter 2 also discusses the results of the investigation of the chain growth mechanism along the C-ON bond. A diradical initiator with one identical nitroxide functional group symmetrically located at each end was synthesized. In addition, a cleavable carbonate linkage was designed into the molecule. The polymerization rate and molecular weight were evaluated and compared to the initiators with a single C-ON bond. Since the initiator includes a hydrolytically cleavable bond, molecular weight analysis before and after hydrolysis was expected to reveal useful information about chain growth kinetics during the polymerization.

The second part of the thesis work was to combine NMRP and step-growth polymerization to prepare polystyrene-*bl*-polycarbonate-*bl*-polystyrene triblock copolymers. Traditionally, polystyrene has been produced by conventional radical

polymerization whereas polycarbonate has been prepared by condensation polymerization. To combine the two different polymerization mechanisms together, a new initiator with both a nitroxyl group and a phenol functional group was synthesized. The phenol group was protected by a *t*-butylcarbonate group during the course of styrene living free radical polymerization initiated by the nitroxyl group. Subsequently, deprotection of the carbonate group returns the phenol functional group as a center for further carbonate condensation polymerization. The structure of PS-*bl*-PC-*bl*-PS block copolymers was evaluated by segment length and glass transition temperature. The details of this study are presented in Chapter 3.

Another route to prepare the copolymer of PS-*bl*-PC-*bl*-PS was also explored and is discussed in Chapter 4. In this case, polycarbonate terminated with the nitroxide functionality was made first, then the styrene monomer was added from the carbon-nitroxyl bond via a living free radical mechanism to form the polystyrene segment. The polymerization efficiency and physical properties are discussed.

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CHAPTER 2:

SYNTHESIS AND REACTIVITY OF FUNCTIONAL ALKOXYAMINE INITIATORS FOR NITROXIDE MEDIATED RADICAL POLYMERIZATION OF STYRENE

2.1. Introduction

Living/controlled radical polymerization can combine some of the desirable attributes of traditional free radical systems with the advantages of traditional living ionic polymerization techniques. Controlled radical polymerization allows for the preparation of various polymers with well-defined architectures, and particularly has potential in the synthesis of block copolymers.[1,2] For any living or controlled polymerization, a critical feature is the nature and efficiency of the initiating system. The original examples of using a stable nitroxyl radical such as 2,2,6,6-tetramethyl-1-piperdinyloxy (TEMPO) to attain "pseudo-living" behavior in the radical polymerization of styrene was described by Georges.[3] In this case, the initiator was benzoyl peroxide and TEMPO was used to mediate the reactivity of the growing radicals as they formed. Good control of the polymerization was achieved and polystyrene (PS) with a fairly low polydispersity of 1.2 was obtained. Recently, much attention has been focused upon synthesis of initiator model compounds that contain an

alkoxyamine bond to understand the mechanism and kinetic details of the nitroxide mediated living free radical (NMRP) process.[4,5,6,7] These studies have demonstrated that, at elevated temperatures, the carbon alkoxyamine bond joining the benzyl unit is thermally and reversibly labile. This reversible capping mechanism dramatically reduces the concentration of active free radicals in the polymerization and thus prevents the chain from unwanted termination and side reactions.[8]

Typically for TEMPO containing initiators, the high dissociation energy of the carbon alkoxyamine bond requires the living/contolled polymerization be conducted at a high temperature, i.e., typically greater than 110 °C.[5] At such temperatures, thermal degradation of the initiator may occur or thermal initiation of the polymerization may result. Therefore, a reduction in polymerization temperature is desired to suppress both thermal initiation and degradation of the alkoxyamine. A number of works have focused on changing the initiator structure to allow it to work effectively at lower polymerization temperatures. Using di-*tert*-butylnitroxide rather than TEMPO, Hammouch demonstrated that living polymerization could be controlled at a relatively low temperature of 90 °C instead of a more typical temperature of 120 °C.[9] It was also found that replacement of a six member ring by two *t*-butyl groups made homolysis of the C-O bond kinetically more favorable for faster polymerization.[10] Puts and Sogah also reported that the asymmetric nitroxide, 2,5-dimethyl-2,5-diphenylpyrrolidin-1-oxyl (DDPO) successfully mediated free-radical polymerization of styrene at low temperatures.[11] The polymerization showed faster kinetics and better molecular weight control compared to TEMPO-mediated polymerization. Hawker *et al.* synthesized a variety of unimolecular alkoxyamine initiators containing various reactive functional

groups.[12] The efficiency of these initiators was evaluated in terms of conversion, molecular weight control, and polydispersity. It was found that, for the benzylic derivatives, the presence of a α-methyl group was essential for the living free radical polymerization. However, a variety of functional groups could be substituted at the β-carbon position, or on the phenyl ring, without affecting the polymerization rate or the polydispersity of the polymers. It was also found that molecular weight control was greater for the unimolecular alkoxyamine initiators than for bimolecular systems. Hawker also investigated the effectiveness of alkoxyamine initiators in the preparation of star and grafted polymers,[13] hyperbranched systems,[14] and low-polydispersity random[15] and block copolymers.[16]

In this work, different TEMPO-containing initiators for alkoxyamine initiated polymerization (AIP) were synthesized. Particularly the study focused on initiators with different ester and carbonate functional groups. In addition, a difunctional initiator with alkoxyamine groups symmetrically located at each end of a carbonate bond was synthesized to compare its efficiency to the mono-functional counterpart. The molecular weight, rate of conversion, and polydispersity were evaluated for each of the initiators.

2.2. Experimental

All reagents were purchased from the Aldrich Chemical Company and were used as received unless otherwise indicated. Styrene was obtained from The Dow Chemical Company and contained 3 ppm 4-*t*-butylcatechol as an inhibitor. Proton and ^{13}C NMR

spectra were recorded in CD_3Cl solution (with chromium acetylacetonate) using a Varian 200-XL spectrometer operating at 200 and 50 MHz frequencies respectively. Mass spectra were recorded using an Innigan SSQ 700 quadrupole spectrometer operating in electron impact and chemical ionization modes. Analytical TLC was performed using commercial Merck plates coated with silica gel (0.25 nm thick).

Polymerizations were conducted in Pyrex ampoules sealed at reduced pressure. Relative polymer molecular weights were established by size exclusion chromatography (gel permeation chromatography, GPC) using a Hewlett-Packard 1090 instrument equipped with a set of 10 μm mixed-bed columns from Polymer Laboratories, Inc., and an ultraviolet detector. Low polydispersity PS standards were used for calibration. Both standards and samples were introduced as 0.25w/w% solutions in tetrahydrofuran (THF). The elution solvent was THF in all cases at a flow rate of 1.0 mL/min.

2.2.1. Preparation of 4-(Acetoxy)ethylbenzene

To a stirred solution of 4-ethylphenol (12.2 g, 0.1 mol) and triethylamine (6.94 g, 0.068 mol) in 125 mL of anhydrous methylene chloride maintained in a dry nitrogen atmosphere was added dropwise over a period of 2 h a solution of 8.87 g (0.1 mol) of acetyl chloride in 75 mL of methylene chloride. Upon complete addition, the mixture was stirred 3 h at room temperature. Triethylammonium chloride was removed by filtration and the methylene chloride solution was washed successively with two 50 mL portions of 10% aqueous sodium hydroxide solution, 50 mL of water, and 50 mL of saturated aqueous sodium chloride solution. The solution was dried over anhydrous

sodium sulfate and the solvent removed by rotary evaporation at reduced pressure. The residual oil was distilled at reduced pressure to yield 4-acetoxyethylbenzene (17.9 g/81.3% yield) as a clear, colorless liquid (b.p. 96-100 °C, 6 torr).

2.2.2. Preparation of Di-*t*-butylperoxyoxalate[17,18]

To 10 mL of a 5.0 M solution of *t*-butyl-hydroperoxide in decane and 4.4 g (0.045 mol) of anhydrous pyridine in 50 mL of pentane maintained at -20 °C was added dropwise over a period of 0.5 h a solution of 2.4 ml (3.2 g, 0.025 mol) of oxaloyl chloride in 25 mL of pentane. The resulting mixture was stirred for an additional 0.5 h with the temperature not exceeding 0 °C. The solid that formed (mixture of pyridinium chloride and product) was removed by suction filtration. The filtrate (pentane solution) was cooled to -78 °C and allowed to stand for crystallization of the product as white needles. The solid was suspended in 50 mL of saturated aqueous sodium chloride solution and extracted with two 15 mL portions of diethyl ether. The ether extracts were dried over anhydrous sodium sulfate, filtered and cooled to -78 °C to afford additional product. Collection of the crystalline material afforded di-*t*-butylperoxalate in 78 % yield as solvent-moist white needles. The di-*t*-butylperoxalate was either used immediately or stored in a freezer at –10 °C until use.

2.2.3 Preparation of 1-phenyl-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (TMPEP)

To a 100 mL round bottom flask equipped with a magnetic stir bar was added 10.0 g of ethylbenzene, TEMPO (2.41g, 21 mmol) and di-t-butylperoxyoxalate (2.42g, 21 mmol). The mixture was warmed to 50°C by an external water bath and the color of the mixture rapidly changed from deep orange to light yellow. The mixture was stirred for an additional hour and the excess ethylbenzene was removed by rotary evaporation at elevated temperature and reduced pressure (90C, 1 Torr). The residual oil was diluted with ethanol and cooled in a refrigerator at 7°C overnight. The crystalline solid that formed was collected and purified by recrystallization from ethanol. The final product of 4.6g was obtained (85% yield).

2.2.4. Preparation of 1-(4-Acetoxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (I)

To a 100-mL, round-bottomed flask equipped with a magnetic stirrer was added 16.0 g of 4-acetoxy ethylbenzene, TEMPO (2.41 g, 21 mmol), and di-*t*-butylperoxyoxalate (2.42 g, 21 mmol). The mixture was warmed to 50 °C by an external water bath and the color of the mixture rapidly changed from deep orange to light yellow. The mixture was stirred for an additional hour and the excess 4-acetoxyethylbenzene removed by rotary evaporation at elevated temperature and reduced pressure (90 °C, 1 torr). The residual oil was allowed to stand in a refrigerator at 7 °C overnight. The crystalline solid that formed was collected and purified by

recrystallization from ethanol/water (70:30). The final product of 5.7 g was obtained (85% yield)

2.2.5. Preparation of 1-(4-Acetoxyphenyl)-1-(2,2,6,6,-tetramethyl-1-piperidinyloxy)-2-*t*-butoxyethane (II)

A stirred solution of TEMPO (2.5 g, 16 mmol) and di-*t*-butylperoxyoxalate (2.41g, 21 mmol) in 4-acetoxystyrene (20.0 g, 123 mmol) was warmed to 50 °C. The color of the mixture changed from deep orange to light yellow over a period of a few minutes. The mixture was stirred for 2 h at 50 °C and the excess 4-acetoxystyrene was removed by rotary evaporation at reduced pressure. The residual liquid was allowed to stand at 7 °C in a refrigerator overnight. The crystalline solid that formed was collected and recrystallized from ethanol/water (70:30). The final product of 6.6 g was obtained (80 % yield).

2.2.6. Preparation of 1-(4-*t*-Butoxycarbonyloxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (III)

To a 100-mL, round-bottomed flask equipped with a magnetic stirrer was added TEMPO (1.7 g, 10.9 mmol), 4-(*t*-butoxycarbonylyoxy)ethylbenzene (9.8 g, 36 mmol) and finally di-*t*-butylperoxyoxalate (9.3 g, 12.3 mmol). The mixture was stirred at 55 °C (water bath) for 1 h. The solution was allowed to cool to room temperature. The solid, which had precipitated, was collected by filtration and recrystallized from absolute ethanol to afford the product as white needles (3.42 g, 83% yield).

2.2.7. Preparation of 1-(4-Hydroxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (III')

Into a dry 50-mL round-bottomed flask fitted with a condenser bearing a nitrogen-inlet tube and a magnetic stirrer was placed 0.42 g (1.15 mmol) of III and 5.0 mL of methylene chloride. To the stirred methylene chloride solution was added a solution of potassium hydroxide (10 wt%, 0.86 g, 1.53 mmol of potassium hydroxide) in methanol. The resulting mixture was stirred at room temperature with the progress of reaction followed by TLC. After 1 h, III had been completely consumed. Solvent was removed by rotary evaporation at reduced pressure and the resulting solid was recrystallized from absolute ethanol to provide light yellow crystals (0.28 g, 94 % yield).

2.2.8 Preparation of Bis{4-[1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethyl]phenyl}carbonate (IV)

Into a 50 mL, round bottomed flask fitted with a magnetic stirrer, a pressure-equalizing dropping funnel, and a Leibig condenser bearing a nitrogen-inlet tube was placed 0.4 g (1.12 mmol) of III' and 5.0 mL of methylene chloride. To the resulting solution was added water (5.0 mL) and a solution of phosgene in toluene (20% (w/w)) corresponding to 0.27 g (0.51 mmol) of phosgene. The mixture was stirred for 5 minutes at room temperature and a 50% aqueous solution of sodium hydroxide (0.056 g, 0.71 mmol) was added. To the stirred mixture was then added 0.1g an aqueous solution of triethylamine (5 wt%). The mixture was stirred at room temperature with the progress of the reaction monitored by TLC. The reaction was complete within 5

minutes. The methylene chloride solution was separated from the aqueous phase, washed successively with two 20 mL portions of saturated aqueous sodium bicarbonate solution and 20 mL of saturated sodium chloride solution, and then dried over anhydrous sodium sulfate. The solution was filtered and the solvent was removed by rotary evaporation at reduced pressure to afford a waxy product that solidified upon the addition of acetonitrile. The white solid (0.23 g 71 % yield) was collected by filtration.

2.2.9. Polymerization

The desirable amount of initiator was dissolved in styrene monomer. The styrene monomer was used without removal of inhibitor. The styrene solutions were loaded into Pyrex ampoules (5mm i.d x 10 mm o.d. x 30 cm) and sealed under reduced pressure (< 6 torr) using the freeze-thaw technique. The sealed ampoules were placed in a silicone oil bath maintained at 140 °C. The ampoules were removed at specified time intervals, allowed to cool to room temperature, opened, and the contents analyzed to determine the extent of monomer conversion to polymer. The polymer molecular weight and molecular weight distribution were determined by GPC analysis.

2.2.10. Hydrolysis of polymer generated using Bis{4-[1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethyl]phenyl}carbonate (IV)

The polymer was dissolved into THF solution and 1g of 10% (w/w) KOH in methanol was added. The polymer solution was stirred at room temperature for 30 minutes. The polymer was precipitated by the addition of methanol. The precipitated polymer was removed by filtration and dried at 50 °C in a vacuum oven for 4 h. The

molecular weight and polydispersity of the polymer before and after hydrolysis were measured using GPC.

2.3. Results and Discussion

2.3.1 Synthesis of Initiator

Methods developed for synthesizing alkoxyamine-containing initiators have often involved the use of Grignard reagents and often require complicated procedures for purification.[6] Recently, it was demonstrated that monofunctional alkoxyamine initiator, 1-phenyl-1-(2,2,6,6-tetramethyl-1-piperdinyloxy)ethane, could be prepared by a simpler technique involving the decomposition of di-*t*-butylperoxide in the presence of a mixture of ethylbenzene and TEMPO.[19] However, due to the high decomposition temperature of the di-*t*-butylperoxide, hydrogen abstraction by the peroxide from ethylbenzene to form the TEMPO adduct required temperatures greater than 100°C. At such temperatures, the TEMPO adduct was unstable and readily eliminated 1-hydroxy-2,2,6,6-tetramethylpiperidine to form styrene.[5] Thus, the isolated yield of the initiator was never greater than 50 %. Table 2.1 shows the yield of initiator can be dramatically improved by replacing the di-*t*-butylperoxide with di-*t*-butylperoxyoxalate (TBPO). Di-*t*-butylperoxyoxalate (TBPO) generated t-butoxy radicals at 50 °C, a temperature much lower than the decomposition temperature of di-*t*-butylperoxide. The *t*-butoxy radicals abstracted a hydrogen atom from the benzylic position of ethylbenzene to generate carbon radicals that were readily trapped by TEMPO to form the adduct. TBPO has a

half-life of decomposition at 50 °C of about 3 minutes so a sufficient amount of *t*-butoxy radicals could be formed in a short period of time.[20] Another advantage to the use of TBPO was that reaction time to obtain TEMPO adduct could be significantly reduced to 1 hour as opposed to 16 hours if di-*t*-butylperoxide was used.

