İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF STAR SHAPED BLOCK COPOLYMERS VIA CATIONIC RING OPENING AND PHOTOINITIATED RADICAL POLYMERIZATIONS

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KATYONİK HALKA AÇILMASI VE FOTO BAŞLATILMIŞ RADİCAL POLİMERİZASYON TEKNİKLERİ İLE YILDIZ TİPLİ BLOK KOPOLİMERLERİN SENTEZİ VE KARAKTERİZASYONU

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LIST OF SYMBOLS

$\mathbf{M_n}$	: Number average molecular weight of polymers
$\mathbf{M_w}$	: Weight average molecular weight of polymers
MWD	: Molecular weight distribution of polymers
PTHF	: Poly(tetrahydrofuran)
PTHFMP	: Poly(tetrahydrofuran) terminated by 2-picoline N-oxide
PMMA	: Poly(methyl methacrylate)
$\mathbf{k_{di}}$, **ki**	: Rate constants of decomposition and initiation
$\mathbf{k_{tc}}$, $\mathbf{kt_d}$	: Rate constants of termination by coupling and disproportionation
$\mathbf{k_p}$	: Rate constants of propagation
ε	: Extinction Coefficient
I, M	: Initiator and monomer respectively
TMAC	: Trimesic acid trichloride
AgOtf	: Silver trifluoro methane sulfonate
PS	: Photosensitizer
PI	: Photoinitiator

SUMMARY

SYNTHESIS AND CHARACTERIZATION OF STAR SHAPED BLOCK COPOLYMERS VIA CATIONIC RING OPENING AND PHOTOINITIATED RADICAL POLYMERIZATION TECHNIQUES

In this study, star-shaped block copolymers consist of PTHF-*block*-PMMA chains were synthesized via combination of cationic ring opening and photoinduced free radical polymerization routs.

The synthesis of star polymers is a challenging task usually achieved following a "living" polymerization route. It has been known that the cationic ring opening polymerization of tetrahydrofuran is living character when the certain conditions are provided .

During the past few years it has been shown that certain pyridinium salts can act directly or indirectly as photoinitiators effective for the cationic and radical polymerization of appropriate monomers.Upon absorption of light, pyridinium salts form reactive species capable of initiating radical polymerization. However, practical applications of some readily accessible pyridinium salts are limited because they do not absorbe light at λ>320 nm. This disadvantage is overcome by using sensitizers such as anthracene.

In the present work, the star-shaped polytetrahydrofurans that were existed nucleus by phenyl ring were synthesized by cationic ring opening polymerization of THF using $C_6H_3(COCl)_3$-$AgSbF_6$\CF_3SO_3Ag as multifunctional initiator systems and terminated by 2-methyl pyridinium N-oxide. The spectral sensitivity of PTHF-MP may be extended to longer wavelengths with the aid of certain sensitizers. Upon irradiation of a solution containing anthracene and PTHF-MP macroradicals are formed via electron transfer from the electronically excited anthracene to the terminal pyridinium ions. In the presence of MMA polymerizable by a free radical mechanism, block copolymer formation would be initiated as in the case of direct irradiation.

UV, GPC, IR and ^{1}H NMR analysis of obtained polymers indicated that star-shaped block copolymers consist of poly(THF-MMA) chains were successfully synthesized.

ÖZET

KATYONİK HALKA AÇILMASI VE FOTO BAŞLATILMIŞ RADİCAL POLİMERİZASYON TEKNİKLERİ İLE YILDIZ TİPLİ BLOK KOPOLİMERLERİN SENTEZİ VE KARAKTERİZASYONU

Bu çalışmada polytetrahydrofuran ve metil metakrilat zincirleri içeren yıldız tipli blok kopolimerlerin sentezi katyonik halka açılması ve foto başlatılmış radikal polimerizasyon teknikleri ile yapıldı.

Son yıllarda yıldız tipli polimerlerin sentezi birçok bilim adamına çalışma konusu olmaktadır. Yapılan çalışmalar göstermiştir ki yaşayan polimerizasyon teknikleri uygulamada iyi sonuçlar vermiştir. Tetrahidrofuranın katyonik halka açılması polimerizasyonu uygun deney ortamı sağlandığında yaşayan karakter taşımaktadır.

Piridinyum tuzlarının uygun monomerlerin katyonik ve radikal polimerizasyonlarında dolaylı ve doğrudan foto başlatıcılar olarak kullanıldığı bilinmektedir. Pridinyum tuzları ışığı absorpladığında radikal polimerizasyonu başlatabilecek aktif merkezler içeren serbest radikaller oluşturmaktadırlar. Bazı piridinyum tuzlarının pratik uygulamalarında bazı problemler yaşanmaktadır mesela uzun dalga boylarında ışığı absorblamadıkları için transparent olmaktadırlar. Bu problemi gidermek için foto duyarlı maddeler kullanılmaktadır.

Bu çalışmada trimesik asid tri klorür, gümüş hekza floro antimon ve tri floro metan sulfat tuzlarından oluşan sistem tetrahidrofuranın katyonik halka açılma polimerizasyonunu başlattı ve sonlandırma aşamasında ışığa duyarlı 2-metil pridinyum N-oxit grupları polimer zincirlerine katıldı. Elde edilen bu polimerler antrasen varlığında polimerik alkoksi radikallere dönüştü ve metil metakrilatın radikal polimerizasyonunda fotobaşlatıcı olarak kullanıldı.

UV, GPC, ^{1}H NMR and IR cihazlarından alınan sonuçlar, PTHF-PMMA segmentleri içeren yıldız tipli polimerlerin başarılı bir şekilde sentezlendiğini göstermiştir.

1. INTRODUCTION

In recent years star-shaped polymers have received significant attention to their desirable properties that arise from a highly branched structure. A star structure is described as a nonlinear polymer composed of multiple backbone chains emanating from junction points. Branching results in a more compact structure than analogous linear structures because of high segment density, which dramatically affects crystalline, mechanical, and viscoelastic properties.

Among all branched architectures, star polymers correspond to the simplest possible assembling of macromolecullar chains in a branched structure since they involve only one central branching point per macromolecule. Star polymers with a price number of arms have been quite useful in providing acute insight into how branching affects the overall properties of polymers in solution or in melt. The synthesis of well-defined star polymers that consist of same size calls for the use of the so-called "living\controlled" polymerization techniques.

The two primary approaches to generate star-shaped polymers are known as "arm-first" and "core first". The arm first approach involves coupling performed linear polymer chains containing functionality at the chain end with a multifunctional coupling agent such as divinylbenzene (DVB). This approach results in a macromolecule with a network like hub of the coupling agent and performed linear polymers attached to the hub. The number of arms resulting from the "arm-first" approach is controlled by varying the molar ratio of the multifunctional coupling agent to the performed linear polymer chains. The "core-first" approach involves the use of multifunctional initiator which initiates the polymerization of multiple linear polymer chains. The "core-first" approach is a priori more attractive, particularly with respect to the functionalization of the star arm ends[1].

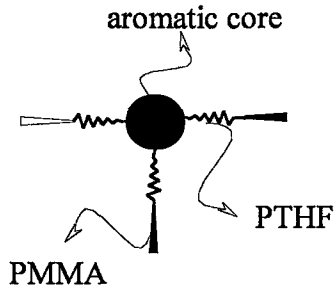
Polymeric macroinitiators synthisized according to "core-first" approach has been growing interest in the preparation of star-shaped block copolymers. For this aim, to

such as N-ethoxy 4 phenyl pyridinium, 2 methyl pyridinium N-oxide, N-ethoxy isoquinolinium and N-ethoxy 2 methyl pyridinium is very feasible to prepare star-shaped copolymers since these photoactive nuchleophiles undergo direct and indirect photolysis. Alkoxy radicals occur after irradiation and these radicals react in the presence of radically polymerizable monomers obviously pure star-shaped copolymers.

Cationic ring opening polymerization is the versatile method to introduce N-alkoxy pyridinium terminal units in polymeric backbone. Sufficiently, strained heterocycles such as ethers, acetals, ortho esters, imino ethers, sulfides, amines, siloxanes and phosphazenes are susceptible to ring opening polymerization under cationic conditions. For this purpose, THF undergoes cationic ring opening polymerization in the presence of suitable macroinitiator system to obtain star polymers.

Indirect photolysis of these polymers in the present of MMA gives guantitative yields of PTHF-PMMA. In our recent study, polyTHFs having terminal pyridinium ions were prepared via cationic ring opening polymerization in the presence of $C_6H_3(COCl)_3$-$AgSbF_6$\CF_3SO_3Ag as tri functional initiator system and terminated by N-alkoxy pyridinium ion. Photoactive polymeric radicals were generated indirectly via the reaction of with electronically excited states of certain sensitizers such as anthracene. This was spectral sensitivity of the initiating systems are shifted longer wavelengths which has importance in UV curing applications. Photoactive PTHFs acted as trifunctional initiator and initiated the radical polymerization of MMA in the present of anthracene.

This system gave quantitative yields of PTHF-PMMA star-shaped block copolymers and expected structure of block copolymer is showed in Scheme 1.1 :



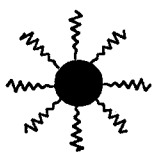
(1.1)

2. THEORETICAL PART

2.1. General definition of polymers

Polymer is a large molecule built up by the linking together of large number of simple chemical units. Monomers are small molecules that combine with each other to form polymer molecule.

Homopolymers are derived from one species of monomer. Polymers that contain more than one type of monomeric repeat unit are called copolymers. By copolymerization two or more monomers in varying ratios and arrengements, polymeric products with an almost limitless variety of properties can be obtained. As shown in Scheme 2.1, there are four basic types of copolymers as defined by the distribution of comonomers A and B, for example. Altough the properties of a random copolymer are intermediate between those of the two homopolymers, block and graft copolymers exhibit the properties of both homopolymers. The properties of an alternating copolymer are usually unique[2]. Copolymers from two, three, four, species of monomers are called bipolymers, terpolymers and quarter polymers.

RANDOM	poly(A-ran-B)	AABAABBBABBAAABABAABBAA
BLOCK	poly(A-block-B)	AAAAAAAAAAAABBBBBBBBBB
ALTERNATING	poly(A-alt-B)	ABABABABABABABABABABAB
GRAFT	poly(A-graft-B)	AAAAAAAAAAAAAAAAAAAAAA B B B B B B B B B B B B B B B B B B B B B B B B B
STAR	poly(A-star-B)	

(2.1)

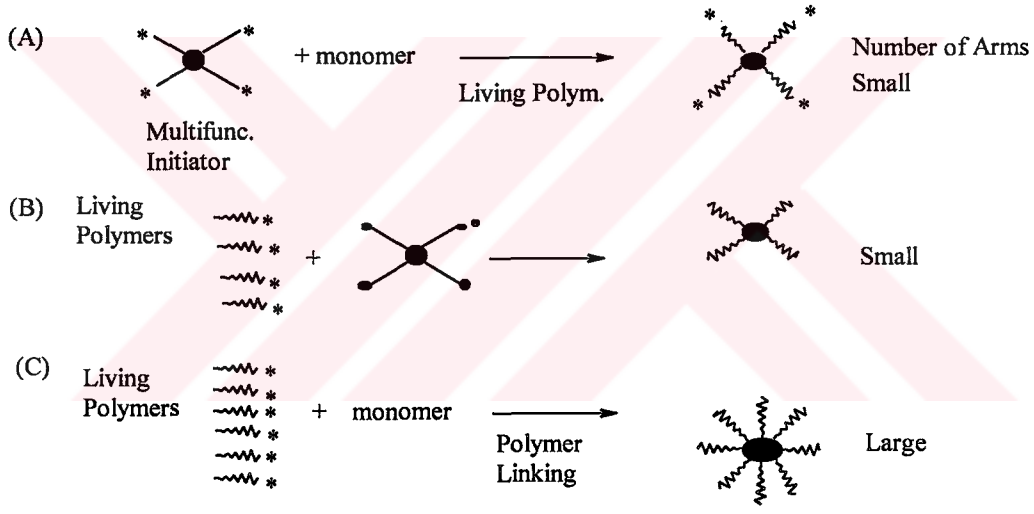
2.2. General methodology of star-shaped polymers

Star polymers three or more branches (arms) sprout from a common core. A star polymer is an example of zeroth generation of dendrimers. The synthesis of star-shaped or multiarmed polymers may be achived at least by three methods via living cationic polymerization, as illustrated in Scheme 2.2:

A. Multifunctional Initiator Method: Living polymerization from a multifunctional initiating system

B. Multifunctional Terminator Method: Coupling of living polymers with a multifunctional terminator

C. Polymer Linking Method: Linking of living polymers with a bifunctional vinyl monomer



(2.2)

2.2.1. Multifunctional initiator method

For example, living polymerization may be initiated with a multifunctional initiating system to grow multiple polymer chains from a central initiator core to give multiarmed or star polymers (Scheme 2.2(A)). The key this approach is of course the development of multifunctional initiators. These multiple initiating systems may involve living ends similar to their monofunctional counterparts, but an additional considiration and design would be needed to ensure the nearly simultaneous initiation from the more than two initiating sites located in a relatively small, single molecule. Obviously, in these multifunctional initiators, steric crowding and

intramolecular side reactions among initiating sites should be minimized by molecular design [3,4].

