İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF POLYMERIC RAFT AGENT BY CATIONIC RING-OPENING POLYMERIZATION

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KATYONİK HALKA AÇILIMI POLİMERİZASYONU İLE POLİMERİK RAFT AJANININ SENTEZİ VE KARAKTERİZASYONU

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ABBREVIATIONS

PTHF : Poly(tetrahydrofuran)
PSt : Polystyrene
RAFT : Reversible Addition-Fragmentation Transfer (RAFT) Polymerization
DTBP : 2,6-ditertiary-butyl-4-methyl pyridine
ATRP : Atomic Transfer Radical Polymerization
CRP : Control Radical Polymerization
M_n : Number Average Molecular Weight
M_w : Molecular Weight
^{1}H-NMR :.Nuclear Magnetic Resonance Spectroscopy
IR : Infrared Spectrophotometer
CTA : Chain Transfer Agent
PDI : PolyDispersity Index
AIBN : 2,2'-azoisobutyronitrile
THT : Tetrahydrothiophene
GPC : Gel Permeation Chromatography
UV : Ultra Violet
THT : Tetrahydrothiophene

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LIST OF SYMBOLS

R : Radical
I : Initiator
M : Monomer
M_n : The number average molecular weight
M_w : The weight average molecular weight
$M_\mathrm{w}/M_\mathrm{n}$: The molecular weight distribution

SYNTHESIS AND CHARACTERIZATION OF POLYMERIC RAFT AGENT BY CATIONIC RING-OPENING POLYMERIZATION

SUMMARY

Block copolymer, poly(tetrahydrofuran)-block-polystyrene abbreviated as (PTHF-*b*-PSt), with controlled molecular weight and narrow polydispersity have been successively synthesized by a combination of cationic ring-opening polymerization and reversible addition-fragmentation chain (RAFT) polymerization. In the first step, cationic ring-opening polymerization of THF was performed using benzyl alcohol, triflic anhydride and 2,6-ditertiary-butyl-4-methyl pyridine (DTBP) as initiating system. The living chain of PTHF was terminated by sodium dithiobenzoate to obtain macro-RAFT agent. Then, block copolymerization of styrene by RAFT process using functional PTHF as a macro-RAFT agent was achieved. The gel permeation chromatography (GPC) and ^{1}H NMR analyses confirmed the structures of the (PTHF-*b*-PSt) block copolymer obtained.

Keywords: Poly(tetrahydrofuran), polystyrene, block copolymers, RAFT polymerization, cationic ring-opening polymerization

KATYONİK HALKA AÇILIMI POLİMERİZASYONU İLE POLİMERİK RAFT AJANININ SENTEZİ VE KARAKTERİZASYONU

ÖZET

Kontrollü moleküler ağırlığına ve dar molekül ağırlığı dağılımına sahip, (PTHF-*b*-PSt) olarak kısaltılımış poli(tetrahidrofuran)-blok-polistiren blok kopolimeri, katyonik halka açılması polimerleşmesi ve geri dönüşümlü katılma-parçalanma transfer (RAFT) polimerleşmesi tekniklerinin birleşimi ile başarılı şekilde sentezlenmiştir. İlk basamakta, başlatıcı sistem olarak benzil alkol, trifilik anhidrid ve DTBP kullanılarak THF'in katyonik halka açılımı polimerleşmesi uygulanmıştır. PTHF'in yaşayan zinciri, makro-RAFT ajanını elde etmek için sodyum ditiyobenzoat ile sonlandırıldı. Sonra, fonksiyonel PTHF'nin makro-RAFT ajanı olarak kullanıldığı RAFT tekniği ile stirenin blok polimerleşmesi başarıldı. Jel yayılım kromatogramı ve ^{1}H NMR analizleri ile (PTHF-*b*-PSt) blok kopolimeri yapısının elde edildiği onaylandı.

Anahtar Kelimeler: Poli(tetrahidrofuran), polystiren, blok kopolimerleri, RAFT polimerleşmesi, katyonik halka açılımı polimerleşmesi

1. INTRODUCTION

Polymers are widely used in all walks of human life and play a vital role in shaping modern man's activities to be as important and comfortable as they are today. The advances in science and technology made in recent decades owe much to development of polymer science. The synthesis and design of new polymeric materials to achieve specific physical properties and specialized applications, and attempt to find interesting applications involving advanced structures and architectures, are in continuous development in the period of the polymer science.

Basically, a polymerization process is based on a repetitive reaction in which a monomer is converted into polymer segment. To achieve such a goal, polymer chemists have a variety of synthetic processes to choose from reactions with very high selectivity when planning a particular synthesis. However, each method has its strengths and its weaknesses, and often requires high-purity reagents and special conditions. Indeed, the need high-purity monomers and solvents, reactive initiators and pure conditions have dramatically limited the industrial application of many techniques.

Free radical polymerization is very important in the field of industrial polymer synthesis and is the preferred route to commercial polymers. It is very is adaptable to many types of monomer under mild conditions. However, the preparation of well defined polymers from unsaturated monomers has been limited by the technology available for conventional free radical polymerization. Certainly, such processes inherently do not allow to control over molar masses and give broad polydispersity since not all the polymeric chains are initiated at the same time because of a lack of control over chain-breaking reactions; i.e., both termination and the transfer steps greatly limit ability to polymer architecture. Living polymerization is an essential technique for synthesizing polymers with controlled structure i.e. polymers with controlled molecular weight and narrow molecular weight distributions. Moreover, living polymerization techniques allow preparation of macromers, macroinitiators, functional polymers, block and graft copolymers and star polymers. This way, the need for specialty polymers having a desired combination of physical properties can be fulfilled. Control of such complex architectures by living polymerization has largely achieved using living anionic or cationic and group transfer polymerization techniques. There are so many different methods to synthesize block copolymers.

Among them, the transformation polymerization is an elegant method which allows to combine various polymerization mechanisms. It is one of the major methods to obtain well defined block copolymers. This way many monomers with different chemical structure can be polymerized to yield block copolymers with novel properties.

Recent advances in controlled free radical (CRP) polymerization have been applied to synthesis of wide range of well-defined specific polymer architectures. Several methods, such as atom transfer radical polymerization (ATRP), stable radical mediated radical polymerization and radical addition-fragmentation chain transfer (RAFT) process have been accepted to be most efficient. Similarly to the other CRP techniques, RAFT polymerization is a smart reply to the drawbacks of conventional free radical polymerization characterized by a low control over the molecular weight distribution (MWD) and the chain architecture. It consists of adding, in the polymerization medium, a reversible chain transfer agent (CTA) which has at least one group that contains the following sequence, –*x*(=S)–S– (with x = C or P). For clarity, only the general case, x = C, which corresponds to thiocarbonylthio compounds. A great number of such compounds have been synthesized by varying the structure of the Z and R groups.

In the presence of (macro)radical species, the CTA induces reversible addition-fragmentation transfer reactions, to create an equilibrium between active species (propagating radicals) and so-called dormant species (thiocarbonylthio-terminated chains) that can become active again, contrary to the dead species (produced via irreversible termination or transfer reactions). This equilibrium is responsible for the control of the polymerization.

Over the past decades, addition-fragmentation reactions have been extended to the polymer field via cationic or radical processes. Also, cationic ring-opening polymerization has some advantages for synthesizing well defined block copolymers. While there is an oxygen inhibition in the free radical polymerization systems, there is no in the cationic ring-opening polymerization systems. Also, this system has less toxicity than other polymerization techniques.

Herein we report that the synthesis of the PTHF-b-PSt by the combination of cationic ring-opening polymerization and RAFT polymerization.

2. THEORETICAL PART

2.1 Cationic Polymerization

2.1.1 Introduction

In the strict sense, cationic polymerizations are defined as chain polymerizations in which the kinetic chain carriers (active species) are positively charged. These ionic species form the growing chain ends of the polymers and can be of different types: in ring-opening polymerizations, they are mostly ''onium ions'' whereas in ''vinyl'' polymerizations, they are carbenium ions. The latter are therefore frequently referred to as ''carbocationic'' polymerizations. The initiation reaction is the formation of the cationic active species (also referred to as ''cationation of the monomer'') and the propagation reaction a nucleophilic attack of the monomer on the active species (Figure 2.1).