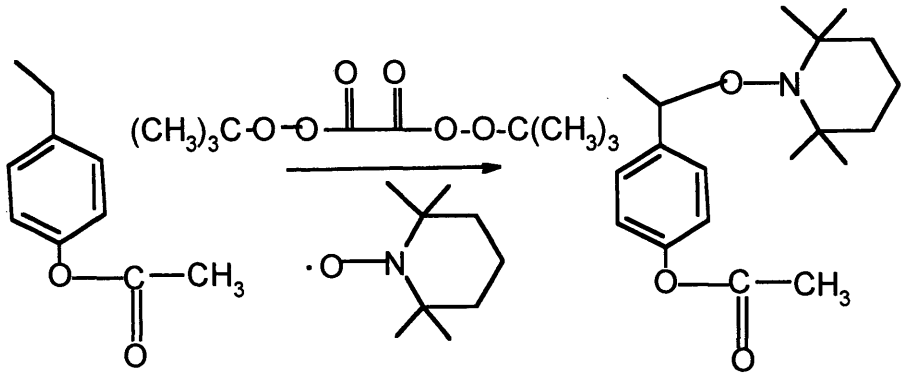
Table 2.1. The Comparison of Reaction Conditions Using Different Peroxides

	Half-life	Reaction Time (hour)	Reaction Temp. (°C)	Yield (%)
di-t-butyl peroxide	10 hr @126 °C	16	120	32
di-t-butyl peroxyoxalate	3 min@ 50 °C	1	50	85

Using TBPO as a carbon radical generator, a variety of functionlized TEMPO initiators suitable for AIP were prepared. The introduction of functional groups into alkoxyamine-containing initiators provides an opportunity to couple conventional radical or step-growth polymerization methodologies with AIP to form various copolymer structures. Initiator I with latent phenol functionality was synthesized by the reaction between 4-acetoxyethylbenzene and di-*t*-butylperoxyoxalate in the presence of TEMPO. A high yield of 85% was obtained and synthesis route is illustrated in Scheme 2.1. The reaction was conducted in an excess of 4-(acetoxy)ethylbenzene which functioned as a solvent as well as a reactant. The hydrogen abstraction efficiency was

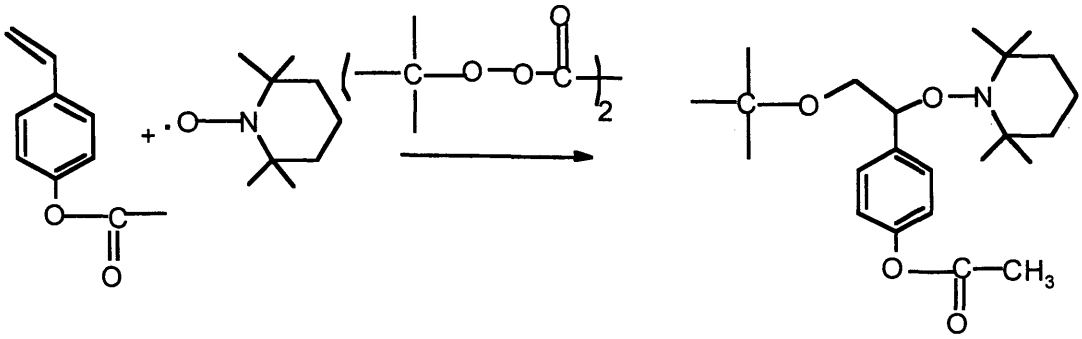
greatly enhanced since radical cage effect from solvent other than 4-(acetoxy)ethylbenzene was minimized. The NMR spectrum of I shows the benzylic proton as a quartet at $\delta = 4.7$ ppm and the aromatic protons at 7.0 and 7.2 ppm respectively. The methyl protons in the acetoxy group appear as a singlet at 2.3 ppm. The protons on the piperidinyloxy ring appeared as a group ranging from 0.6 to 1.6 ppm. The integration of the area under those peaks revealed the ratio of protons was consistent with the desired structure I.

Initiator II was prepared by an alternative radical addition reaction as shown in Scheme 2.2. *t*-Butoxy radical added to the double bond of styrene to form a benzylic radical which was then coupled with TEMPO to generate the adduct. The NMR spectrum of II shows an absorption of the benzylic proton as a triplet at $\delta = 4.7$ ppm and the aromatic protons as two peaks at $\delta = 7.0$ and 7.3 ppm. The methyl and methylene protons on the piperidinyloxy ring as well as the t-butyl protons of the *t*-butoxy group appear as an unresolvable group at 0.7-1.7 ppm. The integration of the area under the peaks reveals the ratio of protons is consistent with the desired structure II.



I

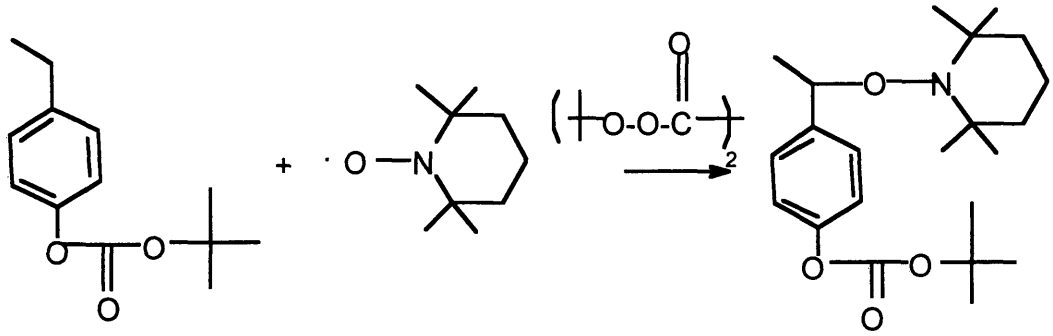
Scheme 2.1. Synthesis of 1-(4-Acetoxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (I)



II

Scheme 2.2. Synthesis of 1-(4-Acetoxyphenyl)-1-(2,2,6,6,-tetramethyl-1-piperidinyloxy)-2-*t*-butoxyethane (II)

Initiator III was prepared in a similar method as for I. The hydrogen atom abstraction reaction between 4-(*t*-butoxycarbonylyoxy)ethylbenzene and the radicals produced from decomposition of di-*t*-butylperoxyoxalate was performed in the presence of TEMPO. The reaction is illustrated in Scheme 2.3. The proton NMR spectrum of III is shown in Figure 2.1. The benzylic proton appears at $\delta = 4.8$ ppm and the aromatic protons are evidenced by two peaks at 7.2 ppm and 7.4 ppm. The protons from methyl and methylene groups on piperidinyloxy ring and the protons from the *t*-boc group emerge as a group at 0.7-1.7 ppm. The integration of the area under the peaks reveals the ratio of protons is consistent with the desired structure III. In addition, ^{13}C NMR (Figure 2.2) shows the carbonate carbon at $\delta = 152$ ppm, the benzylic carbon at $\delta = 82$ ppm and the tertiary carbon of the t-butyl group at $\delta = 83$ ppm. Again the integration of the peaks confirmed the formation of structure III.



Scheme 2.3. Synthesis of 1-(4- *t*-Butoxycarbonyloxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (III)

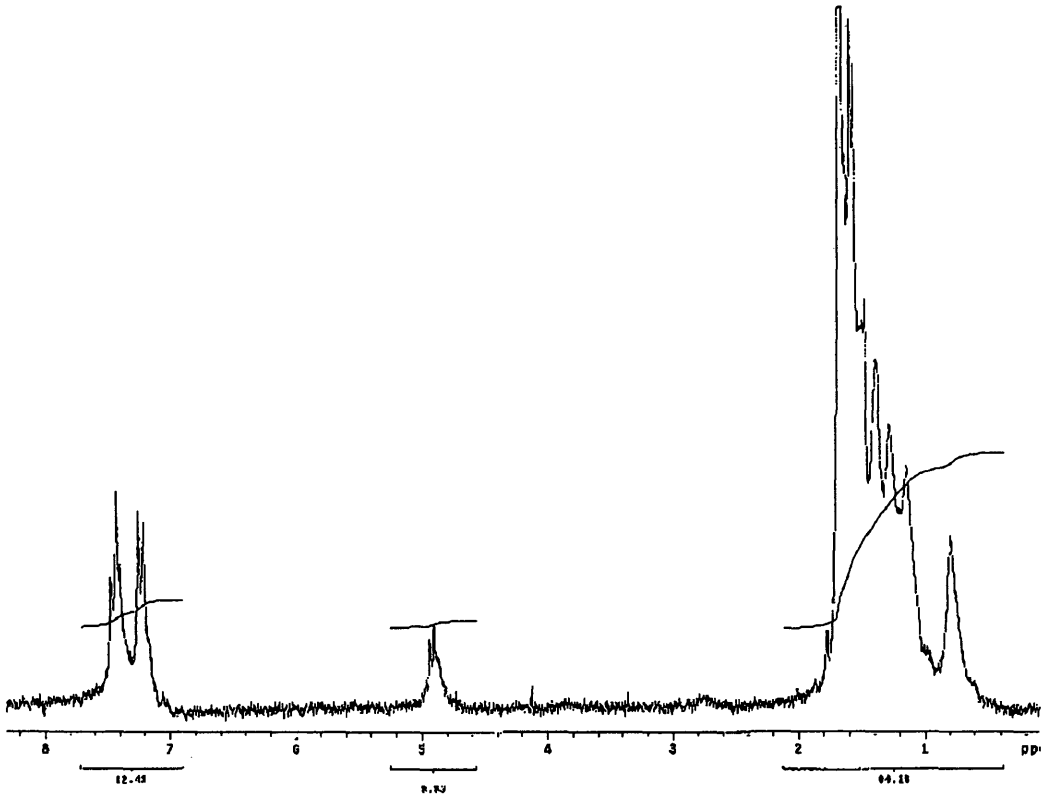


Figure 2.1. Proton NMR Spectrum of 1-(4- *t*-Butoxycarbonyloxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (III)

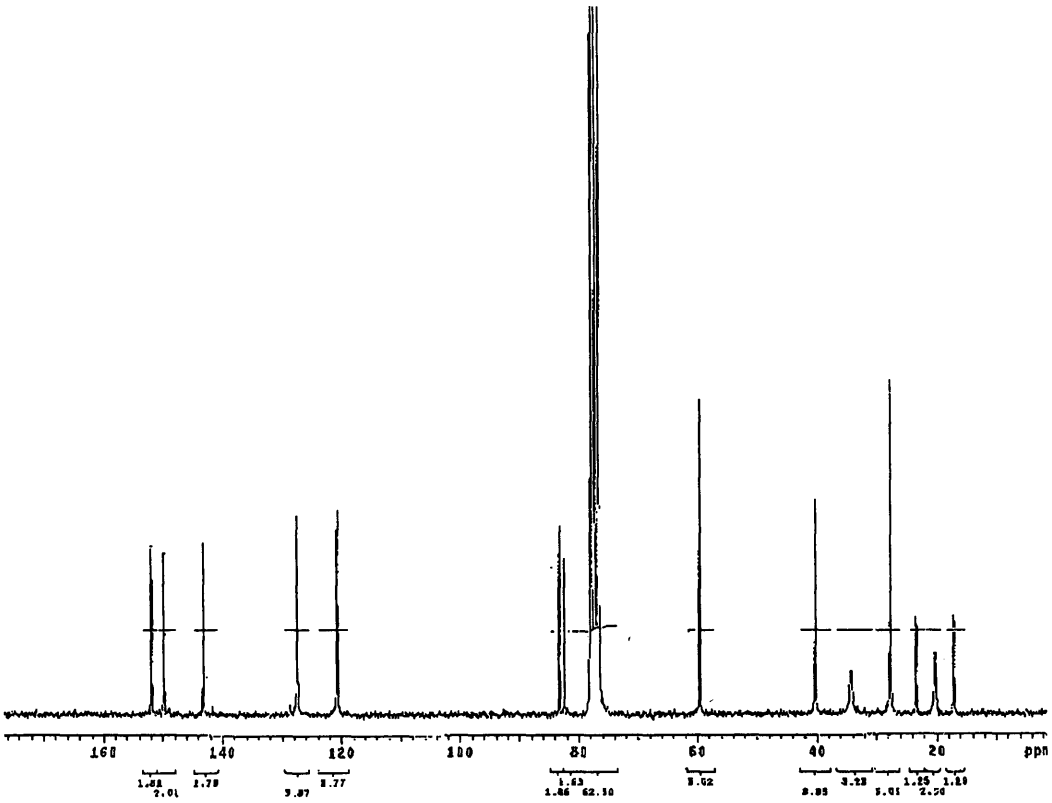
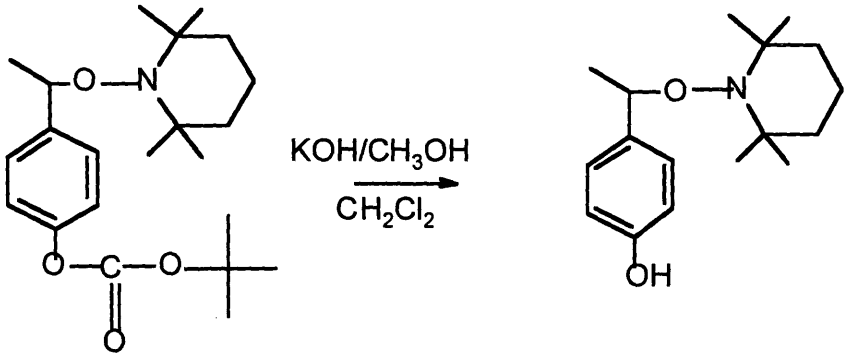


Figure 2.2. Carbon-13 NMR Spectrum of 1-(4- *t*-Butoxycarbonyloxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (III)

Initiators I, II, and III were all monofunctionalized TEMPO adducts that allowed polymer chain growth only in one direction. To perform chain growth from both ends of the initiator, difuctional initiators with two active alkoxyamine bonds are needed. Previous research has evaluated initiators with two active alkoxyamine groups,[21,22] but

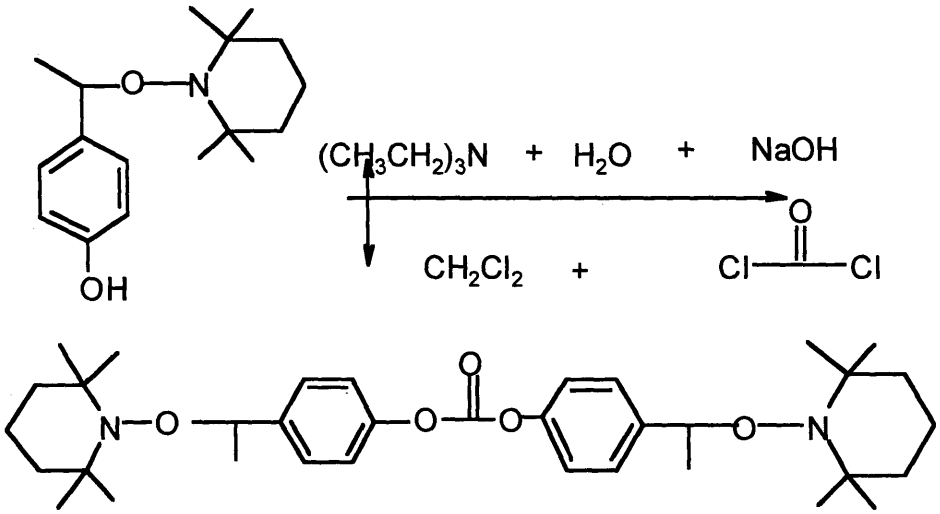
our approach intended to examine an initiator with a cleavable group to evaluate the polymer growth. In order to prepare the difunctional initiator, one synthesis strategy was to first generate a reactive phenol group by hydrolysis of the ester or carbonate groups of the monofunctional compounds (I, II, or III). Coupling of two phenol groups by phosgene allows formation of a difunctional TEMPO adduct. In practice, it was observed that hydrolysis of the carbonate group on III required milder reaction conditions and reduced reaction time, while compounds I and II demanded high alkali concentrations and longer times. The hydrolysis of I and II may be accelerated at elevated temperatures, however the alkoxyamine bond is thermally unstable so that achieving high yield of final product is difficult.



Scheme 2.4. Generation of 1-(4-Hydroxyphenyl)-1-2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (III')

The hydrolysis of III to form the intermediate III' was performed using methylene chloride as a solvent and KOH as a base as shown in Scheme 2.4. The difunctional initiator IV containing two active alkoxyamine groups was generated by combining two phenol functional alkoxyamine intermediates (III') with phosgene. Although homogeneous phosgenation could be carried out using pyridine as a solvent and acid scavenger, the yield was found to be low. Interfacial phosgenation using triethylamine as a phase-transfer catalyst was found more effective to produce high yields. In the interfacial reaction, methylene chloride was used as the organic phase. Sodium hydroxide was used as a base to form the phenolate of III' in the aqueous phase. The reaction resulted in high yield (71%) of IV.

A proton NMR spectrum in Figure 2.3 shows aromatic proton peaks centered at $\delta = 7.2$ ppm and a quartet of methine protons at $\delta = 4.8$ ppm. The methyl and methylene protons on the piperdinyloxy ring appear as a group at $\delta = 0.7$-1.7 ppm. The ^{13}C NMR spectrum in Figure 2.4 clearly indicates the carbonate carbon at $\delta = 150$ ppm. The benzylic carbon appears at $\delta = 81$ ppm. The aromatic carbons show four peaks at $\delta = 148$, 141, 125 and 119 ppm. The methyl group adjacent to the benzylic carbon corresponds to the peak at $\delta = 21$ppm. The mass spectrum in Figure 2.5 further verified structure IV by displaying a protonated molecular peak at 581 and the peaks relevant to the fragments of the difunctional initiator.



