ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF BLOCK COPOLYMER BY MECHANISTIC TRANSFORMATION FROM CATIONIC POLYMERIZATION TO CONTROLLED PHOTOPOLYMERIZATION

M.Sc. Thesis by

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KATYONİK POLİMERİZASYONDAN FOTO POLİMERİZASYONA MEKANİSTİK TRANSFORMASYON YÖNTEMİYLE BLOK KOPOLİMER SENTEZİ

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LIST OF ABBREVIATIONS

M_n	: Number average molecular weight of polymer
M_w	: Weight average molecular weight of polymer
MWD	: Molecular weight distribution
PTHF	: Polytetrahydrofuran
THF	: Tetrahydrofuran
PSt	: Polystyrene
St	: Styrene
Bpy	: Bipyridine
DC	: Dithio carbamate

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SYNTHESIS OF BLOCK COPOLYMER BY MECHANISTIC TRANSFORMATION FROM CATIONIC POLYMERIZATION TO CONTROLLED PHOTOPOLYMERIZATION

SUMMARY

Polymers having photo labile *N,N'*-diethyl dithiocarbamoyl group ($Et_2NC(S)S$-) at their ω-end are widely preferred as they make possible the synthesis of block copolymers with different architectures by means of UV radiation at room temperature. Also atom radical transfer polymerization (ATRP) is one of the most researched areas as it allows controlling molecular weights and molecular weight distributions.

In this study functional polytetrahydrofuran (C-PTHF) containing photo labile $Et_2NC(S)S$- group was employed in the living/controlled photopolymerization of styrene (St) and block copolymers were synthesized.

ω-end functionalized C-PTHF, was obtained by living cationic ring opening polymerization using methyl trifluoromethanesulfonate and the polymerization was quenched by the addition of *N,N'*-diethyl dithiocarbamic acid sodium salt. Afterwards, photo block copolymerization of St was carried out with C-PTHF and cupper chloride (CuCl), as macroinitiator and catalyst respectively.

Photo block copolymerization of St was achieved under 300 nm UV radiation at ambient temperature and without ligand on the contrary of usual ATRP methods. In addition block copolymerization of St with C-PTHF/CuCl/Ligand (Bpy) and C-PTHF/St initiation systems and the self polymerization of St were also performed under the identical conditions to investigate the reaction mechanism.

KATYONİK POLİMERİZASYONDAN FOTO POLİMERİZASYONA MEKANİSTİK TRANSFORMASYON YÖNTEMİYLE BLOK KOPOLİMER SENTEZİ

ÖZET

ω-uç gurubunda foto aktif N,N'- dietil ditiyokarbamoil ($Et_2NC(S)S$-) grubu taşıyan polimerler, doğrudan UV ışını uygulanarak değişik mimaride blok kopolimerlerin sentezini mümkün kıldığından yaygın olarak tercih edilmektedir. Ayrıca molekül ağırlıklarını ve molekül ağırlığı dağılımlarını yüksek oranda kontrol altında tutmaya olanak sağlayan atom transfer radikal polimerizasyonu (ATRP) son yıllarda en çok araştırılan alanlardan biri olmuştur.

Bu çalışmada foto aktif $Et_2NC(S)S$- grubu taşıyan fonksiyonel politetrahidrofuran (C-PTHF), stirenin (St) yaşayan/kontrollü foto polimerizasyonunda ve blok kopolimer sentezinde kullanılmıştır.

ω-ucundan fonksiyonlanmış C-PTHF, metil triflorometansülfonat kullanılarak katyonik polimerizasyon yöntemiyle elde edilmiş ve polimerizasyon N,N'-dietil ditiokarbamik asit sodyum tuzu kullanılarak sonlandırılmıştır. Ardından stirenin foto blok kopolimerizasyonu makro başlatıcı olarak C-PTHF ve katalizör olarak bakır klorür (CuCl) kullanılarak gerçekleştirilmiştir.

Stirenin foto blok kopolimerizasyonu 300 nm UV radyasyonu altında ve oda sıcaklığında klasik ATRP yöntemlerinin tersine ligand kullanılmaksızın gerçekleştirilmiştir. Buna ek olarak, reaksiyon mekanizmasını aydınlatmak üzere C-PTHF/CuCl/Ligand(Bpy) ve C-PTHF/St başlangıç sistemleri ile blok kopolimerizasyon ve aynı zamanda stirenin kendi kendine polimerleşmesi aynı şartlar altında denenmiştir.

1. INTRODUCTION

The synthesis of block copolymers is obviously one of the polymer synthesis areas where living polymerization techniques are most effective and convenient.

Among these techniques, it is characteristic of the iniferter method for producing ω-end functional polymers with photo labile groups, such as diethylthiocarbamoyl ($Et_2NC(S)S$-, DC) through the polymerization course, that it can be applied for the synthesis of polymers with various architectures directly under heat or UV irradiation. In 1982 Otsu *et al* first reported living radical polymerization of vinyl monomers initiated with a thiuram disulfide under UV irradiation and gave this compound the terminology 'iniferter', which means that the compound not only acts as *ini*tiator and trans*fer* agent, but *ter*minator as well [1-3]. This method unfortunately suffers from limitations, such as no good control of the molecular weight and broad molecular weight distribution of the resulting polymer.

Atom transfer radical polymerization (ATRP) is an efficient polymerization method for the synthesis of polymers with well defined architectures and low polydispersities. ATRP is based on a reversible equilibrium between active and dormant species that are formed via atom transfer reactions in the presence of transition metal complexes [4, 5]. In conventional ATRP, generally, the resulting polymers are ω-functionalized with halogen atoms, and further functionalization of these polymeric chains is complicated.

However, presence of a photo labile group that acts as an end-capper by pseudo-halogen transfer will significantly simplify subsequent synthesis of block copolymers. Polymers with a variety of terminal functionalities may be obtained by living cationic polymerization for further block copolymerization. Suitable terminator will result with end functionalized polymers [6], and tetrahydrofuran (PTHF) can be polymerized by living cationic ring opening mechanism [7]. Due to

the oxonium group of the living chain end which can react with nucleophiles, desired end group may be introduced.

In the present study, the results on the preparation of DC terminated PTHF (C-PTHF) by living cationic ring opening polymerization and its use in photo block polymerization of styrene (St) under UV irradiation at ambient temperature are described. The photo labile end group bearing C-PTHF functioned as a macro photoiniferter, allowing block copolymerization. The synthesis of poly (THF-*b*-St) block copolymers was possible and first order kinetic plots were obtained with the C-PTHF/CuCl initiated photopolymerization by the mechanistic transformation from cationic polymerization to controlled photopolymerization.

In addition, according to enlighten the previously described photo block copolymerization, different polymerizations performed under the same conditions by using different starting reactants, e.g. C-PTHF/St/CuCl/Bpy initiation system or only St/CuCl to examine self polymerization of the St..

2. THEORETICAL PART

2.1 Block Copolymers

Block copolymers often provide useful and unique properties which are not attainable in simple homopolymers. This is the result of the thermodynamic incompatibility of the constituent blocks, and leads to microphase separations with various phase morphologies. Therefore, controlling polymer properties through the synthesis of various kinds of block copolymers is a continuing subject. In general, block copolymers may be synthesized either via sequential living polymerization or via reactions of end- functionalized polymers that include living polymers.

2.1.1 Sequential Living Polymerization

$$m\,\mathrm{A} \longrightarrow -(\mathrm{A})_m-* \xrightarrow{n\,\mathrm{B}} -(\mathrm{A})_m-(\mathrm{B})_n- \qquad (2.1)$$

The sequential living polymerization (2.1) of two monomers is perhaps the most straightforward method to synthesize block copolymers, and sometimes the successful formation of block copolymers by this way is taken as evidence for the occurrence of living polymerization. Specifically, monomer A is polymerized according to a living polymerization then from the living end of which another monomer B is polymerized again in a living fashion to form an AB-block copolymer. Thus the synthesis can be carried out simply in a one pot, but the propagation mechanisms for the two monomers should accordingly be the same, which sometimes limits the range of monomer and also segment combinations.

2.1.2 Reactions of End Functionalized Polymers

$$-(\mathrm{A})_m-X + n\,\mathrm{B} \longrightarrow -(\mathrm{A})_m-(\mathrm{B})_n- \qquad (2.2)$$

$$—(A)_m–X + Y–(B)_n— \longrightarrow —(A)_m—(B)_n— \quad (2.3)$$

End group-functionalized polymers, such as telechelic polymers and macroinitiators are important building blocks for the synthesis of tailored multi-segment polymer structures. The reactions of end-functionalized polymers may be divided into two subclasses, the living polymerization from macroinitiators (2.2) and the polymer coupling reactions (2.3). The former uses end-functionalized polymers with a terminal function (*X*) that can initiate the living polymerization of a second monomer. The latter involves two end-functionalized polymers, where the terminal functions, X and Y, react with each other to combine them into a block copolymer.

2.2 Living Cationic Ring Opening Polymerization of Tetrahydrofuran Initiated by Methyl Triflate and Triflic Anhydride

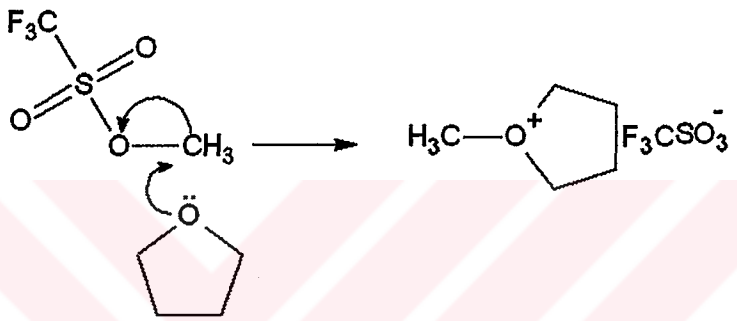
Tetrahydrofuran (THF) is an unsubstituted five-membered cyclic ether, containing four methylene groups connected by an oxygen bridge. Since the ring contains an oxygen atom with two unshared pairs of electrons, THF is a nucleophilic monomer [8].

2.2.1 Initiation

The species which initiates THF polymerization is comprised of a cation and an anion. The polymerization is initiated by a nucleophilic attack of the free electrons of the THF oxygen on the carbon adjacent to the oxygen. The nature of the counter ion, X^-, is very important. It is useful to consider these anions in terms of the position of the elements of which they are composed in the periodic table. The elements that include stable counter ions for THF polymerizations are found almost exclusively among nonmetals in groups VA, VIA, and VIIA. These elements include the most highly electronegative element, F. More firmly bonded elements in a complex ion lead to more stable and more suitable counterions for THF polymerization and fewer side reactions. Whereas maximum stability of the counterion itself is desirable, intermediate stability of the complex is preferable. The complex should not be so stable that polymerization or desired termination reactions are inhibited.

Methyl triflate (methyl trifluoromethane sulfonate, $CH_3SO_3CF_3$) and triflic anhydride (trifluoromethane sulfonic anhydride, $CF_3SO_2OSO_2CF_3$), which are derivatives of trifluoromethane sulfonicacid ($HOSO_2CF_3$), are excellent initiators for the living polymerization of THF. The growing sites are long-living, provided that reaction medium does not contain any transfer agents such as alcohols, ethers, amines or acids.