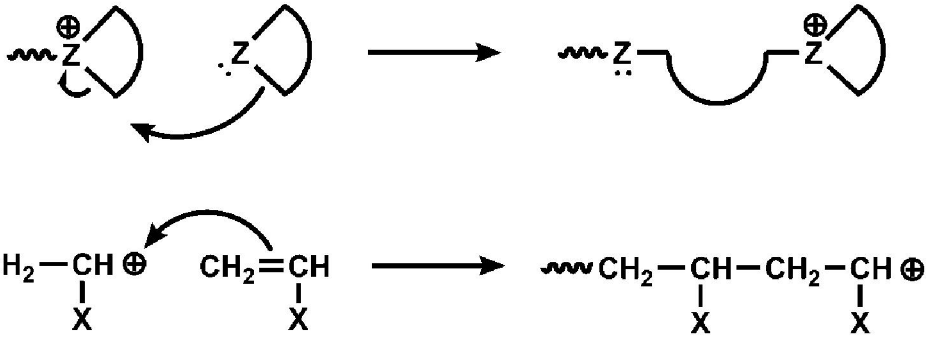
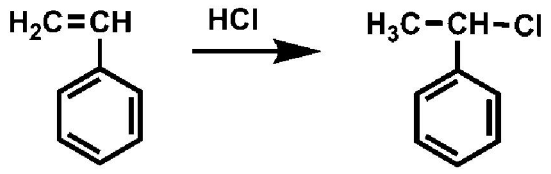


Figure 2.1 : Propagation reactions in cationic ring-opening and carbocationic polymerizations (counteranion omitted).

Condition for an olefinic monomer to be polymerizable by a cationic mechanism is that the active species is stabilized by the substituents on the olefinic group. changing the branch structures found on it. Dendrons are similar to dendrimers but they are not polymers (see Figure 2.1), they are only molecules with high molecular weights and chemical addressable groups.

The reactivity of carbenium ions, even when ‘‘stabilized’’, is very high. This leads to at least three problems for the development of living polymerizations: (1) the rate constants of propagation are very high [1,2], even at low temperatures, which makes control of the reaction difficult, (2) side reactions such as isomerizations, hydride abstraction and different kinds of transfer can take place and (3) the polymerizations are very sensitive to impurities. In any cationic polymerization, the counter anion of the active species plays an important role for the determination of the living character of the polymerization. If this counter ion is too nucleophilic, it will combine with the carbenium ion to form a covalently bonded species, which in principle does not propagate. If this happens, the propagating chain end is destroyed and this reaction is a termination. For example, the reaction of styrene with hydrogen chloride would simply lead to the addition product:



(2.1)

Therefore, it is important that initiating systems are chosen in such a way that the corresponding counter anions are less nucleophilic than the monomer. Typical non-nucleophilic counter ions are BF_4^-, PF_6^-, SbF_6^-, and ClO_4^-. However, if the nucleophilicity of the counter ion is properly tuned, there may exist an equilibrium between the active cationic species and the covalent non-active species which is then called a ‘‘dormant’’ species.

$$\sim CH_2-\underset{R}{CH}\oplus\ X^\ominus \rightleftharpoons \sim CH_2-\underset{R}{CH}-X$$

(2.2)

The control of this kind of equilibria by the proper choice of the initiating system and reaction conditions or by performing the polymerization in the presence of specific (usually weak) nucleophiles, was one of the key factors which have made it possible to perform cationic polymerizations in a living/controlled way. Such mechanism, involving a continuous equilibrium between a dormant and an active chain end has been called ‘‘quasi-living’’. However, according to the latest terminology of kinetics, thermodynamics and mechanisms of polymerization, proposed by IUPAC

Macromolecular Division [3], this mechanism can be designated as ‘‘living’’, provided that the exchange reactions leading to this equilibrium are fast compared to the over-all rate of propagation and, of course, if transfer and termination reactions are absent. In some cases the non-ionic ‘‘dormant’’ species are also able to propagate and in that case, this kind of propagation is, *senso stricto*, not a cationic one. If the propagation occurs by these non-ionic species exclusively, the polymerizations have been termed as ‘‘pseudo-cationic’’ [4] or ‘‘electrophilic’’ [5] polymerizations, the last term stemming from the fact that the active species is a neutral electrophilic function. Controlled/living polymerizations are useful for the synthesis of well-defined polymer architectures and it is often of great importance to be able to introduce functional groups at one or at both polymer chain ends. These groups can, generally speaking, be introduced by two methods: functional initiation and functional termination or end-capping. For ‘‘monotelechelic’’ polymers, i.e. polymers carrying one functional end-group, either method is suitable. For telechelic polymers, the most used method is to initiate the living polymerization with a bifunctional initiator, followed by functional endcapping of both active chain ends. For the synthesis of heterotelechelic polymers, i.e. polymers carrying two different functional end- groups, a combination of functional initiation and termination has to be used. It is clear that the ‘‘controlled’’ polymerization includes also the control of the nature of the endgroups of the formed polymer chains and, hence, the exact knowledge of initiation and (deliberate) termination (end-capping) reactions. The living/controlled carbocationic polymerizations have been developed over a period of 30 years. During that time, a number of reviews and books on this topic have appeared. The first comprehensive book dealing with the chemistry of cationic polymerization is that edited by Plesch in 1963 [6]. Ring-opening polymerizations have been reviewed in Refs. [7–10], carbocationic polymerizations in Refs. [11–17] and Ref. [18] deals with cationic polymerizations in general. Very recently, an exhaustive review on the mechanisms and kinetics of carbocationic polymerizations has been published [19]. A view on the evolution of the topic in the last 30 years can be found in the proceedings of the bi-annual meetings on ‘‘Cationic polymerizations and related processes’’ (since 1998 renamed as ‘‘Ionic polymerizations and related processes’’), which have been organized on a regular bases since 1973.

2.1.2 Early Works

Until the 1960s, pioneering work on carbocationic polymerizations was performed by several groups: David Pepper at Trinity College in Dublin, Ireland; Peter Plesch at Keele University, UK; Pierre Sigwalt at the Universite´ Pierre et Marie Curie, Paris; Vivian Stannett at the University of Maryland, US; Joseph Kennedy at Akron, US; T. Higashimura at Kyoto University, Japan and others. The aim of these studies was in the first place to elucidate the elementary steps of the mechanism of the polymerization mainly by means of kinetics, similar to the studies on anionic polymerizations successfully developed in that same period. However, it became soon clear that the problems encountered in cationic polymerizations were much more complex compared with the anionic systems. In the first place, cationic initiation of alkenes is often a complicated process involving more than one step. Most polymerizations, at that time, were carried out with Lewis acids as ‘‘initiators’’. Already in the late 1940s, Evans, Polanyi, Plesch et al. reported that exhaustively purified, dry isobutene (IB) fails to polymerize when put in contact with BF_3 or $TiCl_4$ and that immediate polymerization ensues upon the introduction of traces of water [20, 21]. Although some cases of direct initiation by Lewis acids have been shown to take place [22, 23], more slowly and at higher temperatures, it is generally agreed that, in ‘‘super dry’’ conditions, most Lewis acids are not capable to initiate the polymerization. In fact, the real initiators are proton donors or cationogenic compounds that are activated by the Lewis acid. Therefore, the presence of minute traces of water or any other proton donor, although necessary to induce polymerization, leads to irreproducible kinetics due to the fact that they are ‘‘impurities’’ and hence present in non-controlled quantities. Pepper investigated the kinetics of the polymerization of styrene initiated by perchloric acid [24, 25]. He reported that at temperatures below -60°C, the polymerization stopped and attributed this to the formation of a perchlorate ester. By raising the temperature above this temperature, the ester became active and polymerization started again. In fact this was a first report of the occurrence of a reversible termination reaction involving two endgroup species: the active propagating chain end and a non-propagating (dormant) chain end. Gandini and Plesch reinvestigated the styrene polymerization initiated by perchloric acid by combination of spectrophotometry, conductivity and kinetics and concluded that ions were absent during propagation and that they only formed when the styrene concentration was less than four times that of the acid. To explain these phenomena, Plesch proposed the concept of ‘‘pseudocationic polymerizations’’ according to which the propagating species are esters, which react directly with styrene in a concerted multicenter mechanism [26, 27]. This concept was also proposed for polymerizations initiated by other strong acids but in 1986, Matyjaszewski and Sigwalt demonstrated that, at least with trifluoromethanesulfonic acid (‘‘triflic acid’’), the ester corresponding to the growing species was unstable, even at -78°C, thus showing that with this acid, propagation with a triflate ester as active species was not possible [28].