Scheme 2.5. *Bis*{4-[1-(2,2,6,6-tetramethyl-1-piperdinyloxy)ethyl]phenyl} carbonate (V)

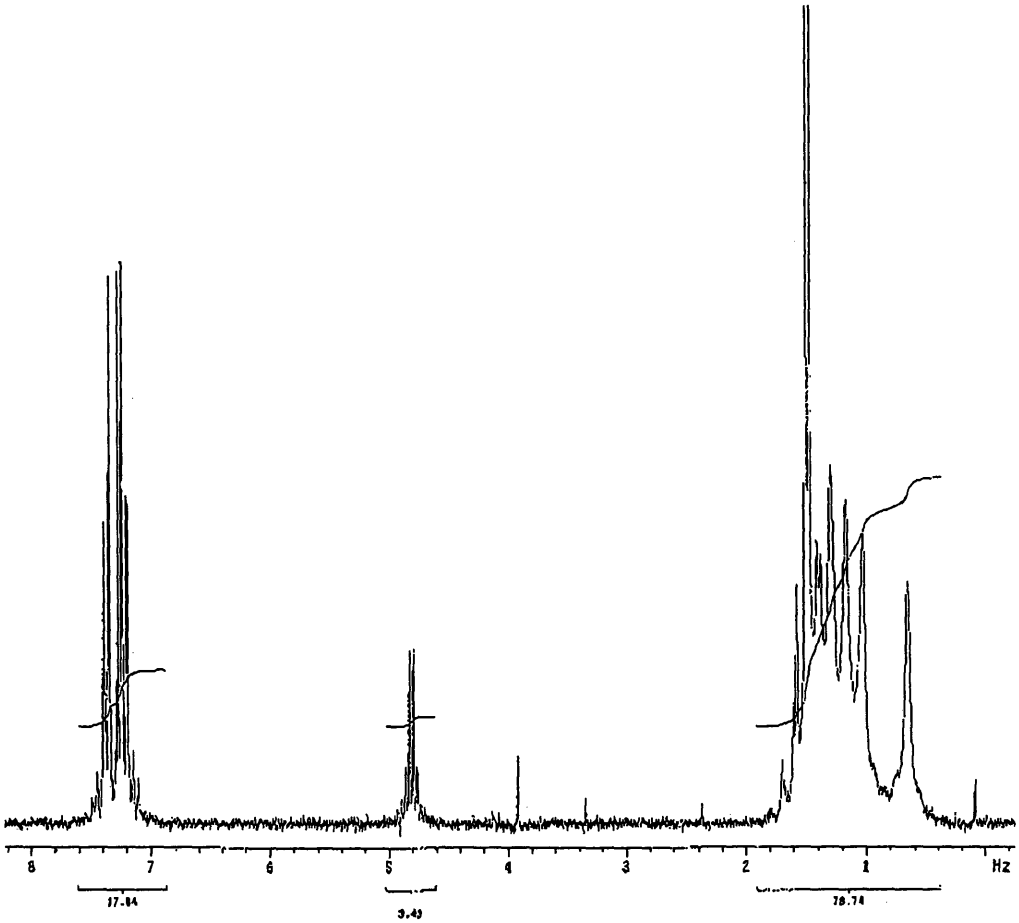


Figure 2.3. Proton NMR Spectrum of *Bis*{4-[1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethyl]phenyl}carbonate (IV)

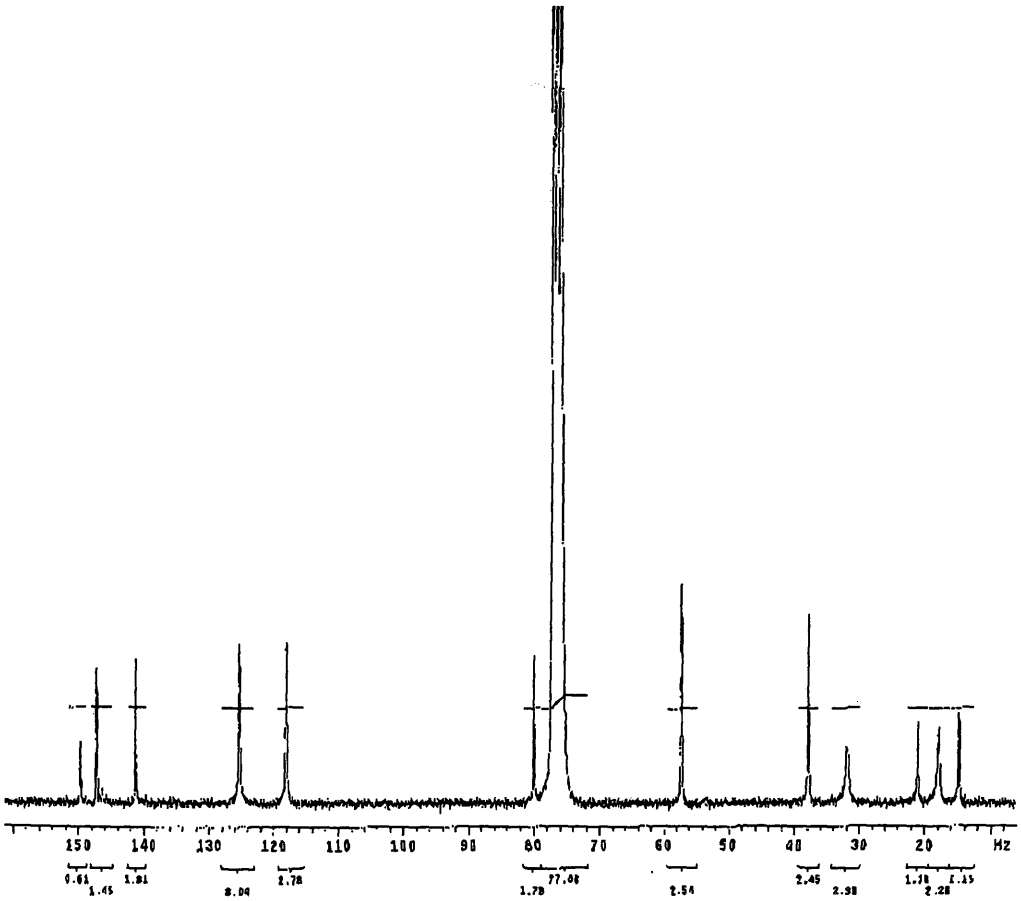


Figure 2.4. C-13 NMR Spectrum of *Bis*{4-[1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethyl]phenyl}carbonate (IV)

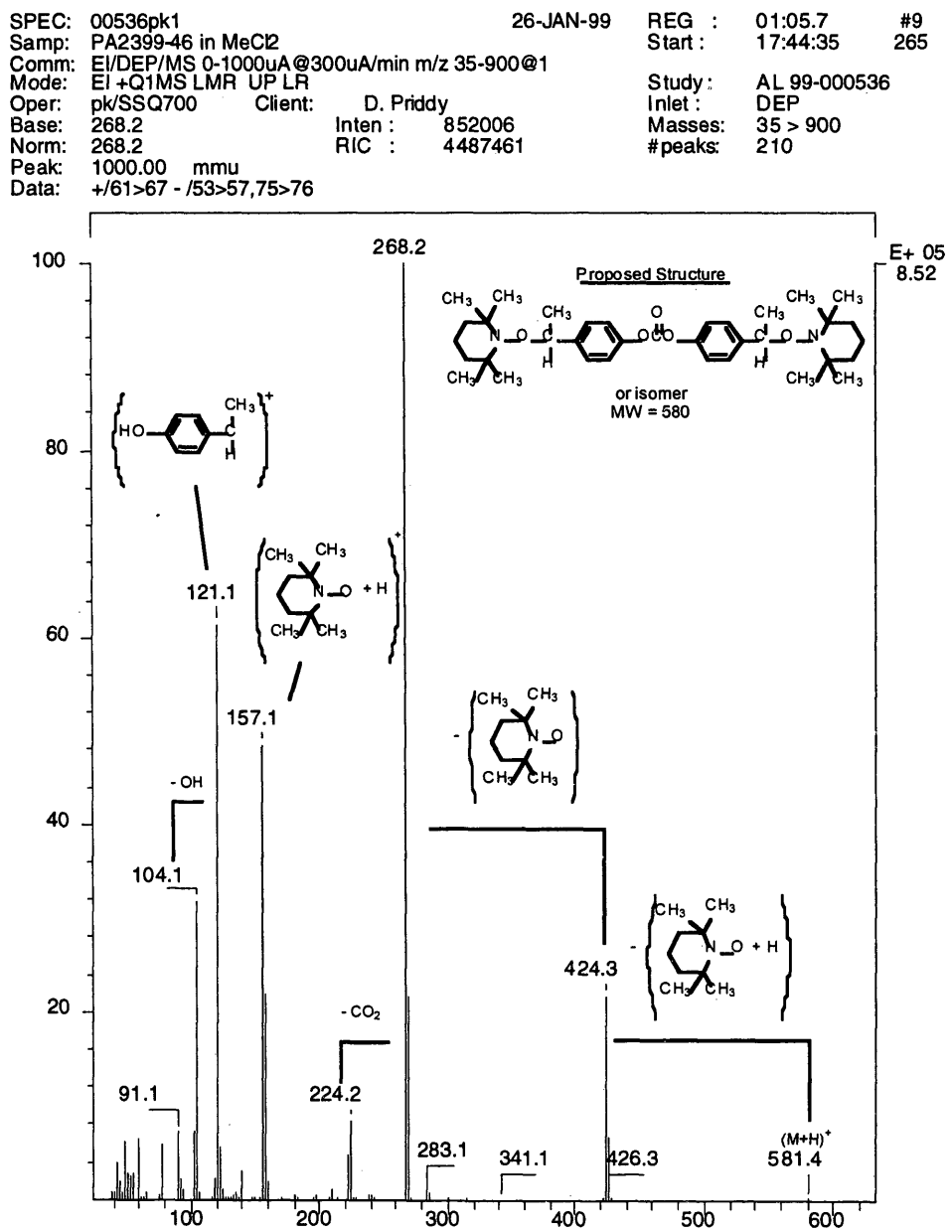


Figure 2.5. Mass Spectrum of *Bis*{4-[1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethyl]phenyl}carbonate (IV)

2.3.2. Polymerization

One way to compare the effectiveness of individual initiators was to evaluate the polymerization of styrene. Figure 2.6 shows a plot of $\ln[M]_0/[M]$ versus polymerization time for styrene at 140 °C using monofunctional initiator I, II and III, where $[M]_0$ is initial monomer concentration and [M] is the monomer concentration after a certain period of time. Unfunctionalized initiator, 1-phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (TMPEP), was used as a control. In order to permit direct comparison, the molar concentration of alkoxyamine was kept the same at 30 mM to maintain an equal initial initiator concentration for each polymerization. Figure 2.8 demonstrates that the polymerization followed first order kinetics in the period of time studied.[23,24] It was found that the kinetics could deviate from the first order as the polymerization continued. The mechanism for the deviation will be discussed later. The functionalized initiators I and III with an acetoxy or *t*-boc group at the *para* position of the phenyl ring were equally as effective as the control TMPEP initiator for the styrene polymerization. In other words, the substitution on the aromatic ring has no obvious effect on the polymerization kinetics. However, it was observed that the polymerization rate using II was significantly slower than I and III. It was speculated that the steric hindrance of the *t*-butoxy group adjacent to the alkoxylamine on II prevented styrene monomer from insertion into the C-O bond leading to a substantial decrease in polymerization rate. Dependence of polymerization rate on the chemical environment of alkoxylamine bond has also been reported by Hawker for copolymerization of polycaprolactone and polystyrene.[25] It was found that when the

alkoxyamine was attached to polycaprolactone as a macromolecule initiator for styrene polymerization, the polymerization rate was enhanced. The rate enhancement could be due to an electronic effect of caprolactone on the alkoxyamine bond. In our case, it is considered that the steric effect is more pronounced than an electronic effect around the labile alkoxyamine initiating center, therefore a slower polymerization rate for II was observed during the time period studied.

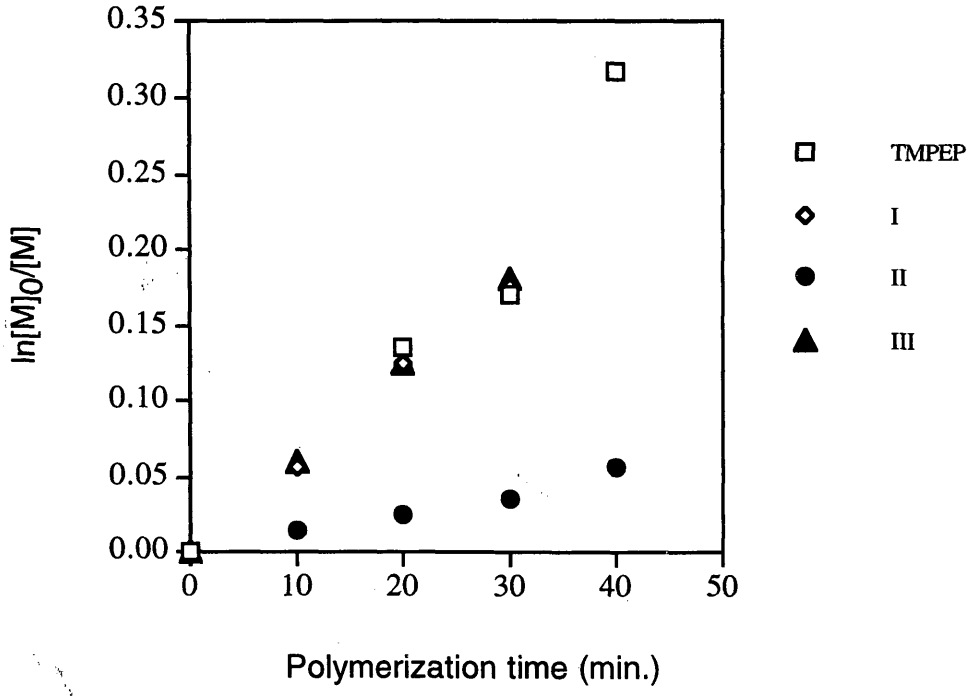
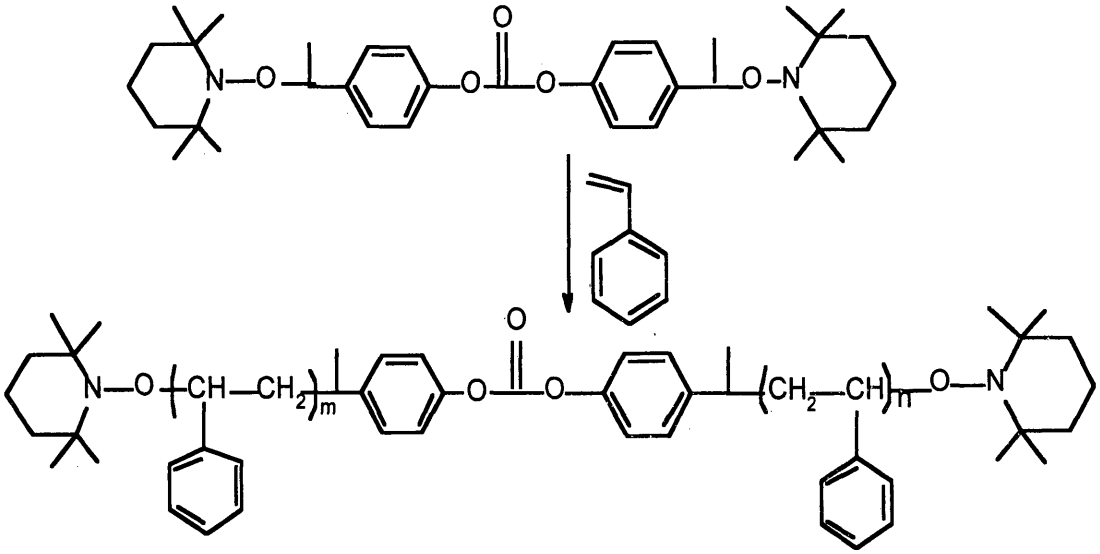


Figure 2.6. Styrene Polymerization at 140 °C Using Different Alkoxyamine-containing Initiators

To evaluate the difference between mono- and difunctionalized alkoxyamine containing initiators in the polymerization, a comparison experiment using IV and III at the same nitroxy group concentration of 60 mM was conducted at 140 °C. Chain propagation during the styrene polymerization using initiator IV is illustrated in Scheme 2.6. Figure 2.7 shows the relationship of monomer conversion versus polymer molecular weight. The molecular weight of the polystyrene initiated by both mono- and di-functionalized initiator increases linearly with monomer conversion indicating the polymerizations followed a living polymerization mechanism. The molecular weight, however, using initiator IV was approximately twice that obtained from III. This suggests that the polymerization did indeed proceed from both ends of the difunctional initiator.



