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İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

**SYNTHESIS OF CYCLOHEXENE OXIDE TYPE  
MACROMONOMERS AND THEIR USE IN  
PHOTOCHEMICAL CATIONIC POLYMERIZATION**

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166285

**Date of submission : 27 December 2004**

**Date of defence examination : 17 January 2005**

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**JANUARY 2005**

**SİKLOHEKZEN OKSİD TÜRÜ  
MAKROMONOMERLERİN SENTEZİ VE  
FOTOKİMYASAL KATYONİK  
POLİMERİZASYONDA KULLANIMLARI**

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**Tezin Enstitüye Verildiği Tarih : 27 Aralık 2004  
Tezin Savunulduğu Tarih : 17 Ocak 2005**

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**OCAK 2005**

## ACKNOWLEDGEMENTS

I would like to thank all the people who encouraged and supported me during my master education.

First of all, working in YAĞCI GROUP was big honour for me. I couldn't understand how time went on. I thank to my supervisor Prof. Dr. Yusuf YAĞCI for his patience and guidance. I wouldn't be able to overcome this work without his promotive support.

I would also like to extend my gratitude to my friends; Oğuzhan AY, research assistant Murat GÜLÇÜR, İ. Gökhan TEMEL, Binnur AYDOĞAN and Dilek EMRE.

It was great pleasure to work with Burçin GACAL, M. Atilla TAŞDELEN, Yasemin YÜKSEL DURMAZ, research assistant Hakan DURMAZ, Dr. Mustafa DEĞİRMENCİ, Dr. Ioan CIANGA, Dr. Faruk YILMAZ, Ali Ekrem MÜFTÜOĞLU, research assistant Demet GÖEN ÇOLAK and Nihan YÖNET.

I dedicated this thesis to my family; my father İbrahim İZGİN, my mother Bahriye İZGİN, and my sweet sister Özge İZGİN, for their endless support.

Thank you all...

January 2005

Öner İZGİN

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## LIST of ABBREVIATIONS

<b>CRP</b>	: Controlled Radical Polymerization
<b>ATRP</b>	: Atom Transfer Radical Polymerization
<b>NMP</b>	: Nitroxide Mediated Polymerization
<b>TEMPO</b>	: 2, 2, 6, 6- Tetramethylpiperidinoxy
<b>SFRP</b>	: Stable Free Radical Polymerization
<b>RAFT</b>	: Reversible Addition-Fragmentation Chain Transfer Polymerization
<b>ROP</b>	: Ring-Opening Polymerization
<b>CROP</b>	: Controlled Ring Opening Polymerization
<b>PI</b>	: Photoinitiator
<b>CTA</b>	: Chain Transfer Agent
<b>GPC</b>	: Gel Permeation Chromatography
<b>NMR</b>	: Nuclear Magnetic Resonance Spectroscopy
<b>UV</b>	: Ultra Violet
<b>M</b>	: Monomer
<b>St</b>	: Styrene
<b>MMA</b>	: Methyl Methacrylate
<b><math>\epsilon</math>-CL</b>	: Epsilon Caprolactone
<b>CHO</b>	: Cyclohexene Oxide
<b>PSt</b>	: Polystyrene
<b>PMMA</b>	: Poly(methyl methacrylate)
<b>PCL</b>	: Poly( $\epsilon$ -caprolactone)
<b>PCHO</b>	: Poly(cyclohexene Oxide)
<b>bpy</b>	: Bipyridine
<b>dpy</b>	: Dipyridyl
<b>THF</b>	: Tetrahydrofuran
<b>On<sup>+</sup></b>	: Onium Salt
<b>Ph<sub>2</sub>I<sup>+</sup>PF<sub>6</sub><sup>-</sup></b>	: Diphenyliodonium Hexafluorophosphate
<b>EMP<sup>+</sup>PF<sub>6</sub><sup>-</sup></b>	: <i>N</i> -Ethoxy-2-Methylpyridinium Hexafluorophosphate
<b>CHMBP</b>	: (3-Cyclohexene-1-methyl )-2-bromopropanoat
<b>CHOMBP</b>	: (3-Cyclohexene oxide -1-methyl )-2-bromopropanoat
<b>PCL-g-PCHO</b>	: Graft copolymer of poly( $\epsilon$ -caprolactone) and poly(cyclohexene oxide)
<b>PSt-g-PCHO</b>	: Graft copolymer of polystyrene and poly(cyclohexene oxide)
<b>PCL-PSt</b>	: Copolymer of poly(cyclohexene oxide) and polystyrene
<b>(PCL-PSt)-g-PCHO</b>	: Graft copolymer of poly( $\epsilon$ -caprolactone)-polystyrene and poly(cyclohexene oxide)

## LIST of SYMBOLS

$f$	: Initiator Efficiency
$\lambda$	: Wavelength
$\epsilon$	: Molar absorption Coefficient
$h\nu$	: Radiation
$R\cdot$	: Radical
$I$	: Initiator
$COI$	: Cointiator
$M$	: Monomer
$C^+$	: Cation
$C^{\cdot+}$	: Radical Cation
$C^-$	: Anion
$S$	: Sensitizers
$E_{1/2}^{Ox}$	: Oxidation potential
$E_{1/2}^{Red}$	: Reduction potential
$M_n$	: The Number Average Molecular Weight
$M_w$	: The Weight Average Molecular Weight
$M_w/M_n$	: The Molecular Weight Distribution
$k_{act}$	: Rate constant of activation step of the initiation in radical polymerization
$k_{deact}$	: Rate constant of deactivation step of the initiation in radical polymerization
$k_p$	: Rate constant of propagation step
$k_t$	: Rate constant of termination step
$M_t^n$	: Transition metal
$DP$	: Degree of polymerization
$R-X$	: Alkyl halide

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# **SYNTHESIS OF CYCLOHEXENE OXIDE TYPE MACROMONOMERS AND THEIR USE IN PHOTOCHEMICAL CATIONIC POLYMERIZATION**

## **SUMMARY**

Recently, there is an enormous interest in the preparation and reactivity of macromonomers having different end functionalities. Controlled / "Living" Radical Polymerization processes have proven to be versatile for the synthesis of polymers with well-defined structures and complex architectures. Among the CRP processes, Atom Transfer Radical Polymerization (ATRP) and Controlled Ring Opening Polymerization (CROP) are the most efficient methods for the synthesis of special homopolymers and copolymers.

Poly( $\epsilon$ -caprolactone) and polystyrene macromonomers were synthesized starting from cyclohexene type alcohol by controlled polymerization techniques. In this process, CROP and ATRP were used as the polymerization methods. The initiation proceeded at the one end of the starting compound while the other was convenient site for the epoxidation. The obtained macromonomers were used in photoinitiated cationic polymerization in the presence and absence of low molecular weight monomers, such as cyclohexene oxide. Moreover, macromonomers possessing poly( $\epsilon$ -caprolactone) and polystyrene segments were also utilized without any additional low molecular weight monomer in conjunction with each other. The structural characteristics of the polymers also were investigated by Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance Spectroscopy (NMR).

# SİKLOHEKZEN OKSİD TÜRÜ MAKROMONOMERLERİN SENTEZİ VE FOTOKİMYASAL KATYONİK POLİMERİZASYONDA KULLANIMLARI

## ÖZET

Son zamanlarda, farklı uç fonksiyonalitesine sahip makromonomerlerin eldesi ve reaktivitesi yoğun ilgi duyulan bir alandır. Kontrollü / “Yaşayan” Radikal Polimerizasyon yöntemlerinin istenen özelliklere sahip ve karmaşık mimaride yapıların sentezinde kullanılabilirliği ispatlanmıştır. Kontrollü Polimerizasyon yöntemlerinden Atom Transfer Radikal Polimerizasyonu (ATRP) ve Kontrollü Halka Açılması Polimerizasyonu (CROP) özel homopolimer ve kopolimerlerin eldesi için en verimli yöntemlerdir.

Poli( $\epsilon$ -kaprolakton) ve polistiren makromonomerleri siklohekzen tipi alkollerden başlayarak kontrollü polimerizasyon yöntemleriyle sentezlendi. Bu aşamada, CROP ve ATRP polimerizasyon yöntemleri olarak kullanıldı. Bu işlemde, başlangıç maddesinin bir ucu polimerizasyondan zincir büyümesine olanak sağlarken diğer ucu ise epoksidasyon reaksiyonu için bir reaktif grup olarak yer almaktadır. Bir diğer uç epoksidasyona açıkken başlangıç bir uçtan gerçekleşecektir. Elde edilen makromonomerler siklohekzen oksid gibi düşük molekül ağırlıklı monomerlerin varlığında ve yokluğunda fotobaşlatılmış katyonik halka açılması polimerizasyonunda kullanıldı. Ayrıca, poli( $\epsilon$ -kaprolakton) ve polistiren segmentleri taşıyan makromonomerler birbirleriyle bağlandı. Polimerlerin yapısal özellikleri Jel Geçirgenlik Kromatografisi (GPC) ve Nükleer Manyetik Rezonans Spektroskopisi (NMR) ile incelendi.

## 1. INTRODUCTION

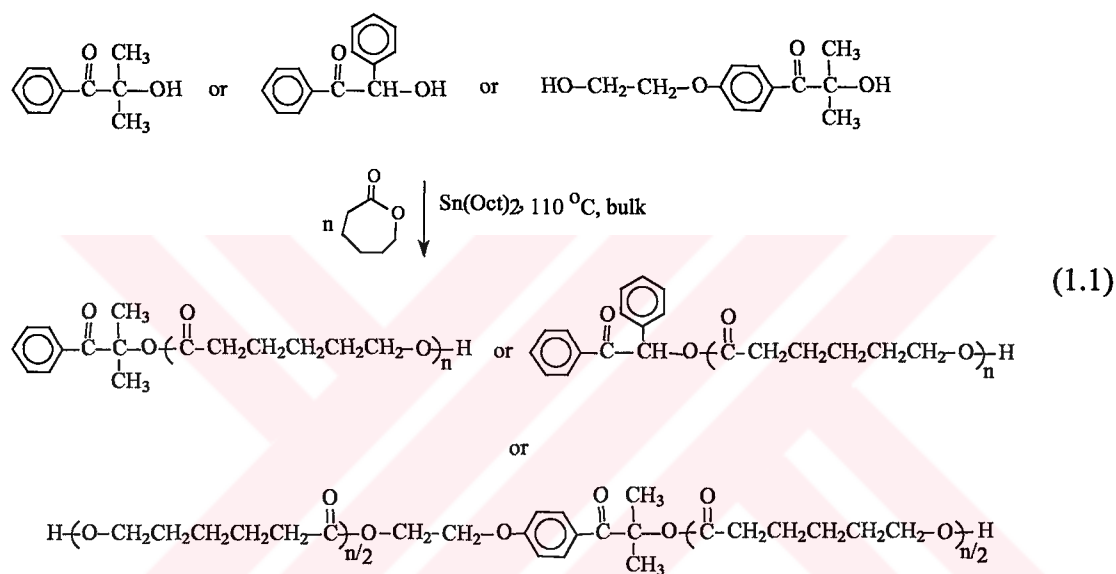
The synthesis of polymers with well-defined compositions, architectures, and functionalities has long been of great interest in polymer chemistry. Typically, living polymerization techniques are employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination [1-3]. Much of the academic and industrial research on living polymerization has focused on anionic, cationic, coordination, and ring-opening polymerizations.

The ring-opening polymerization (ROP) of lactones and lactides has been thoroughly investigated during the last 40 years, due to their versatility in producing a variety of biomedical polymers in a controlled manner. Carothers and coworkers first extensively explored the ROP technique for lactones, anhydrides, and carbonates [4-7]. Since then the method has been applied to a diversity of monomers to produce all types of polymers with well-defined structures or end groups, and a number of initiator and catalyst systems have been developed. In many cases, the resulting polymers exhibit useful properties as engineering materials.

The development of controlled/living radical polymerization (CRP) methods has been a long-standing goal in polymer chemistry. Stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer polymerization (RAFT) are the methods whereby the reactivity of radicals can be controlled and side reactions suppressed.

Polymers with end-functional groups have attracted considerable attention as prepolymers (macromonomers) for synthesizing block and graft copolymers, star polymers, and polymer networks. Macromonomers are usually referred to reactive oligomers or polymers in which a polymerizable functional group is incorporated to the chain end(s). Macromonomers can be synthesized via various methods including anionic, cationic, radical polymerizations and chemical modifications of polymer ends[1]. Because of various applications, particularly in biomedical field, homo- and copolymers of polylactones such as poly( $\epsilon$ -caprolactone) receive interest. Tin

octoate,  $\text{Sn}(\text{O}(\text{O})\text{CCH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9)_2$ , in short  $\text{Sn}(\text{Oct})_2$ , is the most widely used[2] initiator to synthesize designed polymers based on poly( $\epsilon$ -caprolactone). In particular when used in conjunction with hydroxyl functional compounds or prepolymers, telechelics, linear and star-shaped block copolymers or networks can be obtained [3, 8-15] via corresponding alkyl octoate formation. It was previously prepared a new kind of macrophotoinitiators of PCL [16] that have potentiality in initiating light-induced free radical polymerization by using hydroxyl functional photoinitiators in conjunction with  $\text{Sn}(\text{Oct})_2$  in the ring opening polymerization (ROP) of  $\epsilon$ -caprolactone (CL) according to reactions 1.1.



## 2. THEORETICAL PART

### 2.1 Copolymers

Copolymer structures can be described in a variety of ways. Different types of copolymers include statistical, alternating, block, and graft copolymers (Figure 2.1). Statistical copolymers result from a single process where the incorporation of the comonomers follow some statistical law that is due solely to kinetic factors [17]. Alternating copolymerization, is an example of chain copolymerization where each of the monomers adds preferentially to the other and homopropagation is effectively nonexistent [18]. Block and graft copolymers differ in that they contain long sequences of each comonomer either along the backbone or as side chains (grafts) and are often the result of a multi-step process [19].

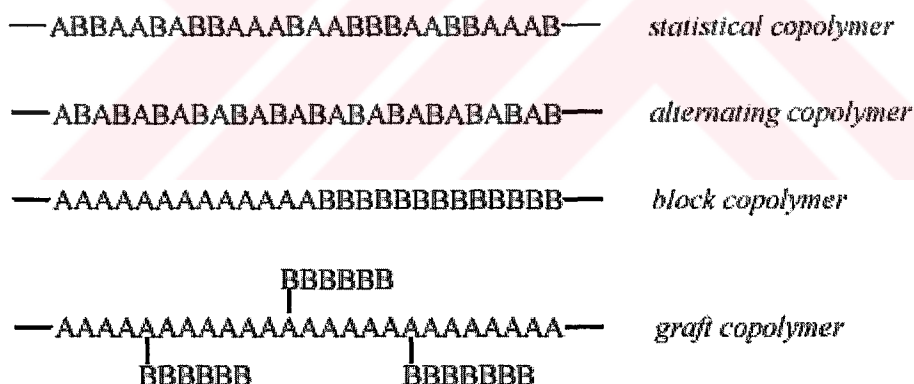


Figure 2.1. Types of copolymer topologies

The manner in which comonomer repeat units are incorporated into the polymer backbone is determined from the reactivities of the monomers and radicals involved in the reaction. Reaction conditions such as solvent and temperature can also have a marked effect on the monomer reactivities and will contribute to the copolymer composition.

Therefore, in only a few select cases of chain copolymerization will the copolymer composition be directly proportionate to the monomer feed. More typically, both the

comonomer feed and instantaneous copolymer composition vary throughout the copolymerization, which results in heterogeneity.

## 2.2 Graft Copolymers

Graft copolymers are composed of a main polymer chain (the backbone) to which one or more side chains (the branches) are chemically connected through covalent bonds. A graft copolymer with one branch can be considered as a miktoarm star copolymer. The backbone and the branches may be homopolymers or copolymers but they differ in chemical nature or composition [20]. The branches are usually equal in length and randomly distributed along the backbone because of the specific synthetic techniques used for their preparation. However, more elaborate recent methods have allowed the synthesis of regular graft copolymers with equally spaced and identical branches and of exact graft copolymers, where all the molecular and structural parameters can be accurately controlled (Figure 2.2).