Another factor that complicated the development of controlled/living carbocationic polymerizations is the tendency of carbenium ions to isomerize to (more stabilized) isomeric structures by means of hydride or carbanion shifts. This was demonstrated in the early 1960s by Kennedy [29,30] for the polymerization of 3-methyl-1-butene (Figure 2.2). When the polymerization is carried out at temperatures above -100°C, the polymer has a structure expected for a normal vinyl type of polymerization. When the polymerization is carried out at -100°C, a polymer with an isomeric structure is formed as a consequence of a hydride shift (transforming the secondary into a tertiary carbenium ion) before each propagation step.

But the biggest problem in the development of living cationic polymerizations was the extremely high reactivity of carbenium ions and their strong tendency to form a double bond by elimination of a proton that starts a new propagation reaction. Recently measured rate constants of propagation for different monomers range from 10^4 to 10^6 L mol^{-1} s^{-1}. Consequently, the control of molecular weight by the ratio of monomer/initiator (as in living anionic polymerizations) is not possible because quantitative initiation in the early stages of the polymerization is not possible. Therefore, the key to controlled/living cationic polymerizations was to reduce the reactivity of the growing chain end without reducing the rate of initiation. By reducing the reactivity of the growing chain end, also the occurrence of transfer reactions could, hopefully, be reduced or eliminated.

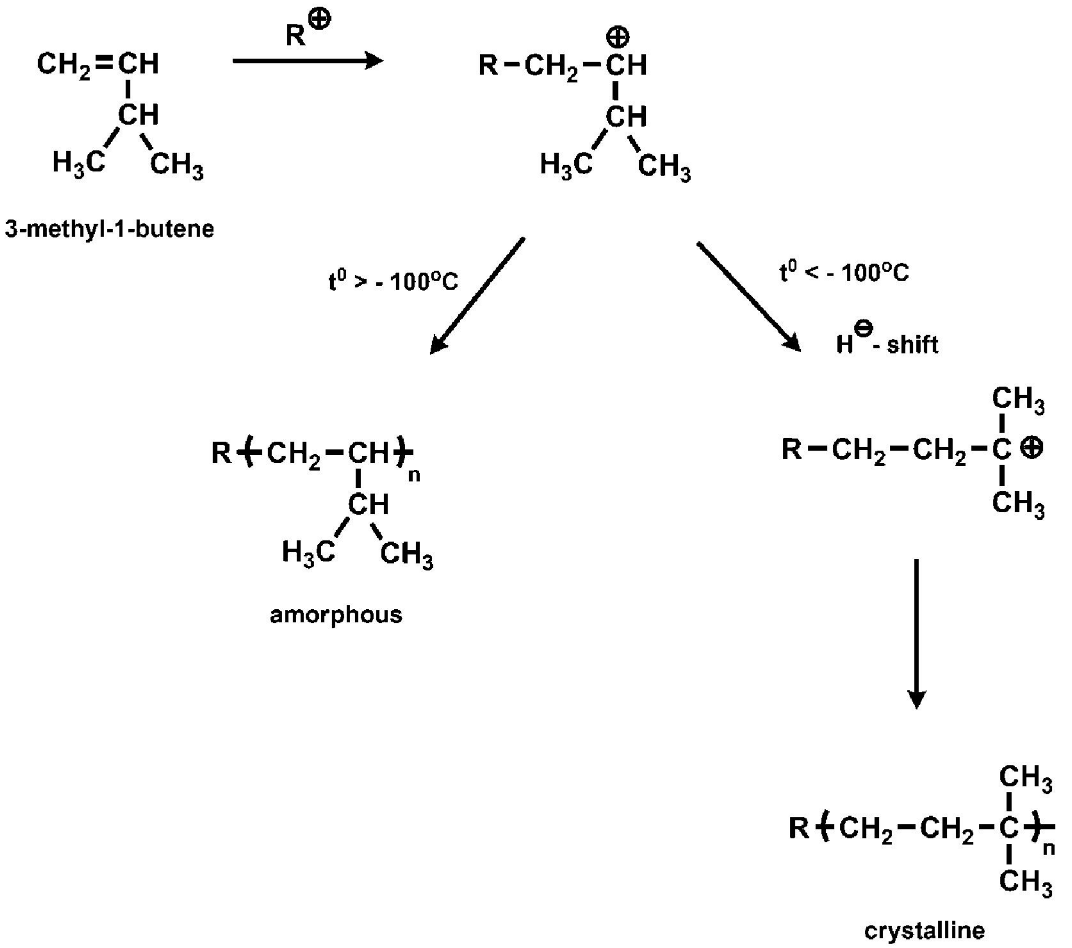
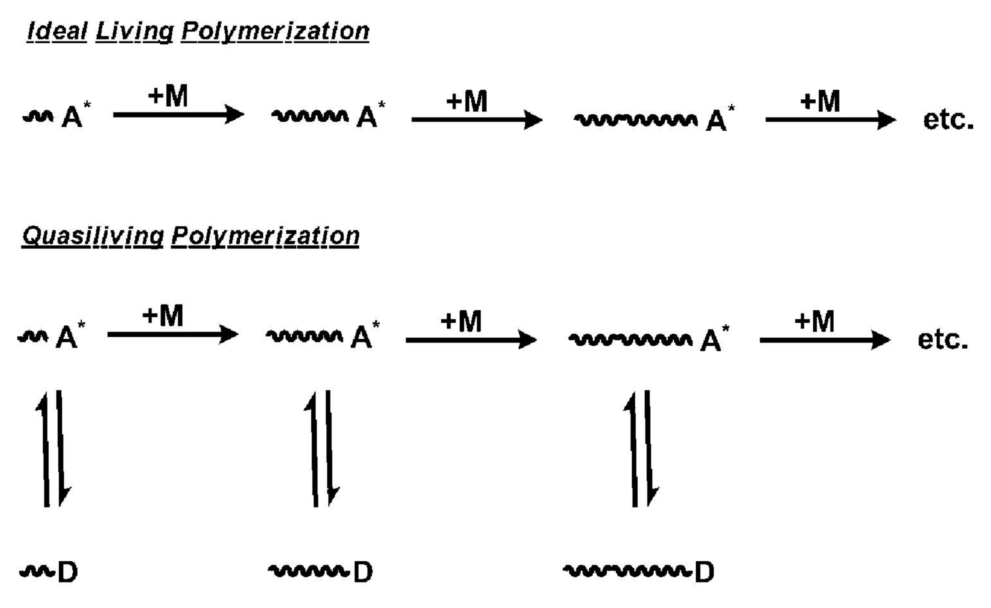


Figure 2.2 : ''Normal'' propagation and propagation, preceded by hydride shift, in the cationic polymerization of 3-methyl-1-butene.

2.1.3 The development of controlled/living systems

In 1984, Higashimura, Sawamoto and coworkers (the ''Kyoto group'') reported that the polymerization of vinyl ethers, initiated with a combination of hydrogen iodide and iodine, leads to controllable polymerizations [31]. Around the same time, Kennedy and his coworkers (the ''Akron group'') made progress in the controlled cationic polymerization of IB using systems leading to what was called ''quasi-living'' and eventually to living systems. Quasi-living polymerizations were defined as polymerizations in which rapidly reversible chain transfer and/or termination are present and the rate of these processes is faster than that of propagation. The difference between ideal living and quasi-living polymerization is illustrated by the following equations:



(2.3)

where A* is active species, D is dormant species and M is monomer. Increasing number of _ signs indicates chain growth and the equilibria between A* and D are rapid relative to monomer addition. From the synthetic point of view, both ideal and quasi-living polymerizations are equally valuable. According to the latest IUPAC nomenclature proposals, this kind of mechanism should be classified under the ‘‘living’’ polymerizations. In the discussions about the mechanism of these ‘‘living’’ systems, another important question arose: are these polymerizations really cationic, in other words are carbenium ions the active species, and, if yes, how is it possible that the reactions become controllable in view of the extremely high reactivity of these species? Or do these reactions occur via other, less reactive, species by other (eventually nonionic) propagation mechanisms? Several such mechanisms have been proposed, some based on the assumption that these polymerizations were to be considered as ‘‘pseudo-cationic’’, in analogy to the mechanism proposed by Plesch for the polymerization of styrene initiated by perchloric acid. This polymerization was believed to occur by a concerted mechanism involving the perchlorate ester as reactive end-group [26]. Also the living vinyl ether polymerizations, described by the Kyoto group, was originally proposed to occur through a ‘‘pseudocationic’’ mechanism in which the monomer was inserted into a polarized covalent carbon–iodine bond by a four-center concerted mechanism. Taking into account the Woodward–Hoffmann rules, this mechanism was changed into a concerted mechanism involving a six-membered transition state [32]. These proposed concerted mechanisms are shown in Figure 2.3.