Scheme 2.6. Chain Growth During Styrene Polymerization Initiated with a Difunctional Alkoxyamine Initiator

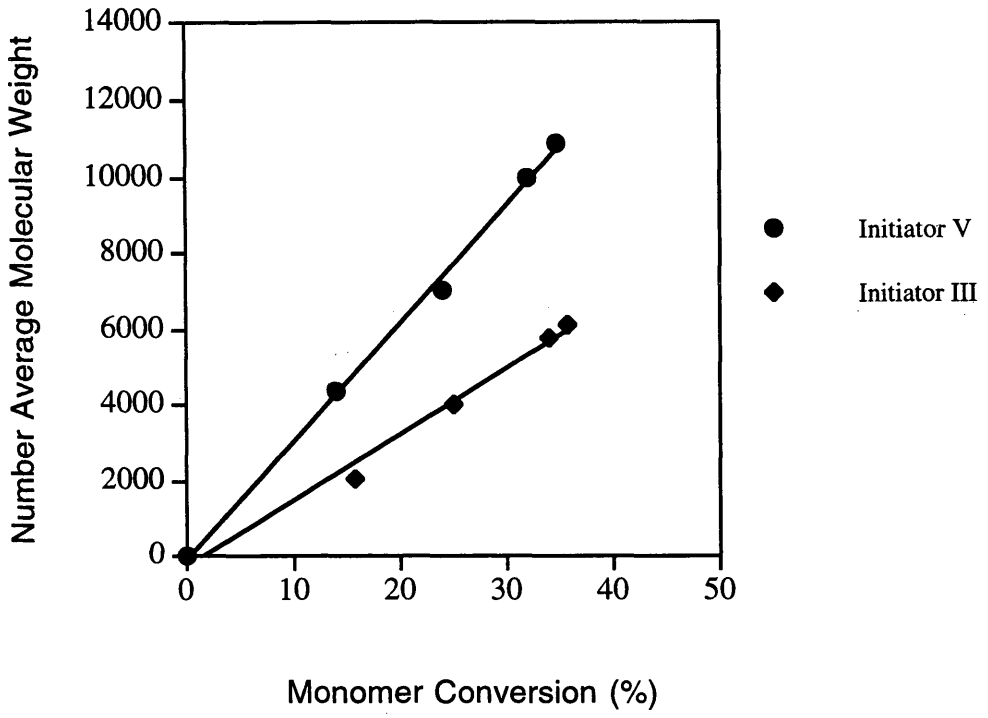


Figure 2.7. Polymer Molecular Weight as a Function of Monomer Conversion for Styrene Using III and V as Initiators

The kinetics of polymerization for mono and difunctionalized initiator was investigated by plotting $\ln[M]_0/[M]$ versus polymerization time, where $[M]_0$ is initial monomer concentration and [M] is time dependent monomer concentration (Figure 2.8). Initiators III and IV showed almost the same polymerization kinetics in the styrene polymerization. The polymerization in general followed first order kinetics but deviated after about 60 minutes (corresponding to about 30% monomer conversion). A similar observation was reported by Fukuda *et al.* where the mechanism and kinetics of

nitroxide-mediated free radical polymerization was studied.[26] The proposed explanation was that as the polymer concentration increases, the polymer radicals become more difficult to diffuse and consequently reduce the chain propagation rate. This explanation is consistent with the greater decrease in reaction rate observed for IV relative to III in the present study. Initiator IV produces a polymer that is twice the molecular weight at a given reaction time and therefore the diffusion would be expected to be relatively more difficult.

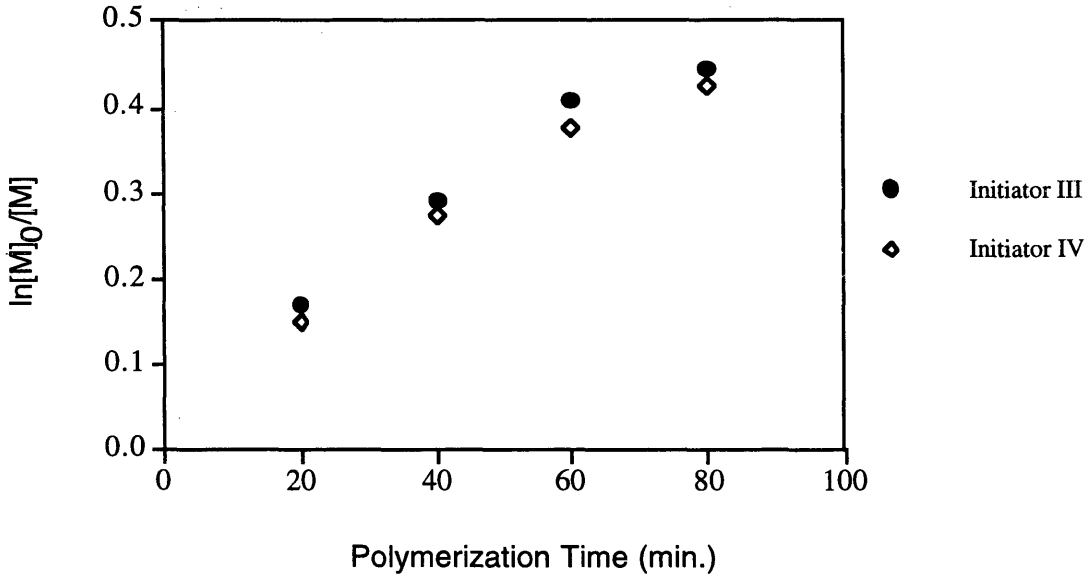
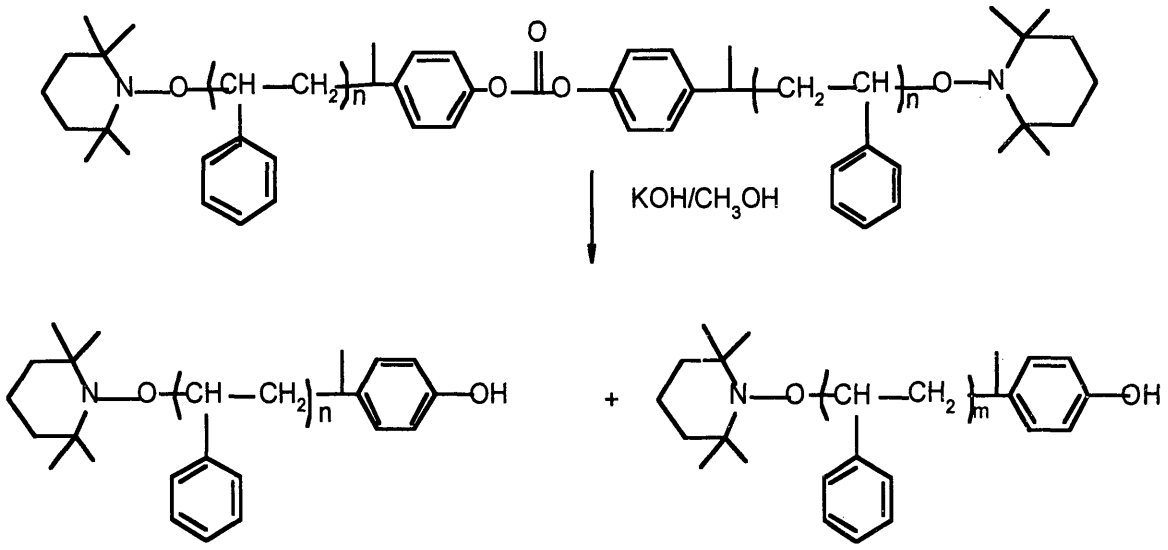


Figure 2.8. Styrene Monomer Conversion as a Function of Polymerization Time Using III and IV as Initiators

To further understand the chain propagation mechanism using difunctional alkoxyamine initiators, the knowledge of the molecular weight distribution of polymer

on each end of the initiator is important. PS using initiator IV contains a carbonate group from the initiator residue that is susceptible to hydrolysis. Therefore, the polymer chains could be cleaved by hydrolysis, providing a convenient method to examine the molecular weight and molecular weight distribution of the polymer produced from initiation from each side of the initiator. The hydrolysis was performed using methylene chloride as a solvent and KOH/CH_3OH as a base as depicted in Scheme 2.7.



Scheme 2.7. Hydrolytic Degradation of PS Containing a Carbonate Linkage in the Main Chain.

Four polystyrene samples made by difunctional initiator IV with different chain length were used in the hydrolysis study. Table 2.2 clearly shows that the molecular weight of each polymer synthesized by the difunctional initiator was reduced after hydrolysis. Theoretically the hydrolysis should result in 50% reduction in number average molecular weight for the polymer and retain low polydispersity if the two alkoxyamine sites are equivalent for the chain initiation and propagation. Alternatively, if the rates of initiation or propagation from the two sites are different, the molecular weight distribution after hydrolysis will broaden. It was observed that the polydispersity of the polymer after carbonate hydrolysis remained almost unchanged. For three of the four samples, the number average molecular weight was reduced to one half of its original value. Sample A showed the molecular weight after hydrolysis was somewhat higher than the anticipated theoretical value. Given that the number average molecular weight of sample A after hydrolysis was low, loss of low molecular weight fraction during polymer precipitation was possible. In conclusion, the two initiating centers on the difucntional initiator appeared to be equivalent since the polydispersity remained low after hydrolysis and polymer chain was determined to be essentially equal in length on each side.

Table 2.2. Change in Polydispersity and Molecular Weight Upon Hydrolysis of Various Carbonate-Containing Polystyrene Samples

Experiment	A	B	C	D
PS M_n Before Hydrolysis (g/mol)	4,100	7,320	9,960	11,100
Polydispersity Before Hydrolysis	1.25	1.21	1.18	1.17
PS M_n After Hydrolysis (g/mol)	3,100	3,810	5,230	5,580
Polydispersity After Hydrolysis	1.19	1.16	1.16	1.15

2.4. Conclusions

Several alkoxyamine containing initiators (I, II, and III) suitable for AIP have been synthesized. Initiator synthesis has been significantly improved by using the low temperature peroxide di-*t*-butylperoxyoxalate. Side reactions are limited because of the low reaction temperature and reduced reaction time. The styrene polymerization using these initiators followed first-order kinetics up to approximately 60 minutes or 30% monomer conversion. After this, deviation from first-order kinetics have been observed. Alkoxyamines bearing an acetoxy or *t*-boc group at the *para*-position of 1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethylbenzene behave normally as AIP initiators while

alkoxyamines having a *t*-butoxy group adjacent to the alkoxyamine group are less reactive due to expected steric hindrance of styrene insertion into the alkoxyamine bond.

Hydroxyl functionality can be easily obtained by converting acetoxy or carbonate groups on the initiator through base catalyzed hydrolysis. A difunctional initiator (IV) containing two active alkoxyamine groups has been generated by coupling the hydroxy-containing alkoxyamine initiator with phosgene. Styrene polymerizations using III and IV as initiators demonstrated controlled polymerization characteristics as the molecular weight of the polymer increased linearly with the monomer conversion. Comparison of polymerization kinetics of mono- and di-alkoxyamines and molecular weight analysis of hydrolyzed product revealed equivalent polymer chain growth from both alkoxyamine sites.

2.5. References

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CHAPTER 3:

PS-*bl*-PC-*bl*-PS FROM PHENOL TERMINATED POLYSTYRENE PREPARED BY NMRP

3.1 Introduction

In 1993, a Xerox research group announced the preparation of low polydispersity polystyrene (PS) using nitroxide mediated radical polymerization (NMRP).[1] This sparked an explosion of research by many groups aimed at determining the commercial value of this technology. Of course it is well understood that, due to the cost competitive nature of a commodity polymer such as PS, NMRP (or alkoxyamine initiated polymerization (AIP)) offers no commercial advantage for the manufacture of the homopolymer. However, NMRP offers an alternative to living anionic polymerization as a method for synthesis of block copolymers, and it provides a synthetic route to block copolymers inaccessible using anionic chemistry. To date, NMRP technology has been utilized to make a variety of block[2,3,4,5] and graft copolymers.[6] For example, the use of NMRP to prepare PS-*bl*-poly(methyl methacrylate) and PS-*bl*-polybutadiene block copolymers has been reported.[4,7,8] There have also been some efforts focused on using NMRP to prepare block copolymers having step-growth polymer segments.[9]

There has been an industrial interest to make polystyrene-*bl*-polycarbonate copolymer due to its balanced physical properties of high strength and toughness. The traditional synthesis of block copolymers relies upon the sequential polymerization of corresponding comonomers by a similar mechanism (e.g., anionic polymerization).[10] Although this strategy may be successful, it has limitations especially when participating monomers follow different synthesis routes. The synthesis of block copolymers of PS and polycarbonate (PC) require two distinctively different polymerization mechanisms. Styrene can be polymerized by either free radical or anionic chain-growth polymerization, however, PC is produced by step-growth polymerization. A strategy needs to be developed in order to combine the two different polymerization processes. Brooks has reported the synthesis of triblock copolymers of PS and PC.[11] The formation of the copolymer required the synthesis of a properly end-functionalized PS. Anionic polymerization of styrene was followed by termination with carbon dioxide and the conversion of the resulting carboxylic acid groups into acid chlorides. The end-functionalized PS was then added as a chain-stopper to a bisphenol-A polycarbonate condensation polymerization to make the triblock copolymer. Jiang also reported the formation of PS-PC triblock copolymer, where hydroxy end-functional PS was produced by ethylene oxide termination of anionically polymerized PS and then the functionalized polymer was used as an end-capper in subsequent reaction with phosgene and bisphenol A.[12] These processes possess several disadvantages due to the rigorous purification conditions required for anionic polymerization of styrene. Consequently, the process adds significant costs to the production of the functionalized PS. To develop a low cost alternative, the preparation of PS-*bl*-PC-*bl*-PS was studied using the combination of AIP and step-growth polymerization. Phenol-functionalized PS was prepared using AIP.

The PS bearing phenol end-groups obtained from this process was further used as a chain stopper in interfacial polycarbonate polymerization. The synthesis and characterization of the PS-*bl*-PC-*bl*-PS block copolymers using this combined procedure will be discussed.

3.2 Experimental

All reagents were purchased from the Aldrich Chemical Company and were used as received unless indicated otherwise. Styrene was obtained from The Dow Chemcial Company and contained 3 ppm 4-*t*-butylcatechol as an inhibitor. Infrared spectra were recorded using a Perkin-Elmer FT-IR spectrometer. Proton and ^{13}C NMR spectra were recorded in CD_3Cl solution (with chromium acetylacetonate) using a Varian 200-XL spectrometer operating at 200 and 50 MHz frequencies, respectively.

Polymerizations were conducted in clean Pyrex ampoules sealed under reduced pressure. Polymer molecular weights were established by gel permeation chromatography(GPC) using a Hewelett-Packard 1090 instrument equipped with a set of 10 μm mixed-bed columns (Polymer Labs) and an ultraviolet detector. Narrow molecular weight distribution PS standards were used for calibration. Both standards and samples were introduced as 0.25% (w/w) solutions in tetrahydrofuran (THF). The elution solvent was THF in all cases and the flow rate was 1.0 mL/min.

Differential scanning calorimetry (DSC) measurements were performed using a DuPont 2000 instrument at a heating rate of 20 °C /min. Temperature calibration was performed with an indium standard. All runs were carried out under a N_2 atmosphere. The glass transition temperature (T_g) was taken as the temperature of the inflection point.

3.2.1. Preparation of 1-(4-*t*-Butoxycarbonyloxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperdinyloxy)ethane (I)

Compound I was prepared as described previously.

3.2.2. Polymerization of Styrene using (I)

A solution of styrene containing I (64 mmol) was loaded into Pyrex ampoules (5mm i.d x 10 mm o.d. x 30 cm) and sealed under reduced pressure (< 6 Torr) using the freeze-thaw technique. The sealed ampoules were placed in a silicone oil bath maintained at 140 °C. The ampoules were removed at different time intervals, allowed to cool to room temperature, opened, and the contents examined to determine the extent of monomer conversion to polymer by precipitating the syrup into methanol.

3.2.3. Removal of the Protecting Group of II by Hydrolysis to Form Phenol Terminated PS (III)

To a 100 mL round-bottomed flask fitted with a magnetic stirrer, condenser and nitrogen inlet, was added aqueous KOH (12.3%, 0.4 g), methanol (0.5 g), and THF (5 g), followed by a solution of III (2.5 g) dissolved in THF (5 g). The mixture was stirred at room temperature for 1 h then concentrated under a stream of nitrogen to a volume of 2 mL and then poured into methanol. The polymer was collected by filtration and dried *in vacuo* for 3 h at 50 °C.

3.2.4. Synthesis of PS-*bl*-PC-*bl*-PS

Step 1: To a 250 mL three necked flask equipped with a mechanical stirrer was added bisphenol A, water and a 50% (w/w) solution of NaOH. After the mixture became homogeneous, methylene chloride was added. The mixture was stirred for 5 minutes. To the above mixture, triphosgene was gradually added. After 5 minutes the solution became very milky. Step 2: NaOH (50% (w/w)) was added and stirring continued for 5 minutes. The agitation was stopped and the aqueous phase analyzed for unreacted bisphenol A by the addition of 1-2 drops of 5 mL 1N HCl (the formation of water insoluble precipitate indicated the presence of unreacted bisphenol A). If unreacted bisphenol A was present, more triphosgene was added until no precipitate formed. Phenol-functional PS was dissolved in methylene chloride and was added to the reaction mixture and stirred for 5 minutes. Step 3: Additional methylene chloride was added and stirring continued for 5 minutes. Triethylamine (0.2 mL) was then added to the solution and the mixture was stirred at room temperature for 30 minutes. Step 4: Finally, more triphosgene was added to reduce the pH to about 8-9. The reaction mixture was allowed to stand and the layers separated. The organic layer was washed twice with water. The polymer was isolated as a film by the evaporation of the solvent in a shallow dish. Copolymers with various compositions were prepared and the amounts of reagents used in the experiments are described in Table 3.1.