2.2.2. Multifunctional terminator method

Alternatively, monofunctional, linear living polymers may be coupled with a multifunctional terminating agent into star polymers (Scheme 2.2(B)). This method highly depends on the development of multifunctional terminators, which should not only fulfill the criteria for monofunctional terminators but also work under the equimolar conditions with the living ends ([quenching site] = [living end]); otherwise, for example, an incomplete reaction of a tetrafunctional terminator might give a triarmed polymer.

In the multifunctional initiation and the multifunctional termination, living polymers grow outward from the initiator core and inward into the terminator core, respectively, but both processes lead to similar polymers. If they operate properly, these methods give multiarmed polymers that carry arms in a precisely controlled or predetermined number per molecule (= the functionality number of the initiator or terminator). On the other hand, it is probably difficult to implant a large number (>10) of initiating or terminating sites into a relatively small molecule.

2.2.3. Polymer linking method

This method is called "polymer linking" or "microgel" method [5-6], adopts a different approach from these two (Scheme 2.2(C)). Namely, when monofunctional, linear living polymers are treated with a small amount of a bifunctional vinyl monomer (usually less than 10 equivalents to the living end), the linear chains are connected together onto a microgel formed from the bifunctional monomer. Because of the low content of the bifunctional monomer, the gellation or cross-linking does not spread over the entire polymerization system under proper reaction conditions, and thereby the resulting polymers are completely soluble in reaction media and thoroughly characterizable.

The microgel method is advantageous over the multifunctional initiation and termination methods in that the product polymers may have a large number of arm chains, often exceeding 50 or sometimes 100. Because microgellation process is statistical, however, there is by definition a distribution in the arm number in a

particular polymer sample. In these regards, the polymer linking method is complementary with the multifunctional initiation and the multifunctional termination.

Common for these three approaches is that living cationic polymerization permits the introduction of a variety of interesting functional groups at specific positions (outer arm layer, arm ends, central core, etc.) of the multiarmed polymer architectures. The combinations of these functional groups and the uniqe molecular topology would lead to physical properties and functions that cannot be found in the conventional linear counterparts.

2.3. General Classification of Polymerization Reactions

In 1929, Carothers suggested a classification of polymers into two groups as addition and condensation polymerization according to the mechanism of polymerization.

2.3.1. Addition polymerization

Addition polymerization of unsaturated monomers lead to the formation of high molecular weight products by chain growth mechanism.

During chain-growth polymerization, high molecular weight polymer is formed early during polymerization and the polymerization yield or the percent of monomer converted to the polymer, gradually increases with time.

In the chain-growth reactions, the initiation is required to begin chain growth by means of a free radical initiator. This free radical R. quickly adds to a monomer to obtain a monomeric radical. This new active monomer adds to another monomer and so on. This growth continues until some termination reaction occurs to make the chain inactive(Scheme 2.3).

I*+ M ⟶ **IM*** (2.3i)

IM* + M ⟶ **IMM*** Initiation (2.3ii)

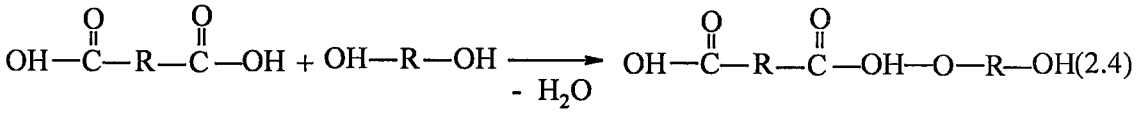
I-(M)* + M ⟶ **I-(M)-M*** Propagation (2.3iii)

I-(M)n + M* ⟶ **Inactive Polymer** Termination (2.3iv)

Chain growth polymerizations are always initiated and initiator fragments are the end groups of the chain, while step growth polymerization is catalysed and catalyst molecules do not become part of the molecules.

2.3.2. Condensation Polymerization

Condensation polymers are obtained by the random reaction of two molecules. Typically, condensation polymerization occurs by the liberation of a small molecule. Typical example of polymer formation begins with one diol molecule reacting with one diacid molecule forming one repeating unit of polyester.

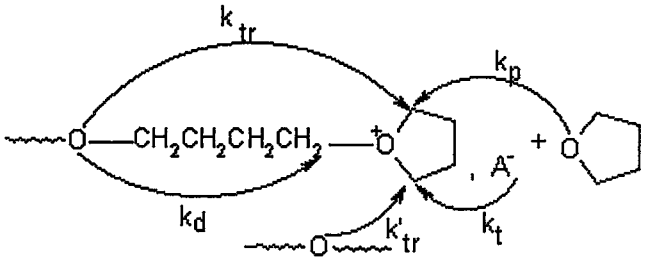


(2.4)

In condensation polymerization molecular weight of polymer increases steadily through out the reaction, so long reaction time is needed to obtain high molecular weight polymer. At any stage all molecular species are present in a calculable distribution and monomer disappears early in the reaction.

2.4. Cationic Ring Opening Polymerization (CROP) of Tetrahydrofuran (THF) Initiated by Multifunctional Initiating System

Sufficiently strained heterocycles such as ethers, acetals, orthoesters, iminoethers, sulfides, amines, siloxanes, and phosphozenes are susceptible to ring opening polymerization under cationic conditions. Typical initiators include strong protonic and Lewis acids, onium and carbenium salts, and some covalent esters and halides. Polymerizations are generally performed in nonnucleophilic solvents such as hydrocarbons and chlorinated solvents, typically at ambient temperatures, although higher temperatures are sometimes necessary. The elementary reactions of a cationic ring opening polymerization are shown in Scheme 2.5 using a tetrahydrafuran polymerization as an example.



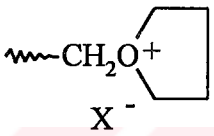
(2.5)

Propagation involves nucleophilic attack of monomer on the growing onium ion. Alternatively, a heteroatom along the polymer backbone may attack the growing

onium ion in a backbiting or an intermolecular chain transfer reaction. Depropagation occurs by intramolecular backbiting at the last unit exocyclic to the ring. Termination occurs by collapse of the ion pair or by attack of an impurity or added nucleophile.

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 where steric interference to potential electron acceptors is low .

THF polymerizes only by a cationic ring-opening mechanism. The propagating species in THF polymerizations is a tertiary oxonium ion[7] (Scheme 2.6):



(2.6)

and must, for reasons of electrical neutrality, be associated with a negatively charged species, the counter ion X^-. The early work of Meerwein and coworkers has shown that polymerization continues only if the propagation rate is faster than the rate of irreversible reaction of the oxonium ion with its accompanying anion[8]. Simple anions like Cl^- are not suitable counterions because the cation-anion complex is suitable with respect to THF and alkyl halides. Stable counterions are complex ions including anions like PF_6^-, AsF_6^-, SbF_6^-, $SbCl_6^-$, BF_4^-, $SO_3CF_3^-$, SO_3F^-, ClO_4^-.

Initiation

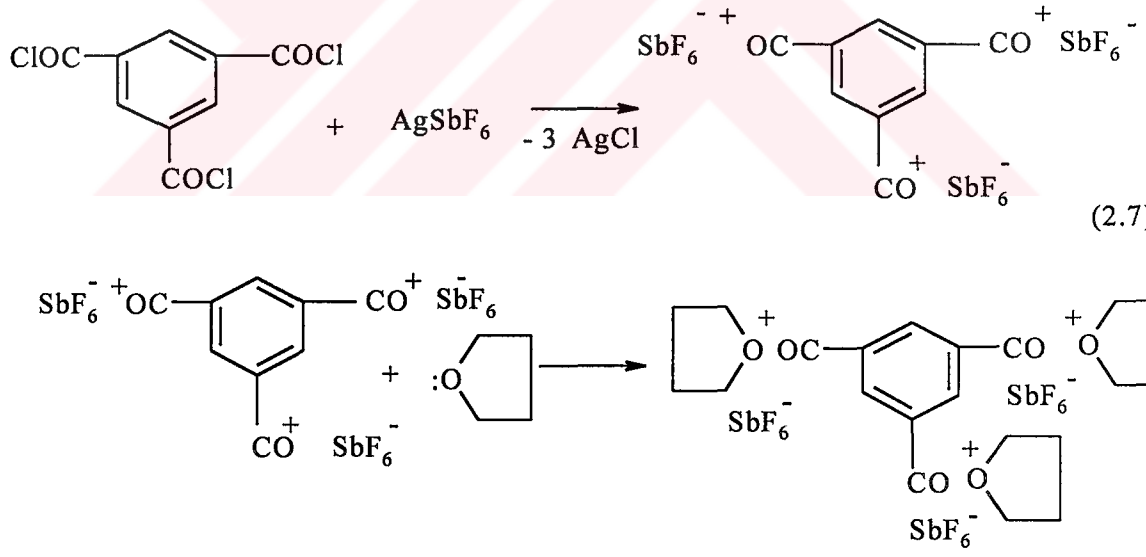
The species which initiates THF polymerization is comprised of a cation and an anion. The polymerization is initiated by a nucleophilic attack of the free electrons of the THF oxygen on the carbon adjacent to the oxygen .

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 comprise 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.

Trimesic acid tri chloride in the presence of silver trifluoromethane sulfonate (CF_3SO_3Ag) and silver hekza fluoro antimonate ($AgSbF_6$) is excellent multifunctional initiator for the cationic ring opening 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.

Tri mesic acid tri chloride as a trifunctional initiator leads to PTHF capable of growing on 3 ends. The mechanism by which the required oxonium ion is formed, is direct alkylation of the oxygen of THF, which is shown in Scheme 2.7 for initiation by silver hekza fluoro antimonate.

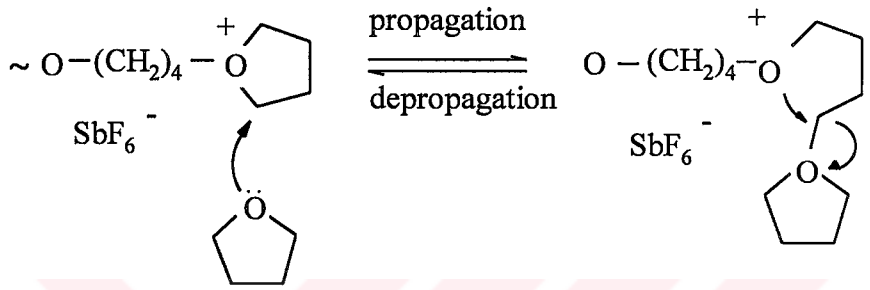


Propagation

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[9-10].

Trifunctional aromatic acid chloride with silver salts as initiators, in addition to the propagation-depropagation reactions involving oxonium ions (2.8), 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.



(2.8)

Termination

The polymerization can be terminated by a variety of nucleophilic reagents such as excess water, tertiary amines, phenolates or lithium bromide. Under the above mentioned conditions, almost any desired end groups can be introduced. We terminated with 2 methyl pyridinium N-oxide and excess methanol.

2.5. Free Radical Polymerization

Free radical polymerizations are initiated by radicals and propagated by macroradicals. These radicals exhibit an unpaired electron. Traditionally, the free radical systems are characterized by 3 main steps: [11]

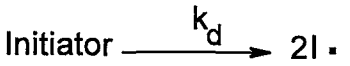
- Initiation
- Propagation
- Termination

Initiation

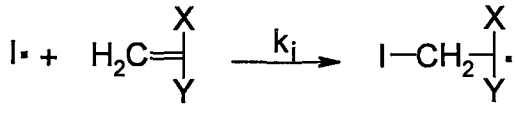
Initiating radicals are rarely formed by monomers themselves but rather thermally, electrochemically from deliberately added initiators.

The initiation consists of two steps in a free radical polymerization:

A dissociation of the initiator to form two radical species.



(2.9)



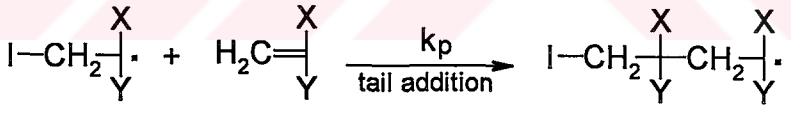
(2.10)

Addition of a single monomer molecule to the initiating radical (association step).

k_d and k_i are the rate constants of decomposition and initiation step.

Propagation

Propagation contains the growth of the monomer. By the successive of large numbers of monomers, it can be figured as shown below where k_p is the rate constant of propagation.