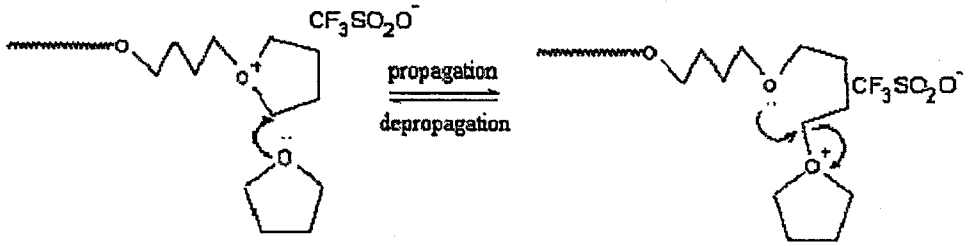
Triflic anhydride as a bifunctional initiator leads to PTHF capable of growing on both ends, whereas methyl triflate produces PTHF, growing at one end only. The mechanism by which the required oxonium ion is formed, is direct alkylation of the oxygen of THF, which is shown in (2.4) for initiation by methyl triflate.



(2.4)

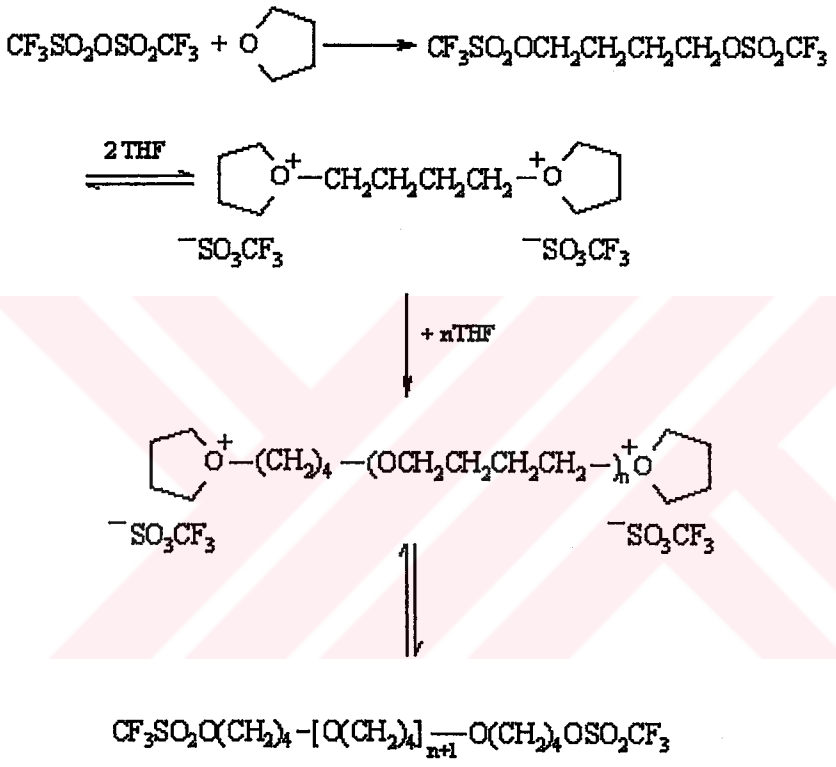
2.2.2 Propagation

The propagating species in THF polymerization is an oxonium ion, and it associates with a negatively charged species. Ring strain of THF is lower than that of three and four membered rings. Thus polymerization is highly reversible, and propagation-depropagation reactions take place [9-12].



(2.5)

With methyl triflate and triflic anhydride as initiators, in addition to the propagation-depropagation reactions involving oxonium ions, the equilibrium between oxonium ion and an ester, formed with the counterion, occurs. At each stage of the polymerization, the oxonium ion-counterion complex is in equilibrium with its corresponding ester. The propagation-depropagation reactions and the oxonium ion-counterion equilibria is shown in (2.5) for the polymerization initiated by methyl triflate and the general mechanism of polymerization initiated by triflic anhydride represented by (2.6).



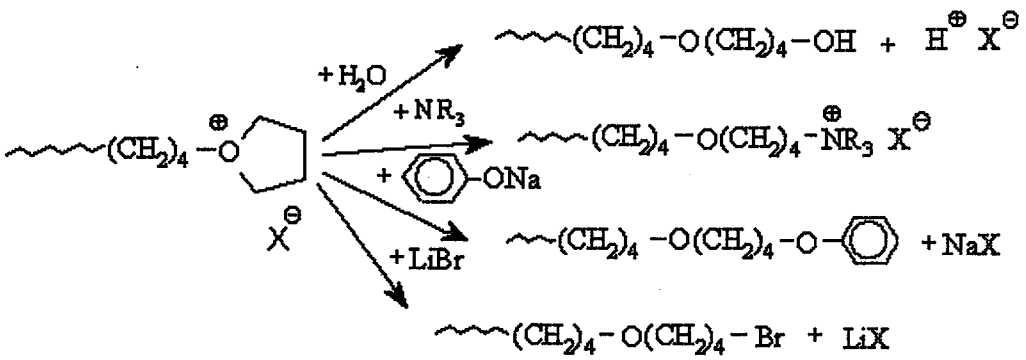
(2.6)

In this type of polymerization, the concentration of growing centers is equal or close to the initial initiator concentration. Polymers with low polydispersity can be prepared, only at low conversions and short times, or if the propagation proceeds at low temperatures. As conversion increases, transfer to polymer oxygen occurs and tends to broaden the molecular weight distribution at longer times and higher temperatures. In addition some cyclization reactions also occur.

2.2.3 Termination

The polymerization can be terminated by a variety of nucleophilic reagents such as excess water, tertiary amines, phenolates or lithium bromide, which are shown in

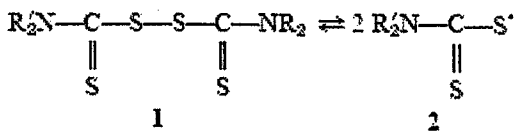
(2.7). Under the above mentioned conditions, almost any desired end groups can be introduced.



(2.7)

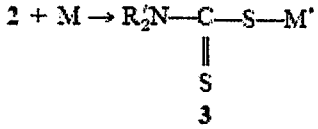
2.3 Iniferter Concepts [13]

The initiating ability of organic sulfur compounds examined and found that various sulfides and disulfides (e.g., phenyl, benzoyl, benzothiazoyl, xanthogene, thiuram, and dithiocarbamate derivatives) could serve as efficient photoinitiators. From kinetic studies, tetraethylthiuram disulfide (**1**; R=C_2H_5) was found to act not only as an initiator but also as a retarder, terminator, and transfer agent. Analysis showed that the resulting polymers had nearly two initiator fragments (**5** in 2.8.d) at the chain ends. Therefore, the polymerization of the monomer (M) with disulfides proceeds via the dissociation of disulfides, initiation, propagation, primary radical (PR) termination, and chain transfer (CT) to disulfides, according to (2.8.a-e) respectively:



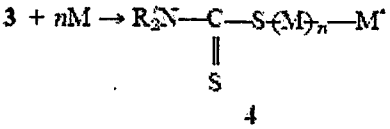
(2.8.a)

1 **2**



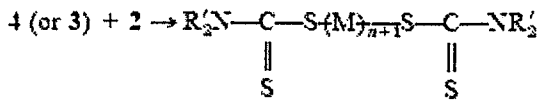
(2.8.b)

3



(2.8.c)

4

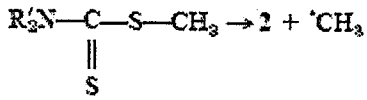


(2.8.d)

5

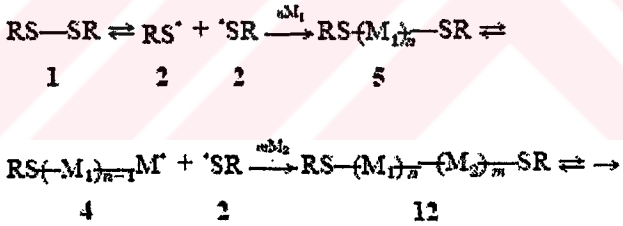
$$4\ (\text{or } 3) + 1 \rightarrow 5 + 2 \qquad \textbf{(2.8.e)}$$

The ordinary bimolecular termination is neglected because primary radical **2** is less reactive for initiation and more reactive for primary radical termination. The chain transfer to **1** also occurs because the chain transfer constants are high values, yielding a relatively low molecular weight (MW) polymer, **5**, with two sulfide end groups similar to those in methyl *N,N*-diethyldithiocarbamate (**6**) that can act as a photoinitiator, as is shown in (2.9):



6 **(2.9)**

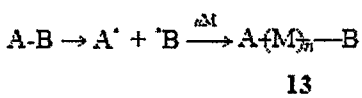
Polymer **5**, obtained from St, was found in 1957 to initiate the photopolymerization of MMA and VAc to give block copolymers (**12** in 2.10), and (2.8.a-e) can be rewritten as (2.10):



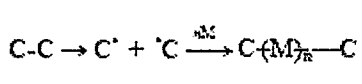
(2.10)

where RS is $R'_2NC(S)S$. **1** and **5** are the monomeric and polymeric initiators, respectively, which can dissociate into PR **2** and propagating radical **4**, respectively. **12** is the resulting block copolymer. In 1982, Otsu proposed for these initiators the name *iniferter* (*ini*tiator–trans*fer* agent *ter*minator) [1].

The iniferters are divided from the structure of their bonds into A–B-type and C–C-type iniferters, which serve as follows:



13 **(2.11.a)**



14 **(2.11.b)**

where A• in (2.11.a) is a reactive radical that participates in initiation and then propagation, and B• is a less reactive or nonreactive radical that principally enters into PR termination to give polymer **13**. In the case of C–C-type iniferters (2.11.b), two C• are less reactive radicals that participate in both initiation and PR termination, leading to polymer **14**, in which n is the total number of inserted monomer molecules.

2.3.1 Living Radical Polymerization with Iniferters

As shown previously, various functional polymers can be synthesized with dithiocarbamate photoiniferters, which can principally induce further radical polymerization. Because radical polymerization proceeds by the low selectivity of a reactive propagating radical, it seems that relatively low-temperature (e.g., room temperature) photopolymerization is better for the controlled synthesis. Therefore, photoiniferters are mainly used in which dithiocarbamate compounds were adopted to easy preparation and functionalization. However, the iniferters cannot always induce living radical polymerization, from which the end groups of polymers produced from some iniferters should further dissociate thermally or photochemically into radicals, which can function as polymeric iniferters. There are some characteristic phenomena in radical polymerizations using these iniferters:

1. The MW of the polymers increases as a function of reaction time.

2. The MWD of the polymers also increases with time from a value of 2, which is obtainable for ordinary radical chain polymerization.

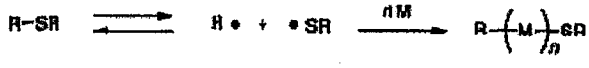
3. The number of iniferter fragments bonded to the polymer end is independent of reaction time.