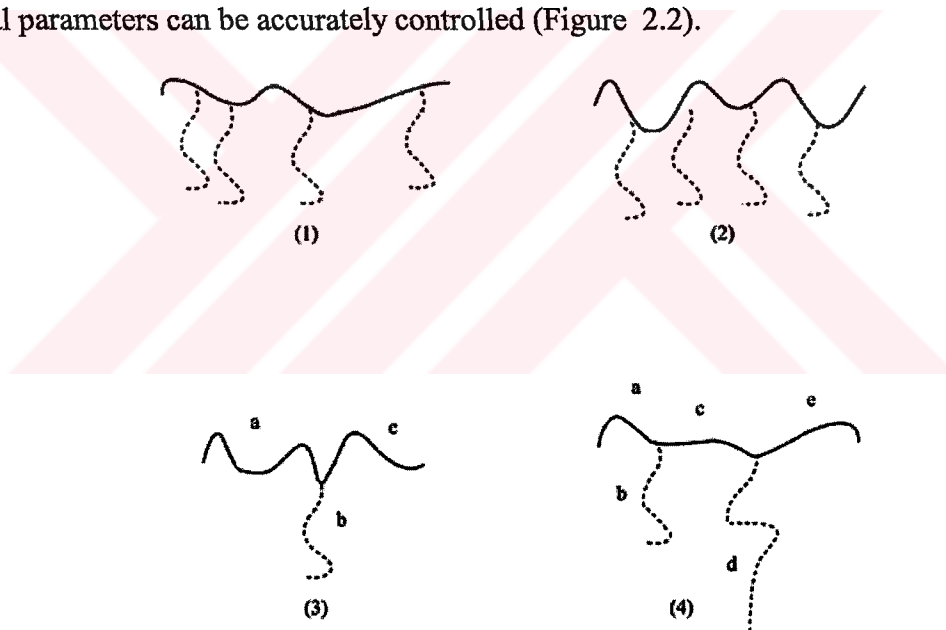


Figure 2.2. Graft Copolymers (1) random graft copolymer (identical branches randomly distributed along the backbone); (2) regular graft copolymer (identical branches equally spaced along the backbone); (3) simple graft copolymer (3-miktoarm star copolymer); and (4) graft copolymer with two trifunctional branch points. Exact graft copolymers.

A simple graft copolymer can be represented as  $A_k\text{-graft-}B_m$  or polyA-*graft*-polyB or poly(A-*g*-B), where  $A_k$  or polyA is the backbone to which the  $B_m$  or polyB branches are grafted. The nomenclature of graft copolymers follows the rules recommended by the IUPAC Commission on Macromolecular Nomenclature [21].

Graft copolymers have been mainly used to modify polymer properties because of their unique mechanical, thermal, dilute solution, and melt properties [22-26].

## 2.2.1 Synthesis of Graft Copolymers

Three general methods have been developed for the synthesis of randomly branched graft copolymers: (1) the “grafting onto”, (2) the “grafting from”, and (3) the macromonomer method (or “grafting through” method) (27) (Figure 2.3).

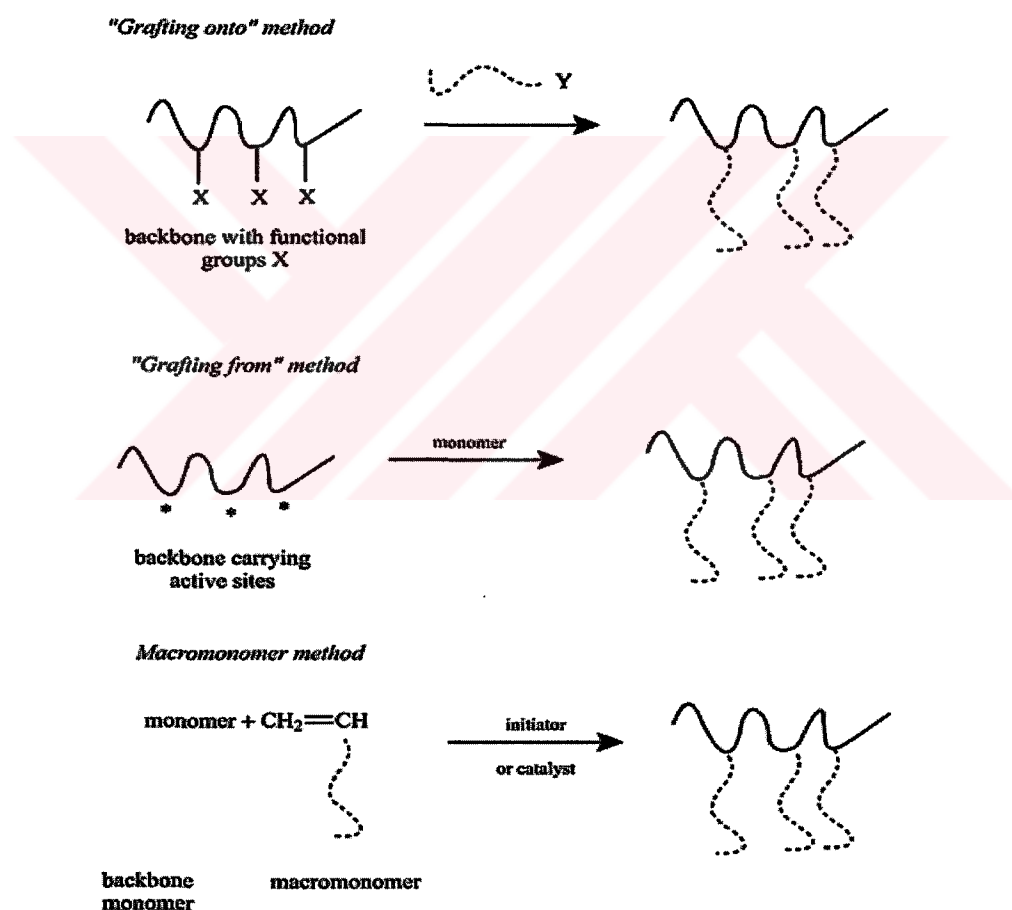


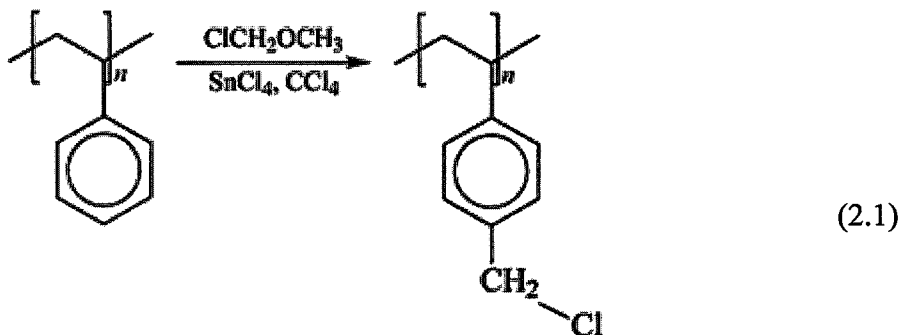
Figure 2.3. Three general methods of synthesis of randomly branched graft copolymers

### 2.2.1.1. "Grafting onto" Methods

In the “grafting onto” method, reaction of preformed polymeric chains having functional groups, with other polymeric chains having active chain ends, takes place.

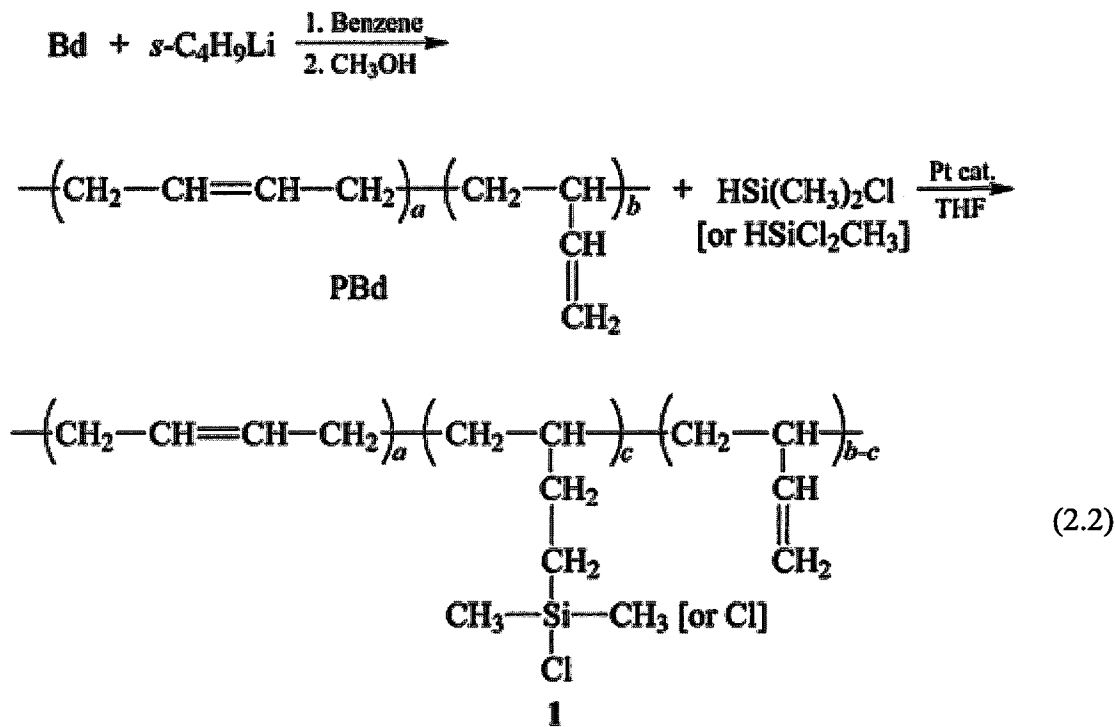


In most cases the incorporation of functional groups is performed by chemical modification of the backbone [28-33]. A common procedure is the chloro(bromo) methylation of polystyrene (Reaction 2.1), and the subsequent reaction with living polymeric chains.



Using this method polystyrene-*g*-poly(ethylene oxide) (PS-*g*-PEO) graft copolymers were prepared [28-31]. The chloromethylation of PS was performed using a CCl<sub>4</sub> solution of PS with chloromethyl methyl ether, with SnCl<sub>4</sub> as the catalyst. The reaction conditions were controlled in such a way so as to give low chloromethyl content (<10 wt).

Well-defined butadiene-styrene graft copolymers (PBd-*g*-PS) were synthesized using hydrosilylation reactions [34]. Catalytic hydrosilylation of the 1,2-Bd units (~10%) of PBd introduced chlorosilane groups (Reaction 2.2). Linking reactions between living PS anions and the Si Cl groups of the backbone (1) gave PBd-*g*-PS graft copolymers with randomly placed single PS branches. When HSiCl<sub>2</sub>CH<sub>3</sub> was used in the hydrosilylation step, difunctional branching sites were introduced in the backbone, resulting in the formation of P(Bd-*g*-S)<sub>2</sub> double grafts.



Block graft copolymers are copolymers having a backbone composed of a diblock copolymer. Grafted chains can be attached to one or both of the backbone blocks (Figure 2.3). Block grafts with a triblock as the backbone are also possible

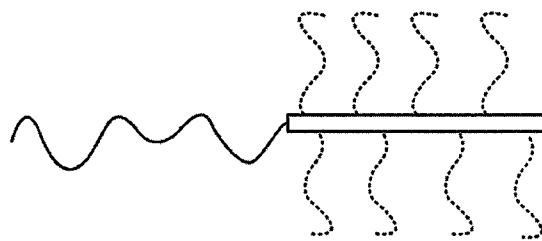
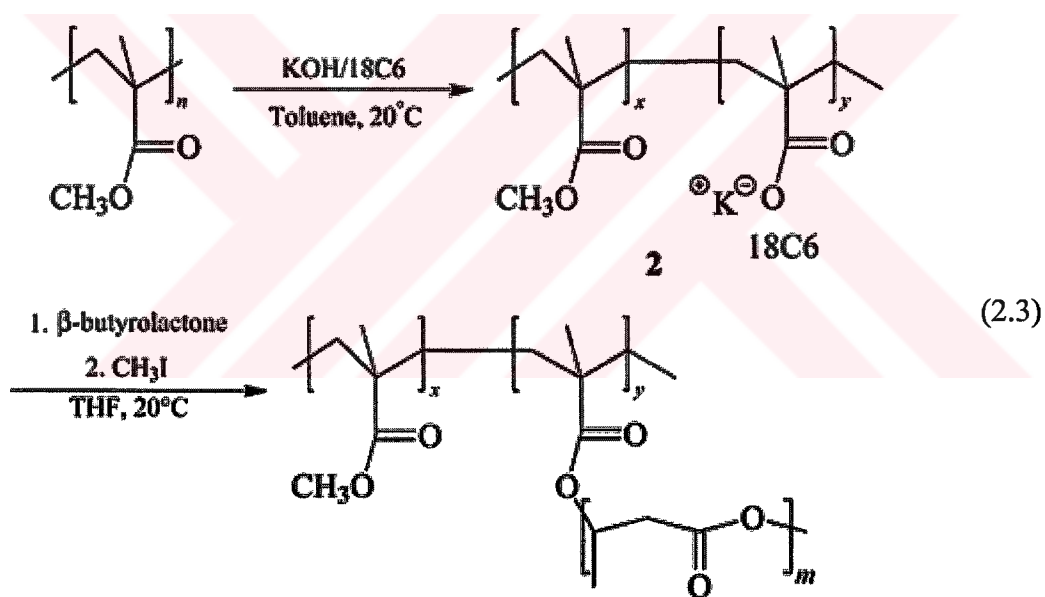


Figure 2.3. Block-graft copolymer. In this case only one of the backbone blocks is grafted.

### 2.2.1.2 “Grafting from” Methods

In the “grafting from” method, the backbone is chemically modified in order to introduce active sites capable of initiating the polymerization of a second monomer. The number of grafted chains can be controlled by the number of active sites generated along the backbone assuming that each one of them participate to the formation of one branch. However, mainly because of kinetic and steric hindrance effects there may be a difference in the lengths of the produced grafts.

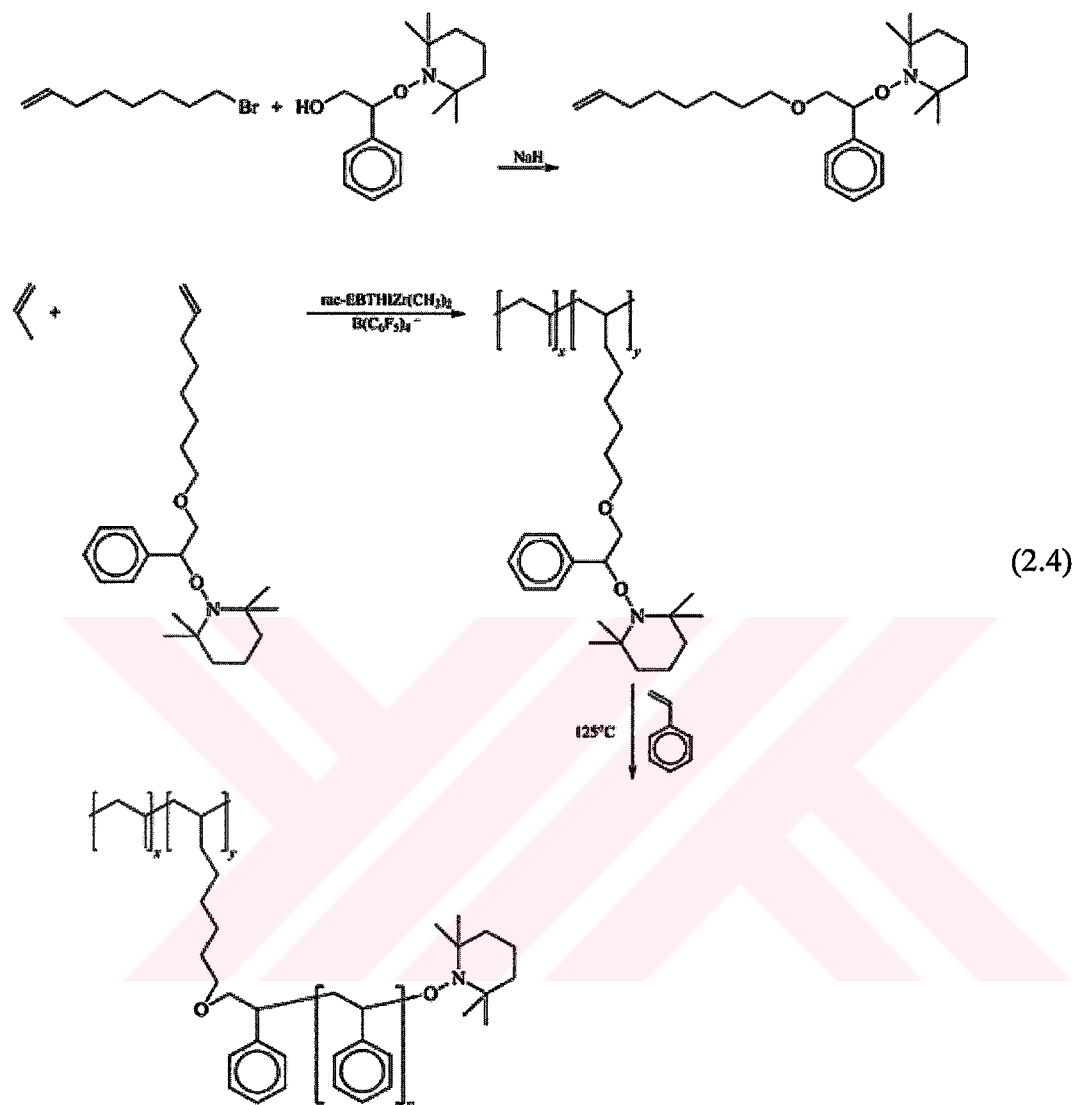
By using the “grafting from” technique, PMMA-g-( $\beta$ -butyrolactone) [35] copolymers were synthesized. Anionically polymerized PMMA was treated with 18-crown-6 complex of potassium hydroxide resulting in a macromolecular initiator (2) (Reaction 2.3).