(2.11)

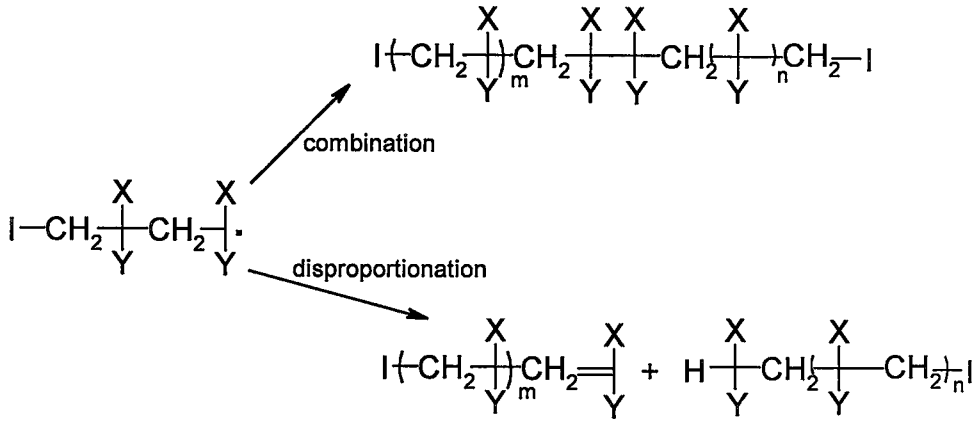
Propagation takes place very rapidly. The value of kp for most monomers are in the range of 10^2-10^4 liter/mole.sec. [11-12]

Termination

The propagating polymer chain stops growing and terminates. Two radicals react with each other by combination, or more rarely, by disproportionation in which hydrogen abstraction from one end to give two dead polymer chains, one is being an unsaturated and the other is saturated.

k_{tc} and k_{td} are the rate constants of termination by coupling and disproportionation, respectively.

Typical termination rate constants are in the range of 10^6-10^8 liter/mole.sec.



(2.12)

2.6. Photopolymerization

Photopolymerization, the utilization of electromagnetic radiation (or light) as the energy source for polymerization of functional monomers, oligomers and polymers is the basis of important commercial processes with broad applicability, including photoimaging and UV curing of coatings and inks. These processes require that light is absorbed by the system and utilized to effect the formation of new chemical bonds. Photopolymerization may be achieved by the utilization of photoinitiators, photocross-linking agents and photocrosslinkable polymers.

2.6.1. Photoinitiators for free radical polymerization

Photoinitiators (PIs) or photoinitiator systems are molecules or combinations of molecules initiating polymerization reactions when exposed to irradiation. The field of photoinitiated polymerizations is of substantial scientific and industrial interest because of applications such as photoresists, flexographic printing plates, photopolymerizable inks, coatings and adhesives.

Unlike most thermally promoted initiators, the radiation sensitive initiators can react at room temperature without additional heating and the cure is completed in a very short time. The monomer, which serves partially as thinner during application, is converted to solid resin, thus avoiding, air pollution by evaporated solvent. These features combine to save time, heating requirements, solvent recover, incineration

systems, and equipment cleaning. Countering these advantages is the greater cost of materials and equipment needed for radiation curing.

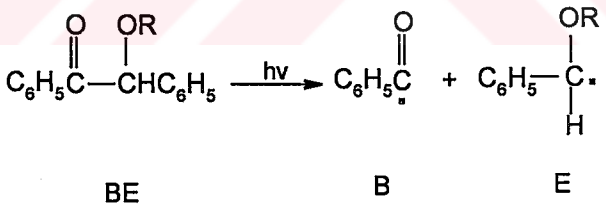
Photoinitiators for radical polymerization[12-13] generally function by intramolecular bond cleavage, notably α-cleavage of an aromatic ketone group in the photoinitiator or intermolecular H abstraction form an H donor by the photoinitiator, notably benzophenone, benzil, and quinone derivatives.

It has been suggested that photoinitiators undergoing intramolecular bond cleavage be classified as type PI1, since initiator radicals are produced by a unimolecular process. Photoinitiators that undergo intermolecular H abstraction may correspondingly be classified as type PI2, since a bimolecular reaction is involved.

2.6.1.1. Intramolecular bond cleavage

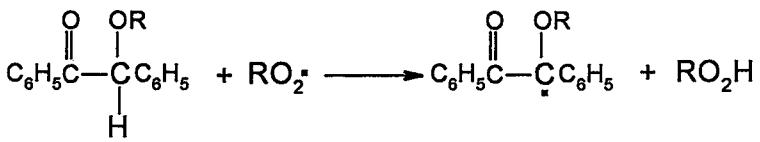
An important criterion for photoinitiators in this class (PI1) is the presence of a bond with a dissociation energy lower than the excitation energy of the reactive excited state, on the one hand, and sufficiently high, on the other hand, to provide thermal stability.

Benzoin ethers represent the first class of photoinitiators utilized in UV curing, predominately in the area of particle-board finishing. Benzoin ethers (BE) undergo photocleavage to produce benzoyl (B) and ether (E) radicals.

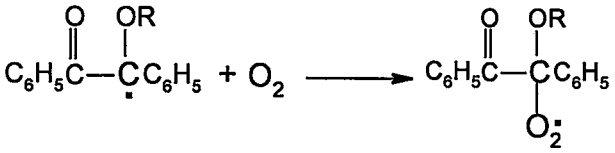


(2.13)

Benzoin ether photoinitiators exhibit poor storage-stability (or shelf life) in the presence of reactive functionality, because the benzylic H atom is readily abstracted by free radical species such as peroxy radicals (RO_2.) shown below [14].

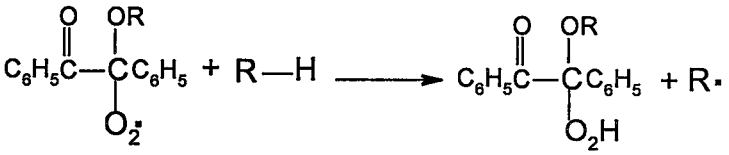


(2.14)

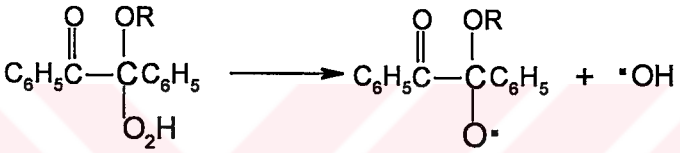


(2.15)

(2.16)



(2.17)



(2.18)

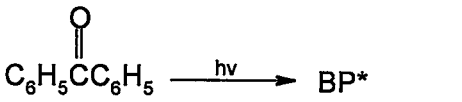
The peroxy radicals, which are poor initiators for polymerization, are converted into initiating B radicals in the absence of light by a chain reaction. Highly reactive hydroxy (HO.) radicals are also formed.

2.6.1.2. Intermolecular abstraction:

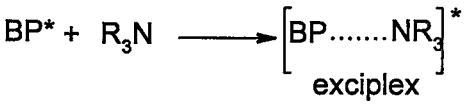
Photoinitiators of this type include benzophenone, Michler's ketone, thioxanthones, benzil and quinones. In contrast to type 1-PI1 photoinitiators, which are capable of generating initiator radicals independently, type 2-PI2 photoinitiators must undergo a bimolecular reaction with H donors. For efficient radical production, this bimolecular H abstraction reaction must compete with nonproductive processes, including quenching of the excited state by oxygen as well as by monomers. Thus a high reactivity of an excited state photoinitiator with the H donor is particularly important when UV curing is conducted in air. Furthermore, the reactivity of the radical derived from the H donor is also critical.

Tertiary amines with abstractable α-H atoms are effective H donors for UV curing of acrylate monomers (and oligomers) in air. This may be attributed to rapid formation of an excited state complex (exciplex) between the excited state photoinitiator and

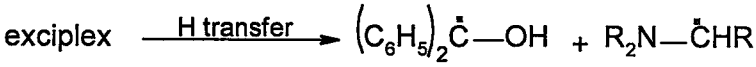
tertiary amines, and initiation of acrylate polymerization by the resulting α-amino radical, as shown below for benzophenone (BP).



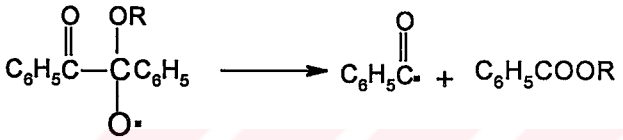
(2.19)



(2.20)



(2.21)

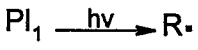


(2.22)

(2.23)

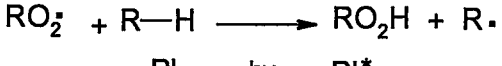
2.6.1.3. Type 1-PI1 and Type 2-PI2 combinations

Mixtures of type 1-PI1 and type 2-PI2 are used to reduced air inhibition in the absence of amines[15]. A possible explanation for the synergistic effect is outlined below.

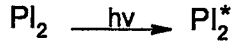


(2.24)

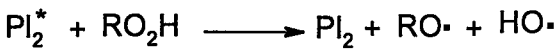
(2.25)



(2.26)



(2.27)



(2.28)

2.6.2. Photoinitiators for cationic polymerization

At ambient temperatures[16] cationic polymerization tends to be dominated by termination and chain-transfer processes. The first commercial system for photoinitiated cationic polymerization of epoxy monomers and oligomers employed aryldiazonium salts with complex metal halide anions[17]. Photolysis of these salts yields Lewis acids (Scheme 2.29), which may initiate cationic polymerization of epoxidesdirectly and react with water (or alcohols) to produce strong protonic acid initiators (Scheme 2.30)

$$Ar{-}N_2^+ + PF_6^- \longrightarrow Ar{-}F + PF_5 + N_2 \qquad (2.29)$$

$$PF_5 + OH_2 \longrightarrow H^+PF_5(OH)^- \qquad (2.30)$$

where Ar= aryl

The low nucleophilicity of the anions, such as PF_6, AsF_6, SbF_6, reduces termination processes and allows cationic polymerization to proceed. Termination of a growing polymer cation (P^+) with these complex anions results in the regeneration of a Lewis acid.

$$P^+ + PF_6^- \longrightarrow P{-}F + PF_5 \qquad (2.31)$$

Low termination rates in these systems contribute to continued polymerization following light exposure, a catalytic activity that is not observed in photoinitiated radical polymerization. The absence of air inhibition further distinguishes cationic from radical polymerization.

The spectral response of diazonium salts may be varied through out the UV-visible range by electron-donating substituents on the aryl ring[18]. However, the evolution of nitrogen limits the practical usefulness of these photoinitiators to films of less then 15μm thickness due to formation of bubbles and pinholes in thicker films.

Thermally stable photoinitiators for cationic polymerization are triaryl sulfonium. (1) and diaryliodonium (2) salts with complex metal halide anions [12,18-20].

Irradiation of these salts results in cleavage of Ar-S (or Ar-I) bonds to yield reactive radical cations.

$Ar_3S^+X^-$ $Ar_2I^+X^-$

(1) (2)

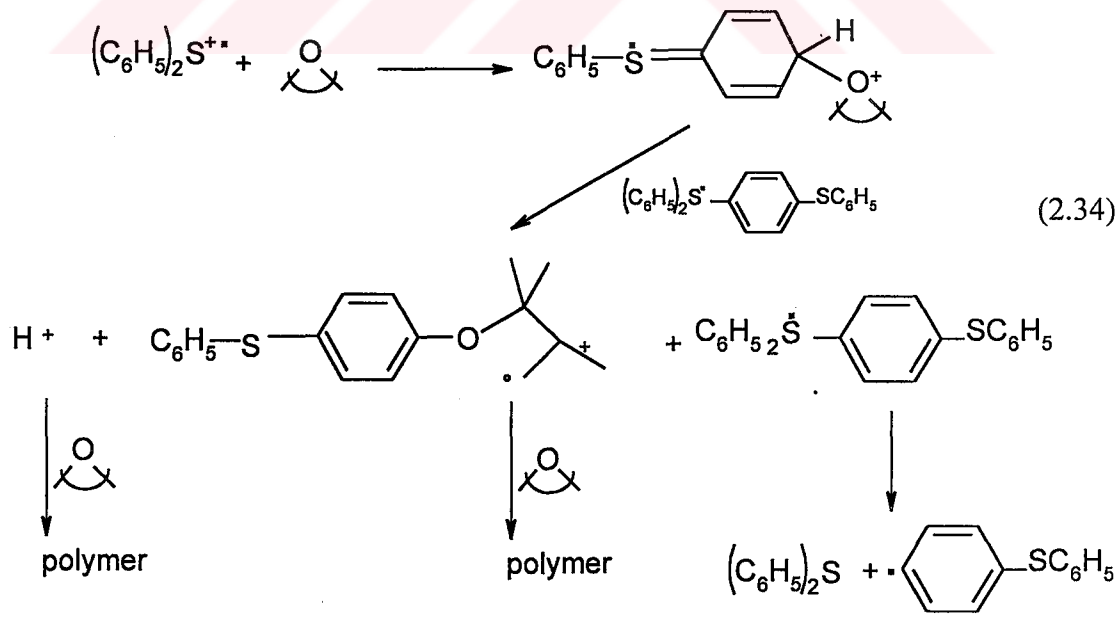
where X= SbF_6, AsF_6, PF_6

$$Ar_3S^+X^- \longrightarrow Ar_2S^+X^- + Ar \quad (2.32)$$

$$Ar_2I^+X^- \longrightarrow ArI^{+\cdot}X^- + Ar\cdot \quad (2.33)$$

Direct evidence for this photocleavage has been obtained from laser-flash photolysis studies[21,22]. The radical cations were found to be highly reactive with nucleophiles, including cyclohexene oxide. Thus the radical cations may directly initiate polymerization of epoxides, which is supported by polymer end-group analysis[23]. Protons (H^+), formed from the reaction of the radical cations with nucleophiles, function as initiators for cationic polymerization, which continues after light exposure as a result of the long lifetime of protons.

Photoinitiated polymerization of epoxides by 4-diphenylsulfoniodiphenylsulfide (3) based on laser flash and end-group analysis studies is shown below (Scheme 2.34).