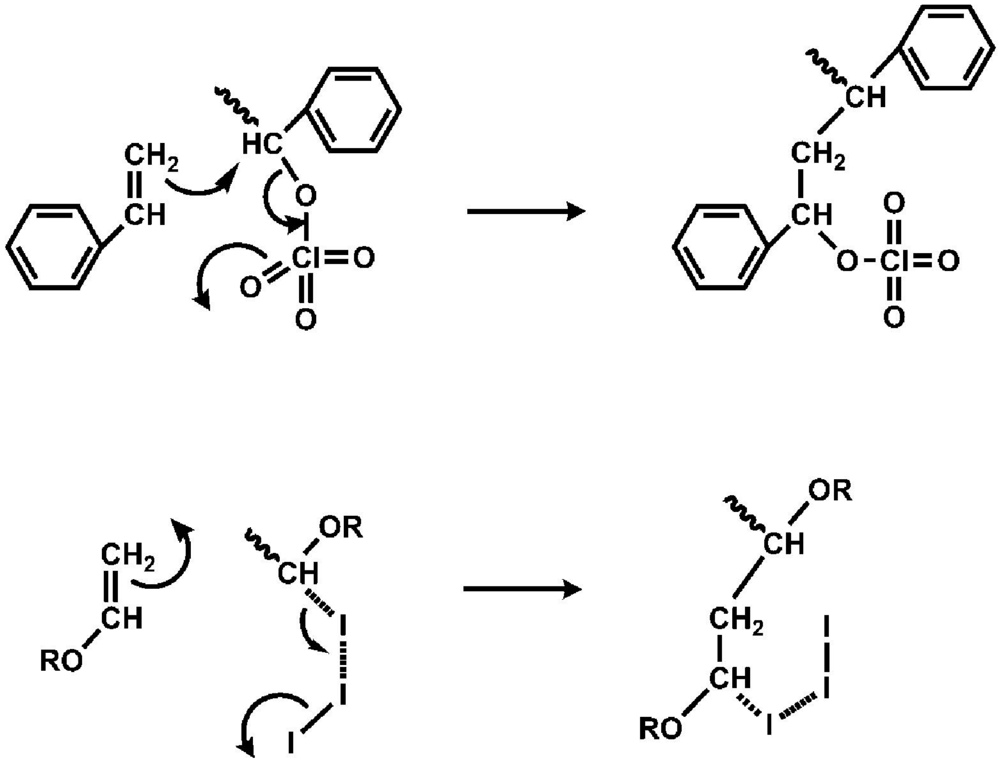
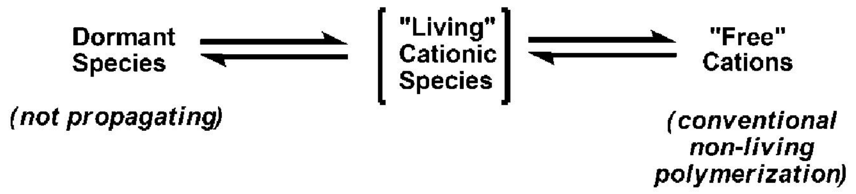


Figure 2.3 : Examples of ‘‘pseudo-cationic’’ propagation mechanisms: the systems styrene/perchloric acid and vinyl ether/hydrogen iodide+iodine.

The assumptions that the living polymerizations occurred by a special type of active species were further substantiated when Kennedy et al. reported that the rate of the polymerization of IB decreased and the livingness of the polymerization increased significantly if the reactions were conducted in the presence of well-chosen electron donors. These electron donors could be formed in situ by the initiation mechanism or intentionally be added to the polymerization mixture. The role of the electron donor was assumed to be the formation of a new type of active center that had a ‘‘reduced cationicity’’ compared to the usual, nonliving, active species [11, p. 59–78].

Thus, not only was there discussion whether the living mechanism was ‘‘pseudocationic’’ or involved equilibrium between a dormant species and an active species (i.e. ‘‘quasi-living’’ polymerization) but also the nature of the active species, leading to living polymerizations, was not clear. It was proposed that it was a structure laying somewhere in between the non-ionic dormant species and the carbocationic (active but non-living) species:



(2.4)

The wealth of available information on the topic was critically reviewed by Matyjaszewski and Sigwalt [33] in 1994. These authors came to the conclusion that the ‘‘new’’ mechanisms leading to ‘‘living/controlled’’ polymerizations could be explained by the occurrence of equilibrium between two species: a cationic, highly reactive species, being present in very low concentrations, and a dormant (non-propagating) species. The dormant species generally is either a covalently bound group (such as a halide), that can be activated by a Lewis acid (the co-initiator), or the reaction product of the carbenium ion with an (added) nucleophile or electron donor which acts as a de-activator. The consequence of this equilibrium is that the over-all rate of propagation (as well as the rates of all other reactions involving the active species) is decreased to such an extent that the initiation reaction can take place in a quantitative way, thus giving rise to the first condition for controlled polymerization: $R_i > R_p$. An important requisite of this system is, however, that the rates of the reactions transforming the active species into dormant species and vise versa have to be rapid in comparison with the overall rate of propagation. If this is not the case, bimodal molecular weight distributions are obtained. The general mechanism of the living/ controlled carbocationic polymerization can then be described as: initiator system, the solvent and the temperature all play a determining role for the ‘‘livingness’’ of the polymerization. As a consequence, it is necessary to establish the conditions for living polymerization for each monomer/initiator/activator or de-activator/ solvent/temperature system. The understanding of the mechanisms of different carbocationic polymerizations has led to renewed interest in the determination of the absolute rate constants of propagation in these living systems [19]. Recently reported kinetic studies yielded new values for absolute rate constants for propagation for ion pairs in living polymerizations of isobutylene [34], styrene [35], p-methoxystyrene [36], p-chlorostyrene [37], 2,4,6-trimethylstyrene [38] and p-methylstyrene [39], determined by two different reaction clock methods: competition experiments and/or kinetic studies of diffusion-limited addition of p-nucleophiles by on-line UV-VIS spectroscopy. Values between 10^4 and

10^6 $Lmol^{-1}$ s^{-1} were obtained and from the independence of the constants on the temperature, it was concluded that propagation reactions in carbocationic polymerizations show no enthalpic barrier. The same authors demonstrated that ion pairs and free ions have similar reactivities [40]. In the following paragraphs, the cationic controlled/ living polymerizations of the three most important families of monomers will be described: vinyl ethers, 1,1-disubstituted alkenes and styrenics, followed by some less important monomers.

2.1.4 Cationic Ring Opening Polymerization of THF

In the last two volumes published by Szwarc (the first of two with M. van Beylen) polymerization of THF is discussed as an example of living ROP [41, 42]. For obvious reasons the treatment given there could not be as extensive there as in the present review or other earlier reviews [43, 44, 45].

An initiator that is suitable for quantitative studies is trifluoromethanesulfonic acid [triflic acid, (CF_3SO_3H)] or its esters. Acid itself is forming in initiation the secondary onium ions that are usually less reactive than the corresponding tertiary onium ions in propagation; like in polymerization of THF (Figure 2.4).

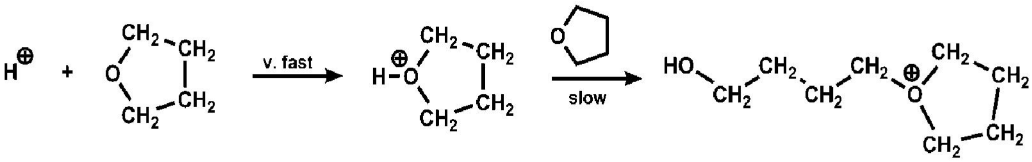


Figure 2.4 : Initiation of THF polymerization with a strong acid.

Esters of triflic acid directly form onium ions of similar structure as propagating species, which are tertiary oxonium ions. The triflic anion of relatively high nucleophilicity may combine with cationic growing species forming the corresponding covalent species (Figure 2.5).