4. The block copolymers are synthesized with polymers isolated from various stages of the polymerization.

These results, except an item (2), are in agreement with the results of living anionic polymerization, discovered by Szwarc [13], and other ionic or coordination polymerizations; accordingly, these polymerizations seem to be performed via a living radical polymerization.

2.3.2 Dithiocarbamate Photoiniferters

As stated previously, dithiocarbamate compounds, which have a diethylthiocarbamylthiyl group [RS in R=$(C_2H_5)_2NC(S)S$] including thiuram disulfides can easily be prepared, purified, and handled, have several advantages and a few disadvantages as iniferters in radical polymerization as follows. First, **1**(RS-SR) and (R-SR) can serve as C–C and A–B-type thermal and photoiniferters for block copolymer synthesis, as in (2.8) and (2.12), respectively:



(2.12)

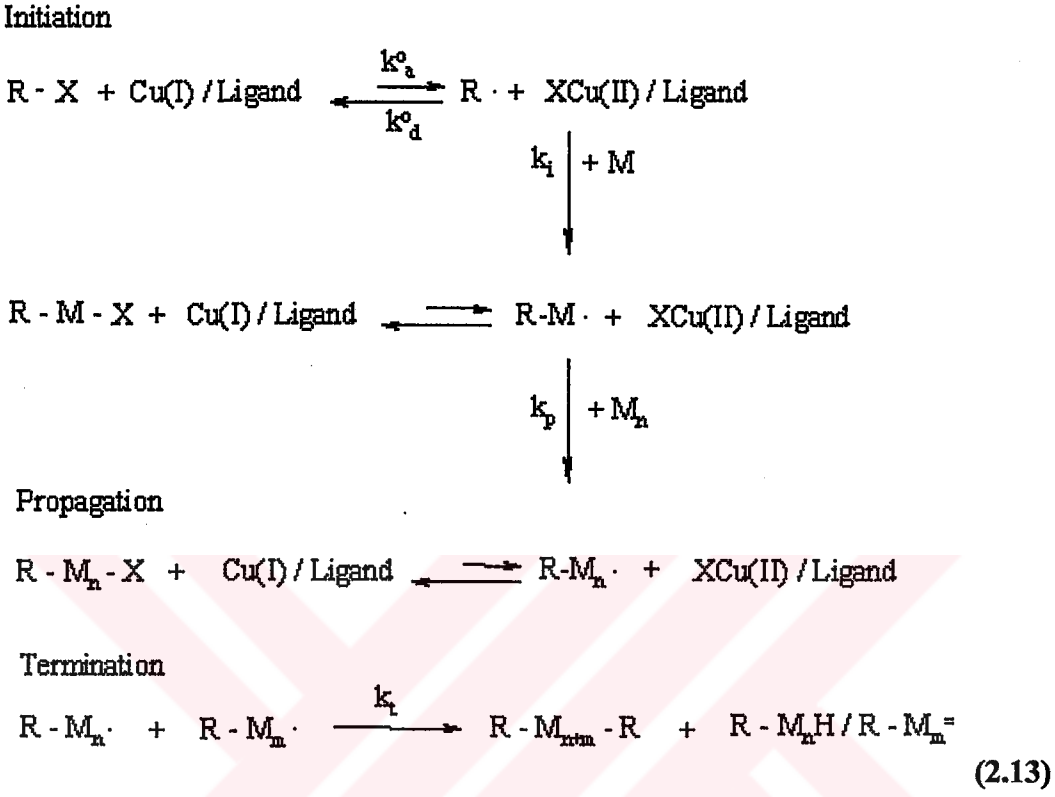
These results show that **1** is an efficient CT agent, and the derived RS serves as a PR terminator, an inhibitor for a bimolecular termination or crosslinking reaction, and a crossrecombinator to reform the RS end group. Second, the RS group in dithiocarbamates, which has a λ_{max} value of 282 nm and an ε value of 10.500, functions as an A–B-type iniferter under the irradiation of light. RS• shows the same reactivity toward the monomer. The iniferter technique using a selected dithiocarbamate is very useful method for various controlled polymer syntheses. An important disadvantage is no polymer being formed with a narrow MWD.

2.4 Atom Transfer Radical Polymerization

Atom Transfer Radical Polymerization (ATRP) is the most versatile polymerization method being able to polymerize a variety of monomers like methyl methacrylate, acrylate and styrene monomers with well-controlled molecular weights and well-defined structures [14-17].

An ATRP system consists of an initiator, a copper(I) halide, ligand(s), and of course, monomer. The general mechanism of ATRP which is schematically represented in (2.13), involves the abstraction of a halogen from the dormant chain by a metal center, such as complexes of Cu^1, in a redox process [18]. Upon halogen abstraction, the free radical formed (the active species) can undergo propagation. However, the free-radical is also able to abstract the halogen back from the metal, reproducing the dormant species. These processes are rapid, and the equilibrium that is established favors the dormant species. By this way, all chains can begin growth at the same time, and the concentration of free radicals is quite low, resulting in a

reduced amount of irreversible radical-radical termination. The final result is that degrees of polymerization (DP) can be predetermined (DP=Δ [M]/ [I_o]) and M_w/M_n is quite low (1.05-1.5), and good control of functionalities is achieved [19].



(2.13)

ATRP is a multi-component system, so concentrations and the structures of all these compounds affect the polymerization rate and the properties of the resulting polymer.

There is a large class of halogenated compounds that can be used as initiators in ATRP. The only requirement is that the initiator must have labile halogen attached to an atom containing radical stabilizing substituents [20].

In ATRP both effective initiation and good control of the polymerization rely heavily on the position of the equilibrium in both the initiation and the propagation steps, and also on reactivities of the radicals generated in the initiation step. Thus, choosing a suitable organic halide and $Cu^{(I)}$ halide is necessary for the controlled polymerization.

Basic requirements for the good catalyst are high selectivity towards atom transfer process and high lability of the resulting $X\text{-}M_t^{n+1}$ species (higher oxidation state of metal). The metal should participate in a one-electron process which would result in oxidative addition/reductive elimination but not in atom transfer process.

Additionally, the metal should have a high affinity for atom/group X, but a low affinity for hydrogens and alkyl radicals. Otherwise, transfer reactions (β-hydrogen elimination) and the formation of organometallic derivatives may be observed reducing selectivity of propagation and control (livingness) of process. The most important factors in selecting good ATRP catalyst are the equilibrium position, dynamics of exchange between dormant and active species. These parameters are related to the redox cycle M_t^n / M_t^{n+1} but it must be remembered that ATRP is not an electron transfer process but an atom transfer process. Thus, the inner coordination sphere of M_t^n must expand to accommodate a new X (halide) ligand. The most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, Ni(II), Ru(II) / $Al(OR)_3$, and Fe(II) / $3PR_3$.

Ligands play a very important role by solubilizing the catalyst and electronically affecting its redox potential in the M_t^n / M_t^{n+1} cycle. Steric effects are equally important, because atom transfer proceeds with the expansion of the coordination sphere of the metal. The most widely used ligands for ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as N,N,N′,N″,N″ pentamethyldiethylenetriamine (PMDETA), Tetramethylethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetraamine (HMTETA), tris[2-(dimethylamino) ethyl]amine (Me_6-TREN) and Alkylpyridylmethaneimines are also used.

Since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper-bpy complex, the employment of simple amines as the ligand in ATRP may lead to faster polymerization rates, enables better control, and thus simple amines are very attractive alternatives to bpy and its derivatives as the ligands [21-22]. It is stated that when PMDETA and HMTETA are used, the ratio of 1:1, when bipy or TMEDA is used, the ratio of 1:2 is sufficient to achieve maximum rates and control of polymerization.

Styrenes, acrylates, methacrylates, acrylonitrile, acrylamides, methacrylamides, N-vinylpyridine and dienes can be polymerized by ATRP, and well defined polymers are achieved.

As a result, atom transfer radical polymerization (ATRP) is a powerful technique allowing the polymerization of a variety of monomers with a high degree of control over the molecular weights and the molecular weight distributions of the resulting

polymers. Additionally, since the polymerization conditions are relatively simple, various types of macromolecular structures can be achieved with a simple polymerization system via this method.

3. EXPERIMENTAL WORK

3.1 Chemicals Used

Tetrahydrofuran (THF, 99.8%, J.T. Baker HPLC grade) was dried over lithium aluminum hydride, subsequently distilled over sodium wire and it was let mixing overnight with sodium/benzophenone then it was distilled prior to use.

N,N'-diethyldithiocarbamic acid, sodium salt trihydrate (Acros), Styrene (St, 99% Aldrich), Methyl trifluoromethanesulfonate (Methyl triflate, Aldrich 99+%), copper chloride (CuCl, Aldrich 99,995+%), 2,2'-bipyridine (Bpy, Aldrich 99+%), Benzene (Aldrich 99+%) and all other reagents were used as received, unless otherwise specified.

3.2 Synthesis of *N,N'*-diethyl Dithiocarbamoyl Polytetrahydrofuran by Living Cationic Ring Opening Polymerization

N,N'-diethyl dithiocarbamoyl polytetrahydrofuran (C-PTHF) was prepared as indicated in a previous work [23]. A graded tube equipped with a nitrogen inlet, and a rubber septum was connected to the vacuum line. The tube was dried by heating under vacuum. After cooling to room temperature, THF (50 ml, 12.3 mol l^{-1}) was distilled into the tube. The flask was disconnected under nitrogen and was placed into a thermostatically controlled bath at 25 °C. Then, the polymerization of the THF was initiated by the addition of methyl triflate (70 µl, 0.0123 mol l^{-1}) for monofunctional PTHF. After 40 minutes, a certain amount was removed from the reaction mixture and injected into methanol as a control sample, afterwards solution of *N,N'*-diethyl dithiocarbamicacid sodium salt in 5 ml of THF (0.123 mol l^{-1}) was introduced into the reaction tube in order to terminate the polymerization, simultaneously. The reaction mixture was then stirred for 60 minutes, and then it was poured into methanol. Polymer was not precipitated in methanol at room

temperature, precipitation was performed by cooling the solution down to -30 °C. The precipitated polymer which was immediately filtered and dried under vacuum was used as macroinitiator.

3.3. Block Copolymerization Reactions

Five different block copolymerization reaction sets have been fulfilled and compared. All of them are shown in the table below. In a typical process all of the reactants were put into a Pyrex tube in 3 ml benzene. The tube was degassed by three freeze-pump-thaw cycles and sealed under argon prior to irradiation at 300 nm at room temperature. When the predetermined reaction time is achieved, the reaction is quenched by addition of methanol. After waiting for a while for evaporation of the solvent, polymer is precipitated from excess of methanol and filtered. For every reaction, samples were taken before degassing and after quenching for gas chromatography measurements.

Table 3.1: List of block copolymerization reactions and molar quantities used [a].

Set	Initiator C-PTHF[b]	Monomer St[c]	Catalyst CuCl[b]	Ligand Bpy[b]
1	$4{,}45.10^{-3}$ M	4,45 M	$4{,}45.10^{-3}$ M	-
2	$4{,}45.10^{-3}$ M	4,45 M	$4{,}45.10^{-3}$ M	$13{,}35.10^{-3}$ M
3	$4{,}45.10^{-3}$ M	4,45 M	-	-
4	-	4,45 M	$4{,}45.10^{-3}$ M	-
5	-	4,45 M	-	-

[a] All experiments performed under 300 nm UV irradiation at room temperature.