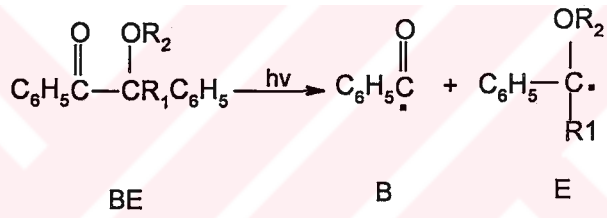


(2.34)

2.7. Pyridinium Salts

Photoinitiated polymerization has gained much attention during the last two decades due to its applications in various industrial areas[24]. In such applications both free radical[25] and cationic photoinitiated polymerizations[26] have been used and the mechnisms of initiation have been studied in detail. Aromatic carbonil compaunds are the most widely used initiators for free radical polymerizations of vinyl monomers[24]. As depicted in reaction 2.34 for benzoin derivatives[27], upon photolysis they undergo α-cleavage to produce the corresponding radicals.

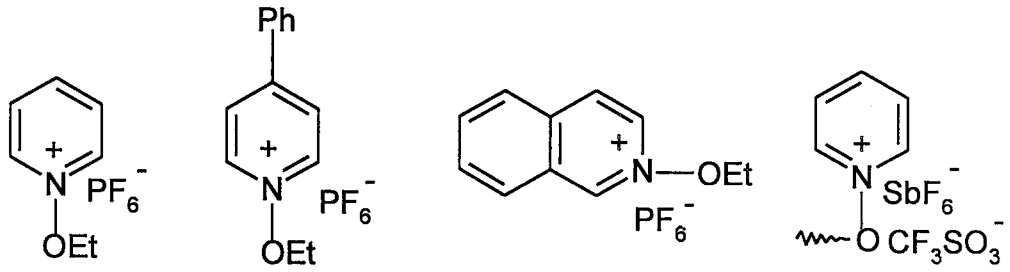
Initiators exhibiting such cleavage with high quantum efficiency show low absorption at wavelengths greater than 350 nm and their use is limited, particularly in pigmented coatings[28,29].



(2.35)

Alkoxy pyridinium salts with non-nucleophilic counter anions (X^-:PF_6,SbF_6, AsF_6,BF_4,CF_3SO_3 etc.) have been used widely used as photoinitiators for cationic and photoinitiated radical polymerization of vinyl monomers. Generally these compounds do noy absorbe light at λ>350 nm and are, therefore, of little technical importance.

N-alkoxy pyridinium and N-alkoxy quinolinium salts of the general structure are capable of acting as photoinitiators for cationic polymerization of cyclic ethers,vinyl ethers and photoinitiated radical polymerization of vinyl monomers.



(I) (II) (III) (IV)

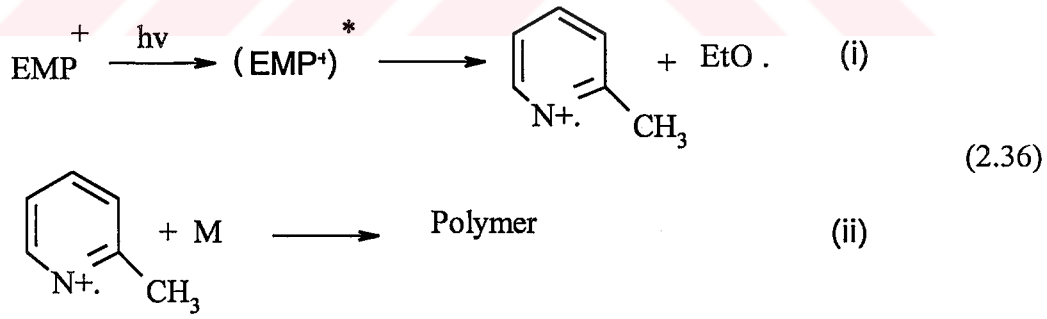
(I) : N-ethoxy-2-metyl pyridinium-hekza fluoro phosphate

(II): N-ethoxy-4-phenyl pyridinium-hekza fluoro phosphate

(III): N-ethoxy-isoquinolinium-hekza fluoro phosphate

(IV): 2-methyl-pyridinium N-oxide-hekzafluoro antimonate\tri fluoro methane sulfonate

Pyridinium salts act directly photoinitiators provided by the irradiation of the performed, at wavelengths corresponding to their absorption bands. If the pyridinium ring is appropriately substituted, the absorption band is shifted to longer wavelengths; e.g. comparing pyridiniumwith biphenyl pyridinium, the absorption spectra of the latter is red shifted. A mechanism put forwerd to explain the ability of pyridinium salts such as $EMP^{+}PF_6^{-}$ (N-ethoxy-2-methyl pyridinium-hekzafluoro phosphate) to induced the polymerization appropriate monomers is shown below (Scheme 2.36 i and 2.36 ii)



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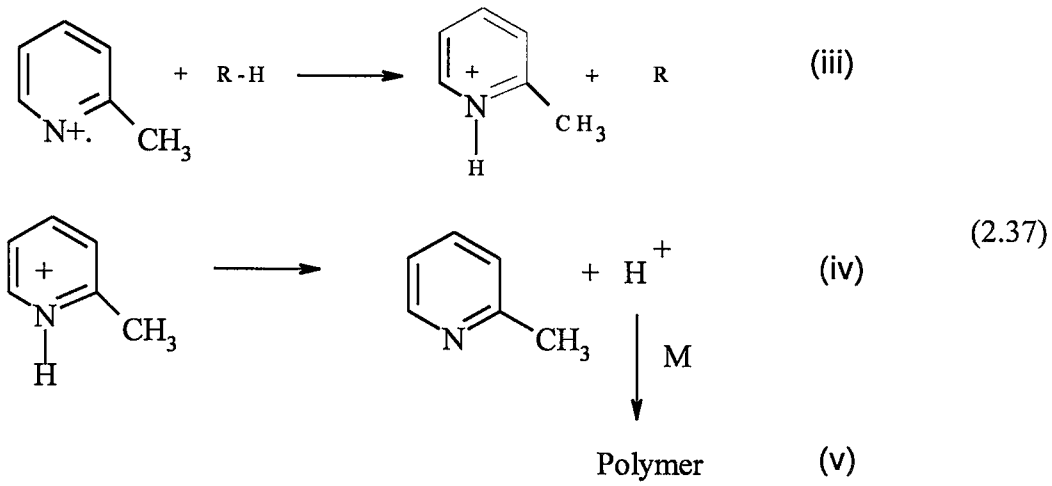
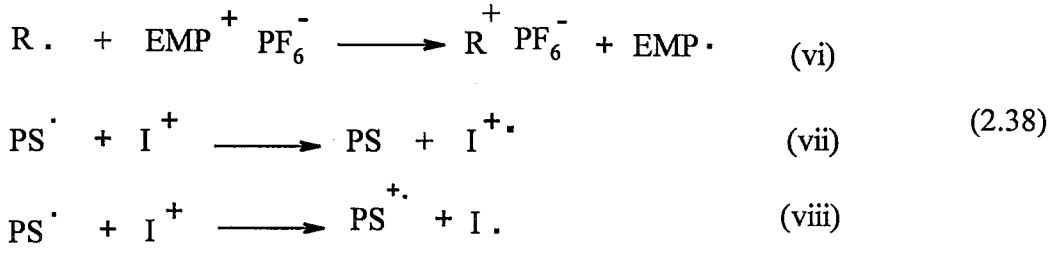


(2.37)

Notably radical cations, formed upon irradiation can be responsible for polymerization. Their mechanism was substatiated by recent flash photolysis studies. In practical aplications photoinitiatiators need to show some absorption at greater than 350 nm. It appears that pyridinium salts have no absorptivity at desired wave lengths. Several systems have been developed to extent their photosensitivity to longer wavelengths (λ>350 nm) which participate in the reaction sequences to yield reactive species capable of initiating cationic polymerization. Depending on their role in the process they may be free radical sources of sensitizers.

Pyridinium salts may also be used asd agents for the oxidation of free radicals. Carbocations formed with the aid of pyridinium salts, e.g. EMP^+, are capable of initiating the polymerization of butyl vinyl ether and cyclohexene oxide.

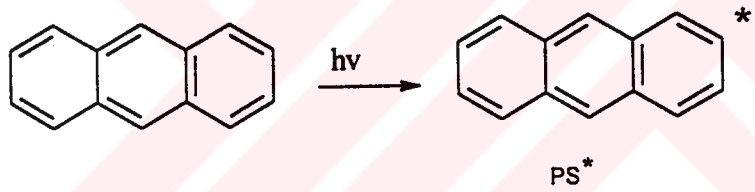


(2.38)

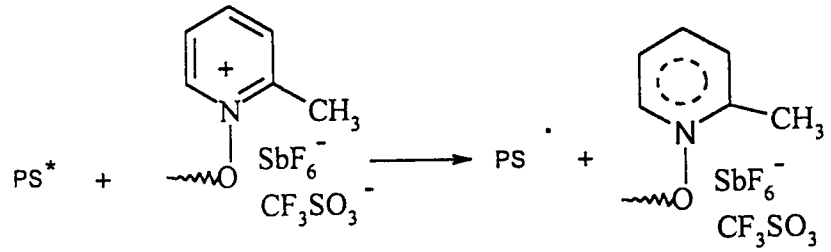
Photosensitization with the aid of appropriate compounds absorbing light at longer wavelengths λ>350 nm can help to extent the applicability of pyridinium salts as photoinitiators. For this purpose, the reactions of EMP^+ with excited states of thioxanthone, anthracene, perylene and phenothiazine were studied by many

scientists. In the ground state these compounds strongly absorb light between 350-400 nm. The sensitization action of the compounds used can be based on either energy transfer from excited sensitizer (PS*) to the pyridinium ion followed by decomposition of the excited pyridinium ion $(I^+)^{\cdot}$ or electron tansfer resulting in the formation of the radical cation of the sensitizer according to reaction (Scheme 2.38 viii).

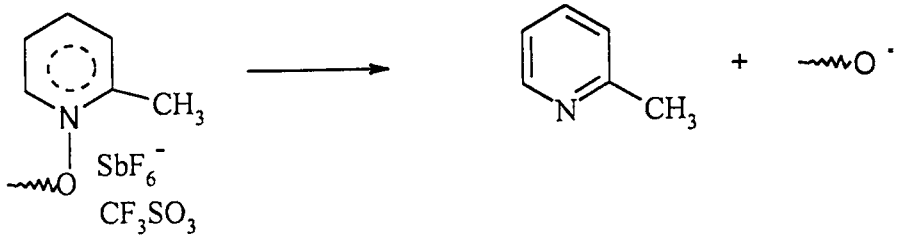
Apart from cationic polymerization, pyridinium salts may also be used as photoinitiators for free radical polymerization of vinyl compounds. In this work, the photosensitized free radical polymerization of methyl methacrylate using polytetrahydrofuran possesing terminal pyridinium ions in the presence of anthracene is studied. Anthracene strongly absorb light at λ>350nm. Dichloromethane solutions containing MMA, photosensitizer and initiator (PTHF $MP^+SbF_6^-\backslash CF_3SO_3^-$) were irradiated in pyrex tubes in a merry-go-round type photoreactor. A possible mechanism for the initiation of free radical polymerization applies to electron transfer between photoexcited sensitizer and the pyridinium ends of PTHF.



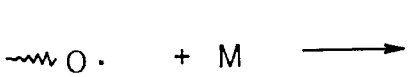
(ix)



(x) (2.39)



(xi)



(xii)

The polymerization of vinyl monomers was initiated effectively upon irradiation of solutions of monomers in dichloromethane containing MP^+ and anthracene. At the irradiation wavelength (λ>350nm) MP^+ transparent and initiationn is caused by light absorbed by anthracene. Notably, the conversion of monomer to polymer was significantly low in the absence of the pyridinium salt. Polymeric alkoxy radical formed according to reaction xii is capable of initiating free radical polymerization. Photosensitized polymerization of MMA in the presence of (PTHF $MP^+SbF_6^-$ \$CF_3SO_3^-$) using constant concentration of anthracene at different irradiation times.

Some experimental results done by Yağcı and co-workers[30] showed that as the concentration of photosensitizer further increased, the percentage conversion drops. This behavior may be attributed to aggregation in solution and resultant self quenching. The polymerization rate was increased increasing pyridinium ion concentration. The results of the photosensitized radical polymerization of MMA by thioxanthone in the absence and presence of EMP^+ showed that the conversion of the polymerization increases in the case of presence of EMP^+.

3. EXPERIMENTAL PART

3.1 Chemicals Used

a) Monomers

Tetrahydrofuran(THF,99,8%,J.T. Baker HPLC grade) was dried for 2h over calciumhydride(CaH_2) and then it was let mixing sodium pelets until the addition of benzophenon ketyl generated a blue colour.The dry THF was distilled into the reaction flask under vacuum prior to use.

Methyl methacrylate(MMA,99%, Fluka) was passed through a column containing basic alumina(Type Brockmann1) to remove inhibitors and then was distilled over CaH_2 under reduced pressure before use.