Cationic grafting techniques have been used for the synthesis on poly(ethyl vinyl ether-g-ethyloxazoline) graft copolymers [36]. A random copolymer of ethyl vinyl ether with a small quantity of 2-chloroethyl vinyl ether was synthesized by cationic polymerization. The pendant alkyl groups were the initiating sites of the cationic polymerization of ethyloxazoline grafts.

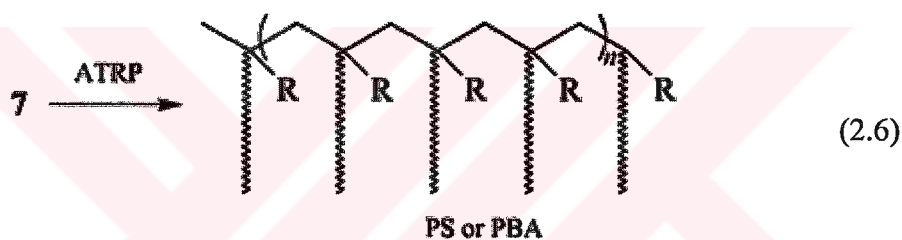
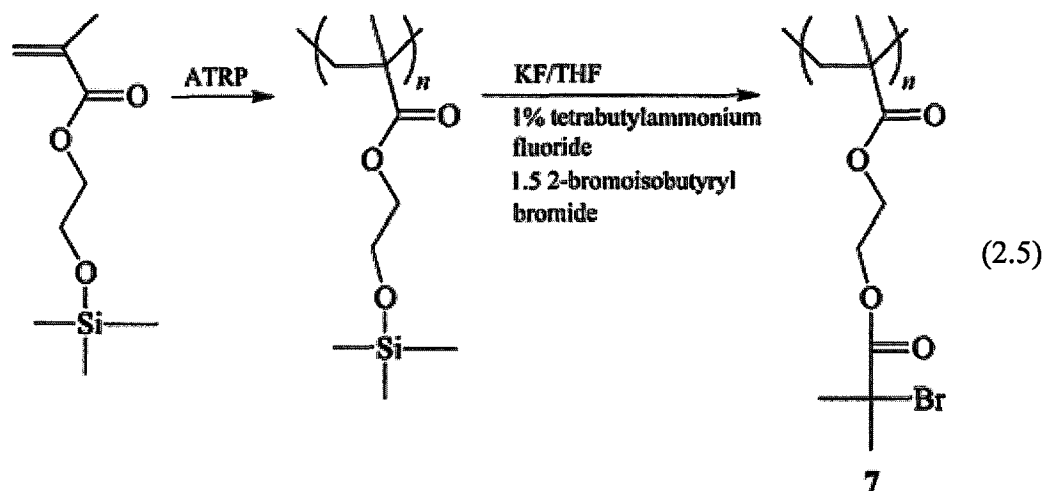
Polypropylene-g-PS copolymers were synthesized by combination of metallocene and TEMPO living free-radical polymerization techniques [37]. The backbone was synthesized by copolymerization of propylene and a TEMPO-functionalized

derivative containing a -double bond. The TEMPO groups were then used for the polymerization of styrene by living free-radical polymerization (Reaction 2.4).



By using ATRP, poly(2-hydroxyethyl methacrylate)-*g*-PS (PHEMA-*g*-PS) and PHEMA-*g*-poly(*n*-butyl acrylate) [38] were synthesized. The backbone, comprised of trimethylsilyl-protected 2-hydroxyethyl methacrylate, was synthesized by using ATRP methodology, followed by deprotection of the hydroxyl group. Subsequent esterification (Reaction 2.5) with 2-bromoisobutyryl bromide resulted in poly [2-(2-bromoisobutyryloxy) ethyl methacrylate].

PS or poly(*n*-butyl methacrylate) were then grafted from the macromolecular initiator (Reaction 2.6). Subsequent analysis revealed that all the initiation sites participated in the polymerization of the second monomer.

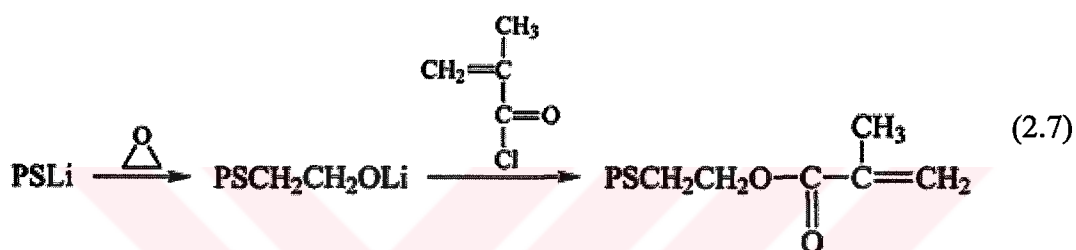


### 2.2.1.3. Macromonomer Method

The synthesis of graft copolymers by the macromonomer method is characterized by its own specific features [39-42]. The number of branches is determined by the ratio of the macromonomer and comonomer molar concentrations and their copolymerization behavior, described by the reactivity ratios  $r_1$  and  $r_2$ . These parameters determine how random the placement of the branches along the backbone will be. It is evident that during the copolymerization the relative concentrations of the macromonomer and the comonomer change with time, leading to the formation of graft copolymers with subsequently different number of branches. In addition, the copolymerization is not homogeneous throughout the course of the reaction since phase separation may occur. For the above reasons it can be concluded that the graft copolymers prepared by this method are generally characterized by increased compositional and chemical heterogeneity.

The synthesis of macromonomers can be accomplished by almost all the available polymerization techniques. Among them, living polymerization methods offer unique control over the molecular weight, the molecular weight distribution, and chain-end functionalization.

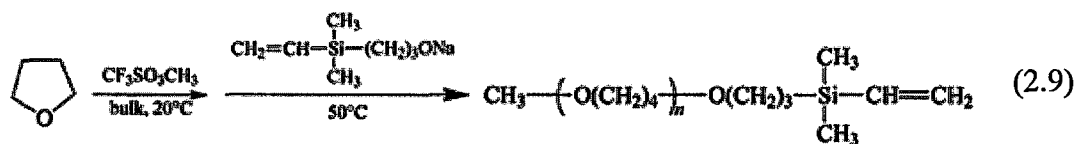
Anionic polymerization is one of the best methods for the synthesis of well-defined macromonomers. Functional initiation or termination by suitable electrophilic reagents is the best ways for the incorporation of the reactive end groups [43]. According to this methodology living polystyryllithium initially reacts with ethylene oxide to form the less reactive alkoxide, followed by the reaction with methacryloyl chloride for the synthesis of the macromonomer (Reaction 2.7) [44].



These macromonomers were then copolymerized with vinyl monomers mainly by free-radical techniques [45] and also other methods as by metallocene catalysts [46] to provide graft copolymers. The reaction of polystyryllithium with *p*-chlorovinylbenzene at low temperatures affords macromonomers with styryl end groups (Reaction 2.8) [47].

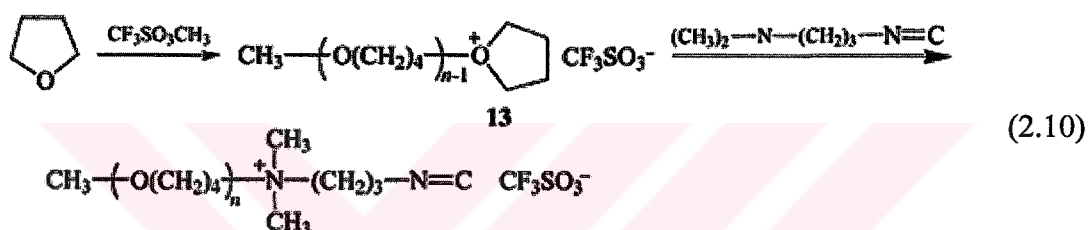


Cationic polymerization has also been used for the synthesis of macromonomers, especially after the development of living cationic polymerization techniques [48]. Macromonomers were prepared by the cationic ring-opening polymerization of tetrahydrofuran (THF) using methyltrifluoromethane sulfonate, followed by termination with 3-sodio-propyloxydimethylvinylsilane to give a macromonomer with vinyl silane end groups [49] (Reaction 2.9).



These macromonomers were copolymerized with vinyl acetate (Vac) using azobisisobutyronitrile (AIBN) as radical initiator to produce PVAc-g-PTHF graft copolymers. Subsequent saponification using NaOH provided poly(vinyl alcohol)-g-PTHF graft copolymers.

Termination of living PTHF (13) with 3-(dimethylamino propyl) isocyanide leads to the formation of macromonomers having end isocyanide groups [50] (Reaction 2.10).



Other examples of graft copolymers prepared using macromonomers, which were synthesized by cationic polymerization, are given in Table 1.

Table 21. Graft Copolymers Prepared by Macromonomers Synthesized by Cationic Polymerization

Macromono.mer	End group	Comonomer	Copolym.	Ref.
Poly(2-alkyl-2-oxazoline)	Diethanolamine	-Caprolactone + 4,4'-methylene di(phenylisocyanate)	Condensation	[51]
Poly(2-alkyl-2-oxazoline)	(Meth)acrylate			[52]
PPO, poly(epichlorohydrin)	(Meth)acrylate	Styrene, MMA	Radical	[53]
Polyisobutylene	Methacrylate	MMA	GTP	[54]

### **2.2.2. Other Present and Potential Applications**

Graft copolymers are steadily assuming an increased importance because of their tremendous industrial application potential [55-66]. Graft copolymers of commercial utility include ABS, obtained by grafting acrylonitrile and styrene monomers onto polybutadiene, high impact polystyrene, a family of poly(butadiene-g-styrene) materials, alkali-treated cellulose-g-acrylonitrile and starch-g-acrylonitrile which are used as “superabsorbent” components in diapers, sanitary napkins, and the like. Graft copolymers containing acrylic monomers are used as pressure-sensitive adhesives [58]. Other graft copolymers are essential materials in oil recovery operations. A large number of commercial paint, printing, and coating formulations involve graft copolymers as dispersion stabilizers, rheology modifiers, and final coating properties improvers (eg, corrosion resistivity, environmental compatibility, etc.) [59-66].

The potential of using graft copolymer micelles and nanoparticles derived from graft copolymers as drug carriers for controlled drug delivery systems and for environmental purification methodologies is high[67-72]. These applications rely on the ability of the micelles to solubilize low molecular weight compounds in their cores. By controlling the molecular characteristics of the copolymers and the chemical nature of the corona, drug containing vehicles of the desired size, loading capacity, release kinetics, targeting capabilities, biocompatibility and biodegradability can be produced. Formulations in the gel and bulk state are also candidates for this kind of application. Size and loading capabilities of the micellar microcontainers are also important in water treatment systems. The application of graft copolymer membranes in separation processes, like removal of deleterious organic compounds from contaminated drinking water, is also of interest [73-75]. With judicious choice of chemical components in conjunction with graft copolymer morphology design, perselectivity and permeability of the resulting membranes can be adjusted.

### **2.3 Macromonomers**

“Macromonomer” or “macromer” is an abbreviation for macromolecular monomer and hence it is a monomer and a polymer at the same time, with a molecular weight of  $10^3 - 10^4$ . It usually contains a polymerizable group on one chain end, so that it can



either homopolymerize to give a regular comb polymer or copolymerize with a conventional monomer to give a graft copolymer, as illustrated in Figure 2.4.

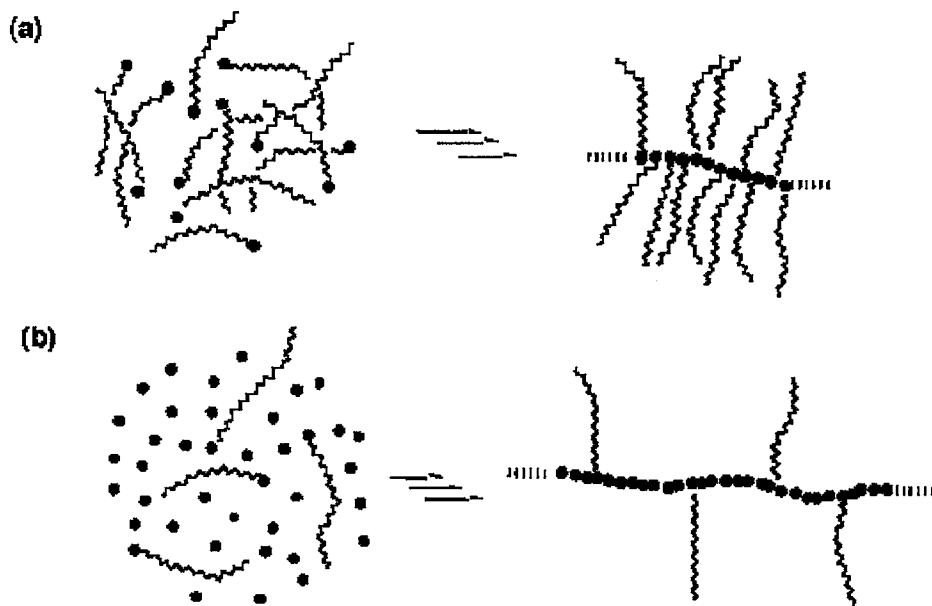


Figure 2.4. Basic scheme of the macromonomer technique.(a) Homopolymerization to a comb copolymer. (b) Copolymerization with a comonomer to a graft copolymer.

Thus the macromonomer technique can be regarded to give access to well-defined branched polymers, at least in the sense that the chain length (degree of polymerization) of the macromonomer, as the branch or the side chain, is usually predetermined and that the chain length and the composition of the backbone or the main chain may also be controlled in principle by the subsequent polymerization or the copolymerization step. With much progress in the syntheses of end-functional polymers, almost all types of conceivable macromonomers are available or at least can be prepared so that we can envisage enormous varieties of branched polymers with different architectures, combinations and compositions.

The first “macromonomer” was introduced by researchers at ICI for the development of well-known, high solids, nonaqueous dispersion (NAD) [77,78]

Secondly, the term “macromer” was introduced as a trade name by Milkovich of CPC International for macromonomers prepared by the end-capping of well-established living anionic polymers prepared from monomers such as styrene and isoprene [79, 80, 44, 45].

The two approaches mentioned have been the bases for subsequent progress which has made macromonomer technique a widely applicable method for the design of a

variety of multiphase, branched polymers. The method may be expected to further increase in importance with a clear understanding and improvement in macromonomer reactivity during polymerization and copolymerization, together with unique developments in macromonomer applications.

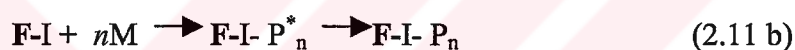
### 2.3.1 The General Synthetic Methods For Macromonomers

Basically, four methods are available (Reaction 2.11 a-d) for introducing a polymerizable functional group into a polymer chain end:

(a) End-capping (termination) of a living polymer by  $x\text{-F}$



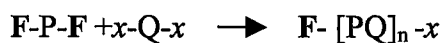
(b) Initiation of living polymerization by F-I



(c) Transformation of end-functional group



(d) Polyaddition



where **F** stands for a polymerizable group, **I** is an initiator fragment, \* is an active (living) chain end,  $x$  and  $y$  are appropriate functional groups, **M** is a monomer, **P** and **Q** are repeating monomer units, and  $n$  is the number of polymerized.