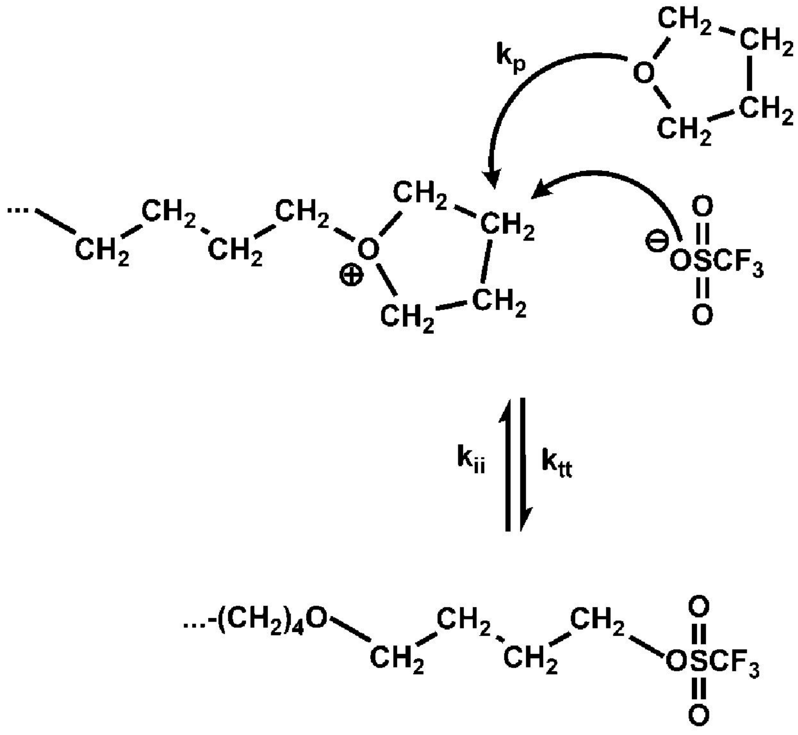


Figure 2.5 : Ionic-covalent species equilibria in THF polymerization.

Propagation proceeds also as nucleophilic attack of the monomer molecule on the carbon atom in the cyclic oxonium ion with rate constant k*p*, as shown in the scheme above for the temporary deactivation.

The pertinent rate constants are k_{tt} and k_{ii} [tt = temporary deactivation and ii = internal (unimolecular) activation]. The importance of deactivation is governed by the nucleophilicity of the studied monomer and, therefore by the ratio of the rate constant of propagation to the rate constant of deactivation. On the other hand, this importance would also depend on the position of equilibrium given in the scheme involving rate constants of deactivation and reactivation. In polymerization of THF the rate of temporary termination is comparable to the rate of propagation.

2.2 Reversible Addition-Fragmentation Transfer (RAFT) Polymerization

The living/controlled radical polymerization (CRP) techniques developed over the past decade have enabled the synthesis of a wide range of macromolecules with well defined architectures, compositions, and functionalities.[46] Among these techniques, the RAFT (reversible addition fragmentation chain transfer) and the MADIX (macromolecular design via interchange of xanthates) processes were introduced at the same time (1998), by the group of Rizzardo at the CSIRO institute[47] and by the group of Charmot at Rhodia Chimie,[48] respectively. Whereas the other main CRP techniques are based on a reversible termination mechanism, i.e., NMP (nitroxide-mediated polymerization) [49–51] and ATRP (atom transfer radical polymerization),[52-53] both RAFT and MADIX processes are based on an identical reversible transfer mechanism.

Similarly to the other CRP techniques, RAFT polymerization is a smart reply to the drawbacks of conventional free radical polymerization characterized by a low control over the molecular weight distribution (MWD) and the chain architecture. It consists of adding, in the polymerization medium, a reversible chain transfer agent (CTA) which has at least one group that contains the following sequence, –x(=S)–S– (with x = C or P). For clarity, only the general case, x = C, which corresponds to thiocarbonylthio compounds. A great number of such compounds have been synthesized by varying the structure of the Z and R groups (Figure 2.6).

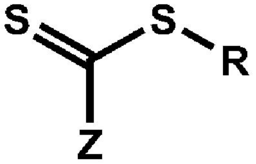


Figure 2.6 : General structure of a thiocarbonylthio compound

In the presence of (macro)radical species, the CTA induces reversible addition-fragmentation transfer reactions (Figure 2.7), to create an equilibrium between active species (propagating radicals) and so-called dormant species (thiocarbonylthio-terminated chains) that can become active again, contrary to the dead species (produced via irreversible termination or transfer reactions). This equilibrium is responsible for the control of the polymerization.

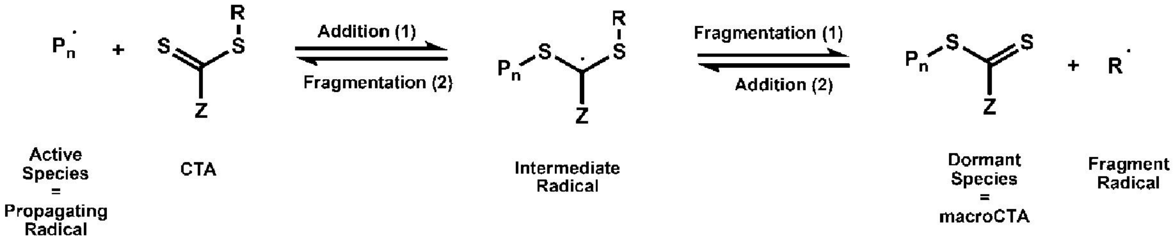


Figure 2.7 : Reversible addition-fragmentation transfer reaction in the presence of a CTA.

Until now, very few articles have given a global overview on the numerous research works dedicated to RAFT polymerization. Several authors have described various aspects of its complex mechanism and kinetics, as well as the numerous polymer architectures that can be obtained.[54–61] In addition, some authors have compiled results about homogeneous aqueous media,[62] dispersed media,[63–66] surface-initiated polymerization,[67] and kinetics modeling[68] including theoretical calculations.[69] Finally, in a very recent highlight article, Perrier and Takolpuckdee nicely reviewed the progresses made in RAFT polymerization since 1998, especially the synthesis and chemical modifications of CTAs, the monomers that have been successfully polymerized by RAFT, and the resulting polymer architectures (block, star and branched polymers).[70]

Over the past decades, addition-fragmentation reactions have been extended to the polymer field via cationic or radical processes.[71] In the case of radical polymerization, these reactions[72] have been used to improve control over molecular weight and chain-end functionality.[73, 74] The main publications concerning this research area up to 1996 are reported in the review of Colombani and Chaumont.[73]

When the chain transfer agent bears a thiocarbonylthio function, the addition-fragmentation reaction becomes reversible. This original mechanism was first established from the research work of Barton and McCombie concerning the addition of stannyl radicals onto dithiocarbonate
derivatives (xanthates).[76–79] It was initially applied to the alcohol deoxygenation reaction,[80] and then extensively developed in organic chemistry (allylation, cyclization[81]), especially by Zard et al.[82–84]

In the polymerization field, the addition of a radical on the very radicophilic thiocarbonyl group of the CTA (much more reactive than a carbonyl group),[74] leads to an IR possessing two weak C–S bonds. This IR undergoes a fragmentation reaction either via pathway 2 to give back the same radical and the same CTA (reversibility), or via pathway 1 to form a newCTAand a new radical (Figure 2.7).

Although it may be amended in some particular cases, the commonly accepted mechanism of the RAFT polymerization [54] is as described in Figure 2.8. The free-radical source is identical to that used in conventional free radical polymerization (e.g., thermoinitiator, photoinitiator). The transfer reaction between the active species and the thiocarbonylthio-containing CTA leads to the formation of dormant species (equilibrium I, sometimes called pre-equilibrium) and to the release of a fragment radical, R., able to initiate a new polymer chain (re-initiation). The dormant species, which also bear a thiocarbonylthio function (macroCTA), induce another reversible addition-fragmentation equilibrium.