[b] [In]:[Cat.]:[L]=1:1:3, (C-PTHF=0.2 g, CuCl=2.64 mg, Bpy=12.5 mg)

[c] [In]:[M]=1:1000 (St=3 ml)

3.4 Analyses and Characterizations

The number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) were determined by Gel Permeation Chromatography (GPC). GPC analyses were performed with an Agilent Model 1100 instrument consisting of a pump, and refractive-index detector, UV dedectors and four Waters Styragel Columns (HR 5E, HR4E, HR 3, and HR 2). THF was used as eluent at a flow rate of 0.3 ml/min at 30 °C. The molecular weight of the polymers was calculated with the aid polystyrene

standards (Polymer Laboratories). Molecular weights of PTHF, which were measured by GPC were multiplied by 0,556 which is an empirical constant for polystyrene standards [24].

Monomer conversion was determined using a Unicam 610 Series Gas Chromatograph equipped with a FID detector using a J&W Scientific 15 m DB WAX Widebore. Injector and detector temperatures were kept constant at 280 °C and 285 °C, respectively. Initial column temperature is 40 °C, finally reaching up to 120 °C with a heating rate of 40 °C/min.

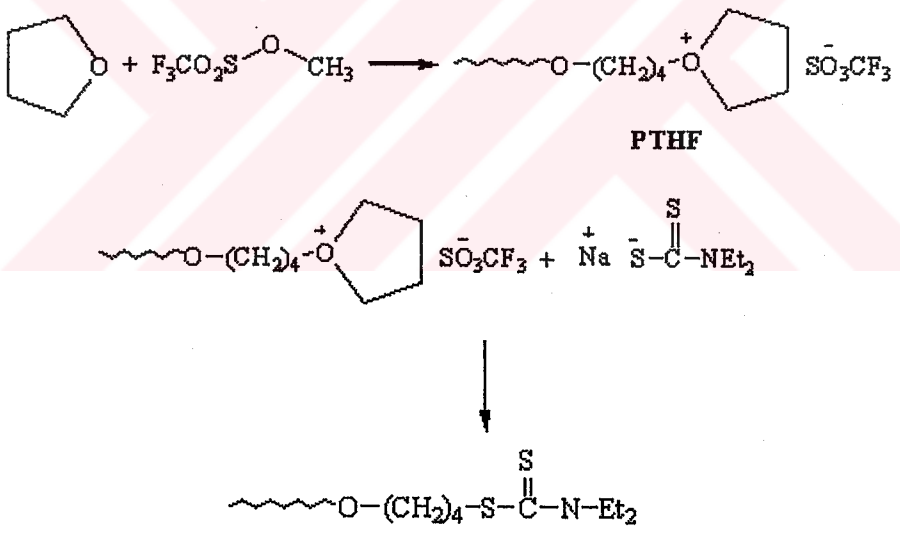
UV-VIS spectra were recorded with a Perkin-Elmer Lambda 2 spectrophotometer using ethyl acetate as solvent.

The ^{1}H-NMR spectra was recorded on a Bruker spectrometer (250 MHz for proton) in $CDCl_3$ solution using tetramethylsilane (TMS) as an internal standard.

4. RESULTS AND DISCUSSIONS

4.1 Preparation of the Macroinitiator

The macroinitiator was synthesized by the living cationic ring opening polymerization of THF with methyl triflate as initiator and the living propagating chain end was quenched with *N,N'*-diethyl dithiocarbamate sodium salt, so that diethyl dithiocarbamate terminated polytetrahydrofuran (C-PTHF) was obtained (4.1). A control sample of PTHF was precipitated before the addition of dithiocarbamate (DC). Due to DC photo labile group, C-PTHF can act as a photoiniferter by the reversible C-S bond dissociation under UV light irradiation.



PTHF

C-PTHF

(4.1)

For living polymerization systems theoretical molecular weight ($M_{n(Theo)}$) can be calculated by the following equation (4.2).

$$M_{n(Theo)} = \frac{[M]_o}{[In]_o} \times MW_o \times Conversion \qquad \textbf{(4.2)}$$

Here $[M]_o$ and $[In]_o$ are the monomer and initiator concentrations, respectively. MW_o is molecular weight of the monomer (for THF=72.11 g mol^{-1}). Molecular weights are measured by GPC and UV and the results are shown in Table 4.1.

Table 4.1: Molecular weights measured and calculated for PTHF and C-PTHF.

Run	$M_{n(Theo)}$	$M_{n(GPC)}$ [c]	$M_{n(GPC\text{-}PTHF)}$ [d]	$M_{n(UV)}$	M_w/M_n
PTHF[a]	7200	13600	7560	-	1.18
C-PTHF[b]	7350	13400	7450	7778	1.09

[a] [THF]=12,3 mol.l^{-1} [Triflate]=0.0123 mol.l^{-1}

[b] [DC]=0.123 mol.l^{-1} in THF.

[d] Obtained by GPC with Pst standards.

[c] Calculated by $M_{n(GPC\text{-}PTHF)}=0.556.M_{n(GPC)}$

Peaks recorded by both RI and UV detectors in GPC were observed at the same elution time. These results shown in Figure 4.1, demonstrate that DC group was introduced into the PTHF chain.

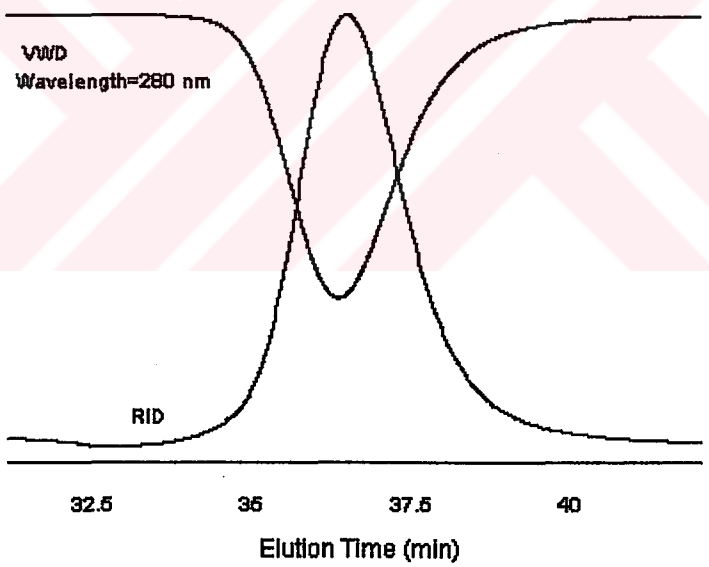


Figure 4.1: GPC curves of C-PTHF with RI and UV detectors. Standard polymer: polystyrene, eluent: THF, 0.3 ml min^{-1}.

The UV-based number average molecular weights of polymers can be calculated by using the Lambert Beer Law given below (4.3):

$$A = \varepsilon \times C \times l \qquad \textbf{(4.3)}$$

where A=Absorbance, ε=Molar extinction coefficient, C=Concentration (mol.l^{-1}), *l*=Cell lenght (cm, *l*=1 cm for the standard system used).

For $M_{n(UV)}$ calculations, ε value of DC group attached to methylene group was measured and calculated with butyl diethyl dithiocarbamate (BuDC). Concentration versus absorbance graphic for BuDC is plotted and extinction coefficient (ε = 12200 l mol^{-1} cm^{-1} in ethyl acetate) was calculated from its slope as mentioned by Lambert Beer law (Figure 4.2).

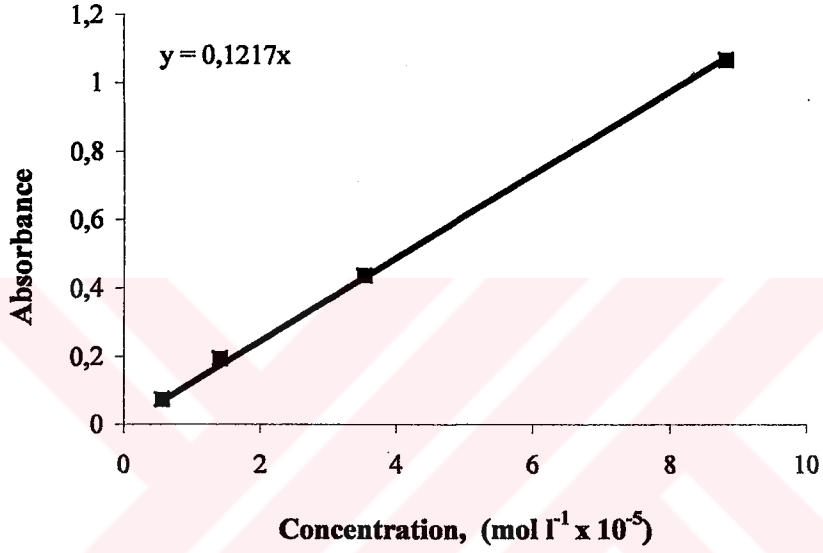


Figure 4.2: Concentration versus absorbance graphic at 280 nm for BuDC.

UV-VIS spectrum of the macroinitiator and BuDC showed maximum absorption at 280 nm which is characteristic for DC groups (Figure 4.3). The concentration (mol l^{-1}) of C-PTHF corresponding to that absorbance value was determined by the Lambert Beer Law, and since the concentration of the polymer in terms of mass (g l^{-1}) was already known, $M_{n(UV)}$ value of the polymer was calculated by dividing these two concentrations to each other (4.4);

$M_{n(UV)}$ = Concentration taken (g l^{-1}) / Concentration calculated (mol l^{-1}) **(4.4)**

The structure of the polymer was also characterized by means of ^{1}H-NMR spectroscopy and the spectrogram is shown in Figure 4.4.