Table 3.1. Formulation for Preparing PS-*bl*-PC-*bl*-PS Copolymers

	Reactant	M_n (g/mol)	Exp No.1 (Amount)	Exp. No. 2 (Amount)
Step 1	Bisphenol A	228	2.60 g /0.0114 mol	2.50 g/0.011 mol
	NaOH 50%	40	1.80 g/0.0225 mol	1.77 g/0.0221 mol
	H_2O		20.0 mL	20.0 mL
	CH_2Cl_2		16.0 mL	15.0 mL
	Triphosgene	296	1.40 g; 0.0047 mol	1.35 g; 0.0045 mol
Step 2	NaOH 50%		1.60 g; 0.020 mol	1.60 g; 0.020 mol
	PS-OH	7016	1.56 g; 2.22e-4 mol	4.80 g; 6.84e-4 mol
Step 3	CH_2Cl_2		7.0 mL	5.8 mL
	Triethylamine		0.20 mL	0.20 mL
Step 4	Triphosgene	296	1.00 g; 0.00338 mol	0.97 g; 0.00328 mol
	Targeted Mn of PC		26,000 g/mol	8,120 g/mol

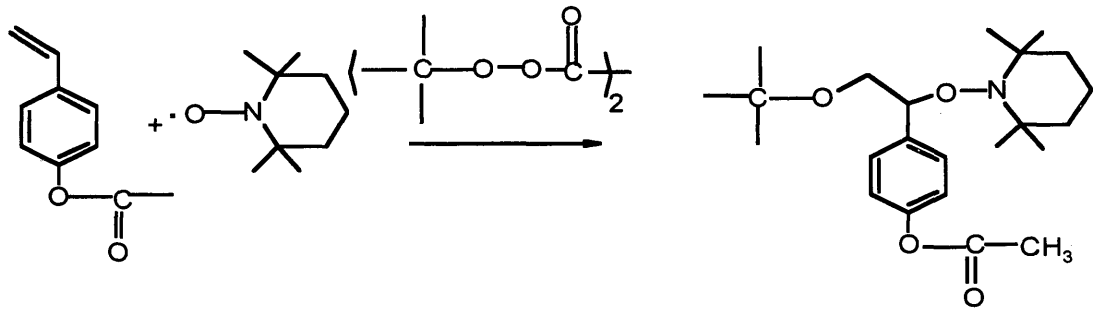
3.2.5 Hydrolysis of PS-*bl*-PC-*bl*-PS Copolymer

One gram of block copolymer was dissolved in 5 g of THF and treated with 1 mL of a 10 % (w/w) solution of potassium hydroxide in methanol. The mixture was stirred at room temperature for 1 h. The polymer was precipitated into methanol and the polymer removed by filtration and dried at 50 °C in a vacuum oven for 4 h. The molecular weight and polydispersity of the polymer before and after hydrolysis were measured by GPC.

3.3. Results and Discussion

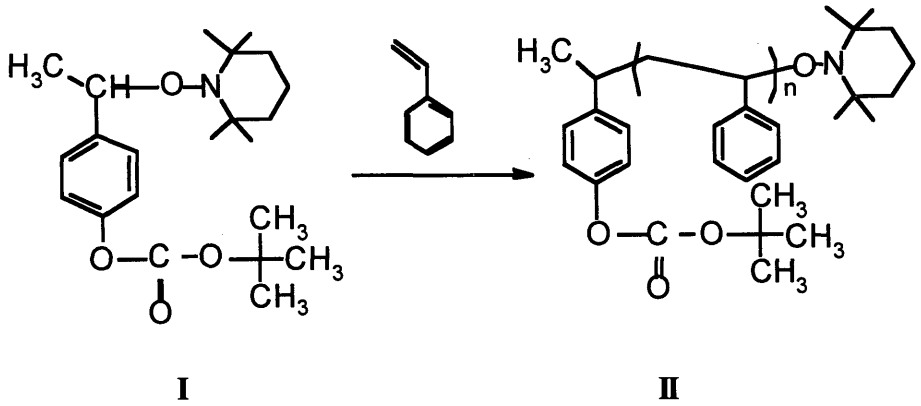
3.3.1. Polymerization

Initiator 1-(4-*t*-Butoxycarbonyloxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperdinyloxy)ethane (I) was synthesized to contain a protected phenol functional group as illustrated in Scheme 3.1. The *t*-boc protecting group was used to prevent the phenol group from interfering with the free radical polymerization of styrene (Scheme 3.2).



I

Scheme 3.1. Synthesis of 1-(4- *t*-Butoxycarbonyloxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane (I)



Scheme 3.2. Synthesis of Polystyrene Using Initiator I

The styrene polymerization behaved in a manner typical for NMRP. The molecular weight increased linearly with the monomer conversion as shown in Figure 3.1, reflecting the living nature of the polymerization. The polymer molecular weight and molecular weight distribution were determined by GPC analysis. The polydispersity of the polymer remained low at about 1.2, which is significantly lower than PS from a conventional free radical polymerization.[19] It was also found that polydispersity was independent of the monomer conversion within the range of the molecular weights studied. Samples with number average molecular weights of 2100 g/mol and 7000 g/mol and polydispersities of 1.23 and 1.18, respectively, were prepared for use in copolymerization.

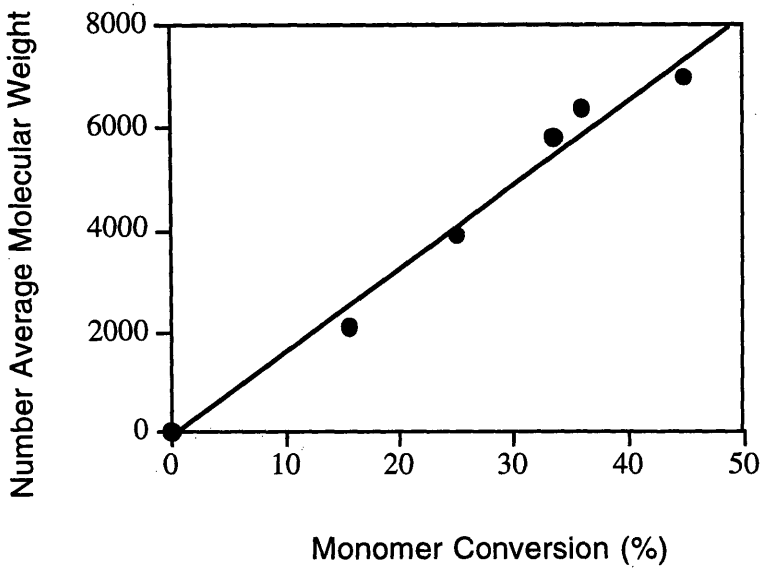
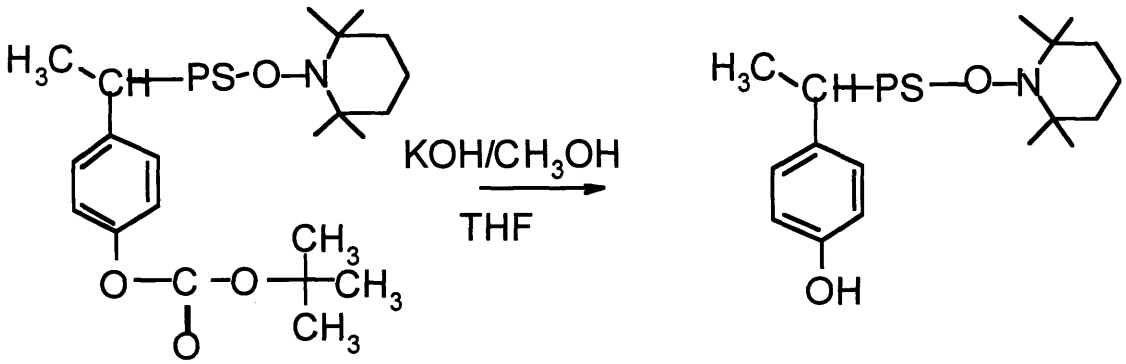


Figure 3.1. Number Average Molecular weight Versus Conversion Using I as an Initiator at 140°C

The phenol end group was generated by hydrolysis of the *t*-boc protecting group on the PS chain end as shown in Scheme 3.3. The phenol-terminated PS was then used as a chain-stopper in the condensation polymerization of bisphenol A and phosgene to form triblock copolymers of PS-*bl*-PC-*bl*-PS as shown in Scheme 3.4.



III

Scheme 3.3. Generation of Polystyrene Containing 1-(4-Hydroxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane III

In order to achieve effective coplymerization of PS with PC and minimize polystyrene homopolymer content, polystyrene with quantitatively functionalized chain-ends is essential. Furthermore, since NMRP (or AIP) is considered as a pseudo living process, radical coupling, chain transfer and disproportionation are possible to occur.[13] The occurrence of some of these reactions will reduce the population of polystyrene chains with *t*-boc functionality and ultimately, phenol functionality. It was observed in earlier work that the number of polystyrene chains with chain-end functional groups decreases as polymerization progresses due to an increased probability of thermal decomposition of the carbon-nitroxy bond and the contribution of thermally initiated

styrene.[5] It was found that polystyrene chains with greater than 90% functionalization were only achieved when the PS's number average molecular weight was kept below 10,000 g/mol.[14] Therefore, to ensure a high percentage of chain end functionality, polystyrene with number average molecular weights of 2,100 and 7,000 g/mol were prepared for copolymerization with PC.

The polystyrene chain ends were probed by ^{1}H and ^{13}C NMR spectroscopy. In order to gain a strong NMR signal for the end group, PS with M_n of 2,100 g/mol was studied. The polymer was dissolved into deuterochloroform to provide a solution suitable for analysis. The ^{13}C spectrum of the polymer is shown in Figure 3.2. The ratio of the integrated peaks for the absorption due to the TEMPO group at δ=17.0 ppm to the absorption of the methine carbon atom of polystyrene at δ=40 ppm indicated that the number average molecular weight of the functionalized polystyrene is about 1980 g/mol. On the other hand, the number average molecular weight of PS including both functionalized and non-functionalized chains was determined to be 2100 g/mol by GPC. This value is within error to that obtained from ^{13}C NMR, indicating a high percentage of functionalized PS chains.

Comparison of the ^{1}H NMR spectrum of initiator with that of the polymer reveals a number of interesting features (Figures 3.3 and 3.4). The absorption for the benzylic proton appears as a quartet at δ = 4.8 ppm in the spectrum of the initiator. However, the spectrum of the polymer in the same absorption region appears as broad peaks at higher field (at about 2.2 ppm). This behavior is fully consistent with the anticipated structure of the polymer in which the electron-withdrawing TEMPO unit is replaced by the polystyrene chain.[15] Two groups of peaks, centered at 5.3 and 5.8 ppm were assigned to the benzylic proton of the styrene unit bonded to the piperidinyloxy

group. Polystyrene tacticity effects cause this methine resonance to be split into two groups.[15]

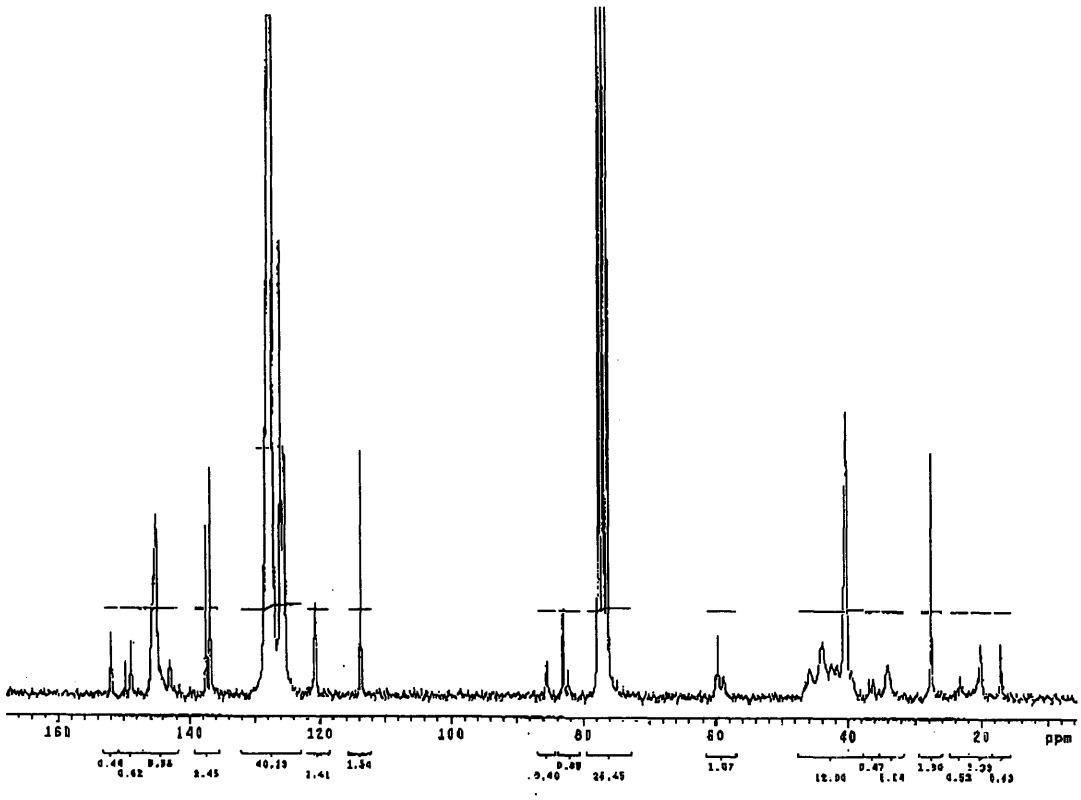


Figure 3.2. ^{13}C NMR of Polystyrene with Number Average Molecular Weight of 2100 g/mol Prepared by Using Initiator I

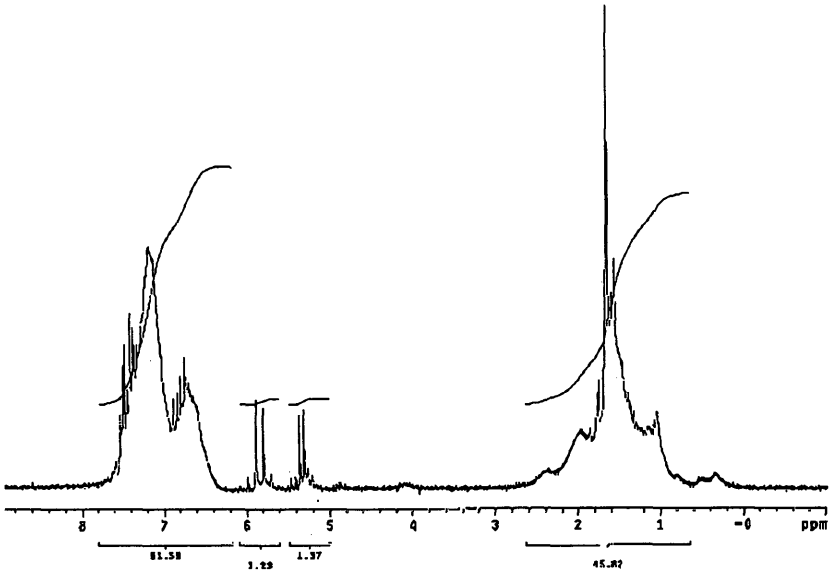


Figure 3.3. ^{1}H NMR of Polystyrene with Number Average Molecular Weight of 2100 g/mol Prepared by Using Initiator I

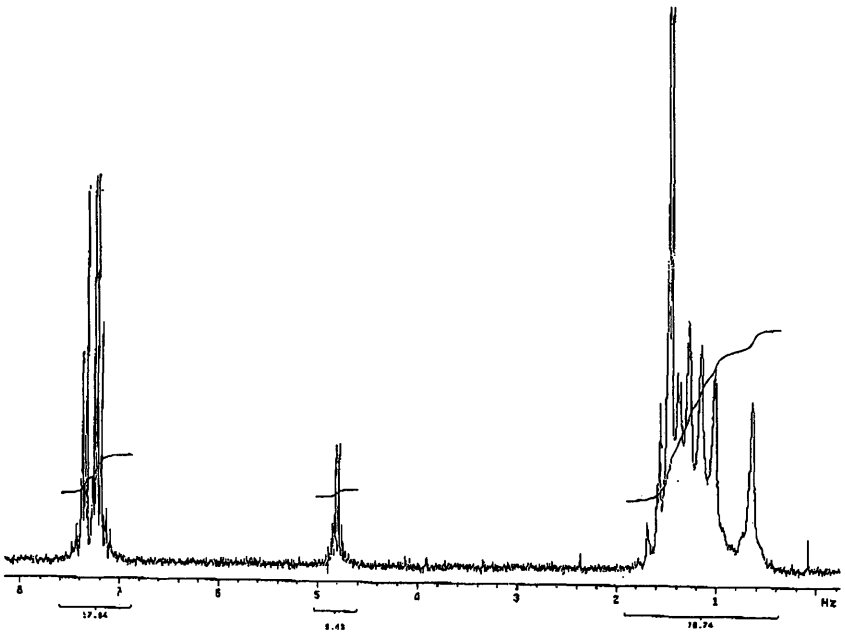


Figure 3.4. Proton NMR Spectrum of 1-(4- *t*-Butoxycarbonyloxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperdinyloxy)ethane

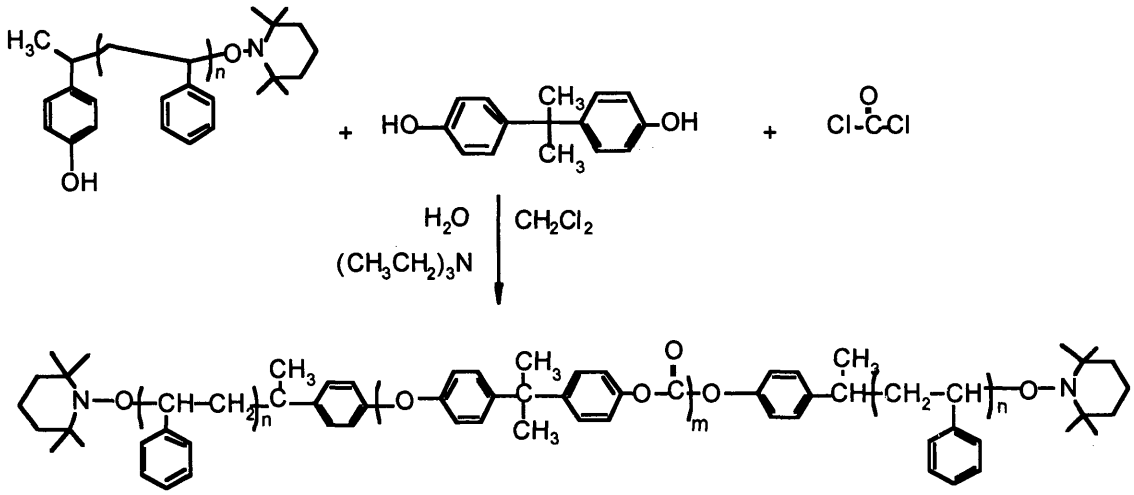
Since it is well known that phenols have an inhibiting effect upon free radical polymerization, it was necessary to protect the phenol functionality of the initiator during styrene polymerization and subsequently remove the protecting group after the PS was formed. Several protecting groups were considered such as acetoxy or *t*-boc groups. We chose the *t*-boc group because it is more readily removed than acetoxy.[16] The hydrolysis reaction of *t*-boc functionalized PS was conducted in THF solution using 10 wt% of KOH in methanol as a reagent. After hydrolysis, the resulting phenol-functionalized PS had about the same molecular weight as before hydrolysis (Table 3.2). In other words, hydrolysis did not change the molecular weight of the PS.