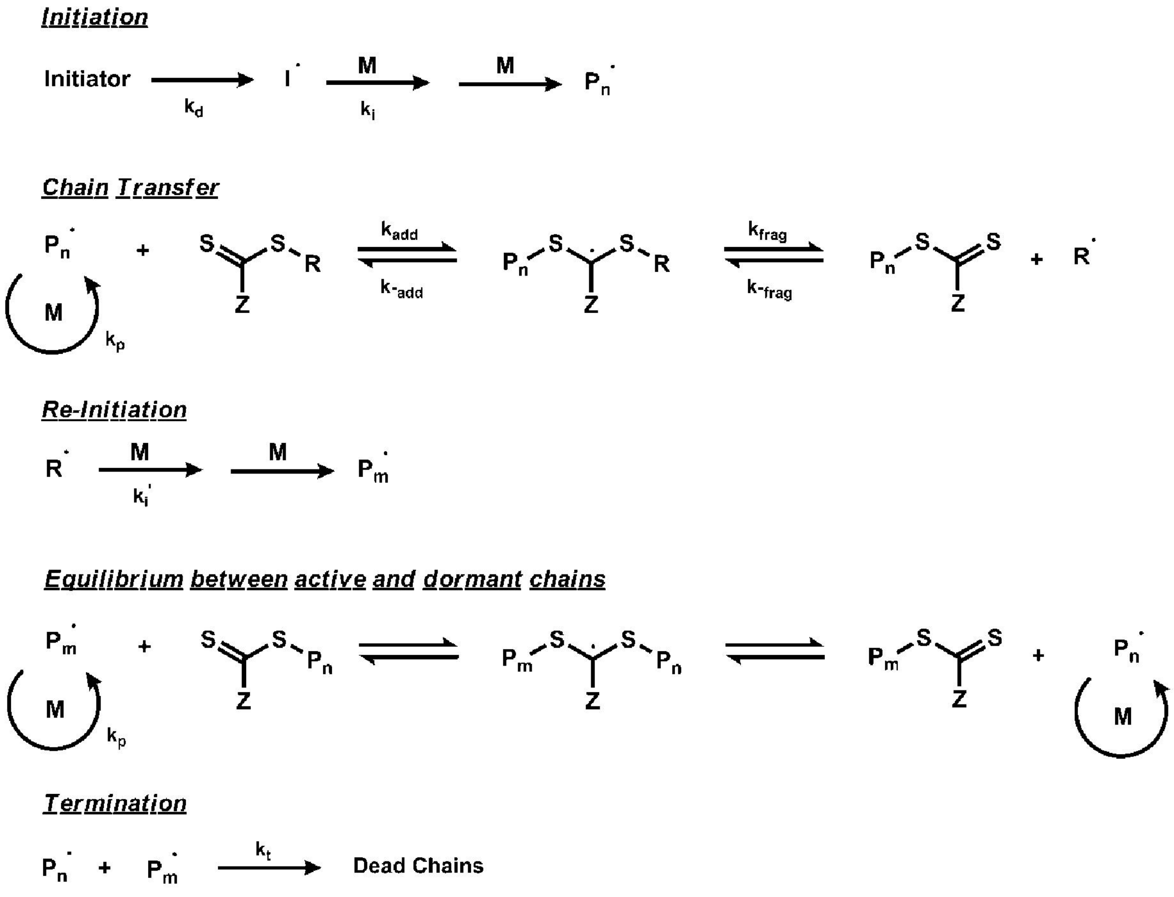


Figure 2.8 : General mechanism of the RAFT polymerization

Of course, like in a conventional free radical polymerization, the active species can also propagate and terminate. However, in a RAFT polymerization, the amount of initiator (the only free-radical source), and thus the concentration of active species, is lower and the termination reactions are minimized. In summary, the polymer chains successively pass from a dormant state to an active state during which they can add monomer units. In contrast to a conventional free radical polymerization, chains grow in parallel during the whole polymerization duration.

A good control of the molecular weight distribution is obtained if the chain growth is homogeneous. The average polymerization degree, DP_n, then increases with conversion and the polydispersity index, PDI, is low and theoretically decreases with conversion. In addition, the number-average molecular weight of the chains, M_n, can be predicted from the conversion and the initial monomer and CTA concentrations (mass of consumed monomer divided by the number of polymer chains). The number of polymer chains corresponds to the sum of the primary radicals, I, and of the fragment radicals, R, that have been efficient, i.e., that have added monomer units. As a consequence, the theoretical M_n can be defined by the following equation:

where nchains is the mole number of chains, $M_{\text{chain ends}}$ is the molecular weight of the chain ends, M_m and n_m are the molecular weight and the initial mole number of monomer, respectively, M_{CTA} and n_{CTA} are the molecular weight and the mole number of CTA that have produced efficient R., respectively, M_i and n_i are the molecular weight and the mole number of efficient primary radicals that stem from the initiator, respectively, and n_c is the mole number of dead chains that result from chain–chain coupling events.

Considering a thermoinitiator that leads to the formation of two identical primary radicals (e.g., 2,2'-azoisobutyronitrile (AIBN)) and neglecting, for simplicity, the possible termination reactions onto IRs, the theoretical M_n equation becomes:

$$\mathbf{Mn} = \frac{\{[\text{monomer}]_0 \times M_m \times \text{conversion}\} + \{f'[\text{CTA}]_0 \times M_{CTA} + 2 \times f \times [\text{initiator}]_0 \times (1-e) \times M_1\}}{f'[\text{CTA}]_0 + 2 \times f \times [\text{initiator}]_0 \times (1-e) \times \left(1-\frac{fc}{2}\right)}$$

where $[\text{monomer}]_0$ is the initial monomer concentration; $[\text{CTA}]_0$ and f_0 are the initial concentration and the initiating efficiency factor of the CTA (see below), respectively, $[\text{initiator}]_0$, k_d, and f are the initial concentration, the decomposition rate coefficient, and the efficiency factor of the initiator (which can vary with experimental conditions and conversion),[85] respectively, t is the polymerization duration, and f_c is the proportion of chain–chain coupling reactions relative to the whole termination reactions.

The CTA initiating efficiency factor, f_0, corresponds to the proportion of the initial CTA mole number that has indeed led to the formation of polymer chains. The initial amount of CTA may not be totally consumed at the considered time t, depending on the CTA transfer constant. [86] Moreover, some side reactions may involve the CTA before its consumption (e.g., hydrolysis in basic aqueous medium),[87] the IRs (e.g., termination),[88] or the fragment radicals (e.g., termination). However, to date, there is no reported study concerning the experimental determination of f, f_0, and f_c in the case of a RAFT polymerization. In this ideal case (low number of initiator-derived chains), *M*n increases linearly with conversion.

Finally, the increase of experimental *M*n with conversion, the agreement between experimental and calculated *M*n values, as well as low PDI values, are experimental criteria that indicate an efficient control of a RAFT polymerization.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Tetrahydrofuran (THF) (99.8%, J.T.Baker)

Pre-dried over magnesium sulfate followed by sodium wire and then distilled from sodium wire and benzophenone immediately before use.

Styrene (%99, Aldrich)

Styrene was purified by usual methods and distilled in vacuum from CaH_2 just before use.

3.1.2 Solvents

Dichloromethane (99.8%, J.T.Baker)

Dichloromethane was dried with P_2O_5.

Anhydrous methanol (Technical)

Stored under nitrogen.

3.1.3 Other Chemicals and Reagents

Benzyl alcohol (≥98%, Aldrich)

Benzyl alcohol was used as received.

Triflic anhydride (≥99%, Aldrich)

Triflic anhydride was used as received.

2,6-Ditertiary-butyl-4-methyl pyridine (DTBP) (≥97%, Aldrich)

It was used as received.

Bromobenzene (99.5%, Carlo-Erba)

Bromobenzene was used as received.

Carbon disulfide (≥99.9%, Aldrich)

Carbon disulfide was used as received.

Benzylbromide (≥98%, Fluka)

Benzyl bromide was used as received.

2,2'-azoisobutyronitrile (AIBN) (98%, Aldrich)

AIBN was used as received.

Sodium methoxide (≥97%, Fluka)

Sodium methoxide was used as received.

Copper(I) bromide (CuBr) (98%, Acros)

Copper(I) bromide was used as received.

2,2'-bipyridine (bipy, 99%, Aldrich)

Bipy was used as received.

Tetrahydrothiophene (THT) (99%, Aldrich)

THT was used as received.

Magnesium (99.8%, Fluka)

Magnesium was used as received.

3.2 Equipments

3.2.1 ^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR)

^{1}H NMR spectra of 5–10 % (w/w) solutions in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 250 and 62.5 MHz, respectively, on a Bruker DPX 250 spectrometer.