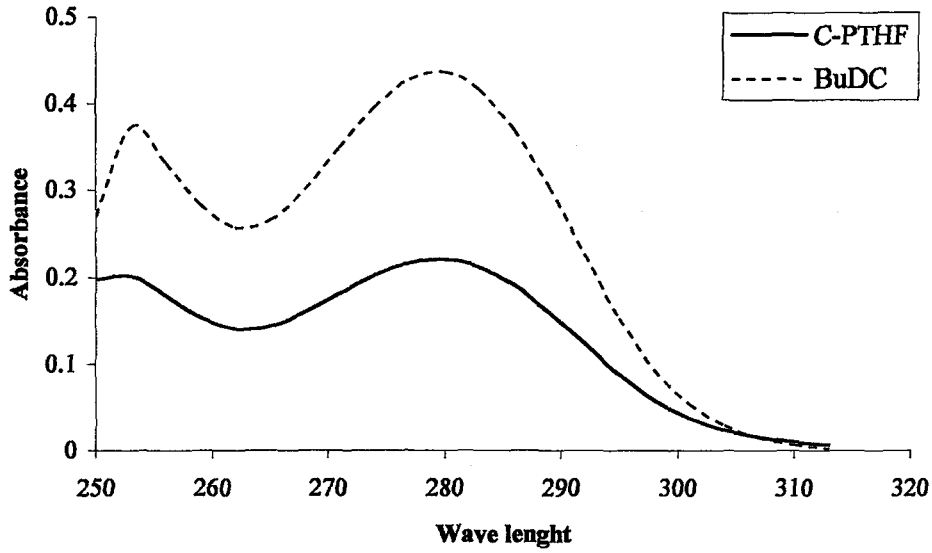


Figure 4.3: UV spectrum of BuDC and C-PTHF. [C-PTHF] =1.87 10^{-5} [BuDC]=3.53 10^{-5}

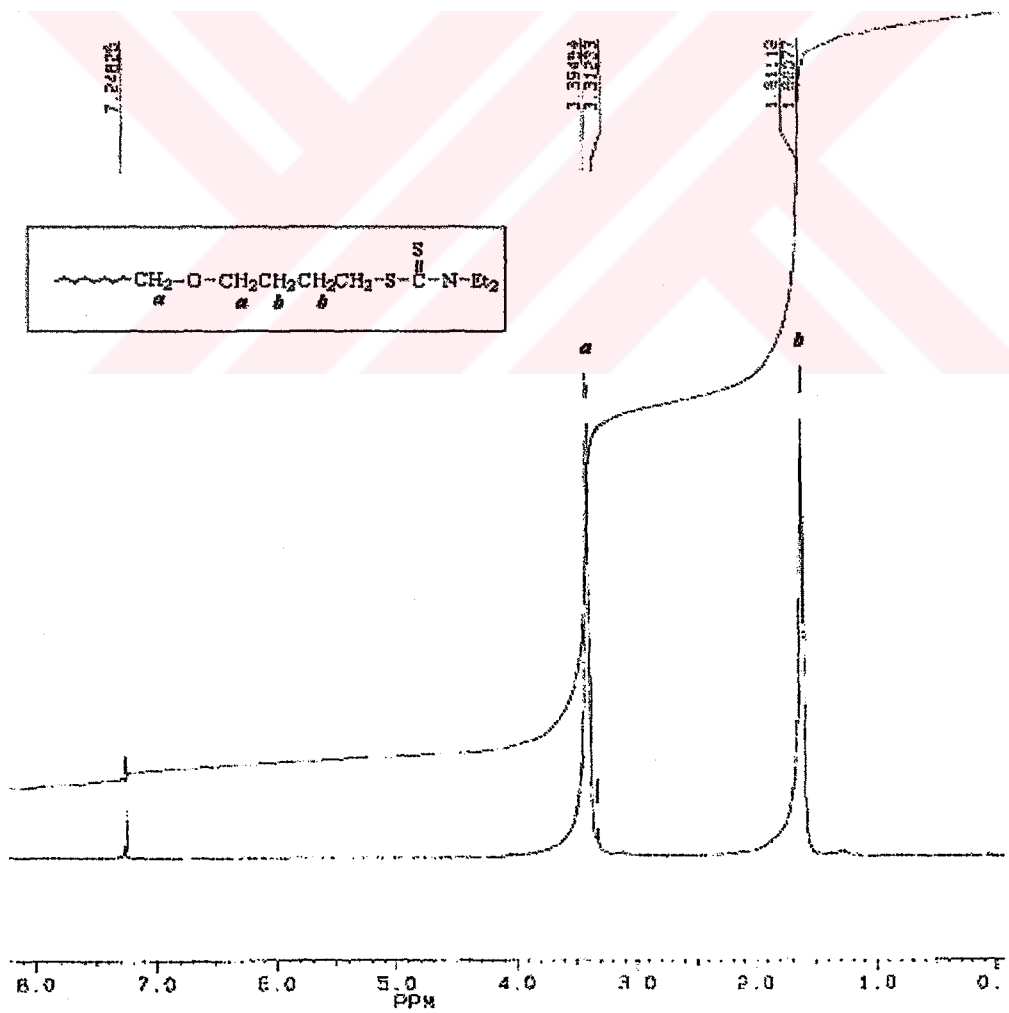
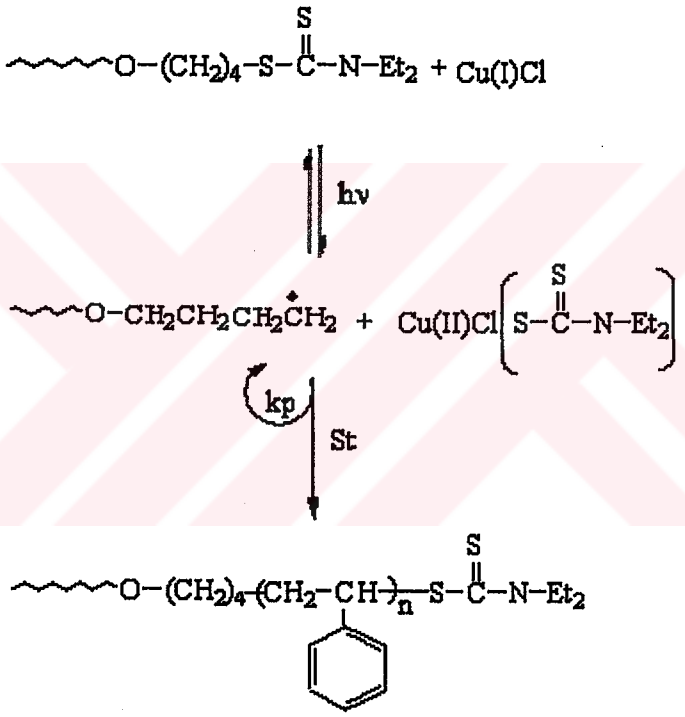


Figure 4.4: ^{1}H-NMR spectra ($CDCl_3$) of the C-PTHF.

^{1}H-NMR spectrum of a typical PTHF displays signals at 3.4 ppm (a) and 1.6 ppm (b) corresponding to two different types of methylene protons, one of which was attributed to the methylene bonding to the oxygen atom (-O-CH_2-) and the other to the methylene group (-CH_2-).

4.2 Synthesis of Block Copolymer by Photopolymerization of St with C-PTHF

The obtained C-PTHF containing photo labile $Et_2NC(S)S$- end group served as a macro photoiniferter for the polymerization of St under UV irradiation (λ_{max}=300 nm) at ambient temperature (4.5).



Poly (THF-*b*-St)

(4.5)

GPC analysis clearly indicates the formation of block copolymer. As can be seen from chromatograms of the block copolymers (Figure 4.4), the peaks obtained from RI detector shift to lower elution time so that to higher molecular weight side, with the increasing polymerization time and the peaks obtained from UV detector also shift to the higher molecular weight side in parallel manner with the RI peaks which demonstrated those polymer chain containing chromophore group was growing.

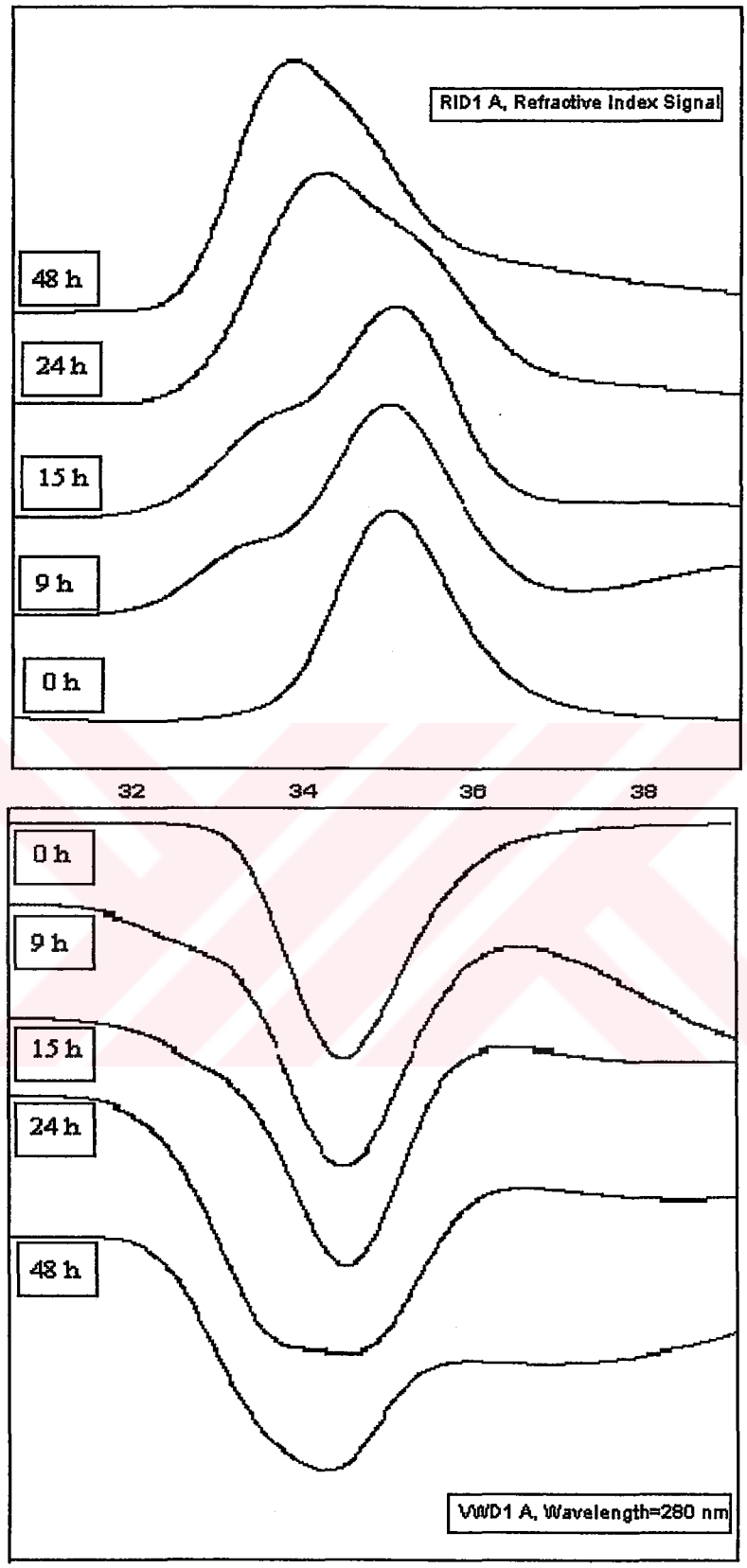


Figure 4.5: GPC profiles of C-PTHF (0 h) and PTHF-PSt block copolymers obtained from RID and UV detectors. λ_{max}=300 nm at room temperature in 3 ml benzene. $[M]_o/[In]_o$=1000:1 (St=3 ml, C-PTHF=0.2 g), [In]/[CuCl]=1:1 (CuCl=2.64 mg) .

The results of the kinetic investigation of the photo block copolymerization are represented in Figure 4.5 and 4.6.