Silver trifluoro methane sulfonate(CF_3SO_3Ag, AgOTf, 99%, Aldrich), silver hekzafluoro antimonate($AgSbF_6$, 98%, Fluka) were used as received.
Anthracene (Merck) was used as recrystallized from EtOH.
Trimesic acid trichloride($C_9H_3Cl_3O_3$,98%,Fluka) was used as received.
2-methyl pyridine N-oxide was used as received (C_6H_7NO,Aldrich).

b) Solvents

Tetrahydrofuran (THF, 99.8%, J.T. Baker) technical grade was used. Dichloromethane (CH_2Cl_2) was purchased from Aldrich and used after distillation over P_2O_5.

Unless otherwise specified, other reagents were purchased from commercial sources and used as received.

3.2. Synthesis of star-shaped poly(tetrahydrofurans) via cationic ring opening polymerization (Initiated by trimesityl chloride-$AgSbF_6$)

A two-necked reaction vessel equipped with an argon inlet and a rubber septum was connected to a vacuum line. It was dried at 130 ^{0}C under vacuum to remove moisture and subsequently cooled to room temperature. After 50 ml THF had been distilled into the reaction vessel which was filled with nitrogen and disconnected from the vacuum line and covered with a rubber septum. After that the reaction vessel was placed into a thermostatically controlled bath. 10 ml THF was injected from reaction vessel under nitrogen and then it was poured under nitrogen into the prepared flask which was containing $AgSbF_6$ ($1.5x10^{-3}$mol), trimesic acid trichloride ($0,51x10^{-3}$mol) was poured under nitrogen into the reaction vessel. The other flask which contained silver hekzafluoro antimonate solution was placed in the same thermostatically bath. After 10min. later, the addition of silver hekzafluoro antimonate solution under nitrogen into the reaction vessel initiated the polymerization of tetrahydrofuran. After a given time on aliquot sample was removed for G.P.C. characterization by a syringe and the polymerization was terminated in the solution of basic methanol solution. The remaining part of the living PTHF was terminated by the addition of a solution of 2-methyl pyridine N-oxide (0,016mol) in dichloromethane (10ml). The polymerization mixture was stirred for 15min. in bath and then 15 min. waited at room temperature. Precipitated AgCl salt was removed by using Sartorious filter. The polymerization mixture was precipitated into methanol and cooled to –30 ^{0}C. Finally the precipitated polymer (PTHF-MP^+/SbF_6^-) was filtered off and dried in vacuo.

3.3. Synthesis of star-shaped poly(tetrahydrofurans) via cationic ring opening polymerization (Initiated by trimesityl chloride-CF_3SO_3Ag)

We applied the same procedure like trimesityl chlorur- $AgSbF_6$ initiation system. The differences between them were trimesicacid trichloride ($7,2x10^{-4}$mol), AgOTf($2,2x10^{-3}$ mol), 2- methyl pyridine N-oxide (0,022mol), at given time and temperatures. Finally the precipitated polymer (PTHF-$MP^+/CF_3SO_3^-$) was filtered off and dried in vacuo.

3.4. Synthesis of star-shaped block copolymers of THF and MMA

3.4.1. Block copolymerization of MMA using PTHF-MP^+/SbF_6^-

The polymer PTHF-MP^+/SbF_6^- ($1,2*10^{-2}$ M, 0,16gr), anthracene (0,053M), methyl methacrylate(4M,1.73ml) and CH_2Cl_2(2,27ml) were sequentially put into a Pyrex tube. The tube was sealed for 15 min under nitrogen prior to irradiation. Irradiation was carried out using a merry-go-round type reactor equipped with 16 Philips 8W/06 lamps emitting light at λ>350nm.

3.4.2. Block copolymerization of MMA using PTHF-$MP^+/CF_3SO_3^-$

The polymer PTHF-MP^+/ PTHF$MP^+/CF_3SO_3^-$ ($1,2*10^{-2}$ M, 0,067gr), anthracene (0,053M), methyl methacrylate(4M,1.73ml) and CH_2Cl_2(2,27ml) were sequentially put into a Pyrex tube. The tube was sealed for 15 min under nitrogen prior to irradiation. Irradiation was carried out using a merry-go-round type reactor equipped with 16 Philips 8W/06 lamps emitting light at λ>350nm.

3.4.3. Fractionation of star-shaped block copolymers

After photolysis of the reaction mixtures, block copolymers were seperated by precipitation in methanol at room temperature. By cooling the supernatant solution to -30^0C and maintaining it at that temperature overnight a second polymer fraction precipitated. Both fractions were dried in vacuo and characterized by the aid of G.P.C,UV,FT\IR and ^{1}H NMR analysis.

3.5. Characterization of Star-shaped Homopolymers and Block Copolymers

^{1}H NMR spectra were recorded on a Bruker AC 250(250 MHZ for proton) in $CDCl_3$ solution using tetramethylsilane as the internal standart. Number-averaged molecular weights(Mn) and molecular weight distributions(Mw/Mn) were determined by Gel Permeation Chromatography(GPC). GPC analysis were performed with a set-up consisting of the Agilent pump and refractive-index detector and three Waters Styragel columns(HR4,HR3, and HR2). THF was used as an eluent at a flow rate of 0,3ml/min. and molecular weights were calculated with the aid of polystyrene standarts. Molecular weights were multiplied by a factor of 0,556 for PTHF [31].

IR spectra were recorded on JASCO FT/IR-5300 spectrophotometer using NaCl disc and THF as solvent. UV-VIS spectra were recorded on a Perkin-Elmer (model lambda 2) spectrophotometer in CH_2Cl_2 solution.

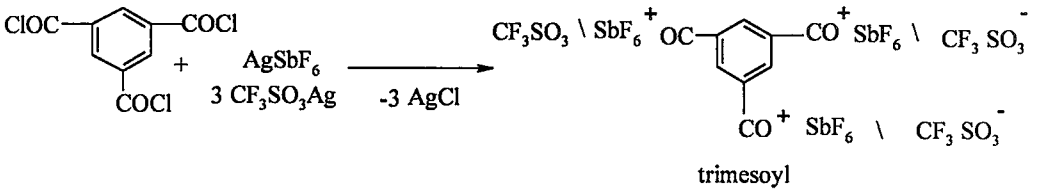
4. RESULTS AND DISCUSSIONS

4.1. Preparation and characterization of PTHF by cationic ring opening polymerization

PTHF terminated by 2-picoline N-oxide was prepared by the cationic ring opening polymerization of THF using trimesic acid trichloride and silver trifluoro methane sulfonate (CF_3SO_3Ag) or silver hekzafluoro antimonate ($AgSbF_6$) as tri functional initiator. They proceed by addition onto the monomer with formation of an ester group and react quantitatively. These initiators led to formation of trifunctional PTHFs, respectively. Polymerizations were terminated by 2-methyl pyridinium N-oxide, the preparation of which is given in Part 3.2 for hekzafluoro antimonate, Part 3.3 for trifluoromethane sulfonate. Trimesic acid trichloride and silver trifluoromethane sulfonate (CF_3SO_3Ag) or silver hekzafluoro antimonate ($AgSbF_6$) initiated polytetrahydrofurans bearing N-alkoxy pyridinium ions at 3 chain ends were formed.

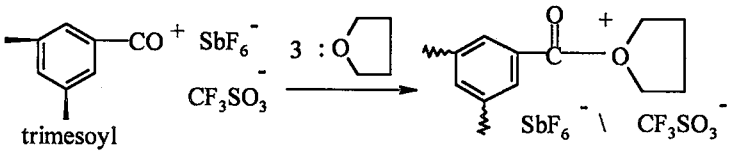
In the first step, trimesic acid trichloride reacted quantitatively with silver hekzafluoro antimonate or silver trifluoro methane sulfonate and silver chloride salt precipitated. The synthesis of trimesoyl is illustrated in Scheme 4.1.

1. Initiation



trimesoyl (4.1)

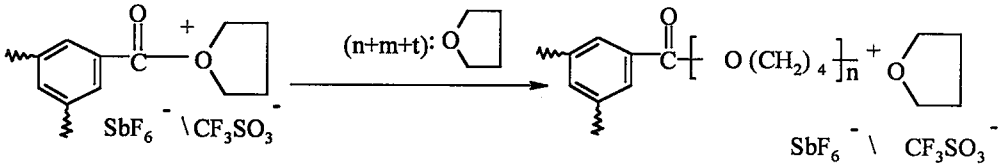
We can conclude that the trimesoyl salt behaves as a tri functional initiator. The carboxonium ion added onto a THF molecule to form ester groups at tri arms. It is represented in Scheme 4.2.



(4.2)

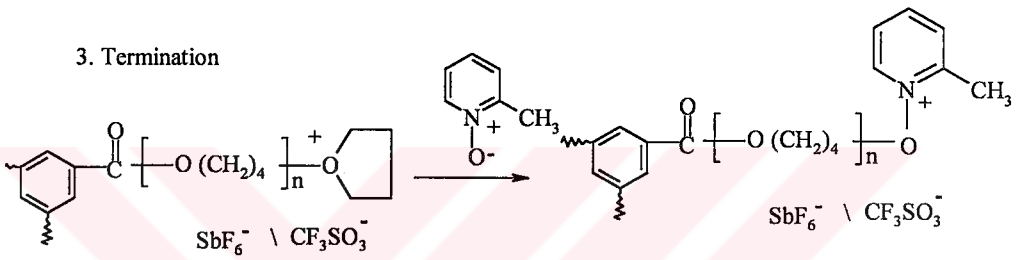
Then another THF molecule adds through a nucleophilic attack(Scheme 4.3).

2. Propagation



(4.3)

3. Termination



(4.4)

At the end of the polymerization time certain amounts of reaction mixtures were taken from the medium and terminated by precipitating in basic methanol solution after a given time. These polymers did not have 2–methyl pyridinium N-oxide at their chain ends, and were used as reference to estimate the termination efficiency . GPC trace of trifunctional poly(tetrahydrofuran), PTHFMP, bearing 2-methyl pyridine N-oxide groups at tri chain ends, is seen in Figure 4.1.

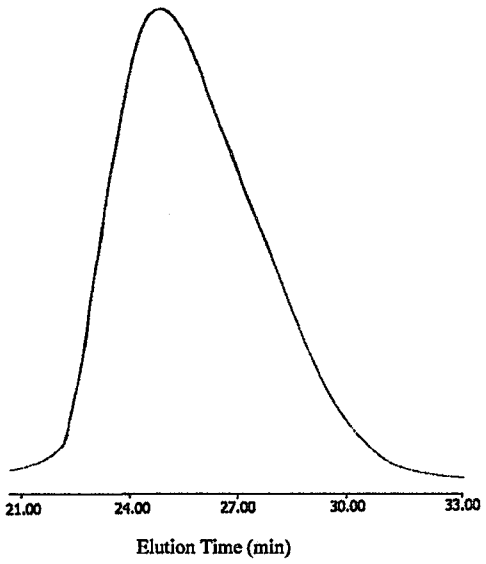


Figure 4.1 GPC trace of PTHFMP terminated by 2-methyl pyridinium N-oxide

Figure 4.2 shows a GPC trace (b) obtained from a polymer prepared by adding a 10-fold excess of 2-methyl pyridinium N-oxide to a batch of PTHF at 0 ^{0}C 25 min after the initiation. The mixture was allowed to stand for a further 15 min at that temperature before precipitation by the addition of excess methanol. Figure 4.2 also shows a GPC trace (b) of a sample obtained by PTHF termination with excess methanol. It may be noted that the maximum position of the PTHF-MP chromatogram corresponds to a longer retention time than that of the methanol-terminated polymer. A relatively long retention time have been found for a PTHF sample containing quarternary ammonium groups by Cunliffe et al[32].

The GPC behavior of PTHF samples having ionic end groups has been explained in terms of specific interactions of the terminal ionic groups with polar ligands on the crosslinked polystyrene matrix.

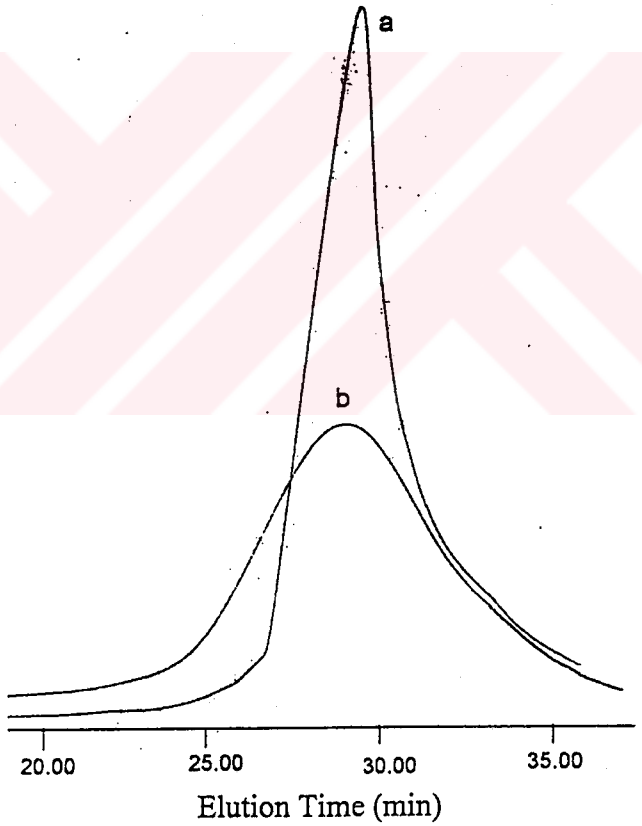


Figure 4.2 GPC traces of (a) PTHF-MP terminated by 2-methyl pyridinium N-oxide and (b) PTHF (terminated by methanol)

The structure of PTHFs terminated at tri ends by 2-methyl pyridinium N-oxide ions confirmed by ^{1}H n.m.r., UV.-VIS, FTIR and G.P.C analysis. The results are

summarized in Table 4.1. In the case of the cationic ring opening polymerization of THF, the theoretical molecular weight of the polymer is calculated by Eq. 4.1:

$$M_{(n,theoretical)} = ([Mo]\backslash[Io]) * MW_{monomer} * (\% \text{ Conversion} \backslash 100) \quad (4.1)$$

where $[I_0]$ $(mol.l^{-1})$is the initiator concentration.