3.2.2 Infrared Spectrophotometer (IR)

IR spectra was recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer.

3.2.3. Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL

GPC columns ($G2000H_{HR}$, $G3000H_{HR}$ and $G4000H_{HR}$), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were 456–42,800, 1050–107,000, and 10,200–2,890,000, respectively. THF was used as an eluent at flow rate of 1 mL min^{-1} at 30°C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Molecular weights were calculated with the aid of polystyrene standards.

3.3 Preparation Methods

3.3.1 Synthesis of Sodium Dithiobenzoate

Magnesium turnings (1.16 g, 0.048 mol) was stirred in dry ether, and then a solution of phenylmagnesium bromide (from bromobenzene (7.475 g, 0.048 mol) was added slowly. After the first bubbles, the reaction mixture was cooled down from outside. Thereafter, the reaction mixture was heated to 40 °C for reflux. After a while, the reaction temperature was cooled down to 0°C and and carbon disulfide (3.62 g, 0.048 mol) was added over 15 min. The reaction was hold in ice-bath for a while. The reaction mixture was stirred overnight at room temperature. Resultant dark orange solid was collected. NaOH (1.9 g, 0.0476 mol) (from saturated solution of NaCl in methanol) was added to the mixture in exothermal ice-bath. Red solid was formed and it remained in ice in 30 minutes. After that, the mixture was heated to 60°C and the mixture remained in an hour. The reaction mixture was dissolved in diethyl ether and then the product was collected after filtration.

3.3.2 Synthesis of Benzyl Dithiobenzoate

Magnesium turnings (1.16 g, 0.048 mol) was stirred in dry ether, and then a solution of phenylmagnesium bromide (from bromobenzene (7.475 g, 0.048 mol) was added slowly. After the first bubbles, the reaction mixture was cooled down from outside. Thereafter, the reaction mixture was heated to 40 °C for reflux. After a while, the reaction temperature was cooled down to 0°C and and carbon disulfide (3.62 g, 0.048 mol) was added over 15 min. The reaction was hold in ice-bath for a while. The reaction mixture was stirred overnight at room temperature. Resultant dark orange solid was collected. Bromobenzene, carbon disulfide and ether was evaporated in vacuum distillation system. Benzyl bromide (4.75 g, 0.028 mol) in methanol was added to the reaction mixture at room temperature. Thereafter, it remained at 60°C for 24 hours. The precipitation was observed in reaction system. The reaction mixture was washed with methanol and the dissolved part was taken. Methanol was evaporated in the rotary system. The resultant solid was dissolved in ethyl acetate and the insoluble salt part was filtered. The mixture was extracted with water and then it was dried. After all, ethyl acetate was evaporated at rotary system and the product was collected.

3.3.3 RAFT Polymerization of Styrene with macro-RAFT Agent.

2,2'-azoisobutyronitrile (AIBN) (1.28×10^{-3} g, 7.84×10^{-6} mol), macroRAFT agent (M_n = 2800 g/mol, M_w/M_n = 1.13) (0.1 g, 3.92×10^{-5} mol), styrene (1.427 g, 0.014 mol) and 0.526 ml benzene as a solvent were placed in a Schlenk tube. Three freeze-pump-thaw cycles were performed and the tube was stirred in oil bath at 60 °C for 6 hours. At end of the reaction, the mixture was diluted with THF and the copper complex was removed out by passing through a neutral alumina column. The diluted mixture was precipitated in hexane and the solid was collected after filtration and dried at room temperature in a vacuum overnight.

3.3.4 Preparation of macro-RAFT agent

A typical procedure is as follows. In a flame-dried two necked flask, 7 ml of CH_2Cl_2, 0.5 ml of DTBP (0.458 g, 2.236×10^{-3} mol), and 0.25 ml of triflic anhydride (0.42 g, 1.496×10^{-3} mol) were placed at 0°C. To this solution, 0.154 ml of benzyl alcohol (0.162 g, 1.496×10^{-3} mol) and 2 ml THF were added dropwise under vigorous stirring, and the mixture was stirred for 1 h at 0°C. The initiator solution was warmed to 25°C, thereupon 48 ml of THF were introduced. The polymerization was carried out at 25°C for 20 min., and 1.4 ml tetrahydrothiophene was added to the reaction mixture. Approximately an hour later, sodium dithiobenzoate was added to the solution. The reaction mixture was stirred overnight at room temperature. The polymer product was recovered by extraction with dichloromethane. The polymer was dried, and then the solvent was evaporated at rotary system. After all, the polymer was precipitated in methanol.

4. RESULTS AND DISCUSSION

In the present work, a combination of reversible addition-fragmentation transfer (RAFT) polymerization and cationic ring opening polymerization was proposed for the preparation of block polymers that can not be prepared by a single mechnism. The first step of the synthetic strategy involves cationic ring opening polymerization of THF. As depicted in Figure 4.1, a well-defined macro-RAFT agent ($M_{n\ \mathrm{GPC}}$ = 2800 g/mol, $M_{n\ \mathrm{NMR}}$ = 2550 g/mol, $M_{n\ \mathrm{theo}}$ = 2500 g/mol, M_w/M_n = 1.13) was prepared by cationic ring opening polymerization in the presence of benzyl alcohol, triflic anhydride and DTBP system.

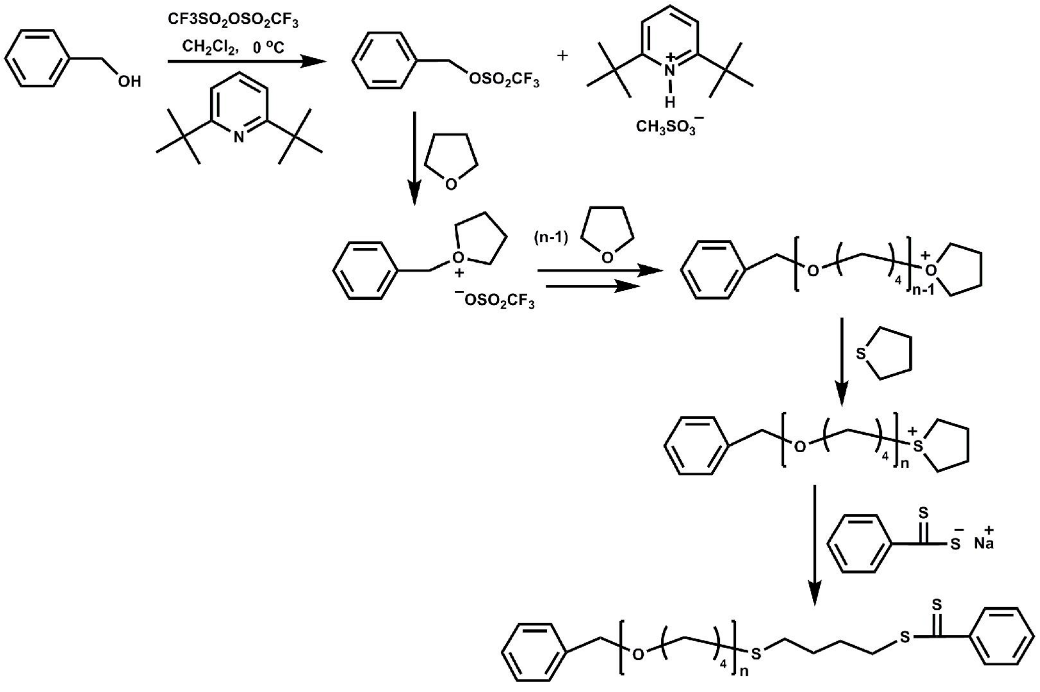


Figure 4.1 : Synthesis of macro-RAFT agent by Cationic Ring Opening Polymerization.