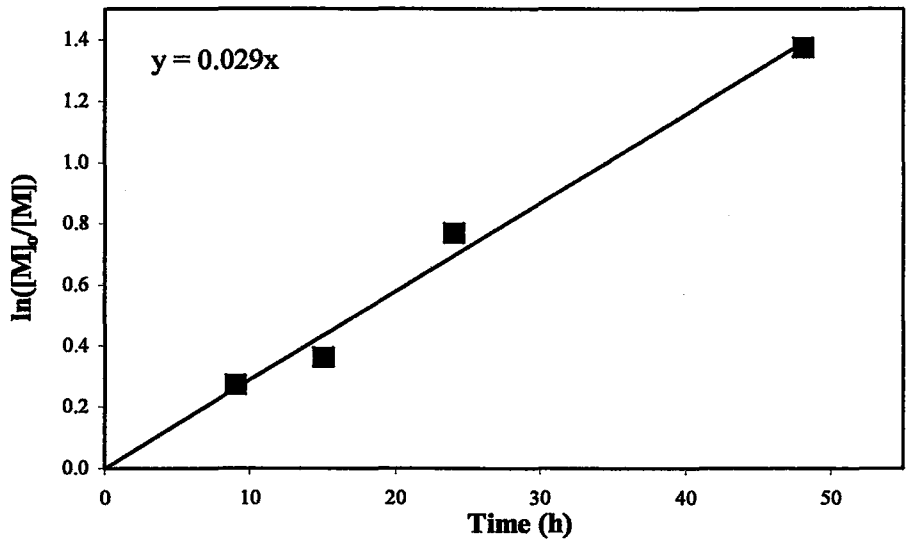


Figure 4.6: Time dependence of ln ($[M]_o/[M]$) for photopolymerization of St by C-PTHF. λ_{max}=300 nm at room temperature in 3 ml benzene. $[M]_o/[In]_o$=1000:1 (St=3 ml, C-PTHF=0.2 g), [In]/[CuCl]=1:1 (CuCl=2.64 mg).

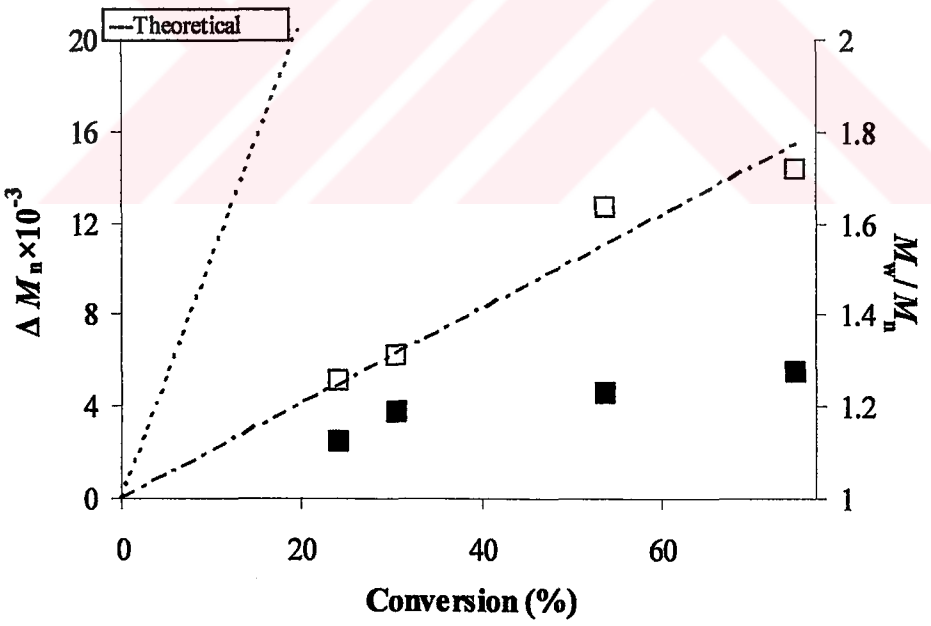


Figure 4.7: Conversion versus molecular weight and polydispersity for photopolymerization of St by C-PTHF. λ_{max}=300 nm at room temperature, in 3 ml benzene. $[M]_o/[In]_o$=1000:1 (St=3 ml, C-PTHF=0.2 g), [In]/[CuCl]=1:1 (CuCl=2.64 mg).

The linear dependence of ln ($[M]_o/[M]$) on reaction time indicated that the concentration of the growing radicals was constant. M_n versus conversion was showed linear relationship with narrow M_w/M_n (<1.3). Relatively low polymerization rate was obtained (8.056×10^{-7} s^{-1}).

In order to confirm the structures of the PTHF-PSt block copolymer, the polymers were also characterized by ^{1}H-NMR, typical spectrum is shown in Figure 4.8 for reaction run 4 and the other runs are shown in Figure 4.9 (a-c). It can be seen that the signals originating from PTHF resonate at about 1.6 and 3.4 ppm, while signals originating from styrene appear at 6.3-7.2 ppm.

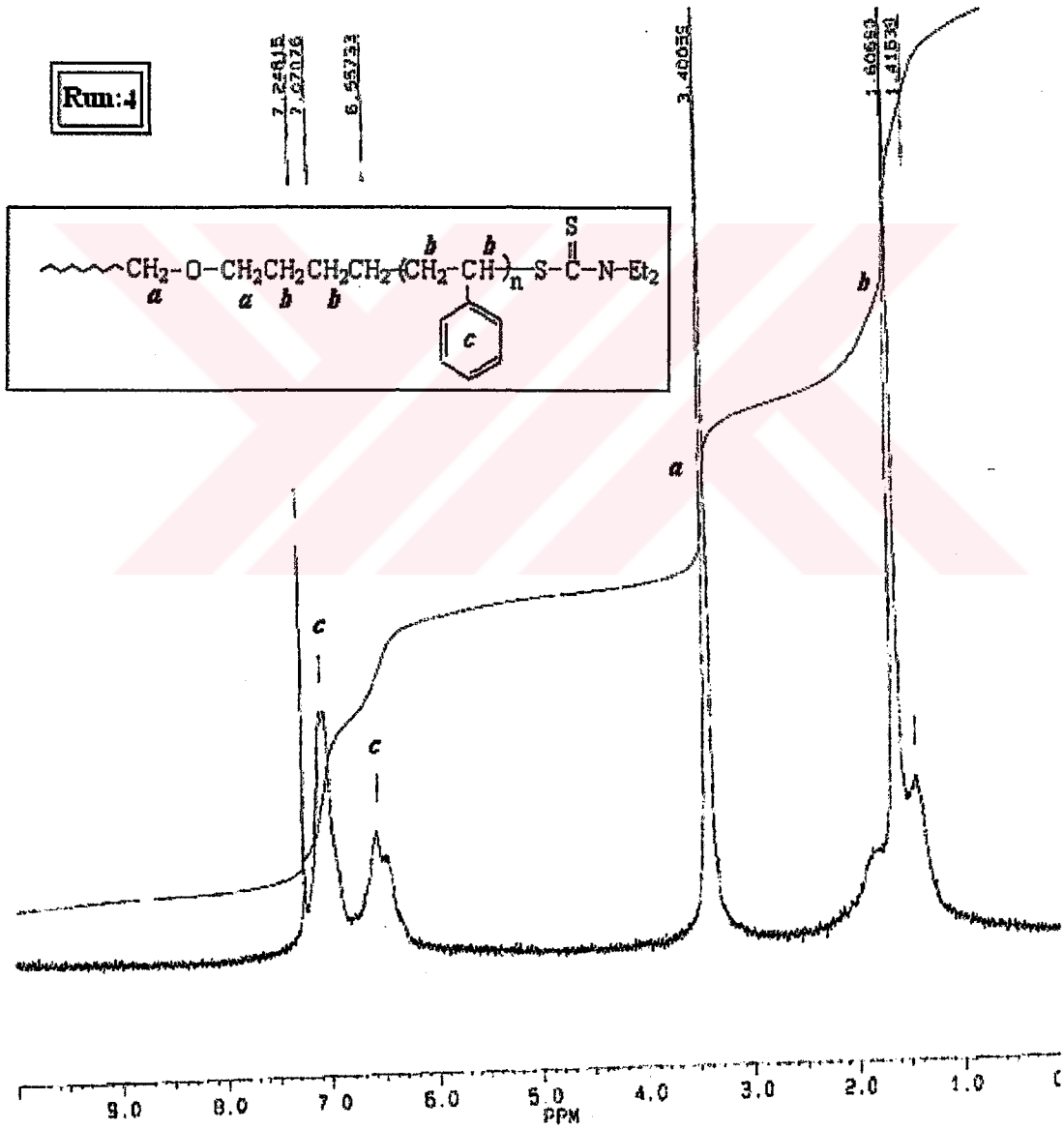
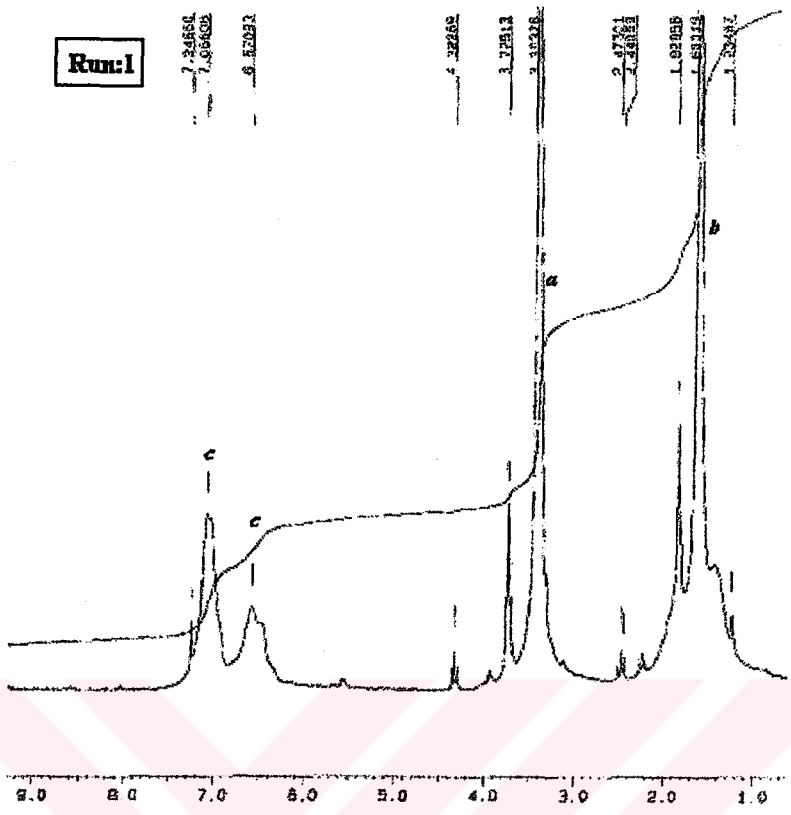
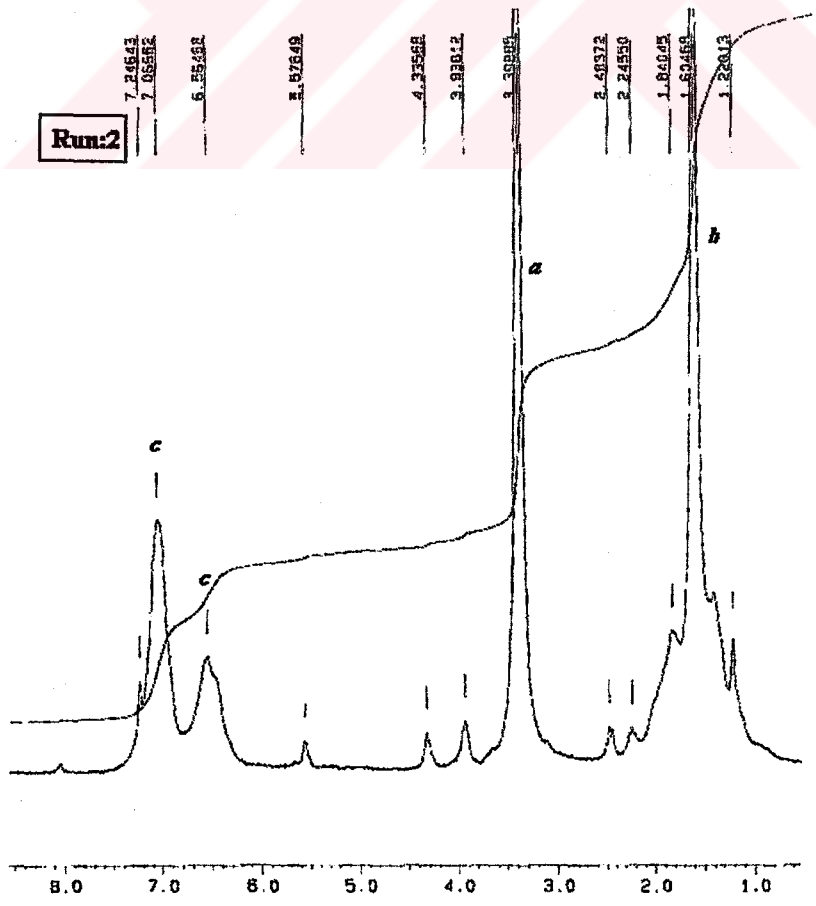