Table 3.2. Molecular Weight and Polydispersity of PS Before and After Hydrolysis

Mn Before Hydrolysis	PD Before Hydrolysis	Mn After Hydrolsyis	PD After Hydrolysis
2,100	1.23	2,260	1.23
7,000	1.18	7,100	1.16

The block copolymers of PS-*bl*-PC-*bl*-PS were prepared using phenol-teminated PS as a chain stopper for condensation polymerization of bisphenol A and phosgene. Due to the toxicity issue of phosgene gas, triphosgene was used as an alternative source of phosgene. Since triphosgene is a solid at room temperature, the handling is much easier and the amount added to the reaction can be controlled precisely with one mole of triphosgene equivalent to three moles of phosgene.[16]

The condensation polymerization of triphosgene and bisphenol A produces bisphenol A polycarbonate. This was performed by an interfacial polymerization procedure. This process proceeded in two discrete steps. Bisphenol A was mixed with water and methylene chloride and subsequently dissolved in the aqueous phase by the addition of sodium hydroxide (NaOH). With good agitation, triphosgene was added while the pH was maintained between 9.0-11.0. Triphosgene reacted with bisphenol A to form organic soluble chloroformate terminated oligomers. Phenol-functional PS was then added to the reaction as a macro-chain stopper and triethylamine was added as a catalyst to promote the condensation of the chloroformate oligmers to PS-*bl*-PC-*bl*-PC copolymer.



Scheme 3.4. Formation of PS-*bl*-PC-*bl*-PS Copolymer by Interfacial Polymerization

PS-*bl*-PC-*bl*-PC copolymers with two different PC segment lengths were prepared. The molecular weight of the PC is governed by the molar ratio of bisphenol A

to the PS macro chain stopper. The targeted molecular weights of PC for the experiments are listed in Table 3.1. The actual molecular weights of PC are listed in Table 3.3, and show that the actual values are slightly lower than the anticipated value. In principle, if the PS chain-end is not quantitatively functionalized with phenol groups, the resultant block copolymer molecular weight will be higher than the targeted value. However, in this case the opposite was observed. In the procedure used, the formation of PC takes place in two stages. First, the disodium salt of bisphenol A in the aqueous alkaline solution is phosgenated in the presence of an inert organic solvent to form chloroformate oligomers. In the second stage, triethylamine catalyzed coupling of the oligocarbonates to high molecular weight polycarbonates occurs.[17] It is speculated that the coupling reaction of the chloroformate oligomers during the second stage is less effective for low molecular weight PC. It was observed that, for high molecular weight PC, the molecular weight deviation between actual M_n and targeted M_n is much less.

Table 3.3. Molecular Weight Characterization of PS-*bl*-PC-*bl*-PS Copolymers Made by Interfacial Polymerization

Exp. No	Mn of Starting PS	PDI PS-OH	Mn PS-PC-PC	PDI PS-*bl*-PC-*bl*-PS	Copolymer Composition
1	7,000	1.18	37,000	2.34	7,000-23,000-7,000
2	7,000	1.18	19,300	4.60	7,000-5,200-7,000

Figure 3.5 shows the GPC chromatogram of phenol-functionalized PS and the copolymer from experiment no. 1. The GPC curves show a monomodal peak that shifts to higher molecular weight indicating the formation of copolymer. A single peak for the copolymer also implies that the copolymer is almost free of PC and PS homopolymers. These results demonstrate that polystyrene was highly functionalized and was mostly incorporated into the copolymer structure.

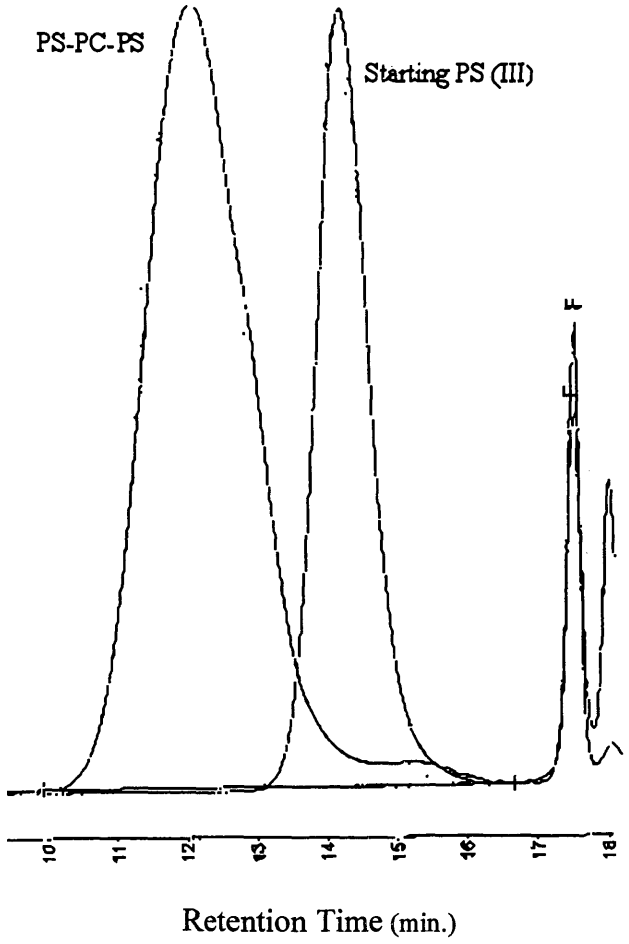


Figure 3.5. Overlay of GPC Chromatograms of Phenol-Functional PS and its Resultant PS-*bl*-PC-*bl*-PS Copolymer (Exp. No. 1)

3.3.2 Copolymer Characterization

Measuring the glass transition temperature (T_g) is an effective way to characterize the copolymer. If the block copolymer is composed of two immiscible blocks, two separate T_gs representing each block will be detected by DSC. However, when the two blocks are miscible with each other, only one T_g appears. It is also well known that the T_g of polymers is a function of their molecular weight. The dependence of T_g on molecular weight can be expressed in the following equation (Eq. 1),[18]

$$T_g = T_g^{\infty} - \frac{A}{M_n} \qquad \text{Eq.(1)}$$

where M_n is the number average molecular weight and T_g^{∞} is a glass transition temperature corresponding to a chain with infinite molecular weight. A is a constant associated with a particular polymer system. T_g^{∞} for PS and PC are 373 K and 432 K, and the factor A are 1.0×10^5 mol K and 1.45×10^5 mol K respectively.[18,19] The calculated T_gs for PS and PC homopolymers as a function of molecular weight are listed in Table 3.4.

Table 3.4 Estimated T_g for PS and PC Homopolymers with Various Molecular Weights

	T_g^{∞}(K)	A (mol-K)	M_n	Calculated T_g (°K)	Calculated T_g(°C)
PS	373	100,000	2,100	278	52
			7,000	346	86
PC	432	145,000	23,000	425	152
			5,200	403	130

The T_gs of the copolymers were measured by DSC. The samples were first heated to 220°C and slowly cooled to room temperature to eliminate the thermal history of the sample. The T_g was then recorded on a second temperature sweep with a heating rate of 20 °C/min. The DSC analysis of the copolymer with composition of PS-*bl*-PC-*bl*-PC (7,000-23,00-7,000) shows two T_gs at 105 °C and 145 °C corresponding well to the T_gs of PS and PC homopolymer, respectively. According to Table 3.4, the T_g of PS with M_n=7,000 should be about 85 °C whereas T_g of PC with M_n=23,000 should be about 152 °C based on Equation 1. An inward migration of T_g of both PS and PC phase was observed. The Tg of the PS phase increased from the expected 85 °C to 105 °C while the T_g of the PC phase decreased from the expected 152 °C to 145 °C. The shift of T_g of the PS and PC segments in the block copolymer indicates partial miscibility between PS and PC at a microstrutural level.[20,21] The degree of shift of T_g is different between PS and PC segment. It was observed that the T_g of PS shifted more to a higher temperature as opposed to the PC shift to a lower temperature, partially due to the higher weight percentage of PC in the copolymer. However, even at the equal weight percentage, it has been reported that there is a greater effect on PC raising the T_g of PS than for PS lowering the T_g of PC because PS is more soluble in PC.[22]

For the block copolymer with composition of PS-*bl*-PC-*bl*-PS of 7,000-5,200-7,000, only one T_g at 107 °C was observed by DSC. It is estimated from Equation 1 that for PC with M_n of 5,200, the T_g should be around 130 °C whereas the T_g of PS with M_n of 7,000 should be about 85 °C. Although, PC and PS are generally incompatible, the observance of only one T_g indicates a high level of miscibility between the low molecular weight PS and PC segments. A similar observation was reported by Landry *et al.,* where

miscibility of the two polymer system showed a strong dependence on the molecular weight.[23]

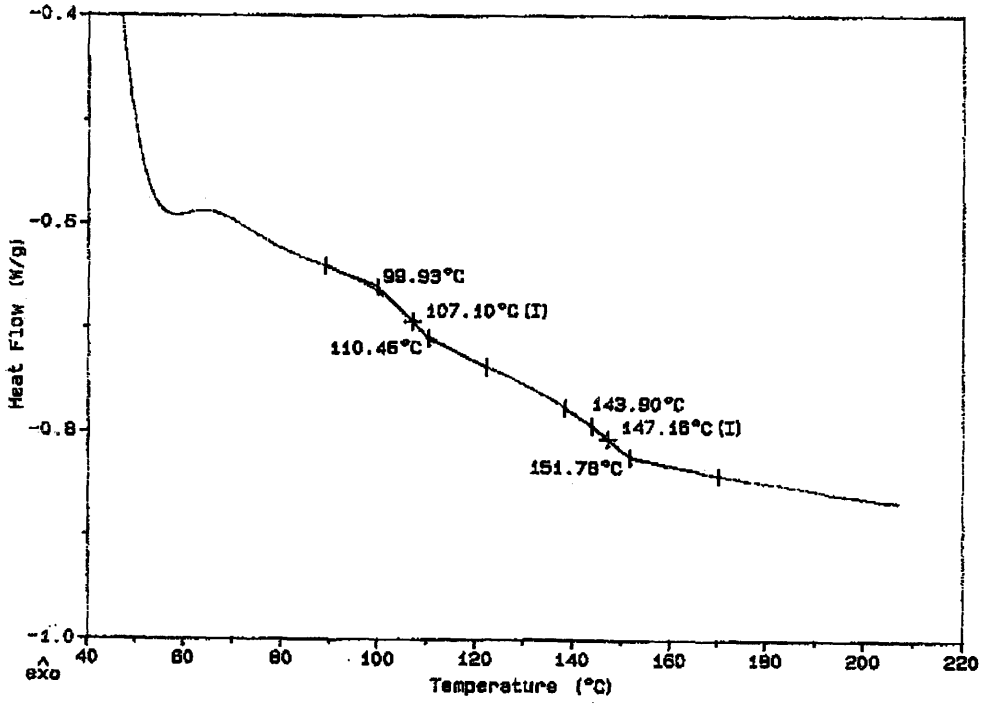


Figure 3.6 DSC of Copolymer PS-*bl*-PC-*bl*-PS(7,000-23,000-7,000)

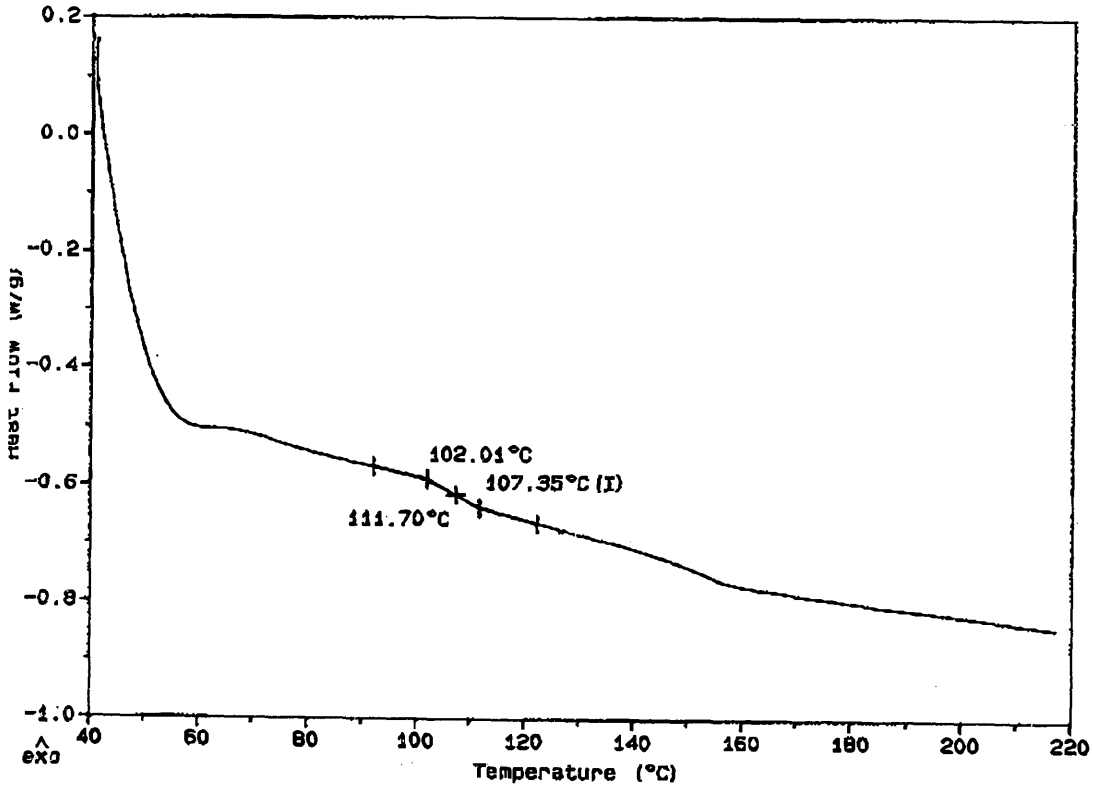


Figure 3.7. DSC of Copolymer PS-*bl*-PC-*bl*-PS (7,000-5,200,7,000)

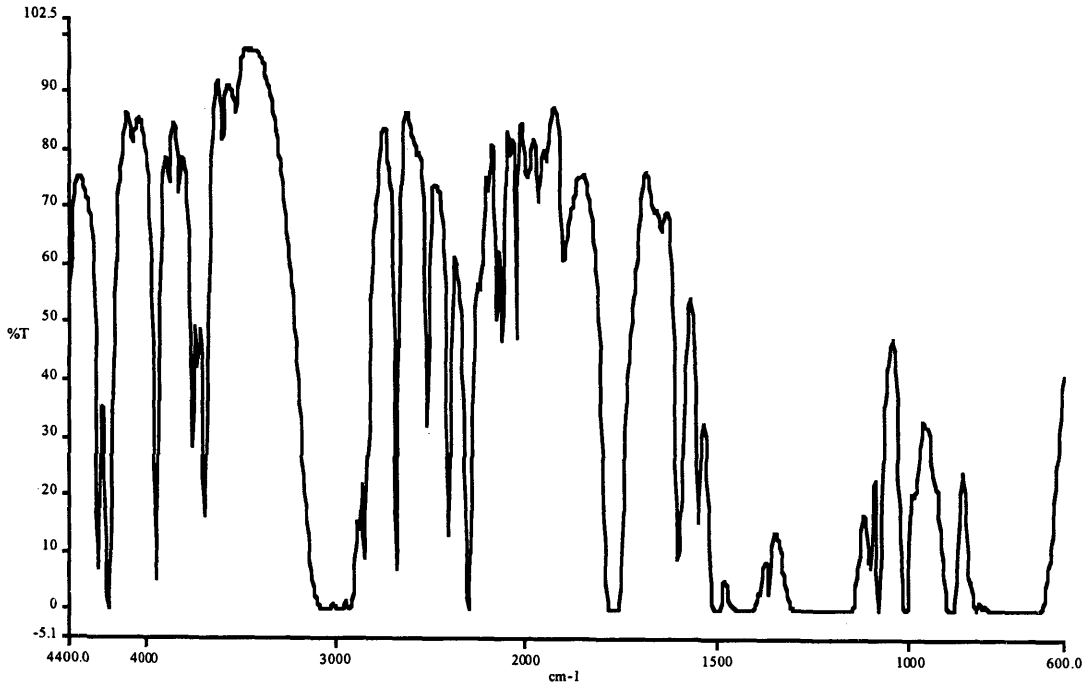


Figure 3.8. FTIR Spectrum of PS-*bl*-PC-*bl*-PS Copolymer

FTIR analysis was used to further confirm the existence of PS and PC segments in the block copolymer structure (Figure 3.8). The spectrum shows the presence of peaks characteristic for both PS and PC segments. Within the region of 1700 to 2000 cm^{-1}, aromatic groups of PS were observed. At 1780 cm^{-1} a C=O stretch was detected. The spectrum shows a series of CH absorption bands within 1200-1500 cm^{-1} characteristic for PS, and within 1200-1300 cm^{-1} a distinct band characteristic for C-O stretching vibration in PC.[24]

TEM analysis showed interesting features of the copolymers. The copolymer was first stained with RuO_4 at room temperature for about 30 minutes and then was

microtomed for TEM analysis. PS was more easily stained than PC, therefore the PS segment showed up as a darker phase in the TEM micrographs. Figure 3.9 displays a TEM micrograph of the copolymer with lower molecular weight PC (experiment no. 2). The micro phase separation between PS and PC is quite obvious with an average domain size of 0.05 μm. TEM of the copolymer with high molecular weight PC revealed an interesting feature as shown in Figure 3.10. Again phase separation between PS and PC is evident, however the morphology and domain size for individual PS and PC segment are quite different from what was seen for low molecular weight PC. Much smaller PS domains, less than 0.01 μm, were observed. The PC domain appeared as a continuous phase with a less defined boundary to the PS phase. This phenomenon can be attributed to the high percentage of PC in the copolymer.