Symmetrically functionalized azo initiators are well known to afford symmetrically telechelic polymers by radical polymerization provided with that recombination or coupling is the termination mechanism as for case of styrene polymerization [81,82], although some ambiguity does remain [83,84](Reaction 2.12).



### 2.3.2. Polymerization and Copolymerization Behaviour Characteristic of Macromonomer

Macromonomer is different in its polymerization or copolymerization reactivity from a corresponding conventional monomer. Macromonomers often homopolymerize with some difficulty because of their high molecular weights as compared to lower molecular weight monomers.

### 2.4. Controlled Radical Polymerization (CRP)

Radical polymerization is a very important commercial process for preparing high molecular weight polymers because it can be used for many vinyl monomers under mild reaction conditions, requiring the absence of oxygen but tolerant to water, and large temperature ranges (-20 to 200 °C). In addition, many monomers can easily copolymerize radically leading to an infinite numbers of copolymers with properties dependent on the proportions of the comonomers. The only disadvantage of conventional radical polymerization is the poor control of macromolecular structures including degrees of polymerization, polydispersities, end functionalities, chain architectures and compositions. Thus, it is desirable to prepare by radical polymerization, new well-defined block and graft copolymers, stars, combs and networks that have not been previously prepared using ionic living polymerizations. Therefore, controlled-“living” radical polymerizations allow for the synthesis of new well-defined and functional materials from a larger range of monomers under simpler reaction conditions than are appropriate for ionic processes [85].

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

A controlled polymerization can be defined as a synthetic method for preparing polymers with predetermined molecular weights, low polydispersity and controlled functionality. Transfer and termination are allowed in a controlled polymerization if their contribution is sufficiently reduced by the proper choice of the reaction conditions such that polymer structure is not affected.

On the other hand, living polymerizations will lead to well defined polymers only if the following additional prerequisites are fulfilled:

- initiation is fast in comparison with propagation

- exchange between species of different reactivities is fast in comparison with propagation

- the rate of depropagation is low in comparison with propagation and the system is sufficiently homogeneous, in the sense of availability of active centers and mixing.

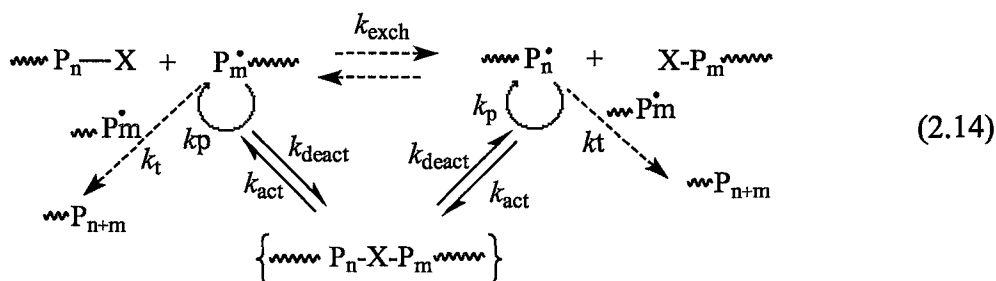
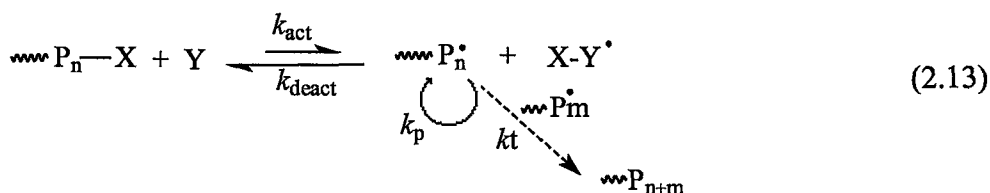
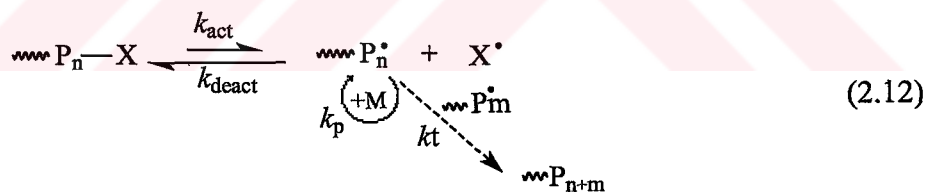
To fairly be termed as "living" a polymerization must meet all of the following criteria.

1. polymerization proceeds until all the monomer has been consumed - further addition of monomer results in continued polymerization
2. the number average molecular weight,  $M_n$  (or  $X_n$ , the number average degree of polymerization), is a linear function of conversion
3. the number of polymer molecules (and active centers) is a constant, which is sensibly independent of conversion
4. the average molecular weight of the polymer can be controlled by the stoichiometry of the reaction
5. narrow-molecular-weight distribution polymers are produced
6. block copolymers can be prepared by sequential monomer addition
7. chain-end functionalized polymers can be prepared in quantitative yield
8. linearity of a kinetic plot of rate of propagation as a function of time
9. linear dependence of the degree of polymerization as a function of time.

The past few years have witnessed the rapid growth in the development and understanding of new “controlled/living” radical polymerization (CRP) methods.[85,86] The achievement of controlled radical polymerizations is one of the most important goals in precision polymerization for polymer chemists. In recent years much effort has been put on the development of pseudo-living free radical polymerization methods. The methods at the forefront fall into one of three

categories: **atom transfer radical polymerization (ATRP)** [87], **nitroxide mediated polymerization (NMP)** or **stable free radical polymerization (SFRP)** [88] and **reversible addition-fragmentation chain transfer polymerization (RAFT)** [89].

All of the CRP methods, shown in below reactions, include activation and deactivation steps (with rate constants  $k_{act}$  and  $k_{deact}$ ), although in RAFT the scheme may be formally simplified to just the exchange process with the apparent rate constant  $k_{exch}$ . Generated free radicals propagate and terminate (with rate constants  $k_p$  and  $k_t$ ), as in a conventional free-radical polymerization. Thus, although termination occurs, under appropriate conditions its contribution will be small (less than a few percent of total number of chains) and these radical polymerizations behave as nearly living or controlled systems (Reactions 2.12-13-14).

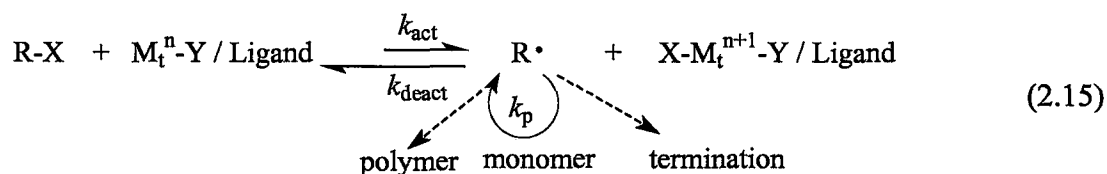


## 2.4.1 Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is one of the most convenient methods to synthesize well-defined low molecular weight polymers [85, 87].

Previously, radical reactions had found limited application in organic synthesis due to the low yields of desired addition and substitution products caused by radical termination reactions. The usefulness of these reactions increased dramatically after discovery that persistent radicals could be used to reduce the stationary concentration of reacting radicals and thereby minimize the contribution of termination. Of the methods developed based on this concept, one of the most useful is atom transfer radical addition (ATRA), so named because it employs atom transfer from an organic halide to a transition-metal complex to generate the reacting radicals, followed by back-transfer from the transition metal to a product to a product radical to form the final product [85,87,90].

Atom transfer radical addition can be extended to ATRP if the conditions can be modified such that more than one addition step is possible. An ATRP system consists of an initiator, a copper (I) halide complexed with some ligand (s), and of course, monomer. ATRP occurs as a repetitive addition of a monomer to a growing radical generated from dormant alkyl halides by a reversible redox process catalyzed by transition metal compounds complexed by amine ligand. If the radical species before and after addition of the unsaturated substrate (monomer) possess comparable stabilization, then the activation-addition-deactivation cycle will repeat until all of the unsaturated substrate present is consumed. This process results in a chain-growth polymerization (Reaction 2.15) [87,90].

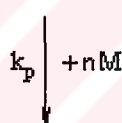
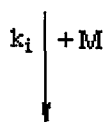
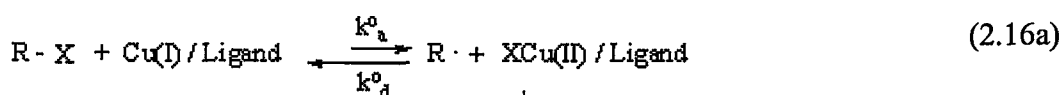


### 2.4.1.1 Mechanism and Kinetics of ATRP

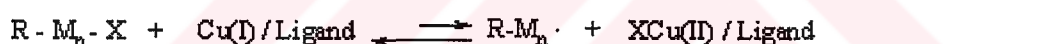
The general mechanism of ATRP which is schematically represented in (Reaction 2.16a-d), involves the abstraction of a halogen from the dormant chain by a metal center, such as complexes of  $\text{Cu}^1$ , in a redox process [85]. Upon halogen abstraction,

the free radical formed (the active species) can undergo propagation. However, the free-radical is also able to abstract the halogen back from the metal, reproducing the dormant species. These processes are rapid, and the equilibrium that is established favors the dormant species. By this way, all chains can begin growth at the same time, and the concentration of free radicals is quite low, resulting in a reduced amount of irreversible radical-radical termination. The final result is that degrees of polymerization (DP) can be predetermined ( $DP = \Delta [M] / [I]_0$ ) and  $M_w/M_n$  is quite low (1, 05-1, 5), and good control of functionalities is achieved [91].

Initiation



Propagation



Termination



The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction is usually negative first order with respect to the deactivator ( $CuX_2/Ligand$ ).

$$R_p = k_{app}[M] = k_p [P\cdot] [M] = k_p K_{eq} [I]_0 \frac{[Cu(I)] [M]}{[Cu(II)X]} \quad (\text{Equation 2.1})$$

The equilibrium constant ( $K_{eq}$ ) depends on the monomer used, for example, in the bulk polymerization of styrene at 110 °C using R-Br and CuBr/dNbpy the equilibrium constant is approximately  $K_{eq} = k_{act}/k_{deact} = 4 \times 10^{-8}$  [92,93].

ATRP is a multi-component system, so concentrations and the structures of all these compounds affect the polymerization rate and the properties of the resulting polymer. For each particular ATRP, a specific initiator, metal, ligands, deactivator, temperature, reaction time and solvent should be selected [85].

#### 2.4.1.2 Components Used in ATRP

##### a) Monomers

Various monomers have been successfully polymerized using ATRP: styrenes, (meth) acrylates, (meth)-acrylamides, dienes, acrylonitrile and other monomers which contain substituents that can stabilize the propagating radicals. Ring-opening polymerization is also possible [87]. The currently used catalyst systems are not sufficient to polymerize less reactive monomers that produce non-stabilized, reactive radicals such as ethylene,  $\alpha$ -olefins, vinyl chloride and vinyl acetate, though copolymerization is sometimes successful [85].

The most commonly used monomers in ATRP are styrenes and MMA.

**(i) Styrene:** Styrene ATRP is usually conducted at 110 °C for bromide-mediated polymerization and 130 °C for the chloride-mediated polymerization [94]. Generally, bulk system is preferred. Solvents may be used for styrene ATRP and nonpolar solvents are recommended.

Well-defined polystyrenes can be prepared with the molecular weight range of 1000 to 90000. In the region from 1000 to 30000, polydispersities ( $M_w/M_n$ ) are less than 1.10 and above 30000 polydispersities increase to within the range of 1.10 to 1.50 due to some side reactions, predominantly HX elimination. These side reactions can be reduced at lower polymerization temperatures [85].

**(ii) Methyl methacrylate:** The standard conditions for MMA ATRP are similar to those of styrene ATRP except that less copper(I) catalyst is needed and the polymerizations are conducted in 50% solution in diphenyl ether or dimethoxy benzene at 90 °C. The use of copper bromide instead of copper chloride leads to more rapidly decreasing polydispersities. This is due to the better efficiency of bromine in the deactivation step. The polymerization is also less controlled when bpy is used instead of dNbpy due to the correspondingly smaller concentration of deactivator.

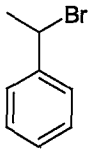
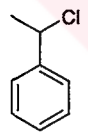
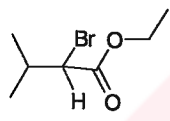
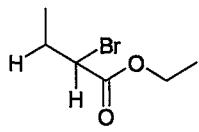
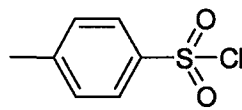


Well-defined poly (methyl methacrylate) has been prepared within the molecular weight range of 1000 to 180000. In the region from 1000 to 90000 the polydispersities are less than 1.10 and above 90000 the polydispersities fall within the range of 1.10 to 1.50 [85].

## b) Initiators

The most frequently used initiator types in ATRP systems are given in Table 2.2.

Table 2.2. Types of initiators used in ATRP systems

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 2-Bromo ethylisobutyrate	Methylmethacrylate
 2-Bromo ethyl propionate	Methylacrylate and other acrylates
 p-toluene sulphonyl chloride	Methylmethacrylate

In general, any alkyl halide with activating substituents on the  $\alpha$ -carbon, such as aryl, carbonyl and allyl groups, potentially can be used as ATRP initiators. Polyhalogenated compounds ( $\text{CCl}_4$  and  $\text{CHCl}_3$ ) and compounds with a weak R-X bond, such as N-Y, S-X and O-X presumably also can be used as ATRP initiators. There is however, an upper limit to the stability of the initiating radicals beyond

which it also becomes an inefficient initiator. For example, trityl halides are poor initiators for ATRP [90].

### c) Transition Metals

Basic requirements for good catalyst are high selectivity towards atom transfer process and high lability of the resulting  $X-M_t^{n+1}$  species (higher oxidation state of metal). The metal should participate in a one-electron process which would result in oxidative addition/reductive elimination but not in atom transfer process. Additionally, the metal should have a high affinity for atom/group X, but a low affinity for hydrogens and alkyl radicals. Otherwise, transfer reactions ( $\beta$ -hydrogen elimination) and the formation of organometallic derivatives may be observed reducing selectivity of propagation and control (livingness) of process. The most important factors in selecting good ATRP catalyst are the equilibrium position, dynamics of exchange between dormant and active species. These parameters are related to the redox cycle  $M_t^n/M_t^{n+1}$  but it must be remembered that ATRP is not an electron transfer process but an atom transfer process. Thus, the inner coordination sphere of  $M_t^n$  must expand to accommodate a new X (halide) ligand. Expansion from tetra to pentacoordinated structure  $Cu(I)/2 \text{ ligand} \rightarrow X-Cu(II)/2 \text{ ligand}$  or pentacoordinated structure  $X_2Fe(II)/3PR_3 \rightarrow X_3Fe(III)/3PR_3$  must be possible. The most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, Ni(II), Ru(II)/Al(OR)<sub>3</sub> and Fe(II)/3 PR<sub>3</sub> [92,93].

### d) Ligands

The position of the atom transfer equilibrium depends upon the nature of the metal and ligands. Generally, more electron donating ligands stabilize better the higher oxidation state of the metal and accelerate the polymerization [90]. Ligands that sterically crowd the metal center prevent the approach of the alkyl halide initiator or end group and therefore are poor ligands for ATRP [85].

The most widely used ligands for ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as N,N,N',N'',N'' pentamethyldiethylenetriamine (PMDETA), Tetramethylethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetraamine (HMTETA), tris[2-(dimethylamino)ethyl]amine (Me<sub>6</sub>-TREN) and alkylpyridylmethaneimines are also used. Examples of ligands used in copper-mediated ATRP are shown in below (Figure 2.5) [95, 96].