Figure 4.8: ^{1}H-NMR spectrum ($CDCl_3$) of PTHF-*b*-PSt. (Run:4 in Table 4.2) $[M]_o/[In]_o$=1000:1 (St=3ml, C-PTHF=0.2g), [In]/[CuCl]=1:1 (CuCl=2.64 mg), Benzene=3 ml. Time=48h.

(a)


Run:1
a
b
c
c
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

(b)


Run:2
a
b
c
c
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

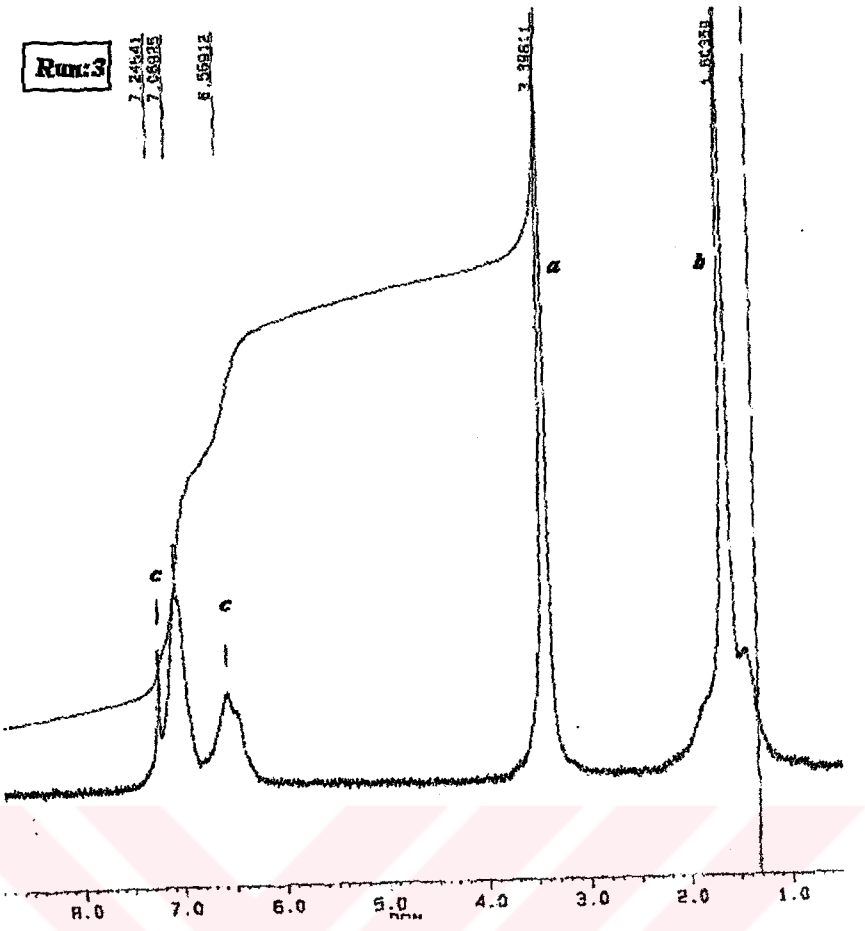


Figure 4.9: ^{1}H-NMR spectrum ($CDCl_3$) of different PTHF-*b*-PSt. (Run:1 in **a**, Run:2 in **b**, Run:3 in **c** from Table 4.2). $[M]_o/[In]_o$=1000:1 (C-PTHF=0.2 g, St=3 ml) [In]/[CuCl]=1:1 (CuCl=2.64 mg), Benzene=3 ml. Time=9, 15 and 24 hours respectively.

$M_{n(NMR)}$ values and number average degree of polymerization of respective blocks in the copolymer was also estimated from the intensity ratio of -O-CH_2- protons at 3.6 ppm of the PTHF (a in Figure 4.8) to the aromatic protons of styrene at 6.3-7.2 ppm (c in Figure 4.8). Number of the THF units is found from $M_{n(GPC,THF)}$ value (7450 g mol^{-1} from Table 4.1) and for the calculation of the $M_{n(NMR)}$ of the block copolymer, $M_{n(GPC)}$ value of the C-PTHF (13400 g mol^{-1} from Table 4.1) is used to obtain a comparative result to the $M_{n(GPC)}$. Calculations are shown below. The overall results are compiled in Table 4.2.

$(THF)_x$—$(St)_y$

x = (7450-150) / 72.11 = 101

Integral of aromatic peaks = 5y

Integral of methylene protons = 4x

→ x/y is evaluated.

→ x is known, y is evaluated.

$M_{n(NMR)}$ = y * MW_{St} + 13 400

Representative calculation for run 4 from Table 2:

5y = 23.143 4x = 17.472

x/y = 0.9437 x = 101 → y = 107

$M_{n(NMR)}$ = 107.104 + 13 400 = 24 528

Table 4.2: Photo block copolymerization of St by using C-PTHF under 300 nm UV irradiation at room temperature. $[M]_o/[In]_o$=1000:1 (St=3 ml, C-PTHF=0.2 g) [In]/[CuCl]=1:1 (CuCl=2.64 mg), Benzene= 3 ml.

Run	Time (hour)	Conversion[a] (%)	$M_{n(GPC)}$[b]	M_w/M_n[b]	$M_{n(NMR)}$[c]	Units[c]	
						THF	St
0	0	-	13 400	1.09	-	101	-
1	9	24	18 600	1.12	18 100	101	45
2	15	31	19 600	1.19	20 100	101	64
3	24	54	26 100	1.23	21 600	101	79
4	48	75	27 700	1.27	24 500	101	107

[a] Calculated by GC measurements.

[b] Obtained by GPC with PSt standards.

[c] Calculated by 1H-NMR results as shown before.

Comparison experiments with different initiation reactants were also carried out under the identical conditions to investigate the photo block copolymerization mechanistically. During the first experimental set (Run: 1-4) copolymerization was

initiated with C-PTHF/CuCl and for the other sets (Run: 5-19) different polymerizations were realized. The results are summarized in Table 4.3.

Table 4.3: Photo block copolymerization of St under 300 nm UV irradiation at room temperature.

Run	Initiator[a]	Catalyst[b]	Ligand[c]	Time (hour)	Conversion (%)	$M_{n(GPC)}$	M_w/M_n
1	C-PTHF	CuCl	-	9	24	18 600	1.12
2	C-PTHF	CuCl	-	15	31	19 600	1.19
3	C-PTHF	CuCl	-	24	54	26 100	1.23
4	C-PTHF	CuCl	-	48	75	27 700	1.27
5	C-PTHF	CuCl	Bpy	9	21	14 000	1.82
6	C-PTHF	CuCl	Bpy	15	29	16 000	1.79
7	C-PTHF	CuCl	Bpy	24	46	17 600	1.57
8	C-PTHF	CuCl	Bpy	35	46	23 600	1.36
9	C-PTHF	-	-	9	18	28 260	1.68
10	C-PTHF	-	-	15	34	28 600	1.80
11	C-PTHF	-	-	24	38	30 500	1.90
12	C-PTHF	-	-	35	38	29 000	1.72
13	-	CuCl	-	9	8	22 900	2,92
14	-	CuCl	-	15	12	24 200	2.65
15	-	CuCl	-	24	15	42 400	2.05
16	-	CuCl	-	35	20	49 600	2.14
17	-	-	-	9	2.5	30 700	1.80
18	-	-	-	15	13	31 400	1.84
19	-	-	-	24	15	40 800	2.13

[a] $[M]_o/[In]_o$=1000:1 (St=3 ml, C-PTHF=0.2 g) Benzene=3 ml

[b] [In]/[CuCl]=1:1 (CuCl=2.64 mg)

[c] [CuCl]/[Bpy]=1:3 (Bpy=12.5 mg)

For each polymerization set, kinetic results were examined and shown below.

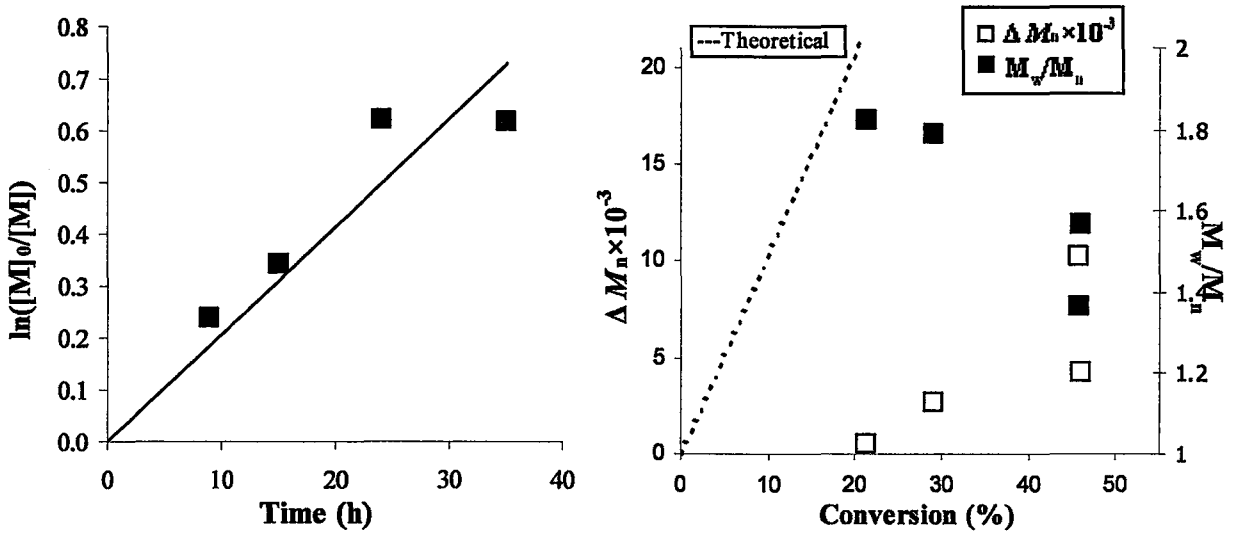


Figure 4.10: Reaction time versus ln ($[M]_o/[M]$) and conversion versus molecular weight and polydispersity for C-PTHF/St/CuCl/Bpy (Run:5-8). $[M]_o/[In]_o$=1000:1 (C-PTHF=0.2 g, St=3 ml), [In]/[CuCl]/[Bpy]=1:1:3 (CuCl=2.64 mg, Bpy=12.5 mg), λ_{max}=300 nm at room temperature in 3 ml benzene.