As can be seen from Table 4.1 there is good agreement between the molecular weight values determined by G.P.C. and the theoretical values.

Table 4.1 Preparation and characterization of PTHFs with tri arms terminated by 2-methyl pyridinium N-oxide

Polymer	Initiator System	Time (min.)	Temp. (°C)	[Mo]\[Io]	Conv. (%)	Mn_{th} [a]	Mn [b*]	Mn [c]	Mn [d]	MWD [e*]
PTHFMP-1	TMAC\$AgSbF_6$	80	25	1200	8	7000	17000	21000	6500	1,36
PTHFMP-2		240	0	400	31	9000	9700	11000	12000	1,51
PTHFMP-3	TMAC\CF_3SO_3Ag	10	25	286	19	3900	4000	2000	3500	1,26
PTHFMP-4		25	25	286	21	4200	4500	4300	3000	1,26

[a] $M_{n,th}$ = [Mo]\[Io] * MW (monomer) * (% conv./100), [THF] = 12,3 mol\l (bulk)

[b] Obtained by GPC molecular weight of PTHF terminated by 2-methyl pyridinium N-oxide on the basis of the polystyrene standarts and calculated by

Mn [b] = 0,556 x Mn GPC

[c] Determined by UV measurements in dichloromethane at 266 nm.

[d] Determined by ^1H NMR comparing the integrals of the $-CH_3$ protons of 2-methyl pyridine N-oxide and $-OCH_2-$ protons of PTHF

[e*] Obtained by GPC based on the calibration with polystyrene standarts

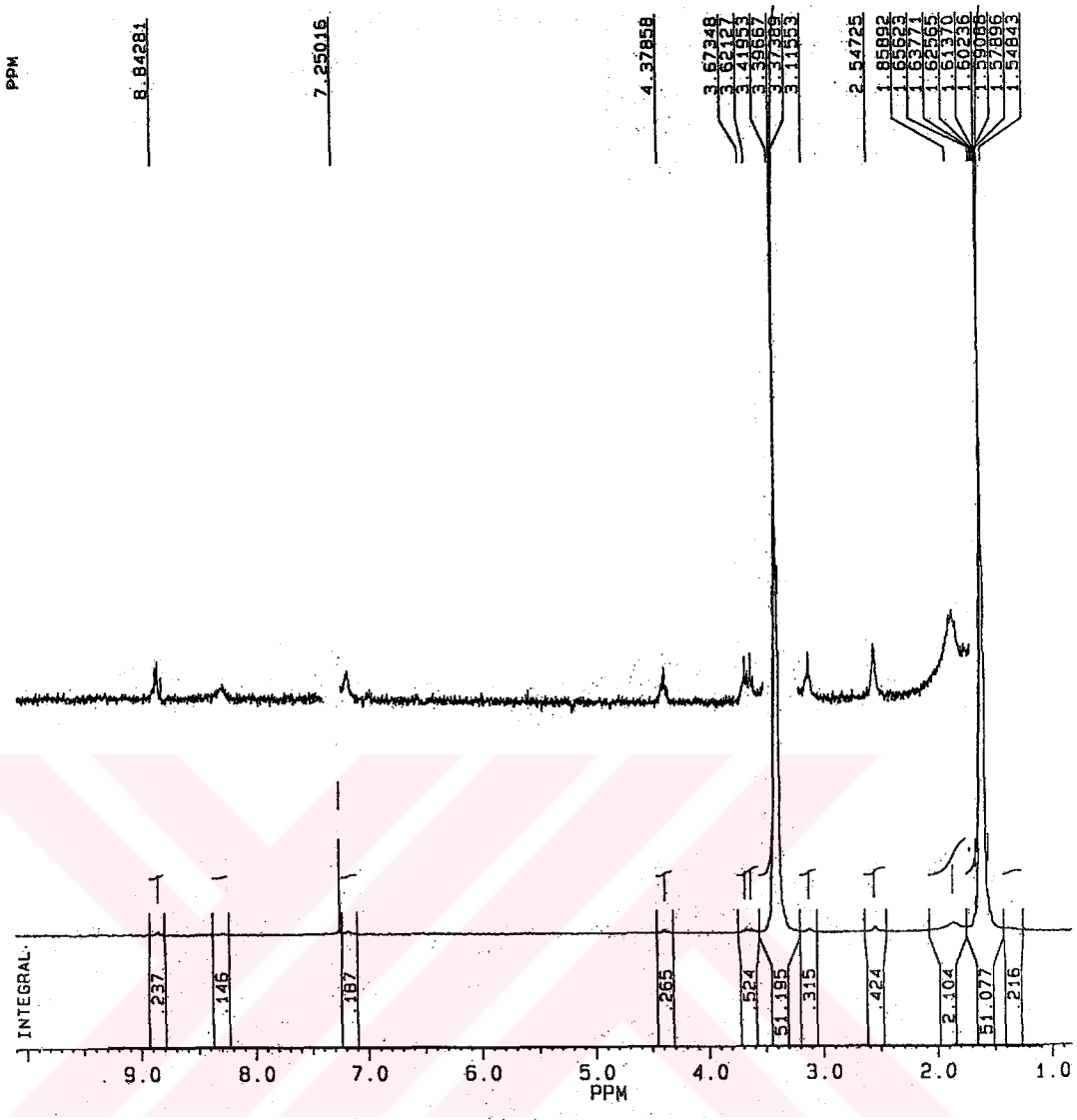


Figure 4.3 The ^{1}H-NMR spectra of PTHFMP-1

The ^{1}H-NMR spectra (Fig.4.3) showed that PTHF initiated $C_6H_3(CO)_3^+ \setminus SbF^-_6$ initiator system and terminated 2-methyl pyridinium N-oxide was formed. The ^{1}H-NMR spectrum of a typical PTHF-MP sample exhibits signals in the range of 7-9 ppm corresponding to aromatic protons of central core. Based upon a comparision of the ratio of –O-C$\underline{H_2}$ CH_2 CH_2 C$\underline{H_2}$-O of PTHFs to C$\underline{H_3}$ of 2-methyl pyridinium N-oxide, the molecular weights of the polymers were calculated (Table 1). According to the spectra; –OC$\underline{H_2}$ – groups in PTHF at 3,39 ppm; C$\underline{H_3}$ groups in 2-methyl pyridinium at 2,54 ppm.

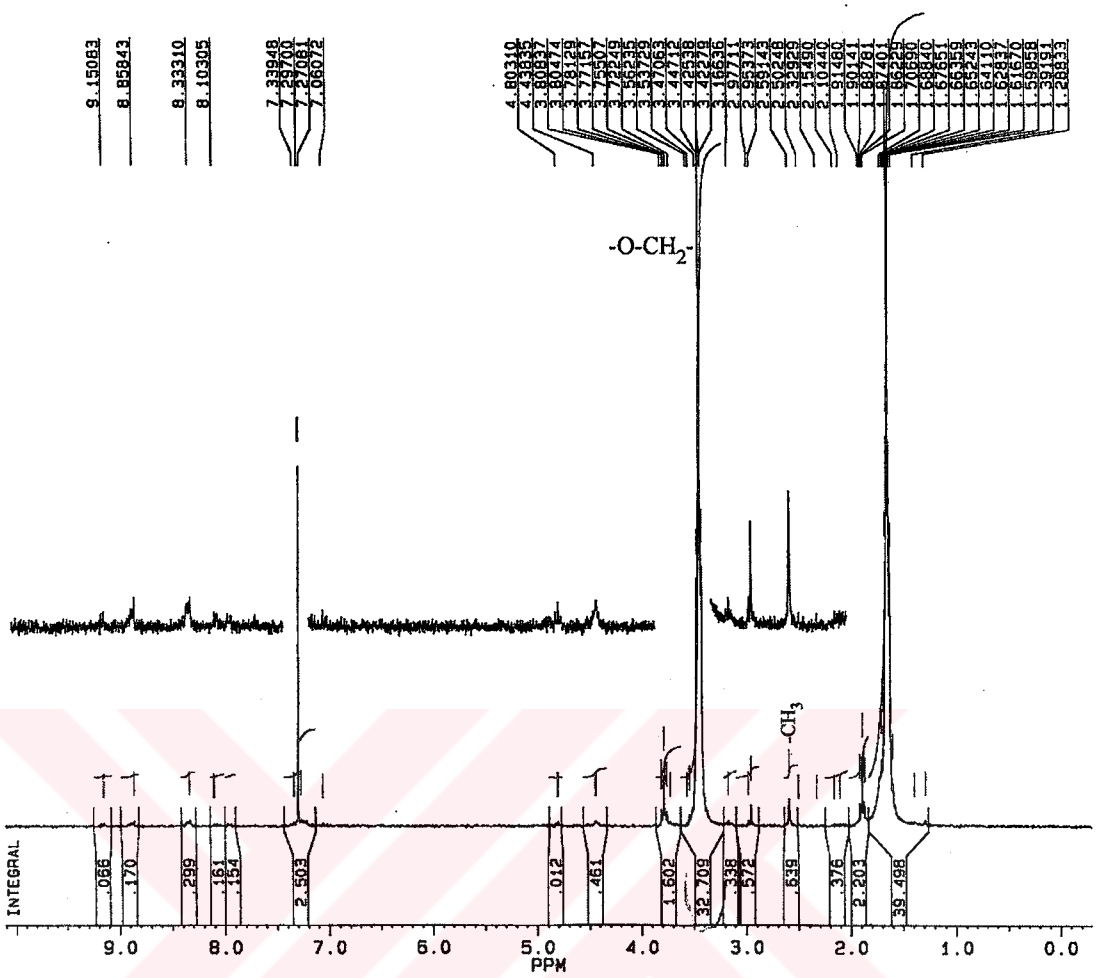


Figure 4.4 The ^{1}H-NMR spectra of PTHFMP-4

According to the Figure 4.4 –O<u>CH$_2$</u>– groups in PTHF at 3,42 ppm; <u>CH$_3$</u> groups in 2-methyl pyridinium at 2,5 ppm.

The structure of the polymers was assigned by means of UV spectral measurement . The UV spectra of the polymers show absorbtion bands characteristic of those of the corresponding low molecular weight pyridinium ions. The relationship between the absorbance and the wavelength of the 2-methyl pyridinium N-oxide –labelled polymers, given in Figure 4.5, provides an evidence that the 2-methyl pyridinium N-oxide molecule was surely incorporated into the polymer.