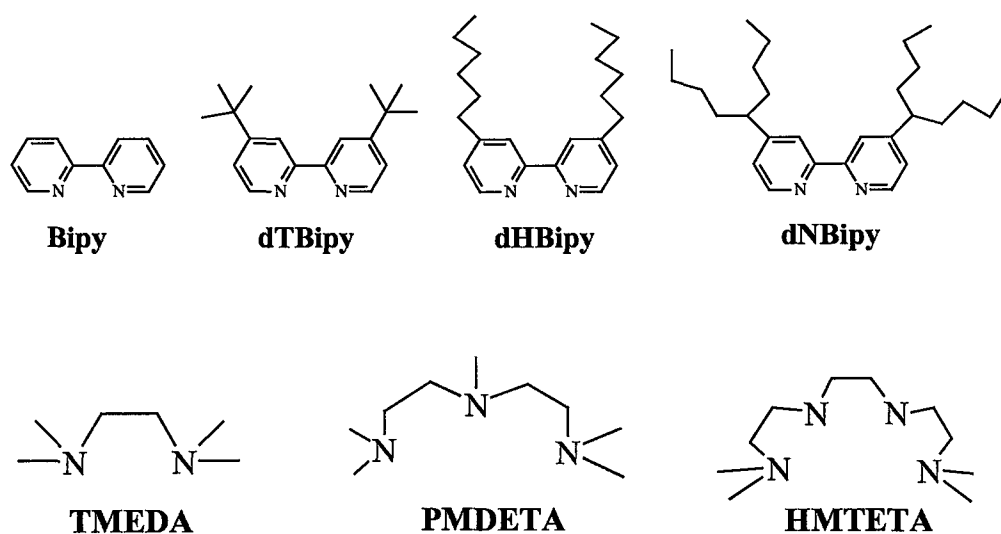


Figure 2.5. Some of the most frequently used ligands.

### e) Deactivators

The deactivator plays a vital role in ATRP in reducing the polymerization rate and the polydispersity of the final polymer. In the limit that the rate of deactivation is too slow or does not occur, and then ATRP simply becomes a redox initiated polymerization. For copper-catalyzed ATRP, the deactivator is the corresponding copper (II) halide complex (e.g.  $2\text{dNBpy}/\text{CuX}_2$ ) [90].

In most systems the concentration of deactivator continuously, but slowly, increases due to slow termination by radical coupling [90].

*As a conclusion*, ATRP is robust polymerization system that can polymerize a wide variety of monomers including styrenes, methacrylates, acrylates and acrylonitrile. The reaction conditions are not stringent because only the absence of oxygen is required to conduct the polymerizations. The polymer end groups can be transformed to other functional groups, such as amines and a range of polymers with different architectures and compositions can be prepared by relatively simple means. The combination of synthetic versatility and simplicity makes ATRP a powerful technique for use in designing and preparing new and unusual materials [90].

## 2.5 Controlled Ring-Opening Polymerization

Aliphatic polyesters are an attractive class of polymer that can be used in biomedical and pharmaceutical applications. One reason for the growing interest in this type of

degradable polymer is that their physical and chemical properties can be varied over a wide range by, e.g., copolymerization and advanced macromolecular architecture. The synthesis of novel polymer structures through ring-opening polymerization has been studied for a number of years. The development of macromolecules with strictly defined structures and properties, aimed at biomedical applications, leads to complex and advanced architecture and a diversification of the hydrolysable polymers.

Degradable materials with new mechanical properties and modified degradation profiles have been produced and characterized. The increasing demands of a larger number of biomedical applications have resulted in an increasing interest in producing macromolecules through controlled polymerization.

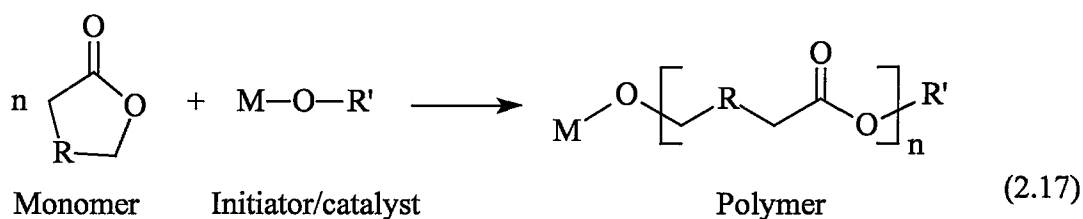
### **2.5.1 Ring-Opening Polymerization (ROP)**

Polylactones and polylactides can be prepared by two different approaches, by the polycondensation of hydroxycarboxylic acids or by the ring-opening polymerization (ROP) of cyclic esters. The polycondensation technique is less expensive than ROP, but it is difficult to obtain high molecular weight polymers, to achieve specific end groups, and to prepare well-defined copolyesters.

There are several reasons for studying the polymerization of cyclic esters. First, to exploit the potential of synthetic polymer chemistry to prepare a variety of polymers with control of the major variables affecting polymer properties. Experimental conditions have to be optimized in order to find the best polymerization system for a desired technological or industrial process. Factors such as economy, toxicology, and technical apparatus development are important. A second reason for studying ROP is to enable various advanced macromolecules, including homopolymers with well-defined structures or end groups, to be prepared, as well as copolymers with different architectures, e.g., block, graft, or star copolymers. The physical, mechanical, and degradation properties of these various macromolecules are studied to determine the structure-to-property relationship. The third reason for studying these kinds of systems is that they are valuable models for the examination of the kinetics [97] mechanisms [98] of elementary reactions in polymerization.

## 2.5.2 Ring-Opening Polymerization of Cyclic Esters

Poly lactones and poly lactides of high molecular weight are exclusively produced by the ROP of the corresponding cyclic monomers. A polyester is formed when cyclic esters are reacted with a catalyst or initiator. Reaction 2.17 presents the reaction pathway for the ROP of a cyclic ester.



R = (CH<sub>2</sub>)<sub>0-3</sub>, M = Metal

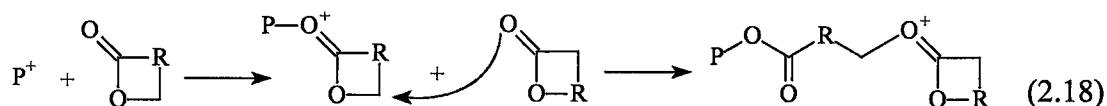
Each macromolecule formed generally contains one chain end terminated with a functional group originating from the termination reaction and one terminus end capped with a functional group originating from the initiator. By altering the catalyst or initiator and the termination reaction, the nature of the functional groups can be varied to fit the application of the polymer. The types of initiator and end group play important roles in determining both the thermal stability and hydrolytic stability of the resulting polyester [99]. Functional groups accessible to post-polymerization reactions can also be introduced into the polymer structure in this way.

The ring-opening reaction can be performed either as a bulk polymerization, or in solution, emulsion, or dispersion. A catalyst or initiator is necessary to start the polymerization. Under rather mild conditions, high-molecular weight aliphatic polyesters of low polydispersity can be prepared in short periods of time. Problems associated with condensation polymerization, such as the need for exact stoichiometry, high reaction temperatures, and the removal of low molecular weight by-products (e.g., water) are excluded in ROP.

Depending on the initiator, the polymerization proceeds according to three different major reaction mechanisms [100], *viz.*, cationic, anionic, or “coordination-insertion” mechanisms [101-103]. In addition, radical, zwitterionic [104], or active hydrogen [100] initiation is possible, although such techniques are not used to any great extent. Here we focus on the “coordination-insertion” mechanism and the other methods are described only briefly.

### 2.5.2.1 Cationic Ring-Opening Polymerization

Among the cyclic esters, 4-, 6-, and 7- membered rings form polyesters when reacted with cationic catalysts [100]. The cationic ROP involves the formation of a positively charged species which is subsequently attacked by a monomer (reaction 2.18). The attack results in a ring-opening of the positively charged species through an  $S_N^2$ -type process.

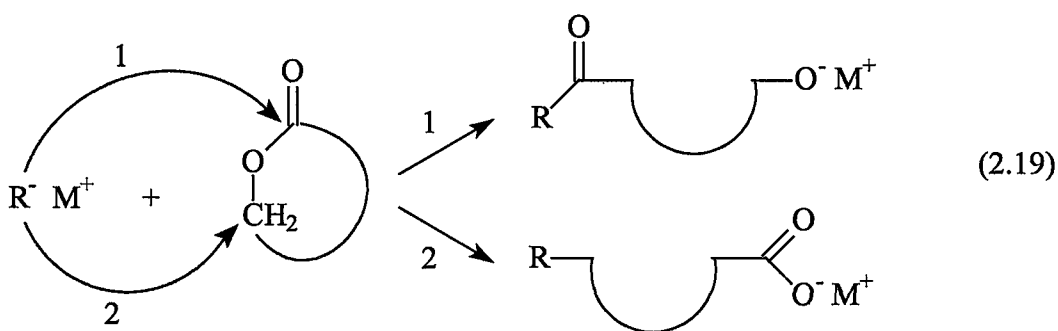


P= Polymer

The cationic polymerization is difficult to control and often only low-molecular weight polymers are formed. When the bulk and solution polymerization of 1,5-dioxepan-2-one (DXO) with cationic initiators were studied, the highest molecular weight achieved was about 10,000. More detailed reviews on cationic ROP have been published by Penczek and coworkers [105,106].

### 2.5.2.2 Anionic Ring-Opening Polymerization

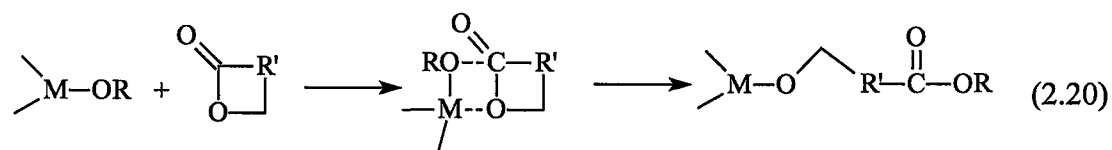
Anionic ROP of cyclic ester monomers takes place by the nucleophilic attack of a negatively charged initiator on the carbonyl carbon or on the carbon atom adjacent to the acyl oxygen, resulting in linear polyester. Reaction 2.19 shows the reaction pathway for the ROP of a cyclic ester by anionic initiation, ring-opening of monomer by 1) acyl-oxygen bond cleavage and 2) alkyl-oxygen bond cleavage [107]. The propagating species is negatively charged and is counter-balanced with a positive ion. Depending on the nature of the ionic propagating chain end and the solvent, the reacting complex varies from completely ionic to almost covalent.



One of the best controlled methods leading to high molecular weight polymers is anionic polymerization carried out in a polar solvent. The Jedlinski group developed living anionic ROP methods for 4- and 5-membered ring lactones and has reported well-defined polymers and copolymers of high molecular weight [108]. The anionic ring-opening of four-membered rings ( $\beta$ -lactones) occurs through alkyl-oxygen or acyl-oxygen cleavage giving a carboxylate or alkoxide. Larger lactones, such as  $\epsilon$ -caprolactone ( $\epsilon$ -CL) or lactide, react only by an attack of the anion on the carbonyl carbon atom with acyl-oxygen scission and the formation of an alkoxide as the growing species. A problem associated with the anionic ROP is the extensive back-biting, and in some cases only polyesters of low molecular weight are achieved.

### 2.5.2.3 Coordination-Insertion Ring-Opening Polymerization

The pseudo-anionic ROP is often referred to as coordination-insertion ROP, since the propagation is thought to proceed by coordination of the monomer to the active species, followed by insertion of the monomer into the metal-oxygen bond by rearrangement of the electrons [101,102]. Reaction 2.20 shows a schematic presentation of the proposed reaction pathway for the ROP of a cyclic ester by the coordination-insertion mechanism. The growing chain remains attached to the metal through an alkoxide bond during the propagation. The reaction is terminated by hydrolysis forming a hydroxy end group. With functional alkoxy-substituted initiators, macromers with end groups active in post-polymerization reactions are produced.



The coordination-insertion type of polymerization has been thoroughly investigated since it may yield well-defined polyesters through living polymerization [102]. When two monomers of similar reactivity are used, block copolymers can be formed by sequential addition to the "living" system.

### 2.5.3 Initiators for the ROP of Lactones and Lactides

The synthesis of novel initiators and the ROP of existing or new monomers and macromers substituted with functional groups provide a very interesting and promising strategy for producing structurally advanced macromolecules.

A large variety of organometallic compounds, e.g., metal alkoxides and metal carboxylates, has been studied as initiators or catalysts in order to achieve effective polymer synthesis [109]. Many reactions catalyzed by metal complexes are highly specific and, by careful selection of metal and ligands, reactions can be generated to form a desired polymer structure. The covalent metal alkoxides with free *p* or *d* orbitals react as coordination initiators and not as anionic or cationic initiators. Figure 2.6 shows some of the most frequently used initiators and catalysts used in ROP of lactones. a) stannous octoate and b) aluminum isopropoxide

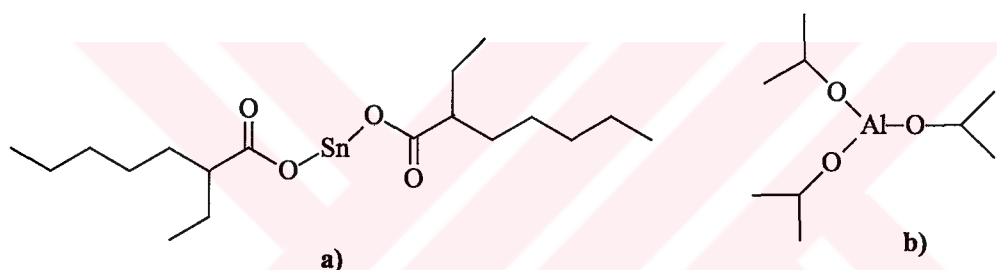
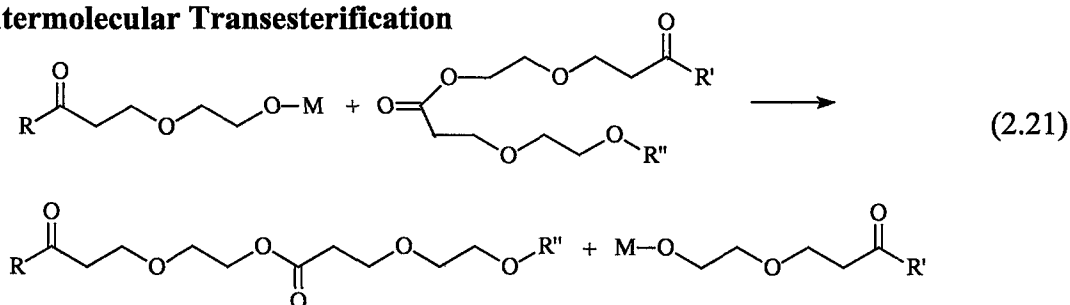


Figure 2.6 Some of the most frequently used initiators.

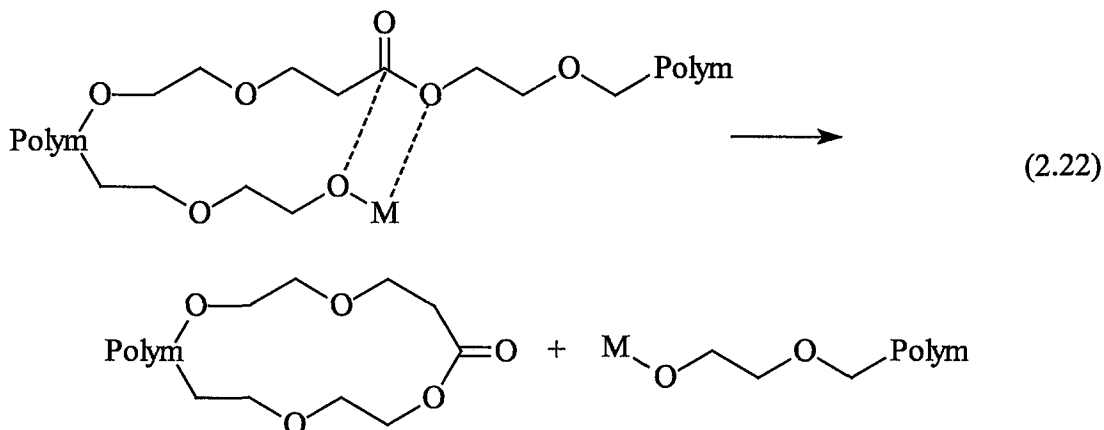
It is well known from the ROP of lactones and lactides that the catalyst or initiator causes transesterification reactions at elevated temperatures [110], or at long reaction times (reactions 2.21 and 2.22) [111].