To further confirm the formation of PS-*bl*-PC-*bl*-PS block copolymer, hydrolysis of the block polymer by breaking the carbonate linkages in the PC was performed. The procedure allowed the measurement of the molecular weight of the remaining PS (Scheme 3.6) as a final check of the copolymer structure. The molecular weight change before and after hydrolysis is shown in Table 3.5. The molecular weight of the copolymer reduced upon hydrolysis and the remaining PS matched the starting PS molecular weight. Figure 3.11 shows the GPC profile of the block copolymers after hydrolysis and the starting phenol-functional polystyrene before copolymerization. The two GPC profiles overlap well implying the whole functionalized polystyrene chain is indeed attached to polycarbonate segment and there is little or no PS degradation taking place during polymerization.

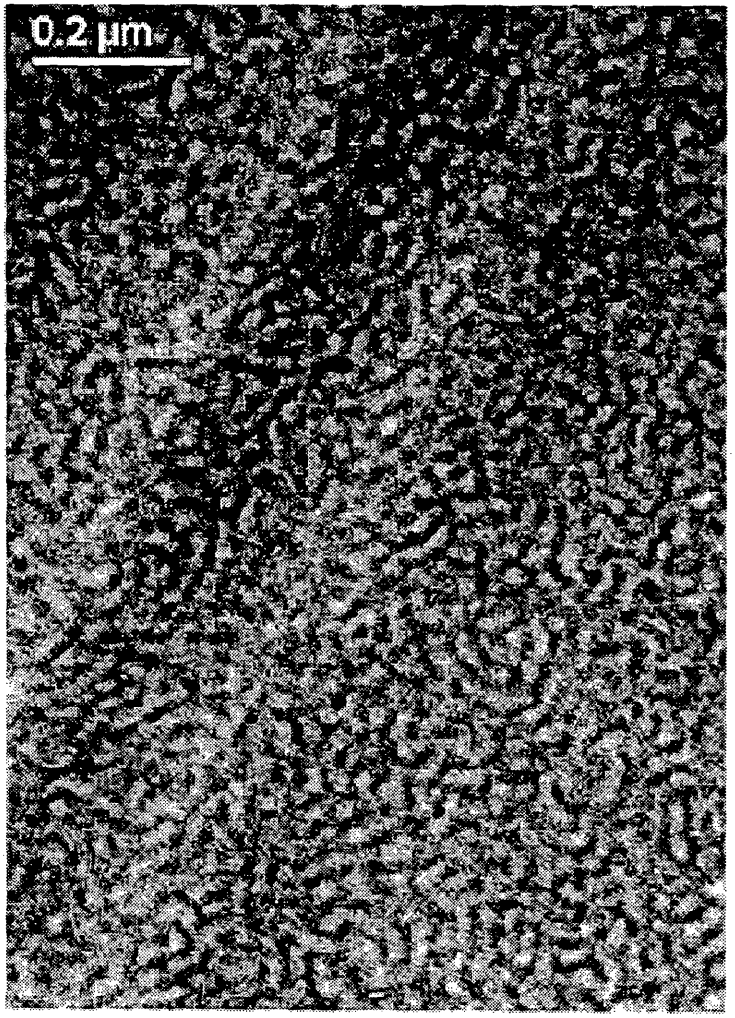


Figure 3.9. TEM of PS-*bl*-PC-*bl*-PS Copolymer from Exp. No. 2 (7,000-5,200-7,000)

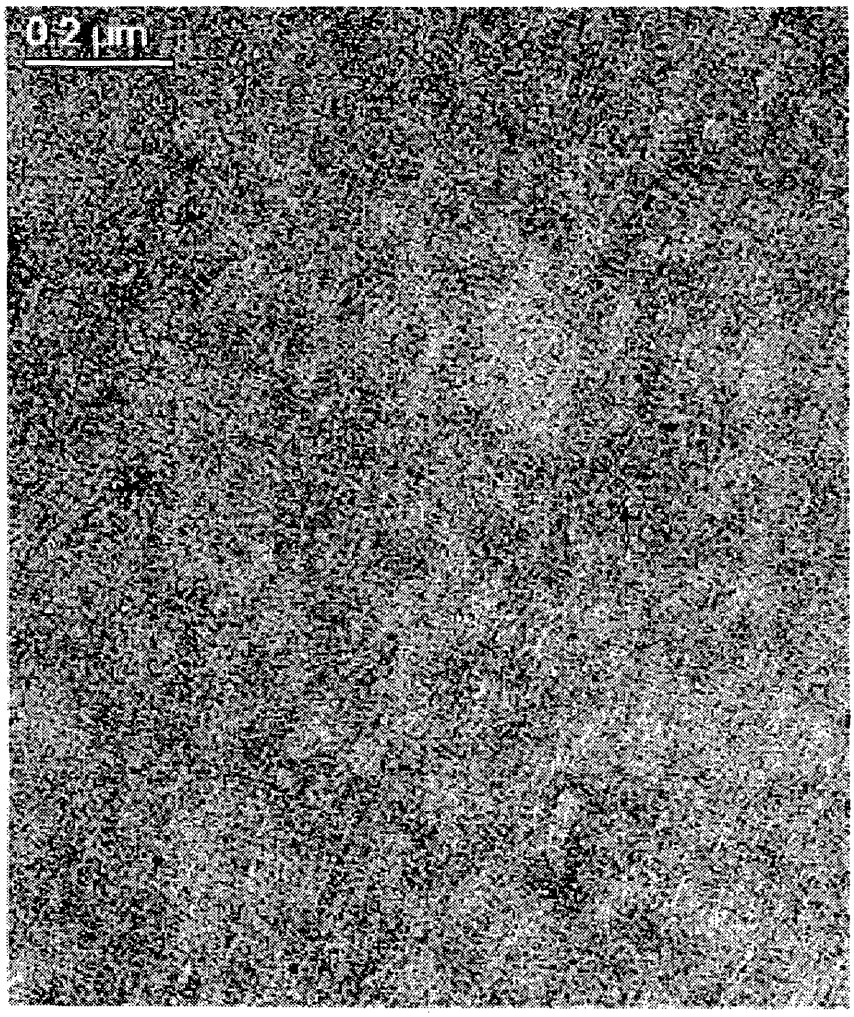
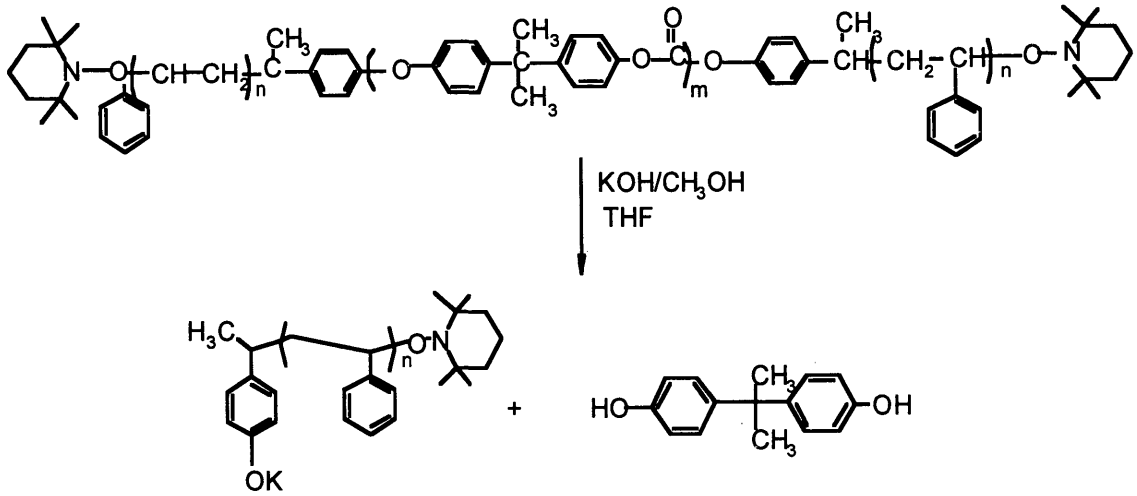


Figure 3.10. TEM of Copolymer PS-*bl*-PC-*bl*-PS (7,000-23,000-7,000)



Scheme 3.6. Hydrolysis of PS-*bl*-PC-*bl*-PS Block Copolymer

Table 3.5. Molecular Weight Change of Phenolate PS (III), its Copolymer and Hydrolysis Products of the Copolymer

Exp. No	M_n (g/mol) of Starting PS	PDI PS-OH	M_n (g/mol) PS-*bl*-PC-*bl*-PC	M_n (g/mol) after hydrolysis	PDI after hydrolysis
1	7,000	1.18	37,100	7,200	1.15
2	7,000	1.18	19,300	7,200	1.15

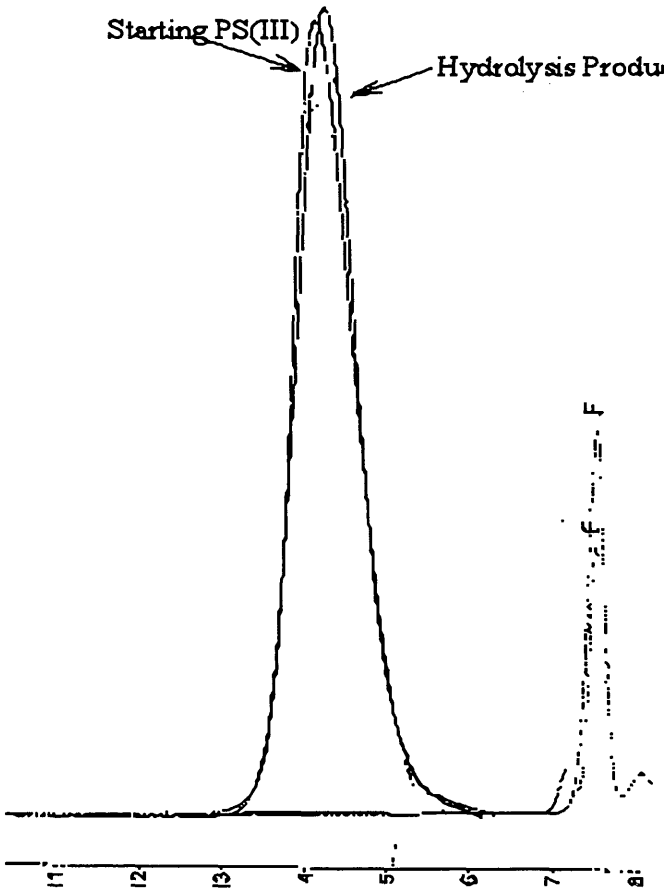


Figure 3.11 Overlay of GPC Chromatograms of Initial Phenol-functional PS and PS From Hydrolysis of PS-*bl*-PC-*bl*-PS Copolymer (Exp. No. 1)

3.4. Conclusions

Two block copolymers of PS-*bl*-PC-*bl*-PS (7,000-23,000-7,000 and 7,000-5,200-7,000) have been prepared by AIP of styrene with a functional initiator followed by interfacial polycarbonate polymerization. PS bearing *t*-boc groups was first obtained by

using 1-(4-*t*-butoxycarbonyloxyphenyl-1-2,2,6,6-tetramethyl-1-piperdinyloxy)ethane as an initiator for styrene polymerization. The *t*-boc group protects the phenol functionality during free radical polymerization of PS. Hydrolysis of the *t*-boc group on the PS chain end to form a reactive phenol group enables the functionalized PS to act as a macro chain-stopper for bisphenol A and phosgene condensation polymerization to form triblock copolymer. NMR analysis showed high chain end functionality on PS and GPC analysis confirmed near complete incorporation of PS into the block copolymer. DSC analysis of the block copolymer with high PC molecular weight shows two T_gs at 107 °C and 145 °C. An inward shift of the two T_gs indicates partial miscibility (phase mixing) between the PS and PC. The block copolymer with low molecular weight PC shows only one T_g at 107 °C by DSC indicating that miscibility between the PS and PC is greatly increased at a molecular level. FTIR confirms that PS and PC both exist in the copolymer. TEM analysis clearly shows the microphase separation of PS and PC phases, which further confirms the formation of block copolymer. The hydrolysis of the block copolymer was performed to cleave the carbonate bonds in the PC and demonstrated PS was indeed attached to PC.

3.5. References

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CHAPTER 4:

SYNTHESIS AND EVALUATION OF NITROXYL TERMINATED POLYCARBONATE MACROINITIATOR AND ITS APPLICATION TO FORM PS-*bl*-PC-*bl*-PS TRIBLOCK COPOLYMERS

4.1 Introduction

Nitroxy mediated radical polymerization (NMRP) has drawn much attention since Georges et al. reported the controlled polymerization of styrene in the presence of the TEMPO radical.[1] One of the major advantages of this technology is the stability of the initiation and propagation center in different chemical environments due to the reversible capping mechanism.[2] This nature allows the initiator to be used in various combination of polymerization procedures to produce polymers with novel structures.[3] Recently, a number of publications have focused on the design and synthesis of new types of functionalized initiators that can be used for sequential polymerization to obtain well-defined linear polymer,[4] block copolymer,[5] and other complex macromolecular architectures using the combination of living nitroxy mediated radical polymerization with other polymerization procedures.[6] By using 1-hydroxy-2-phenyl-2-(2',2',6',6'-tetramethyl-1-piperidinyloxy)ethane, Hawker et al. demonstrated that polycaprolactone-polystyrene block copolymer can be formed by first ring opening polymerization of ε-

caprolactone followed by NMRP of styrene.[7] The similar work by Yoshida showed that polycaprolactone-polystyrene block copolymers could be prepared using aluminum tri(4-oxy-TEMPO) initiator for anionic polymerization of ε-caprolactone with TEMPO (2,2,6,6-tetramethyl-1-piperdinoxy) attached at the terminal end, and then performing NMRP of styrene.[8] In this paper, the synthesis of TEMPO terminated polycarbonate will be presented. The TEMPO functionalized PC was subsequently used as a macroinitiator for NMRP of styrene to form PS-*bl*-PC-*bl*-PS triblock copolymers. Evaluation of polymerization efficiency for the TEMPO terminated PC as macroinitiator in terms of conversion and molecular weight will be discussed.

4.2 Experimental

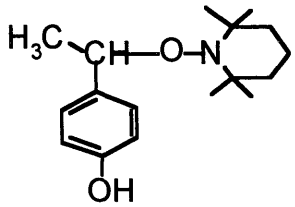
Polymer molecular weights were established by size exclusion chromatography (gel permeation chromatography, GPC) using a Hewlett-Packard 1090 instrument equipped with a set of two 10 μ mixed-bed C columns from Polymer Laboratories, Inc., and an ultraviolet detector. Narrow molecular weight distribution polystyrene standards were used for calibration. Both standards and samples were introduced as 1% (w/w) solutions in tetrahydrofuran. The elution solvent was THF in all cases at a flow rate of 1.0 mL/min. Differential scanning calorimetry (DSC) measurements were performed using a DuPont 2000 instrument at a heating rate of 20° C /min. Temperature calibration was performed with an indium standard. All runs were carried out under a N_2 atmosphere. The glass transition temperature (T_g) was taken as the temperature of the inflection point.

4.2.1 Preparation of 1-(4-hydroxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperdinyloxy)ethane (I)

Compound I was synthesized as previously described.