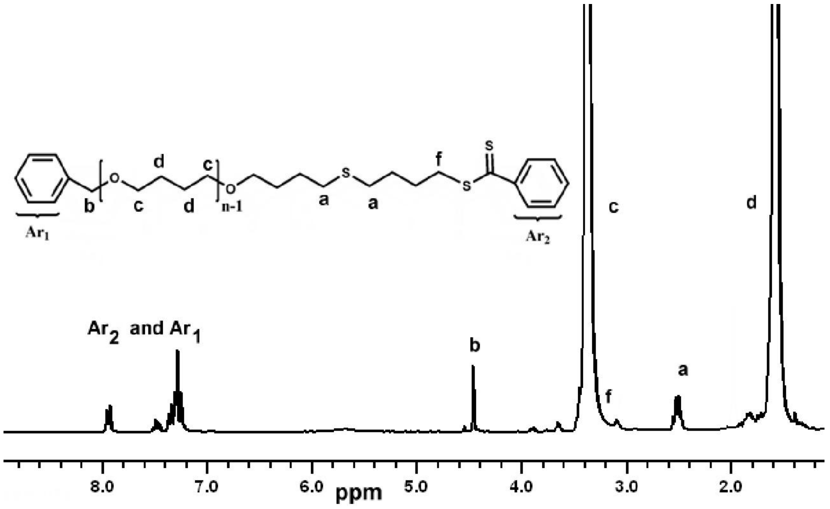


Figure 4.2 : ^{1}H NMR spectrum of macro-RAFT agent recorded in $CDCl_3$.

The ^{1}H NMR spectra of macro-RAFT agent was presented in the Figure 4.2. As can be seen, the peak representing the methylene protons adjacent to the sulfur atom appears at around 2.50 ppm. The signal at 3.10 ppm was attributed to the proton located next to dithiobenzoate group. The peaks belonging to the protons of the aryl group1 and aryl group2 appear at 7.25 ppm and 7.95 ppm, respectively.

In the second step, functional PTHF obtained this way was used as a macro-RAFT agent for the polymerization of styrene. According to the reactions presented in Figure 4.3, this process is expected to yield block copolymers of THF and St

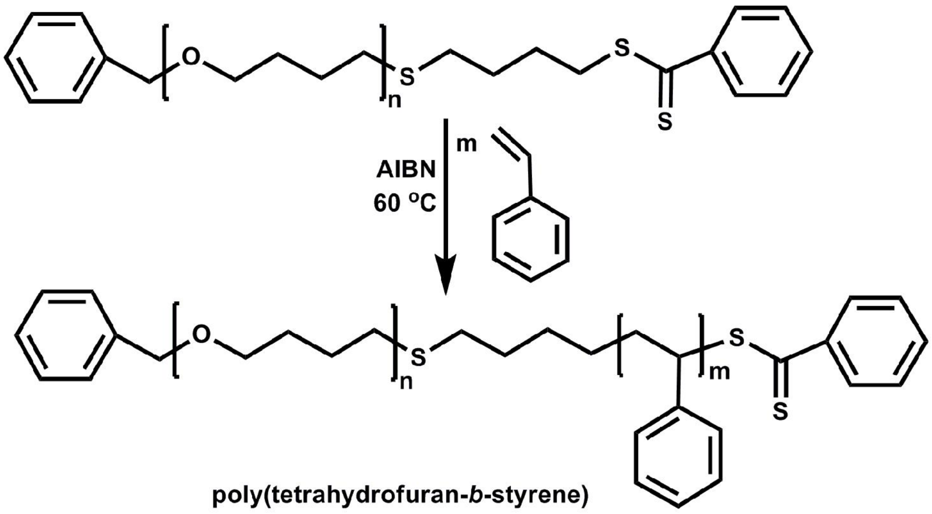


Figure 4.3 : Block copolymerization of styrene by RAFT process using functional PTHF as a macro-RAFT agent.

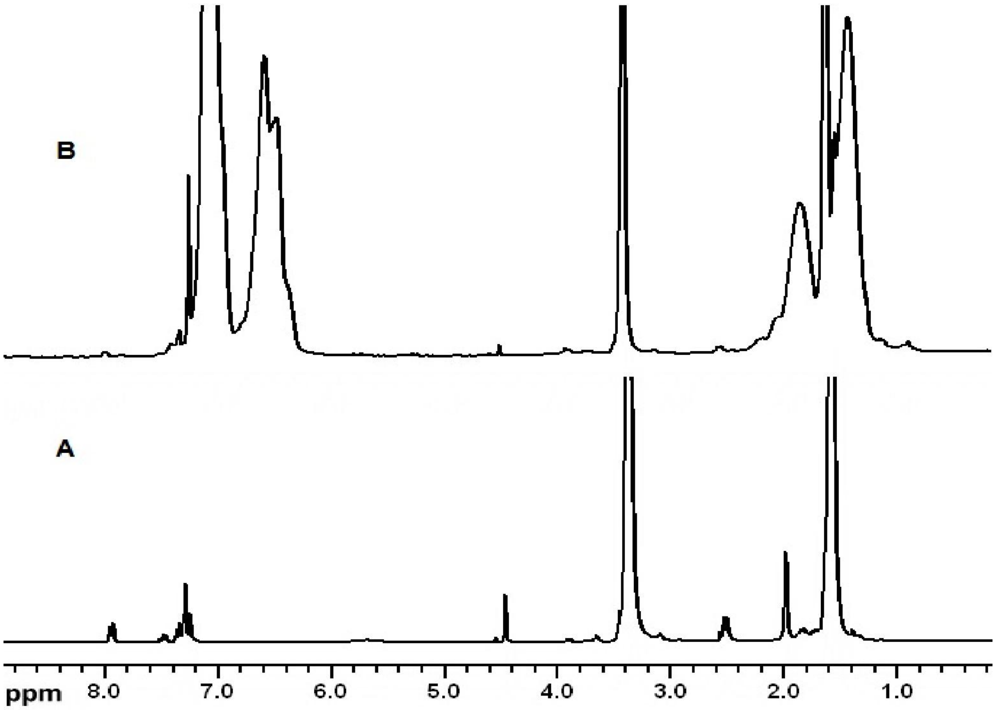


Figure 4.4 : ^{1}H NMR spectra of macro-RAFT agent and block copolymer.

The structure of the block copolymer was analyzed by ^{1}H NMR spectroscopy. A typical spectrum is shown in Figure 4.4 (B). The new peak centered at 6.5~7.2 ppm was assigned to the protons of the aromatic groups from the PSt segment is evidence for the successful block copolymerization. The remained characteristic peaks of RAFT agent around to 2.5 and 3.1 ppm are also proof of the controlled character of this polymerization.

Figure 4.5 represents GPC chromatograms of the precursor PTHF and the block copolymer obtained after RAFT polymerization. For comparision, the chromatogram of polymer obtained in the absence of a RAFT agent was also included. All the GPC curves show a unimodal distribution and the elution peaks shift to the lower elution volume after RAFT polymerization. Expectedly, the polymer in the absence of RAFT agent gave much higher molecular weights. Moreover, molecular weight obtained from GPC consistent with obtained from ^{1}H NMR and theoretical values.

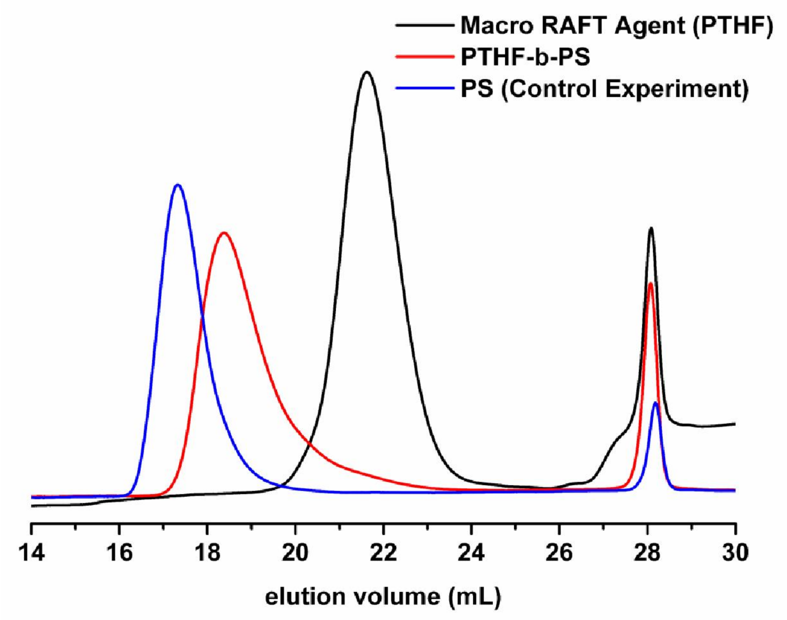


Figure 4.5 : GPC traces of macro-RAFT agent (PTHF) (M_n = 2800), its RAFT polymerization product with styrene and polystyrene control experiment.

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