#### Intermolecular Transesterification





### Intramolecular Transesterification (back-biting)



Intermolecular transesterification reactions modify the sequences of copolyesters and prevent the formation of block co-polymers. Intramolecular transesterification reactions, i.e., back-biting, cause degradation of the polymer chain and the formation of cyclic oligomers. Both types of transesterification reaction broaden the molecular weight distribution (MWD).

As displayed in the proposed scheme, each intramolecular transesterification randomly breaks the polymer chain. In this way, an attack on the polymer chain leads to a free residual polymer and a new randomized, modified polymer. Consequently, an original copolymer with a block-like structure would be converted to a randomized copolymer after undergoing  $n$  transesterifications.

Parameters that influence the number of transesterifications are temperature, reaction time, and type and concentration of catalyst or initiator [112]. Depending on the metal used, the initiator is more or less active towards side-reactions such as transesterification reactions [112]. The relative reactivity of different metal alkoxide initiators towards chains already formed has been reported to be:

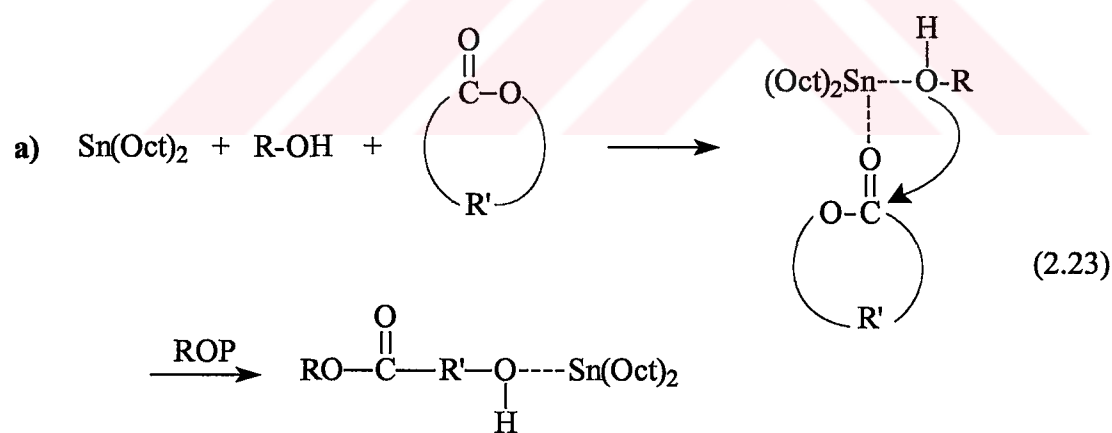


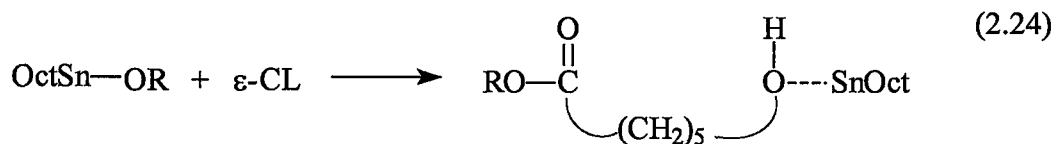
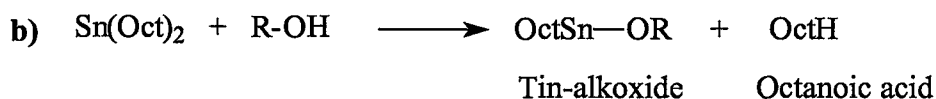
#### *a) Tin (II) 2-Ethylhexanoate*

Tin (II) 2-ethylhexanoate, commonly referred to as stannous octoate  $[\text{Sn}(\text{Oct})_2]$ , is a frequently used catalyst in the ROP of lactones and lactides [113].  $\text{Sn}(\text{Oct})_2$  has been approved as a food additive by the American Food and Drug Administration (FDA). The mechanism of polymerization has been widely discussed. Despite several

proposals [114] over a long period of time, it is not until now that the ROP mechanism is about to be elucidated [115,116]. The  $\text{Sn}(\text{Oct})_2$  is not thought to be the actual initiator since the molecular weight does not depend on the monomer-to- $\text{Sn}(\text{Oct})_2$  molar ratio. The most promising mechanism is a “coordination-insertion” mechanism where a hydroxy functional group is thought to coordinate to  $\text{Sn}(\text{Oct})_2$ , forming the initiating tin alkoxide complex.

Investigations of the coordination-insertion mechanism have resulted in two slightly different reaction pathways. Kricheldorf and coworkers have proposed a mechanism [116] where the co-initiating alcohol functionality and the monomer are both coordinated to the  $\text{Sn}(\text{Oct})_2$  complex during propagation. Penczek and coworkers have presented a mechanism [115] where the  $\text{Sn}(\text{Oct})_2$  complex is converted into a tin alkoxide before complexing and ring-opening of the monomer. Direct observation of this tin-alkoxide complex has been reported by using MALDI-TOF spectroscopy for both lactide [115] and  $\epsilon$ -CL polymerization. Reactions 2.23 and 2.24 show the two different proposals. The main ROP mechanism proposals with  $\text{Sn}(\text{Oct})_2$  as catalyst, a) complexation of a monomer and alcohol prior to ROP and b) formation of a tin-alkoxide before ROP of CL





The Sn (Oct)<sub>2</sub> catalyst is a strong transesterification agent, and the resulting copolymers normally have a randomized microstructure [111]. An increase in reaction temperature or reaction time increases the amount of transesterification reactions.

The ROP of lactide with Sn(Oct)<sub>2</sub> is fairly slow and it is desirable for economic and commercial reasons to increase the rate of polymerization. The addition of an equimolar amount of triphenylphosphine increases the rate and, as an additional advantage, this compound delays the occurrence of the undesirable back-biting reactions.

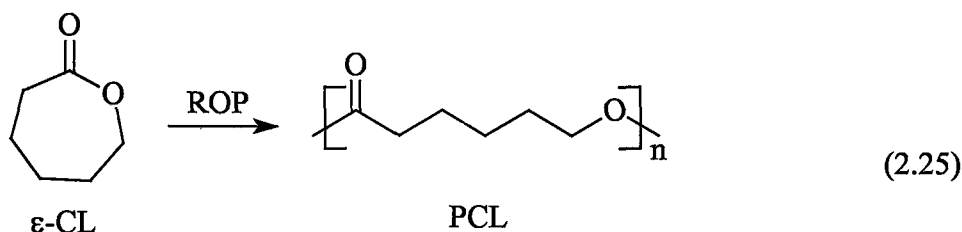
**b) Aluminum Tri-Isopropoxide**

**c) Tin (IV) Alkoxides**

**d) Tin (II) Alkoxides**

**2.5.4 Poly(ε -Caprolactone) and Copolymers**

Poly(ε-CL) has been investigated thoroughly because of the possibility of blending this aliphatic polyester with a number of commercial polymers such as PVC and bisphenol A polycarbonate. It is of interest as a packaging material and in biomedical applications since it is degradable and its degradation products are non-toxic. Reaction 2.25 shows the monomer (ε-CL) structure and the resulting repeating unit.



The poly( $\epsilon$ -CL) material has a long degradation time, which is usually a disadvantage in medical applications. The in vivo degradation of poly(D-LA) was 2.8 times faster than that of the poly( $\epsilon$ -CL) chain cleavage under the same conditions [117]. Different approaches have been used to copolymerize  $\epsilon$ -CL to increase the degradation rate. Copolymers of  $\epsilon$ -CL and D-LA of all compositions degraded much more rapidly than their component homopolymers [117]. This observation has been attributed to morphological differences, specifically a reduction in crystallinity and a lowering of the glass transition temperature.

Random copolymers of  $\epsilon$ -CL with 1,5-dioxepan-2-one (DXO) have been investigated [118]. The copolymers were crystalline up to a DXO content of 40%, and it was concluded that the DXO units were incorporated into the poly( $\epsilon$ -CL) crystals. The block copolymerization has also been investigated and the resulting material was shown to exhibit thermoplastic elastomeric properties [119].

In conclusion, a number of architectures may be produced as a result of the great versatility of the ROP of cyclic esters. Different strategies have been applied for the design of new polymeric materials. A careful selection of the appropriate initiator or catalyst for ROP of a specific system is crucial. The broad range of initiators and catalysts offer different advantages and possibilities. Sn(Oct)<sub>2</sub> is rather easy to use, but it is also a strong transesterification catalyst and it cannot therefore be recommended for the synthesis of advanced molecular structures.

For living ROP with the ability to control molecular architecture and weight, aluminum alkoxides can be used, the propagation being characterized by the almost total absence of side-reactions. The reaction is usually performed in solution at low temperatures. The sensitivity towards hydrolysis is however a limitation.

Tin alkoxides, on the other hand, are less sensitive to hydrolysis and can be used for controlled ROP and the synthesis of macromolecules with advanced architecture (tri-block, star, or comb polymers). Cyclic tin alkoxides offer a convenient pathway for tri-block copolymerization.

Lanthanide-based initiator systems offer a fourth possibility, permitting the block copolymerization of lactones with compounds such as ethylene, tetrahydrofuran, L-LA, trimethylene carbonate, and methyl methacrylate. Detrimental side reactions

such as macrocyclic formation, transesterification, and racemization are absent and the reactions are extremely fast.

## 2.6 Photoinitiated Polymerization

When polymerizations are initiated by light and both the initiating species and the growing chain ends are radicals, we speak of *radical photopolymerization*. As for other polymerizations, molecules of appreciably high molecular weight can be formed in the course of the chain reaction. Playing the predominant role in technical polymer synthesis, vinyl monomers can be mostly polymerized by a radical mechanism. Exceptions are vinyl ethers, which have to be polymerized in an ionic mode. Light induced *ionic* polymerization has been reviewed elsewhere [120,121].

Regarding initiation by light it has to be pointed out that the *absorption* of incident light by one or several components of the polymerization mixture is the crucial prerequisite. If the photon energy is absorbed directly by a photosensitive compound, being it monomer itself or an added initiator, this photosensitive substance undergoes a homolytic bond rupture forming radicals, which may initiate the polymerization. In some cases, however, the photon energy is absorbed by a compound that itself is not prone to radical formation. These so called sensitizers transfer their electronic excitation energy to reactive constituents of the polymerization mixture, which finally generate radicals. The radicals evolved react with intact vinyl monomer starting a chain polymerization. Under favorable conditions, a single free radical can initiate the polymerization of a thousand molecules. The spatial distribution of initiating species may be arranged in any desired manner.

Light induced free radical polymerization is of enormous commercial use. Techniques such as curing of coatings on wood, metal and paper, adhesives, printing inks and photoresists are based on photoinitiated radical vinyl polymerization. There are some other interesting applications including production of laser video discs and curing of acrylate dental fillings.

In contrast to thermally initiated polymerizations, photopolymerization can be performed at room temperature. This is a striking advantage for both classical polymerization of monofunctional monomers and modern curing applications. Photopolymerization of monofunctional monomers takes place without side reactions

such as chain transfer. In thermal polymerization, the probability of chain transfer is high which brings about a high amount of branched macromolecules. Hence, low-energy stereospecific polymeric species, namely of syndiotactic configuration, may be obtained by photopolymerization. Another important use refers to monomers with low ceiling temperature. They can only be polymerized at moderate temperatures, otherwise depolymerization dominates over polymerization. By means of photopolymerization these monomers are often easily polymerizable. Furthermore, biochemical applications, such as immobilization of enzymes by polymerization, do also usually require low temperatures. As far as curing of coatings or surfaces is concerned it has to be noted, that thermal initiation is often not practical, especially if large areas or fine structures are to be cured or if the curing formulation is, like for dental fillings, placed in a surrounding that should rather not be heated.

Radical photopolymerization of vinyl monomers played an important role in the early development of polymerization. One of the first procedures for polymerizing vinyl monomers was the exposure of monomer to sunlight. Blyth and Hoffman [122] reported on the polymerization of styrene by sunlight more than 150 years ago.

Photocurable formulations are mostly free of additional organic solvents; the monomer, which serves as reactive diluent, is converted to solid, environmentally safe resin without any air pollution. UV curing is often a very fast process, taking place as pointed out above without heating. If the polymerization mixture absorbs solar light and the efficiency of radical formation is high, photocuring can be performed with no light source but sun light. These features make photopolymerization an ecologically friendly and economical technology that has high potential for further development.

### **2.6.1 Photoinitiated Free Radical Polymerization**

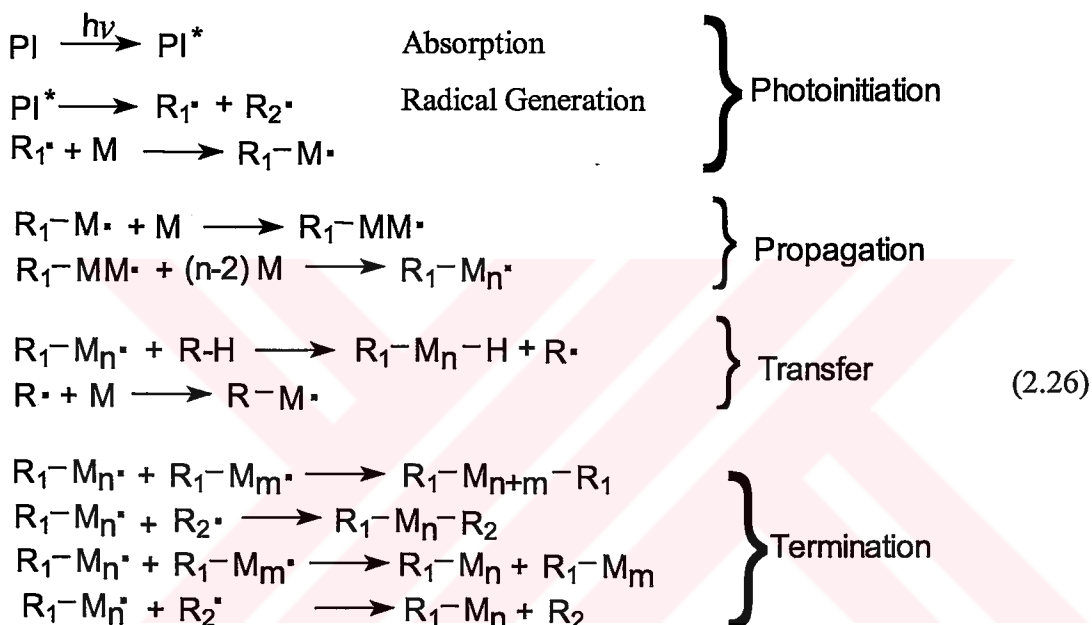
Photoinitiated free radical polymerization consists of four distinct steps:

- 1) **Photoinitiation:** Absorption of light by a photosensitive compound or transfer of electronic excitation energy from a light absorbing sensitizer to the photosensitive compound. Homolytic bond rupture leads to the formation of a radical that reacts with one monomer unit.
- 2) **Propagation:** Repeated addition of monomer units to the chain radical produces the polymer backbone.

3) **Chain transfer:** Termination of growing chains by hydrogen abstraction from various species (e.g., from solvent) and concomitant production of a new radical capable of initiating another chain reaction.

4) **Termination:** Chain radicals are consumed by disproportionation or recombination reactions. Termination can also occur by recombination or disproportionation with any other radical including primary radicals produced by the photoreaction.

These four steps are summarized in reactions 2.26.



Notably, the role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating radicals. The reaction of these radicals with monomer, propagation, transfer and termination are purely thermal processes; they are not affected by light. Since in this chapter the genuine photochemical aspects are to be discussed, propagation, transfer and termination reactions are not depicted as long as it is not necessary for the understanding of a reaction mechanism. Instead, the photochemically produced initiating species are highlighted by a frame.

## 2.6.2 Photoinitiated Cationic Polymerization

During the past decade photoinitiated polymerization have received considerable attention and practically applied in variety of areas, including printing inks, adhesives, surface coatings, microelectronics and printing plates [121,123,124-127].

The advantages of photoinitiated polymerization over conventional thermal polymerization lie in the high speed reaction at ambient temperature, low energy consumption and solvent free formulation. Photoinitiated polymerization is typically a process that transforms a monomer into polymer by a chain reaction initiated by reactive species (free radicals or ions) which are generated by UV irradiation.

Much effort has been devoted to free radical systems [121,126] mainly due to the availability of a wide range of photoinitiators and the great reactivity of acrylate-based monomers. Despite the most popular industrial application based on the photoinitiated free radical photopolymerization there are some drawbacks associated with this type polymerization such as the inhibition effect of oxygen and post-cure limitations which may affect the properties of the final product. UV initiated cationic polymerization holds considerable promise in future, particularly as a means of overcoming volatile emission, toxicity and molecular oxygen inhibition limitations.