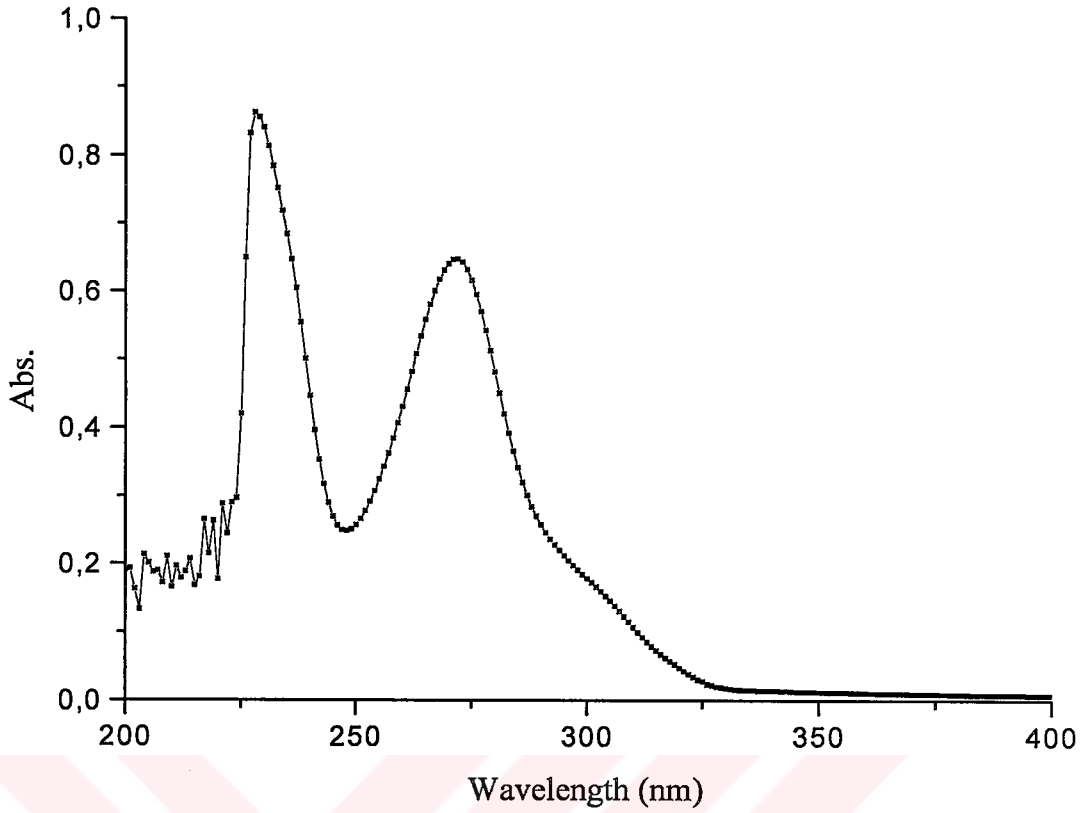


Figure 4.5 UV spectra of PTHF bearing 2-methyl pyridinium N-oxide

Absorbance value of polymers, changed linearly with respect to its concentration. This is of importance in the calculation of its molar absorbtion coefficient,ε. The absorbance of the 2-methyl pyridinium N-oxide-labelled polymers, at a certain concentration, are measured at a certain wavelength, and with the aid of ε value, the M_n of the polymers are calculated from their UV spectra.. The UV-based number average molecular weights of polymers can be calculated by using the Lambert Beer Law(Eq. 4.2) that dictates the equation given below.

$$A = \varepsilon * C * L \qquad (4.2)$$

A = Absorbance

C = Concentration (mol / l)

L = Distance (cm), through which the light passes, in our experiments L = 1 cm

ε=5925 at λ=266 nm for 2- methyl pyridinium N-oxide [33]

The concentration, (mol/l), corresponding to that absorbance value is determined by the Lambert Beer Law given in Eq. 4.3. Since the concentration of the polymer in terms of (mass / volume) is already known, M_n value of the polymer can be calculated by dividing these two concentrations to each other and multiplying 3 due to tri armed polymers:

M_n = Concentration taken (mass/volume)*3/Concentration calculated (mol / l) (4.3)

The composition of the polymers was analysed via IR measurements. According to the IR spectra; the characteristic carbonyl band at 1728,38 cm^{-1}.

C_6H_3-(COO-(CH_2)$_4$-O ~~~)$_3$ and the ether band at 1110 cm^{-1}. Therefore, we can state that the initiation mechanism proceeds by formation of an ester group and the propagation mechanism proceeds by formation of an ether group(Figure 4.6). Similar IR spectra were observed for the other polymers.

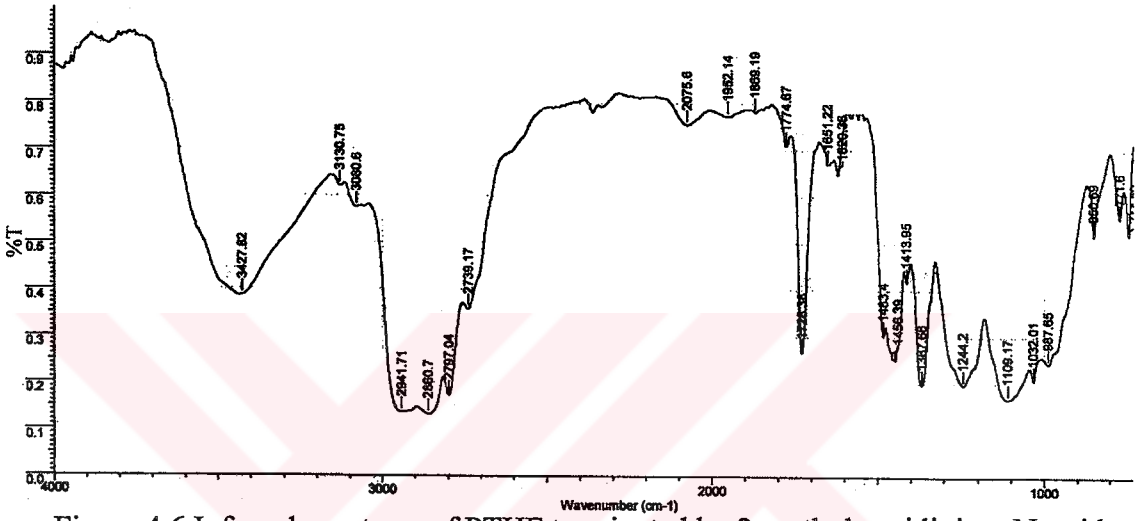


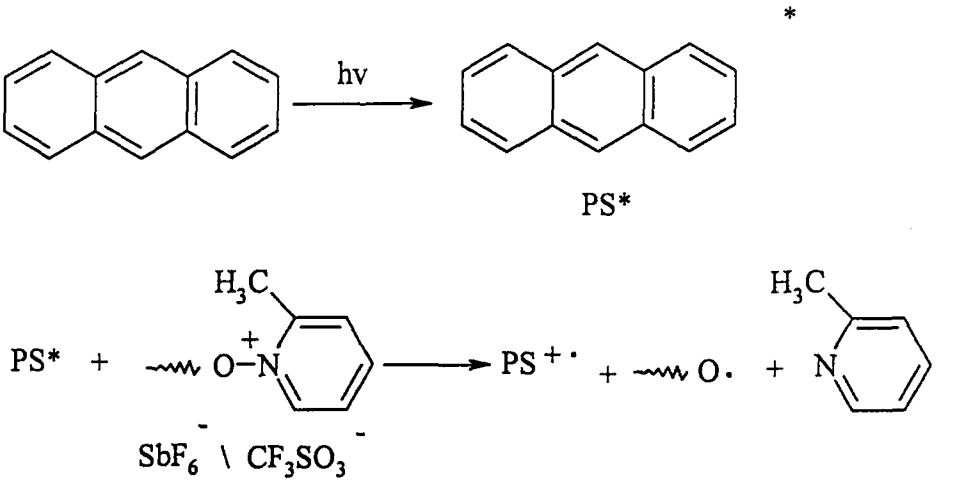
Figure 4.6 Infrared spectrum of PTHF terminated by 2-methyl pyridinium N-oxide

4.2. Preparation and characterization of star shaped block copolymer (PTHF -*block*-PMMA)

Pyridinium salts are used as initiators for cationic and photoinitiated radical polymerization, directly or indirectly. Pyridinium salts do not have absorbance at wavelengths in which photosensitizers are efficient. Generally pyridinium salts form active centers in the presence of photosensitizers such as anthracene, prylene, phenotiazin.

In the present study, obtained polymers (Part 3.1) terminated 2-methyl pyridinium N-oxide were used to initiate the radical polymerization of PMMA in the present of anthracene. According to the absorption characteristics of PTHFMP were involved in order to transform these polymers into block copolymers containing MMA. PTHF-PP and PTHF-IQ absorb light at relatively long wavelengths, i.e. at 300-350nm. Upon direct irradiation at these wavelengths polymeric alkoxy radicals are produced and that have been studied by Hızal and co-workers [33]. The spectral sensitivity of PTHF-MP may be extended to longer wavelengths with the aid of

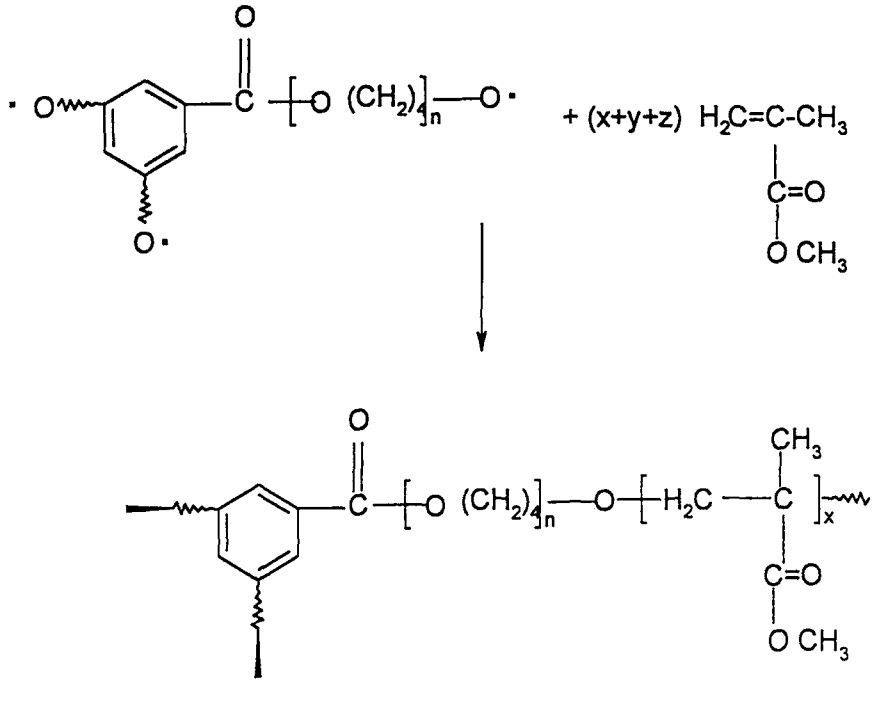
certain sensitizers. Upon irradiation of a solution containing anthracene and PTHFMP macroradicals were formed via electron transfer from the electronically excited sensitizer(PS). The representation of the synthesis is seen in Scheme 4.5:



(4.5)

The action of anthracene as a photosensitizer for synthesis of polymeric alkoxy radicals is showed in Scheme 4.5

In the presence of MMA polymerizable by a free radical mechanism, block copolymer formation at tri arms would be initiated as in the case of direct irradiation (Scheme 4.6). Results for star-shaped block copolymer formation are summarized in Table 4.2.



(4.6)

For the photoinitiated radical polymerization of MMA; cationically prepared PTHFs having 2-methyl pyridinium N-oxide at their 3 chain ends were used as initiator in the presence of anthracene as photosensitizer. In this case, alkoxy radicals formed by electron transfer initiate free radical polymerization.of MMA in dichloromethane solution and star-shaped block copolymers were formed.

IR, UV, ^{1}H NMR and GPC analysis were done for all of the polymers. The results are presented in Table 4.2 for PTHF-PMMA star-shaped block copolymers.

% conversion was calculated by Eq. 4.4;

$$\% \text{ Conversion} = (W / M) * 100, \quad (4.4)$$

where W is the weight of the formed polymer and M represents the mass of the monomer (MMA) initially taken(E.q. 4.5).

$$[W = (M_{\text{polymer precipitated at 25 }^0C} + M_{\text{polymer precipitated at–30 }^0C}) - \text{Minitiator}] \quad (4.5)$$

During the course of polymerization it was observed that conversion and molecular weight of the polymers was increased with irradiation time (Table 4.2).

The molecular weight distribution of the block polymers obtained from PTHFMP-CF_3SO_3 becomes broden with both increasing irradiation time.

Table 4.2 Preparation and characterization of star shaped PTHF-PMMA block copolymers

Initiator	$[I]_o*10^2$(mol.l^{-1})	Time(h)	Conv.(%)	Mn^a	Mn^b	Mn^c	MWD^d
PTHFMP-1	0,79	10	29	60500	15000	69000	1,26
PTHFMP-2	1,2	4	7	52000	23000	62000	1,4
		6	20	57000	15000	75000	1,37
		10	39	56000	22000	86000	1,27
PTHFMP-3		10	37	32000	18000	57000	1,44
PTHFMP-4		4	10	47000	9000	23000	1,39
		6	24	48000	17000	34000	1,4
		10	52	35000	15000	32000	1,56

[MMA] = 4 $mol.l^{-1}$ in dichloromethane, [Anthracene] = 5,3 * 10^{-2} $mol.l^{-1}$, Vt = 4 ml, $\lambda > 350$ nm

[a] Mn,GPC of polymers precipitated in methanol at 25 ^{0}C based on calibration with PS standarts

[b]Mn,GPC of polymers precipitated in methanol at –30 ^{0}C based on calibration with PS standarts

[c]Determined by ^{1}H NMR comparing the content of the –O CH_3 protons of MMA and –O CH_2- protons of PTHF

[d] Molecular weight distribution of block copolymers precipitated at 25 ^{0}C

Figure 4.7 shows GPC traces of the initial PTHFMP and of block copolymer fractions precipitated at room temperature and at –30 ^{0}C. The peaks show unimodal molecular weight distribution.