4.2.2 Preparation of TEMPO Terminated Polycarbonate

To a 250 ml three necked flask equipped with a mechanical overhead mixer was added 2.5 g (0.011 mol) bisphenol A , water (20 ml) and 1.77 g (0.022 mol) of 50% NaOH solution. After the bisphenol A reacted into solution, 15 ml of methylene chloride and 0.18 g (0.65 mmol) (I) were added into the flask. The mixture was stirred for 5 minutes. To the mixture, 1.35 g triphosgene (4.56 mmol, 1.25 mol phosgene/mol of bisphenol A) was added to the flask gradually. The mixture was stirred at 500 rpm for 5 minutes. The solution became very milky at this moment. 1.61 g 50% NaOH was added and stirred for 5 minutes. 6 ml of additional methylene chloride was added and stirred for 5 minutes. At this point, the aqueous phase was analyzed and 0.2 ml of triethylamine was added to the solution. The mixture was stirred at room temperature for another 30 minutes. The viscosity of the mixture was observed to increase. Finally, 0.97 g triphosgene was added to reduce the pH to about 8-9. The reaction mixture was allowed to stand to separate the layers, then the organic layer was separated and washed with water twice. The polymer was obtained by evaporation of the solvent. GPC molecular weight: M_n = 9,740, M_w = 18, 900, PDI = 1.98



I

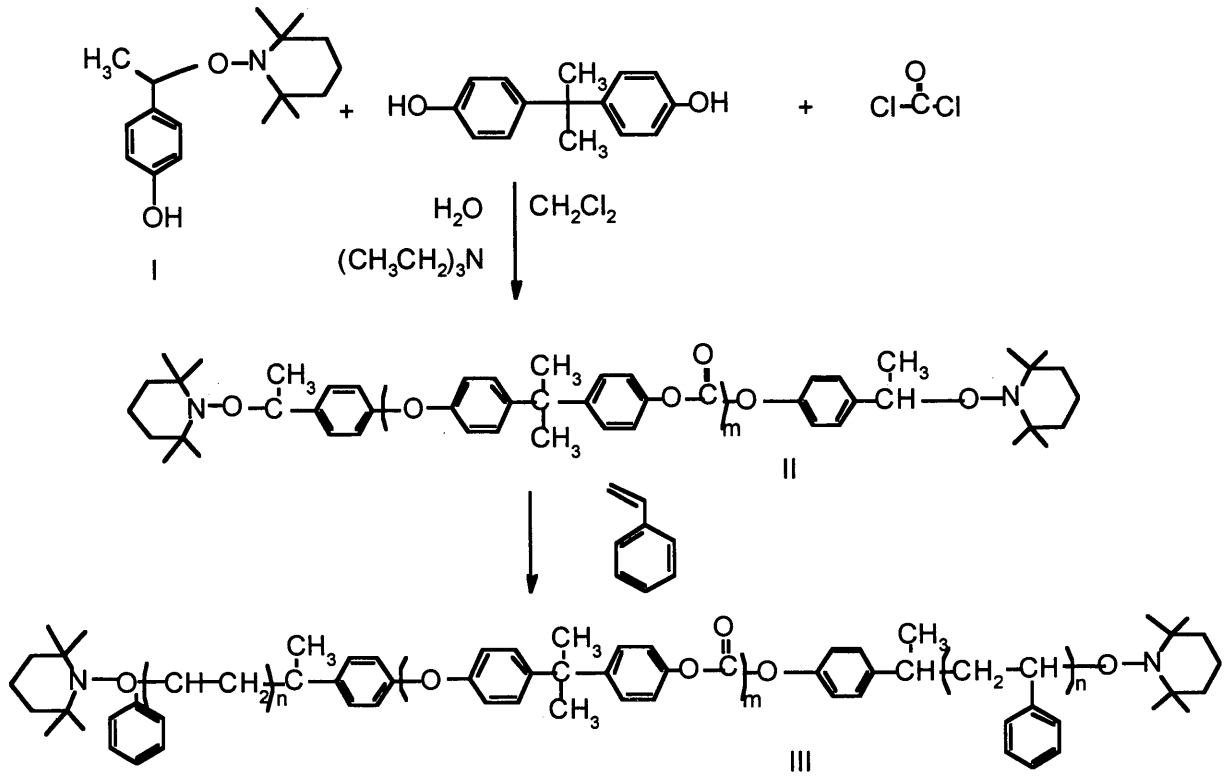
Figure 4.1 1-(4-hydroxyphenyl)-1-(2,2,6,6-tetramethyl-1-piperdinyloxy)ethane (I)

4.2.2 Copolymerization

The above polymer of 2.8 g was equally divided into four portions then loaded into Pyrex ampoules (5mm i.d x 10 mm o.d. x 30 cm). In each ampoule, 4.2 gram of styrene was added. The ampoules were sealed under reduced pressure (< 6 torr) using a freeze-thaw technique. PC of this molecular weight is not soluble in styrene at room temperature. The sealed ampoules were placed in a silicone oil bath maintained at 140°C. Polycarbonate was observed to dissolve after the ampoules were placed into the oil bath. The ampoules were removed at different time intervals to vary the polymerization time and therefore, the molecular weight. The ampoule was allowed to cool to room temperature, opened, and the contents examined to determine the extent of monomer conversion to polymer. The polymer molecular weight and molecular weight distribution were determined by GPC analysis.

4.3 Results and Discussion

The basic strategy to form PS-*bl*-PC-*bl*-PS block copolymer using the dual functional compound I is shown in Scheme 1. Compound I contains both a mono-phenol group useful as a chain stopper for polycarbonate polymerization and an alkoxyamine group connected through a secondary benzylic group which is an effective initiation center for the subsequent NMRP of styrene.[9] Polycarbonate of a calculated molecular weight was obtained with TEMPO on the chain ends by using I as a chain stopper. Subsequently, without further chemical transformation, TEMPO terminated PC was used as a macromolecular initiator for the NMRP of styrene to result in a PS-*bl*-PC-*bl*-PS triblock copolymer.



Scheme 4.1 The Preparation of Triblock Copolymer Using Functionalized Polycarbonate Initiator

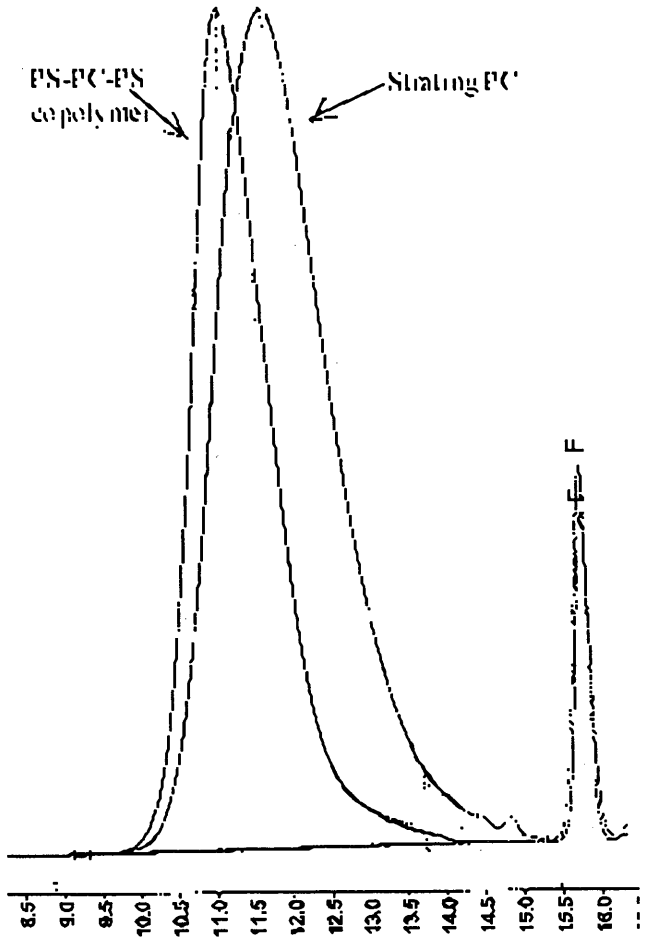
Polycarbonate with GPC molecular weight of M_n = 9,740 g/mol was prepared by an interfacial condensation polymerization of bisphenol A and triphosgene in the presence of compound I as a chain stopper. The molecular weight of the PC was controlled by the ratio of bisphenol A to TEMPO functionalized chain stopper I. The polydispersity of the polycarbonate was 1.98, which is typical for condensation polymerization. The copolymerization proceeded by dissolving TEMPO terminated PC into styrene monomer. It was known that PC has a very limited solubility in styrene monomer at room temperature; however, its solubility increases with increasing

temperature.[10] It was found that at 140 °C in the sealed ampoule, about 14 wt % of PC could be dissolved into styrene monomer within one minute to result in a homogeneous solution. The molar concentration of [PC-TEMPO] was 15 mmol. The styrene polymerization was performed at 140 °C and samples were removed at different time intervals (20, 40, 60, and 80 minutes) to prepare copolymers with different PS chain lengths. The results of the copolymerization are depicted in Table 4.1

Table 4.1. Characterization of the Copolymers with Different PS Chain Length

Polym. time (min.)	Styrene monomer conversion (%)	M_n (g/mol) of the copolymer	PDI	PS M_n (g/mol) in the copolymer	T_g (°C)	wt % of PS in the copolymer
0	0	9,740	1.98	0	122.0	0
20	12.1	13,100	1.51	2,400	109.6	18.3
40	23.6	17,700	1.45	8,000	107.4	45.2
60	29.4	19,000	1.47	9,300	106.5	48.9
80	36.2	20,900	1.47	11,200	105.5	53.6

Figure 4.2 depicts the GPC profiles for functionalized PC and the final triblock copolymer after 80 minutes of polymerization at 140° C. The measured polydispersity of the copolymer is 1.47 as compared to 1.98 before the copolymerization. The shift of the GPC peak to higher molecular weight and narrower distribution of the GPC peak after copolymerization supports that PC had indeed inititated the styrene polymerization to form PS-*bl*-PC-*bl*-PS.



Retention Time (min)

Figure 4.2. The GPC Profile of Starting Prepolymer PC (II) and its Resultant Copolymer (III) Obtained After 80 Minutes at 140 °C

Figure 4.3 shows a straight line for the plot of number average molecular weight of the copolymer against conversion for the copolymerization, which confirms the living/controlled character of the polymerization. Further evidence of efficient NMRP of styrene is that after 80 minutes, the total molecular weight of the PS segment is only M_n = 11,000 g/mol as opposed to an expected molecular weight of homopolystyrene approximately 10 times higher than that number if conventional free radical polymerization had occurred.[11]

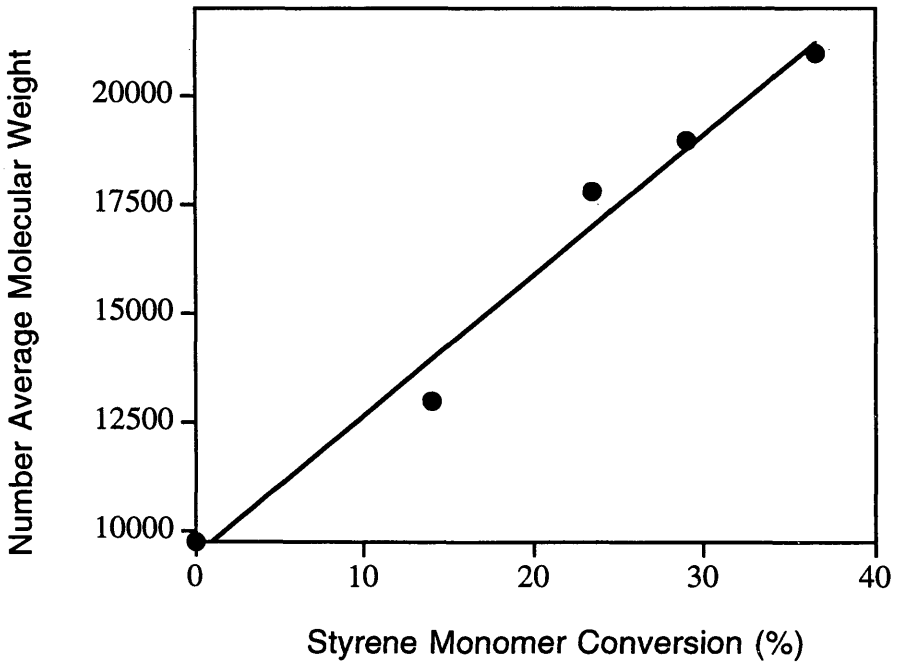


Figure 4.3 Plot of Number Average Molecular Weight Versus Styrene Conversion in the Polymerization of Styrene using II as Macroinitiator.

To further investigate the efficiency of TEMPO-terminated PC as a macroinitiator for styrene polymerization, the styrene monomer conversion using macroinititiator II was compared to that using monofunctional initiator 1-phenyl-(2,2,6,6-tetramethyl-1-piperdinyloxy)ethane (TMPEP). From the relationship of $\ln[M]_0/[M]$ versus time (Figure 4.4) where $[M]_0$ is the initial styrene monomer conversion concentration and [M] is the monomer concentration at a given time, it is clear that the overall polymerization efficiency of the macroinitator is similar to the monofunctional initiator TMPEP (except at the beginning of the reaction where a slightly slower polymerization rate has been observed for macroinitiator II). It has been reported that the attachment of an alkoxyamine group to the chain end of poly(ε-caprolactone) may significantly enhance the rate of its copolymerization with styrene to form block copolymer of poly(ε-carprolactone)-*bl*-polystyrene.[7] In contrast, the opposite result was observed when TEMPO was attached to the chain end of polytetrahydrofuran to form polytetrahydrofuran-*bl*-polystyrene). The polymerization rate of styrene monomer to form the block copolymer was significantly depressed while the monomer conversion was low.[12] In this study, it was found that the efficiency of the small molecule initiator and the polycarbonate macroinitiator has no significant difference for the NMRP of styrene.

In addition, as shown in Figure 4.4, styrene polymerization for both initiators followed first order kinetics up to about 40 minutes of the polymerization. After that time, both polymerizations deviated from the linear line of $\ln[M]_0/[M]$ versus time presumably due to the increased viscosity of the polymer which may cause slower mass transfer and reduce the polymerization rate.

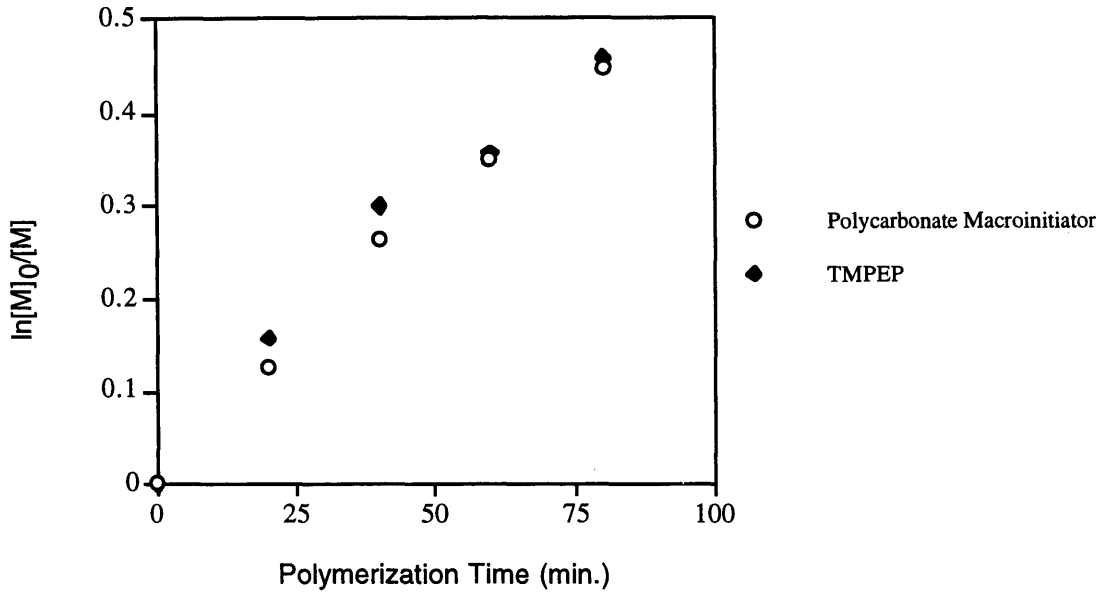


Figure 4.4 Comparison of Polymerization Efficiency of Monofunctional Initiator (TMPEP) and the Polycarbonate Macroinitiator (II) for Styrene Polymerization

The T_g of a polymer is a function of the molecular weight and can be expressed by equation 1.[11] Measurement of the glass transition temperature (T_g) of PS-*bl*-PC-*bl*-PS with different PS segment lengths has revealed interesting features. The T_g for the polycarbonate with TEMPO chain ends and M_n = 9,740 g/mol was determined to be 122°C as measured by DSC. According to equation 1, the T_g of polystyrene with different molecular weights can be estimated theoretically (Table 4.2).

$$T_g = T_g^{\infty} - \frac{A}{M_n} \qquad \text{Eq. 1}$$

Table 4.2. Theoretical Calculation of Polystyrene T_g as a Function of Molecular Weight given Tg^{∞} = 373 K and A = 100,000 (mol·K)[13]

M_n (g/mol)	Calculated T_g (K)	Calculated T_g (°C)
2,400	331.3	58.3
8,000	360.5	87.5
9,300	362.2	89.2
11,200	364.0	91.0

The T_gs of the four block copolymers with different PS chain length and different weight percentage of PS in the copolymers are listed in Table 4.1. For the block copolymers, only one T_g was observed for all cases indicating the PS and PC segments show miscibility for the particular molecular weights obtained. The general trend shows that the T_g of the block copolymer decreases with increasing molecular weight and increasing weight percentage of the PS segment.

4.4 Conclusions

In conclusion, it has been demonstrated that using duel functionalized compound (I), block copolymer PS-*bl*-PC-*bl*-PS with various PS chain lengths can be prepared by the sequential combination of step-growth polymerization of PC with NMRP of styrene. Polycarbonate with TEMPO-functionalized chain ends served as a macroinitiator for styrene polymerization. The copolymer molecular weight increases linearly with

monomer conversion supporting the fact that the styrene polymerization proceeded according to a living/controlled mechanism. GPC profiles further confirm the formation of PS-*bl*-PC-*bl*-PS triblock copolymer. The polycarbonate macroinitiator is determined to be as effective as a small molecule monoinitiator indicating that attachment of PC on the alkoxyamine does not interfere with the polymerization efficiency for NMRP of styrene. Single glass transition temperatures for the copolymers with different PS molecular weights implies that PS and PC segments are miscible in the block copolymers.

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