In the presence of Bpy photo block copolymerization was seemed controlled in the earlier stage with higher polydispersities compared to the first set, but at prolonged reaction time (35 h) termination and transfer reactions can be seen from Figure 4.10.

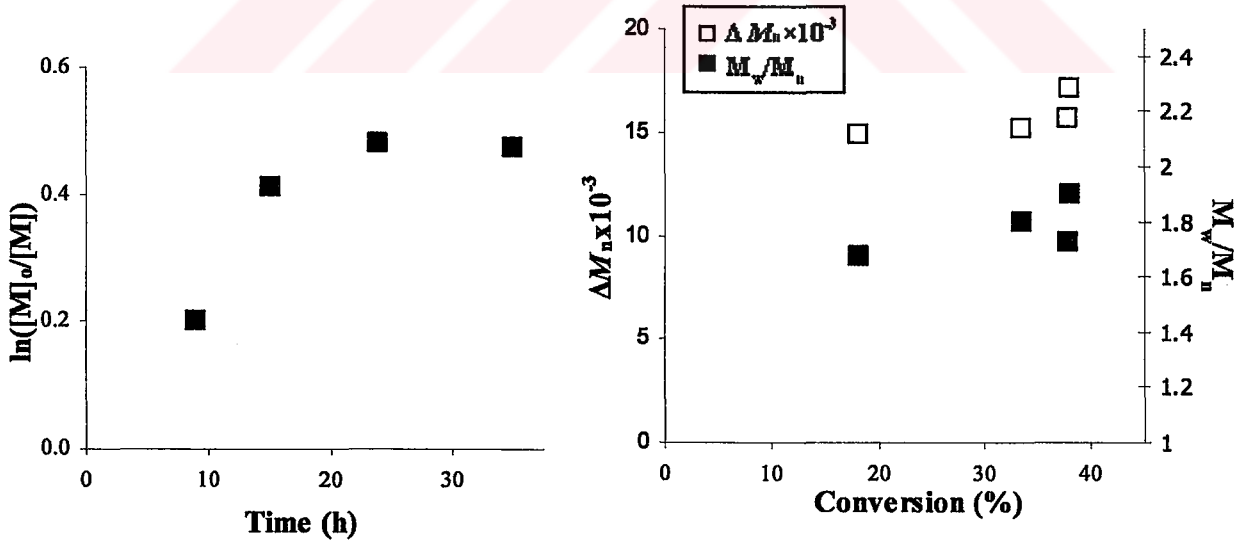


Figure 4.11: Reaction time versus ln ($[M]_o/[M]$) and conversion versus molecular weight and polydispersity for C-PTHF/St (Run: 9-12). $[M]_o$/ $[In]_o$=1000:1 (C-PTHF=0.2 g, St=3 ml). λ=300 nm at room temperature in 3 ml benzene.

For the third set, representative one for the classical iniferter system, kinetic plot was not linear and termination was favored. On the other hand polydispersities was relatively high. M_n values were not changed significantly with time.

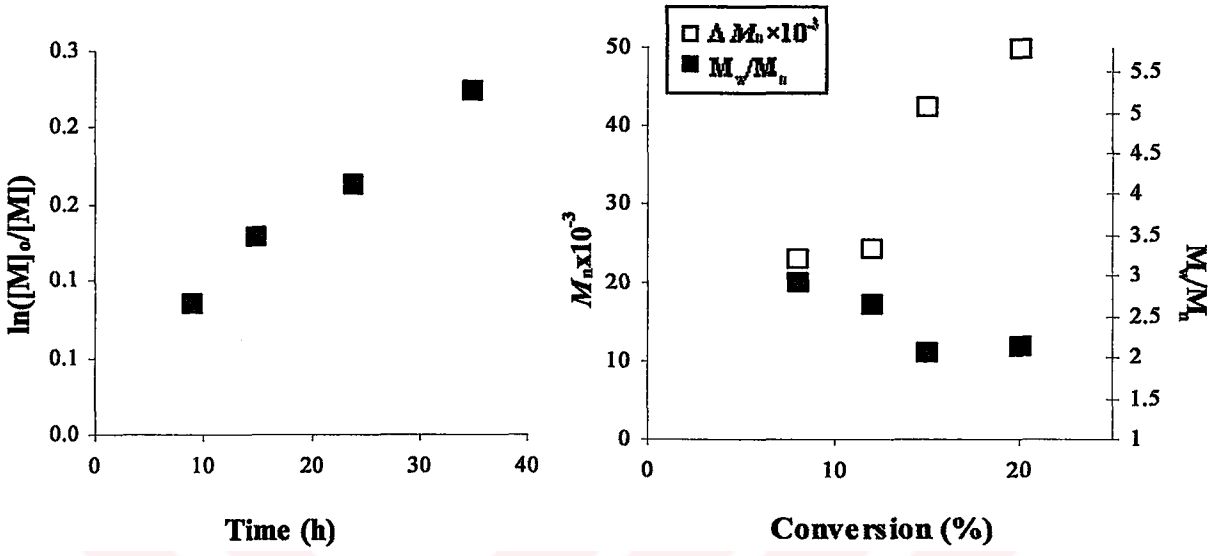


Figure 4.12: Reaction time versus ln ($[M]_o/[M]$) and conversion versus molecular weight and polydispersity for St/CuCl (Run: 13-16). (St=3 ml, CuCl=2.64 mg). λ=300 nm at room temperature in 3 ml benzene.

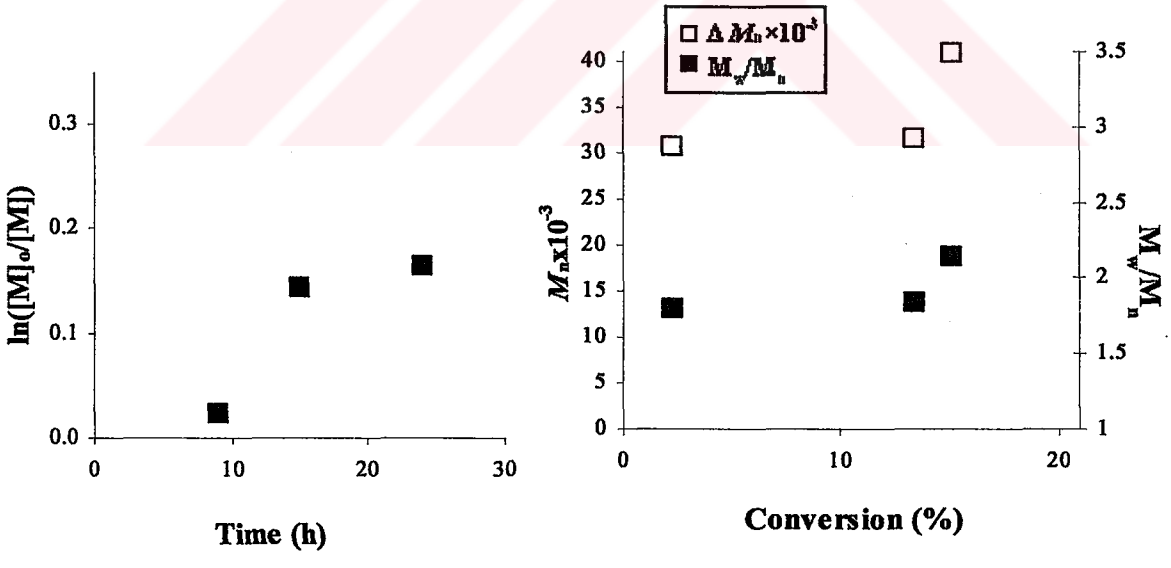


Figure 4.13: Reaction time versus ln ($[M]_o/[M]$) and conversion versus molecular weight and polydispersity for St (Run: 17-19). St=3 ml. λ_{max}=300 nm at room temperature in 3 ml benzene.

The last two sets of polymerization were carried out according to observe self polymerization of St under UV irradiation with the identical concentrations, first in

the presence of CuCl (Figure 4.12) then St by self (Figure 4.13). The self polymerization of St was uncontrolled with high molecular weights and molecular weight distributions (Fig 4.13). In the presence of CuCl, although molecular weight distributions were relatively high, the both kinetic and M_n versus conversion plots (Figure 4.12) showed unexpectedly linear relationship which is a promising result for controlled fashion in photo induced radical polymerization system. One can notice that by CuCl addition to the St self polymerization using UV irradiation introduces well defined polymer. Further investigation would be carried out.

5. CONCLUSIONS

Initially, PTHF was synthesized by living cationic ring opening polymerization and the reaction was ended by *N,N'*-diethyl dithiocarbamate to achieve intended end functionalization. Characterization analyses clearly revealed that C-PTHF synthesized was well defined with narrow polydispersity and contained photo-labile DC groups as end-cappers.

Afterward, C-PTHF was used as macroinitiator for the photo block copolymerization of St in which, CuCl was introduced to the system to obtain controlled results. A plot of semilogarithm of monomer concentration, $\ln([M]_0/[M])$, versus time gave a straight line, indicating that the kinetic of polymerization was first-order. Molecular weights of St increased with time and low polydispersities were obtained. Block copolymers were also characterized with ^{1}H-NMR and the composition of block copolymer was calculated. Furthermore, different polymerizations having altered reactants were carried out under the identical conditions to compare with the previous case (first set). When the same copolymerization was realized in the presence of ligand (Bpy), in second set, kinetic plot showed deviation from linearity especially at the last point and also the polydispersities were higher than previous ones. During the third set, classical iniferter system was tested with C-PTHF and St without CuCl nor Bpy, and the results was as expected far from controlled copolymerization. Forth and fifth sets were performed to observe self polymerization of St under the identical conditions in the presence and absence CuCl, respectively.

In conclusion, it was observed that the photo block copolymerization of St with C-PTHF in the presence of CuCl was the most controlled one between the whole sets tested. The reaction was slow and the M_n values measured by different methods were below than theoretical ones but these were expected results because of the nature of photo iniferter reactions which show slow initiation. The adaptation of the CuCl from ATRP concept to the iniferter concept method gave encouraging results.

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