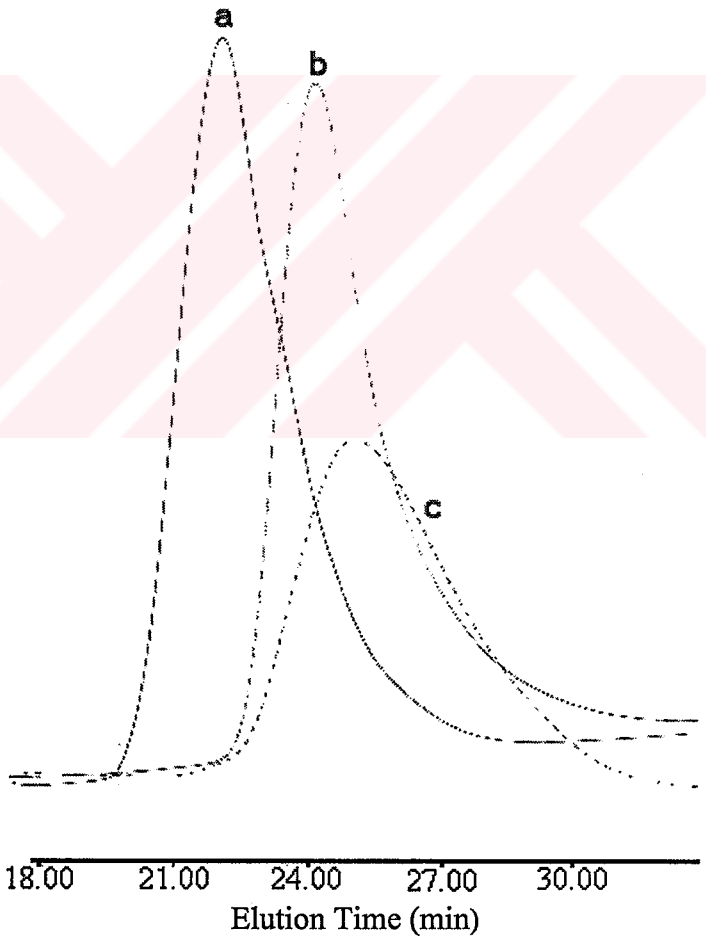


Figure 4.7 GPC traces of star block copolymer obtained from PTHFMP and precipitated from methanol solution (a) 25 ^{0}C and (b) –30 ^{0}C and (c)PTHF (terminated by methanol)

It is possible to fractionate resulting block copolymers with different MMA segment lengths by means of precipitated them at different temperatures. As can be seen from Figure 4.7, block copolymers with long chains were showed their peaks firstly. It is provided that the intensity of peaks are shown from ^1H NMR spectrums of polymers.

The UV absorption spectra of PTHFMP and PTHF-PMMA shows that the fractions do not contain residual initiating polymer and 2-methyl pyridinium N-oxides are seperated from chain ends. These spectra no longer contain the strong absorbtion band ($\lambda \approx 266$) of the pyridinium end groups indicating their complete conversion. It is seen in Figure 4.8.

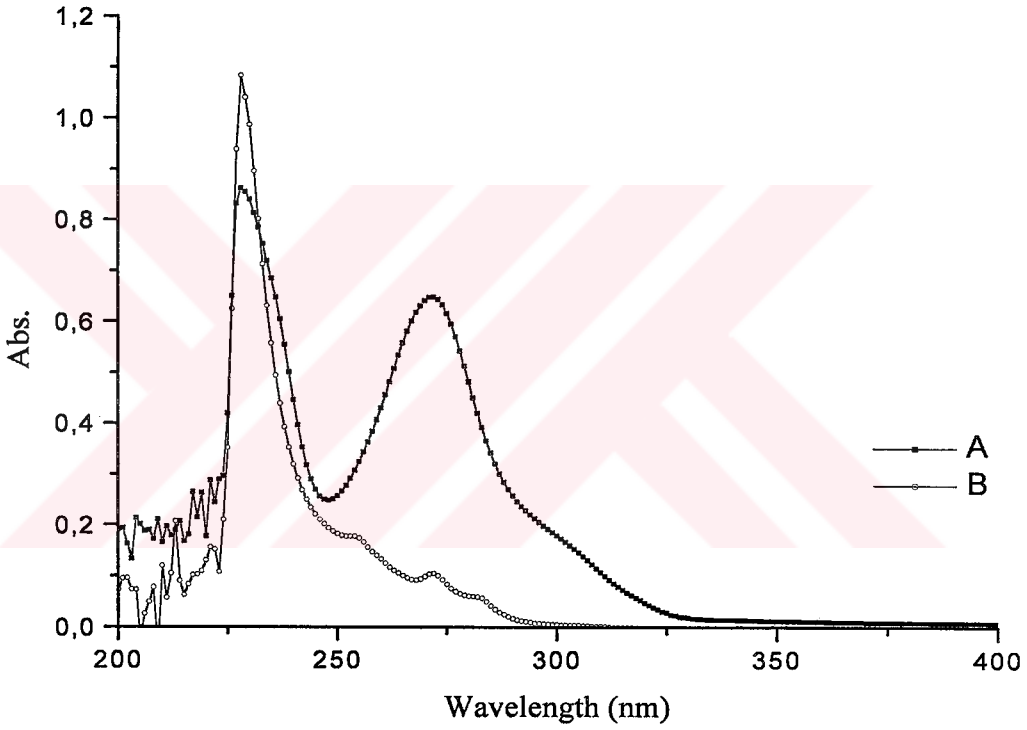


Figure 4.8 UV spectra of (A) PTHFMP in CH_2Cl_2, (B) PTHF-PMMA in CH_2Cl_2

The polymer fraction precipitating at $-30\ ^0C$ consist of a copolymer with short MMA segments. Similar observations were obtained for mono and difuctional initiator systems[33]. This was corroborated by recording the ^1H NMR analyses of the two block copolymer fractions(Figure 4.9 and 4.10).

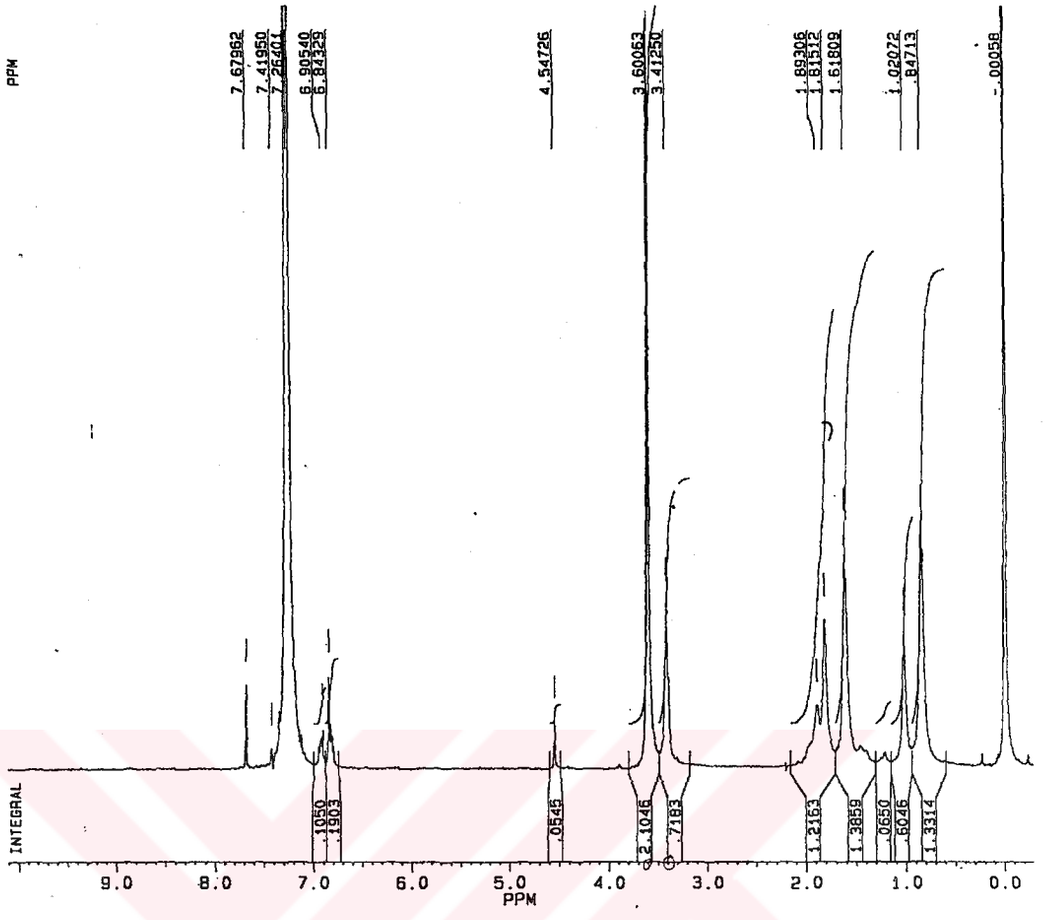


Figure 4.9 ^{1}H NMR spectrum of star-shaped block copolymers obtained from PTHF-MP and precipitated with methanol at room temperature in $CDCl_3$ with TMS

On the basis of a comparison of the ratio of $-OCH_3$ protons of the MMA group at 3,7 ppm to $-O-CH_2-$ protons of the PTHF at 3,3 ppm, the molecular weights of the block copolymers were calculated. Obviously, the polymer fraction precipitating at $-30\ ^{0}C$ consist of a copolymer with short MMA segments(Figure 4.10).

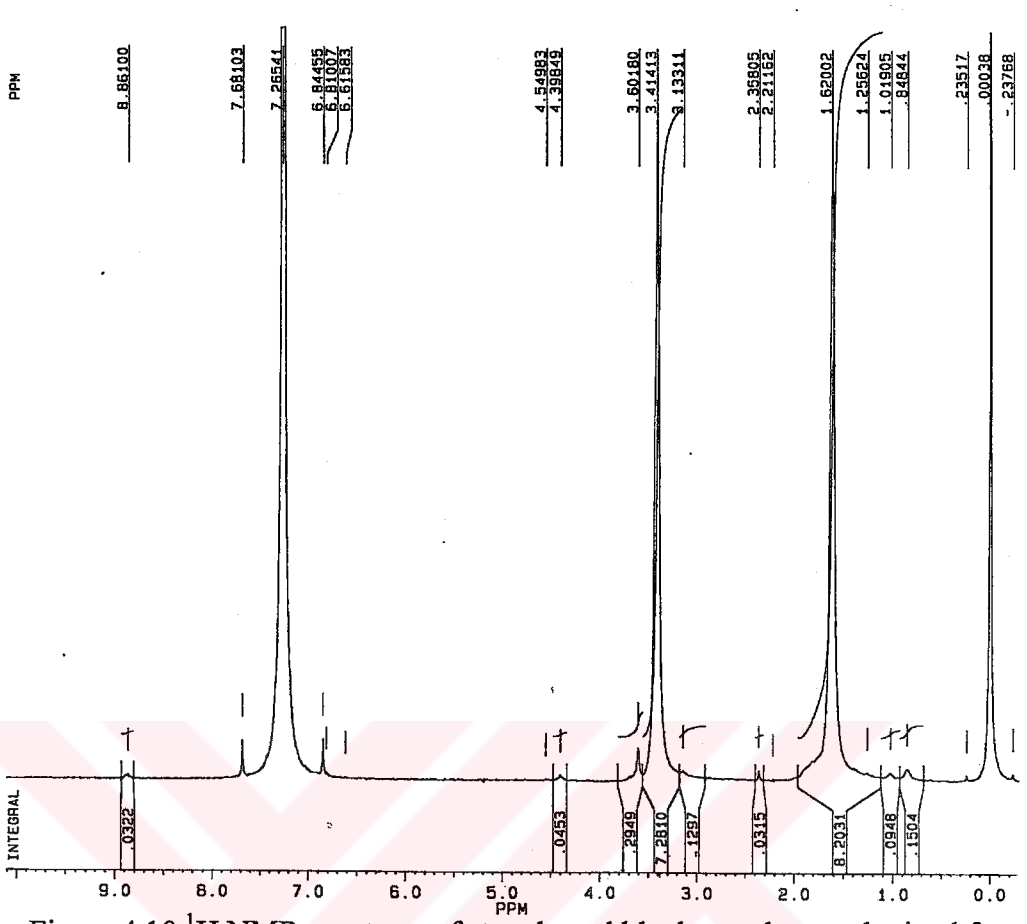


Figure 4.10 ^{1}H NMR spectrum of star-shaped block copolymer obtained from PTHF- MP and precipitated with methanol at -30 ^{0}C in $CDCl_3$ with TMS

The IR measurements of block copolymer fractions showed the composition of polymers. According to the measurements; the characteristic carbonyl streching band of MMA at 1730 cm^{-1}, the ether streching band of PTHF at 1149 cm^{-1}.

5. CONCLUSIONS AND RECOMMENDATIONS

In conclusion, Star-shaped polymers having PTHF-PMMA segments were succesfully synthesized via cationic ring opening (CROP) and photoinitiated radical routes.

This work demonstrates that the oxocarbenium salts presented above are useful initiators for the cationic ring opening polymerization of THF. The propagating chains are terminated by 2-methyl pyridinium N-oxide. By using photosensitizers, the absorbance of pyridinium salts are shifted to longer wavelengths. It is provided that pyridinium salts can be used in industry for UV curing applications. The photoinitiating capability of these polymers provides a versatile method for preparing star shaped block copolymers as selected suitable initiator such as trimestyl-hekzafluoro antimonate\trifluoro methane sulfonate.

According to the analysis, the observed molecular weights of star shaped homopolymers and block polymers measured by GPC were in reasonably agreement with the theoretical molecular weight and calculated from those of ^{1}H NMR. Block copolymers with various molecular weights and narrow molecular weight distributions were prepared. GPC analysis shows a unique peak. Trimesoyl salt exhibits an induction period of about 15min. and fairly slow initiation .

These studies are showed that cationic ring opening and photoinitiated radical polymerization methods are useful techniques in order to prepare star shaped block copolymers.

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