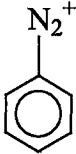
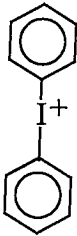
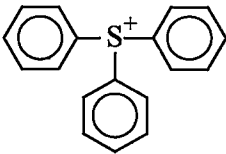
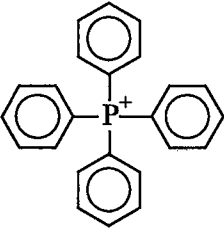
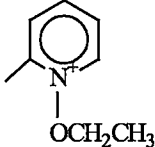
Although the cationic polymerization exhibits several advantages it has not as yet achieved the commercial significance of radical polymerization in UV curing applications. This was mainly because of the limited choice of the cationic photoinitiators and monomers that were commercially available until recently. This situation changed with two significant improvements. First, cationically polymerizable important classes of monomers such as vinyl ethers and epoxides became commercially available. Second, a new class of cationic photoinitiators with non-nucleophilic counter ions such as  $\text{SbF}_6^-$  and  $\text{AsF}_6^-$  has been utilized [128].

Since the photoinitiator is one of the most important part of a UV initiated polymerization, many research efforts have been devoted to understand what type of photoinitiators is applicable to generate cations. Among the various types of photoinitiators that can lead to the formation of cation as a result of UV light induced fragmentation, onium salts have found considerable application in UV curing and photorezist technology.

Onium salts are the most widely used cationic photoinitiators. These salts are compounds containing heteroatoms, with a cationic center on the heteroatom. As counterions, mostly inorganic metal complex anions are used. The onium salts depicted in Table 2.3 were used for light induced cationic polymerization.



Table 2.3. Onium Salts for Externally Stimulated Cationic Polymerization

				
Aryl diazonium salt	Iodonium salt	Sulphonium salt	Phosphonium salt	N-alkoxy pyridinium salt

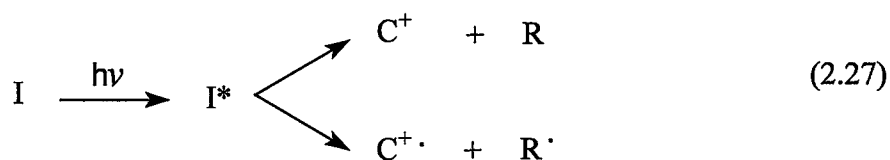
The polymerization by onium salts does generally start only after an external stimulation such as irradiation or heating. However, in a few cases dark polymerizations at room temperature have been observed [129].

The photochemistry of these novel classes of photoinitiators is well documented [121,123,124-127]. Onium salts used in cationic photopolymerization mainly absorb the wavelengths of light between 225 and 350 nm [124,128,130,131]. Alkoxy pyridinium salts are also treated as onium salts since the chemistry of these salts resembles that of classical onium salt initiators, such as iodonium and sulphonium salts.

The photoinitiator (onium salt) can form a cation directly upon irradiation or the generation of a cation can depend upon the interaction of a sensitizer and a photoinitiator. This latter process is termed indirect excitation of the photoinitiator (indirect photolysis).

### 2.6.2.1 Direct Photolysis

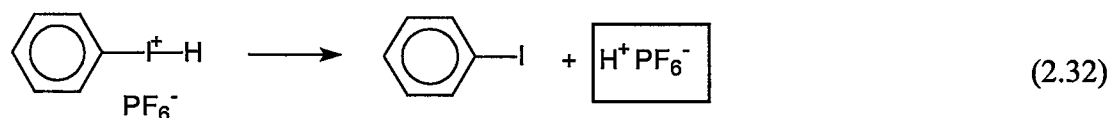
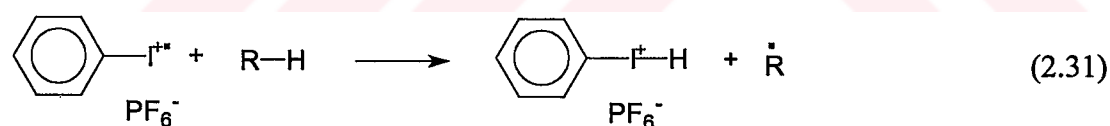
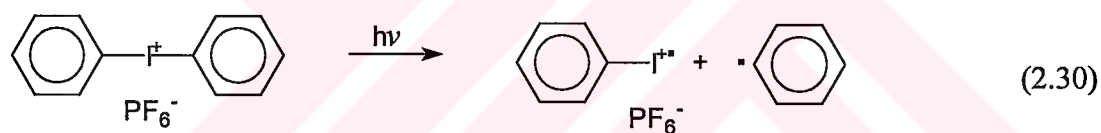
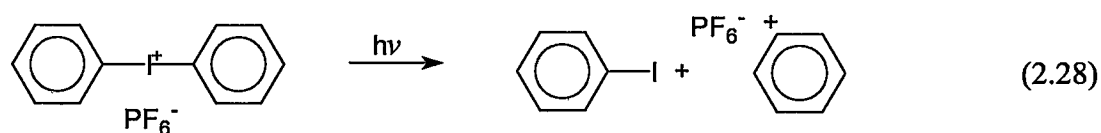
If onium salt initiators I absorb light, electronically excited initiator I\* species are produced. The latter undergo a heterolytical or homolytical bond rupture leading to cations C<sup>+</sup> or radical cations C<sup>+·</sup>, respectively (Reaction 2.27).



In some cases, these entities are able to react directly with monomer molecules starting a cationic polymerization. Frequently, C<sup>+</sup> or C<sup>+·</sup> is inert towards the

cationically polymerizable monomer in the manner necessary for initiating the polymerization. This often observed lack in reactivity is mostly explainable in terms of bulkiness of the species  $C^+$  and  $C^{+\cdot}$  produced in the primary reaction. However, both  $C^+$  and  $C^{+\cdot}$  are often able to react with the monomer or solvent molecules thus releasing the Brønsted acid  $H^+$ . Being highly reactive to all sorts of cationically polymerizable monomers, protons will act as initiating species in these circumstances.

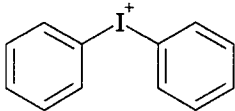
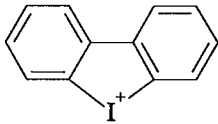
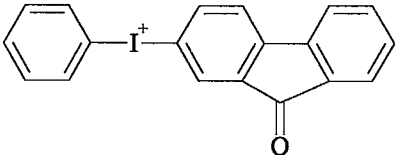
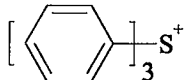
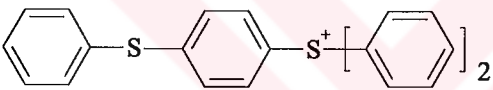
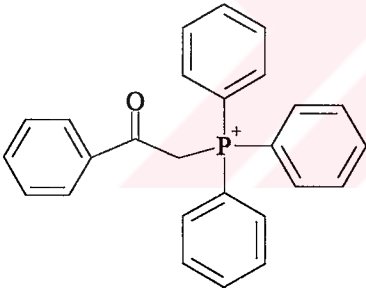
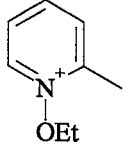
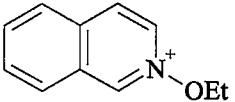
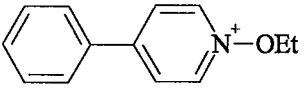
The mechanism of onium salt initiation is depicted on the example of diphenyliodonium hexafluorophosphate (Reactions 2.28-32)



### 2.6.2.2 Photosensitization of Cationic Polymerization (Indirect Photolysis)

For practical applications, onium salts should absorb light appreciably at wavelengths longer than 350 nm. where the commercially available medium and high pressure mercury lamps emit much of their radiation. Since this requirement is not fulfilled for certain easily available onium salts several systems were developed to extend the applicability of the onium salt photoinitiators.

Table 2.4. UV Absorption Characteristics of Selected Onium Salts

Cation	Anion	$\lambda_{\text{max}}$ (nm)	$\epsilon_{\text{max}}$ (l mol <sup>-1</sup> cm <sup>-1</sup> )
	BF <sub>4</sub> <sup>-</sup>	227	17800
	AsF <sub>6</sub> <sup>-</sup>	264	17300
	AsF <sub>6</sub> <sup>-</sup>	366	745
	AsF <sub>6</sub> <sup>-</sup>	227	21000
	PF <sub>6</sub> <sup>-</sup>	230 300	24330 19500
	SbF <sub>6</sub> <sup>-</sup>	257	32000
	PF <sub>6</sub> <sup>-</sup>	266	5925
	PF <sub>6</sub> <sup>-</sup>	337	4220
	PF <sub>6</sub> <sup>-</sup>	310	21440

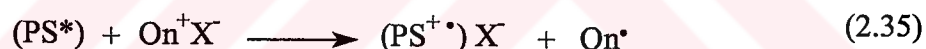
In these case additives are present which participate in the reaction sequence to yield reactive species capable of initiating the cationic polymerization. In the following

sections depending on the role played by the additives in the initiation of the polymerization three modes of indirect initiation will be discussed.

Photosensitization is very attractive way to initiate cationic polymerization since the triggering of the initiation may be extended to much longer wavelengths where the photoinitiator is transparent and photosensitizers such as heterocyclic and polynuclear aromatic compounds absorb the incident light. Photosensitization is considered as an energy transfer process which occurs from the excited photosensitizer molecule (PS\*) to the ground state photoinitiator (PI) producing the excited state of the latter.



However, in many cases, photoinduced decomposition of the cationic photoinitiator was observed via electron transfer since most onium salts are capable of oxidizing these sensitizers in exciplex formed between sensitizer and onium salt.



Depending upon the two components involved the photosensitization can occur through energy transfer or electron transfer. The basic requirement for the energy transfer is the excitation energy of the sensitizer  $E^*(\text{PS})$  should be higher than that of excited onium salt  $E^*(\text{On}^+)$ . On the other hand the electron transfer is energetically allowed, if  $\Delta G$  calculated by (extended Rehm- Weller equation) [132] is negative. °

$$\Delta G = F [ E_{\text{ox}}^{1/2}(\text{PS}) - E_{\text{red}}^{1/2}(\text{On}^+) ] - E^*(\text{PS}) \quad (\text{Eq:2.2})$$

Where  $E_{\text{ox}}^{1/2}$  and  $E_{\text{red}}^{1/2}$  are half wave oxidation and reduction potential of photosensitizer and photoinitiator respectively,  $F= 97 \text{ kJ mol}^{-1} \text{ V}^{-1}$ , is the conversion factor and  $E^*(\text{PS})$  is the excitation energy of photosensitizer.

## 1. Classical Energy Transfer

Energy may be transferred from excited sensitizer (PS\*) to onium salt (PI) by either resonance excitation or exchange energy transfer. Depending on the two components involved, energy transfer may proceed either excited singlet or in triplet state.

Diphenyliodonium cations were excited to their first excited triplet state by energy transfer from *m*-trifluoromethyl acetophenone [133]. As can be seen from Tables 2.5 and 2.6, the energy transfer is energetically allowed. Electron transfer in the exciplex can be totally excluded, since the oxidation potential of *m*-trifluoromethylacetophenone is relatively low. In the case of triphenyl sulfonium salt energy transfer may occur from sensitizers with triplet energies above 314 kJ mol<sup>-1</sup>.

Table 2.5. Halfwave Oxidation Potentials  $E_{1/2}^{ox}(PS)$  (vs SCE) and Triplet or Singlet energies  $E^*(PS)$  of Commonly Used Photoinitiators

Photosensitizer	$E_{1/2}^{ox}(PS)$ (V)	$E^*(PS)$ (kJ mol <sup>-1</sup> )
Acetophenone	2.9	308 (E <sub>t</sub> )
Benzophenone	2.7	290 (E <sub>t</sub> )
Thioxantone	1.7	277 (E <sub>t</sub> )
Anthracene	1.1	319 (E <sub>s</sub> )
Perylene	0.9	277 (E <sub>s</sub> )
Phenothiazine	0.6	239 (E <sub>t</sub> )
<i>m</i> -Trifluoromethyl acetophenone	2.7	305 (E <sub>t</sub> )
Xantone	-	311 (E <sub>t</sub> )

It has been shown that photosensitized decomposition of onium salt follows different route from that observed for direct photolysis of the onium salts [134,135]. This can be attributed to the different spin multiplicities involved in the corresponding decompositions.

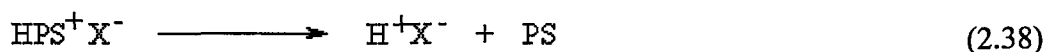
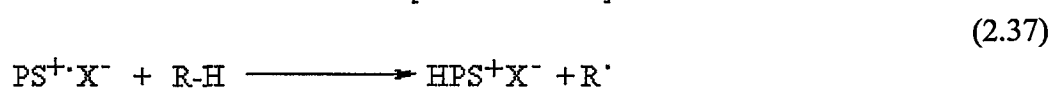
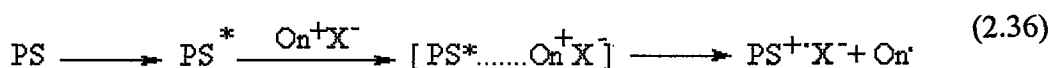
It should be pointed out that the energy transfer sensitization is not a technically useful process due to the high energy requirements.

Table 2.6. Reduction Potential and Triplet Excitation Energies of Selected Onium ions

Onium Cation	$E^{\text{red}}_{1/2}$ (V) (vs SCE)	$E^*_t$ (kJ mol <sup>-1</sup> )
	0.35	-
	-0.2	268
	-1.1	314
	-0.7	-
	-0.5	-

## 2) Electron Transfer via Exciplex

Many aromatic hydrocarbons such as anthracene, phenothiazine, perylene are able to sensitize the decomposition of onium salts via electron transfer. The irradiation of the sensitizer is followed by the formation of a complex between excited sensitizer molecules and ground state onium salt. In this complex, one electron is transferred from the sensitizer to the onium salt giving rise to the generation of sensitizer radical cation as a result of homolytic cleavage of the corresponding onium salt. The radical cations themselves initiate the polymerization of appropriate monomers or, alternatively, interact with hydrogen donor constituents of the polymerization mixture (such as solvent or monomer) resulting in the release of Brønsted acid. For this type cationic initiation, the following general scheme holds (Reactions 2.36-38);



Since the oxidation potentials of sensitizers  $E^{ox}_{1/2}$  are easy to determine, the calculation of  $\Delta G$  can indeed be applied in order to predict whether or not an oxidation would take place as presented for the example of typical onium salts in Table 2.7.

Table 2.7. Sensitization of Onium Salts;  $\Delta G$  in  $\text{kJ mol}^{-1}$

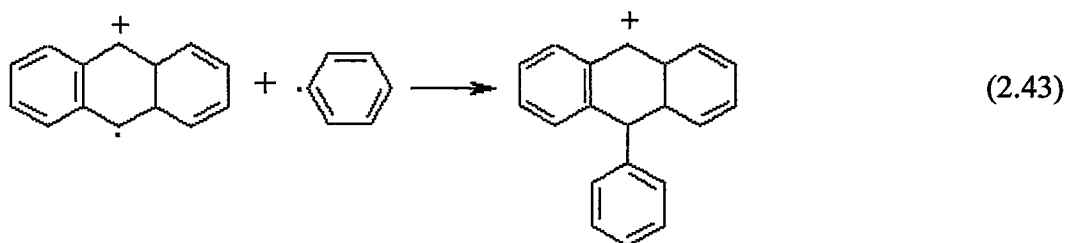
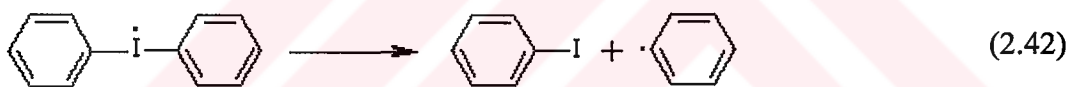
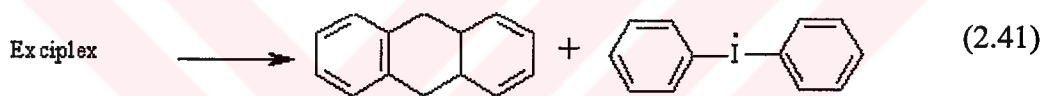
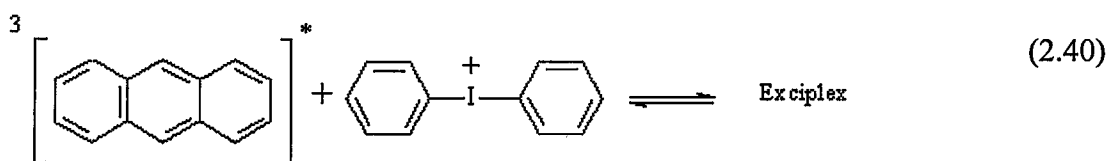
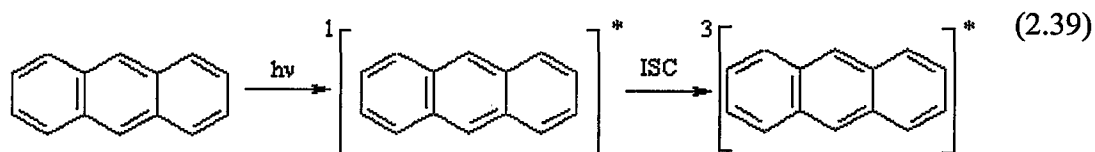
Sensitizer	$\Delta G$	Sens <sup>a</sup>	$\Delta G$	Sens <sup>b</sup>	$\Delta G$	Sens <sup>a</sup>
Benzophenone	-8	+	+39.8	-	+88	-
Acetophenone			+41.2	-		
Thioxanthone	-92	+	-44.2	+	+4	-
Anthracene	-193	+	-144.4	+	-96	+
Perylene	-171	+	-121.8	+	-71	+
Phenothiazine	-159	+	-112.9	+	-63	+

<sup>a</sup>Polymerization of the diepoxide, 3,4-epoxycyclohexylmethyl-3,4- epoxy cyclohexane carboxylate

<sup>b</sup>Polymerization of cyclohexene oxide

However not all sensitizers are suitable in conjunction with onium salts. The requirements are low oxidation potentials,  $E^{ox}_{1/2}(PS)$ , and relatively high excitation energies  $E^*(PS)$  of the sensitizer. It should also be noticed that only onium salts with high (low negative) reduction potentials  $E^{red}_{1/2}(On^+)$ , such as diphenyliodonium or alkoxy pyridinium salts are easily reduced by sensitizers.

The sensitization of onium salts ( $\text{Ar}_2\text{I}^+$  and  $\text{Ar}_3\text{S}^+$ ) by anthracene has been investigated in detail in a number of papers [136-138]. Exciplex formation is followed by a partly loss of anthracene's aromatic system as concluded from the decrease in the sensitizer fluorescence. Notably, similar coupling reactions of radical cations with the radicals formed from the salts were also observed with alkoxy pyridinium salts [139].



counter ion is omitted.

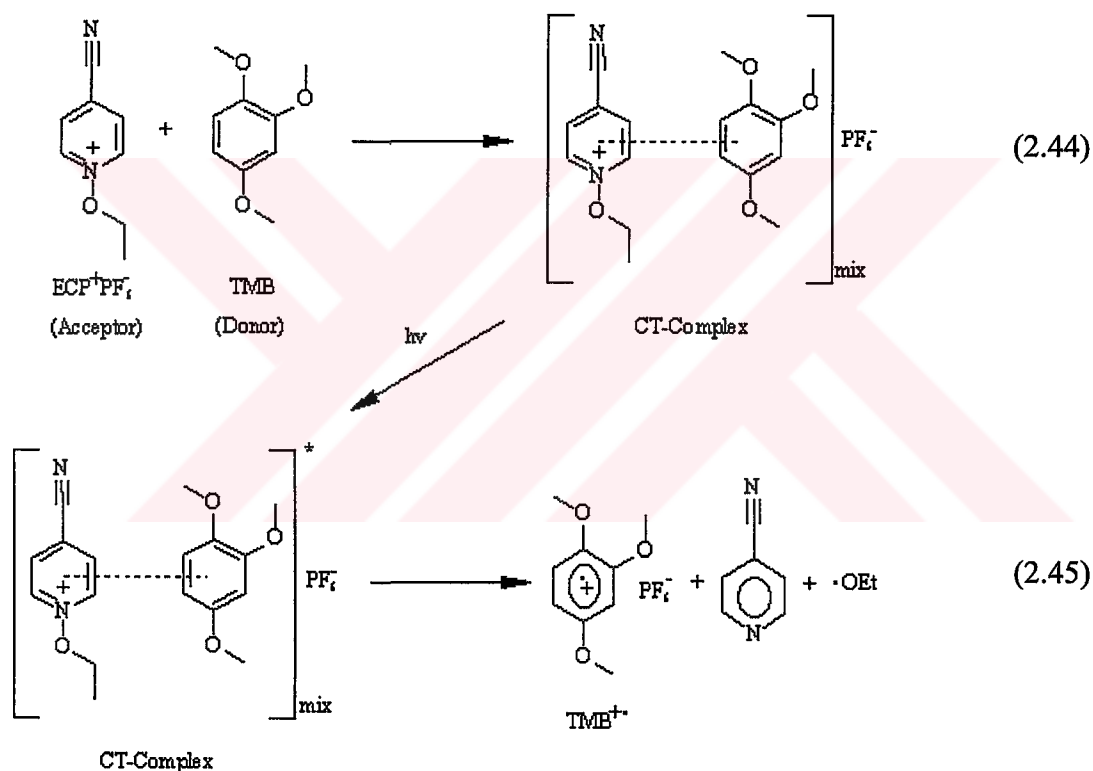
The sensitization of thioxanthone follows only partly the general mechanism described for the exciplex formation [139]. To some extent, this sensitization is based upon the oxidation of photolytically formed radicals.

### 3) Charge Transfer Complex Initiated cationic polymerization

Pyridinium salts are capable of forming charge transfer (CT) complexes with electron rich donors such as methyl- and methoxy-substituted benzene [140].



Notably, these complexes absorb at relatively high wavelengths, where the components are virtually transparent. For example, the complex formed between *N*-ethoxy-4-cyano pyridinium hexafluorophosphate and 1, 2,4-trimethoxy benzene possesses an absorption maximum at 420 nm. The absorption maxima of the two constituents are at 270 and 265 nm for the pyridinium salt and trimethoxybenzene, respectively. It was found that the CT complexes formed between pyridinium salts and aromatic electron donors act as photoinitiators for the cationic polymerization of cyclohexene oxide and 4-vinyl cyclohexene oxide. The mechanism illustrated in reactions 2.44 and 2.45 for the initiation of the cationic polymerization has been suggested [140].



Since the proton scavenger 2,6-di-*tert*-butylpyridine did not noticeably influence the polymerization, the initiation by Brønsted acid that could be formed after an interaction with hydrogen donor components can be excluded. Notably, the CT complexes described above are applicable for the photoinitiation of epoxide monomers but not for the photoinitiation of vinyl ethers and *N*-vinyl carbazol. The latter monomers are already polymerized in a dark reaction upon addition of these complexes.

### **3. EXPERIMENTAL WORK**

#### **3.1 Materials and Chemicals**

##### **3.1.1 Monomers**

###### **Styrene (St) (Fluka)**

It was washed with aq. 5% NaOH to remove inhibitors, then water, dried with CaH<sub>2</sub> several hours and distilled under reduced pressure (50 °C/25 mm Hg). Middle fraction was collected and immediately used.

###### **Epsilon Caprolactone ( $\epsilon$ -CL)**

It was vacuum distilled over calcium hydride just before use.

###### **Cyclohexene Oxide (CHO) (Fluka)**

Cyclohexeneoxide (CHO) was a product of Aldrich, it was vacuum distilled from calcium hydride (CaH<sub>2</sub>) before used as initiator.

##### **3.1.2 Solvents**

###### **Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) (Lab-scan)**

Methylene chloride was used as solvent for dissolving bulky polymer formations, also as a solvent in organic reactions. It was first washed with conc. H<sub>2</sub>SO<sub>4</sub> until the acid layer remained colourless, then washed with water, aq. %5 NaOH and then water again. It was pre-dried with CaCl<sub>2</sub> and distilled from CaH<sub>2</sub>.

###### **Chloroform (CHCl<sub>3</sub>)**

It was used as solvent in organic reaction. Firstly, it was refluxed with P<sub>2</sub>O<sub>5</sub>, after that it was distilled from CaH<sub>2</sub> over molecular sieves.

###### **Tetrahydrofuran (THF) (J.T. Baker)**

It was used as eluent for chromatography as received (HPLC grade). Also it was used for precipitation of polymers in ATRP reaction agent.

### **Methanol (Technical)**

It was used for the precipitation of polymers without further purification.

### **3.1.3 Initiators and Other Chemicals**

#### **3-cyclohexene-1-methanol**

3-cyclohexene-1-methanol was a product of Aldrich, no further purification was applied.

m-chlorobenzoic acid

m-chlorobenzoic acid was a product of Aldrich, no further purification was applied

#### **Sodiumbicarbonate (NaHCO<sub>3</sub>)**

Sodiumbicarbonate (NaHCO<sub>3</sub>) was a product of Merck, it was used as received.

#### **Stannous 2-ethyl-hexanoate (stannous octoate )**

Stannous 2-ethyl-hexanoate (stannous octoate ) was a product of Sigma, it was used as received.

#### **Diphenyliodonium hexafluorophosphate (Ph<sub>2</sub>I<sup>+</sup>PF<sub>6</sub><sup>-</sup>) (Fluka)**

It was used as received.

#### **2 – Bromopropionyl bromide (Aldrich)**

It was used without further purification.

#### **Copper (I) Bromide (CuBr) (Aldrich)**

It was used as received.

#### **2, 2'-Dipyridyl (dpy) (Merck)**

It was used as a ligand for ATRP without further purification

#### **Pyridine (Lab-Scan)**

It was used as received.

And the other chemicals were used as received.

## 3.2 Equipments

### 3.2.1. Photoreactor

Rayonet photoreactor equipped with 16 Philips 8W / O6 lamps emitting light nominally at 300 nm was used.

### 3.2.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

<sup>1</sup>H-NMR analyses were recorded on a Bruker 250 MHz NMR Spectrometer.

### 3.2.3 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) analyses were performed with a set up consisting of a Waters 515 apparatus equipped with three Waters ultrastyrigel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min and a refractive index detector. Molecular weights of polymers were calculated with the aid of polystyrene standards. Molecular weight of PCL macromonomer was calculated by using following conversion formula [143]:

$$M_{\text{PCL}} = 0.259M_{\text{PSt}}^{1.073}.$$

## 3.3 Preparation Methods

### 3.3.1 Synthesis of Atom Transfer Radical Polymerization (ATRP) Initiator

#### 3.3.1.1 Synthesis of (3-cyclohexene-1-methylol)-2-bromopropanoat ( CHMBP)

3-Cyclohexene-1-methanol (10 mL, 0,0856 mol ), triethylamine (TEA) (14 mL, 0,1027 mol ) and 150 mL CH<sub>2</sub>Cl<sub>2</sub> were added in to two- necked round bottom flask fitted with a magnetic stirrer, nitrogen inlet-outlet and addition funnel containing 2-bromopropanoyl bromide (9,964 mL, 0,094 mol) and 30 mL CH<sub>2</sub>Cl<sub>2</sub>. The flask was placed in an ice-water bath. The solution of 2-bromopropanoyl bromide was added dropwise over a period of 1.5 h under nitrogen. Then the mixture was allowed to reach room temperature, and stirred at that temperature over the night. The resulting solution was washed with 20% aqueous NaHSO<sub>3</sub> (1x 100 mL ) and separated organic layer was drawn off. The aqueous phase was diluted with an equal volume of saturated aqueous NaHCO<sub>3</sub>, cautiously mixed, and the remainder of the organic layer was withdrawn. The combined organic layers were washed with saturated

NaHCO<sub>3</sub> (3x 100mL, solid NaCl added to last wash ) dried (MgSO<sub>4</sub>), filtered and distilled in vacuum evaporatory.

Also this compound was purified by column chromatography with TLC control. Eluent was mixture of ethylacetate and hexane (with ratio of 1:4)

C<sub>10</sub>H<sub>15</sub>O<sub>2</sub>Br (M<sub>w</sub> = 247,13 g)

### 3.3.1.2 Synthesis of (3-cyclohexene oxide-1-methylol)-2-bromopropanoat (CHOMBP)

Epoxidation of initiator with cyclohexene end group was performed under inert atmosphere.. The initiator with cyclohexene end group (2 g), sodium bicarbonate (0,48g, 5,70 mmol) and (3-cyclohexene-1-methanol)-2-bromopropanoat (2 g, 0,00846 mol), m- chloroperoxy-benzoic acid (3 g, 0,0173 mol ) and 200 mL CH<sub>2</sub>Cl<sub>2</sub> were added into 250 mL round bottom flask. The mixture was refluxed for 8 h. The reaction mixture was cooled with an ice bath , diluted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL) , and filtered through sintered glass with CH<sub>2</sub>Cl<sub>2</sub> wash (4x50 mL). The resulting solution was washed with 20% aqueous NaHSO<sub>3</sub> (1x 100 mL ) and separated organic layer was drawn off. The aqueous phase was diluted with an equal volume of saturated aqueous NaHCO<sub>3</sub>, cautiously mixed, and the remainder of the organic layer was withdrawn. The combined organic layers were washed with saturated NaHCO<sub>3</sub> (3x 100mL, solid NaCl added to last wash ) dried (MgSO<sub>4</sub>), filtered and distilled in vacuum evaporatory. This product was purified through column chromatography, too. Eluent (Ethyl acetate-Hexane) ratio was 4:6.

C<sub>10</sub>H<sub>15</sub>O<sub>2</sub> , Mw = 264 g/mol Yield :0,8527 (32 %)

Yield: 100 %

### 3.3.2 General Procedure for Ring-Opening Polymerization (ROP)

Calculated amounts of monomer ( $\epsilon$ -caprolactone), stannous octoate and photoinitiators (Ph<sub>2</sub>I<sup>+</sup>PF<sub>6</sub><sup>-</sup>) were added under nitrogen in previously flamed and nitrogen- purged schlenk tubes equipped with magnetic stirrer. The detailed polymerization conditions are given in Table 4.1. The  $\epsilon$ -CL polymerizations were carried out in bulk at 110 °C. After a given time, the polymerizations were terminated by cooling the tubes to the room temperature, then diluted with CH<sub>2</sub>Cl<sub>2</sub>

and poured into ten-fold excess of cold methanol. The polymers were collected after filtration and drying at room temperature in a vacuum for three days.

### 3.3.2.1 Preparation of Poly( $\epsilon$ -caprolactone) with Cyclohexene end group

3-cyclohexene-1-methanol (0.30 g, 2.60 mmol), monomer ( $\epsilon$ -caprolactone) (5.83 g, 51.0 mmol) and stannous octoate (2.70 g, 6.66 mmol), were added under nitrogen in previously flamed and nitrogen-purged schlenk tube equipped with magnetic stirrer. The  $\epsilon$ -CL polymerization was carried out in bulk at 110 °C. After 5 days the polymerization was terminated by cooling the tube to the room temperature, then diluted with  $\text{CH}_2\text{Cl}_2$  and poured into ten-fold excess of cold methanol. The polymer with cyclohexene end group was collected after filtration and drying at room temperature in a vacuum for three days.

Yield: 100 %,  $M_n$  GPC = 2500,  $M_w/M_n$  = 1.3  $M_n$ , NMR = 1720

### 3.3.2.2 Preparation of Poly( $\epsilon$ -caprolactone) Macromonomer

Epoxidation of poly( $\epsilon$ -caprolactone) with cyclohexene end chain group was performed under inert atmosphere at 0 °C. The polymer with cyclohexene end group (5 g), sodium bicarbonate (0.48 g, 5.70 mmol) and 60 mL  $\text{CH}_2\text{Cl}_2$  were added into a 250 mL three-necked round bottom flask fitted with a condenser, a magnetic stirrer, nitrogen inlet-outlet, and an addition funnel containing 3-chloroperoxybenzoic acid (1.45 g, 8.40 mmol) and 40 mL  $\text{CH}_2\text{Cl}_2$  mixture. The flask was placed in an ice-water bath. The solution of 85% 3-chloroperoxybenzoic acid was added dropwise over a period of 2 h under nitrogen. Then the mixture was allowed to reach room temperature, and stirred at that temperature over the night. The solution was washed three times with water. Finally, the solution was dried with  $\text{MgSO}_4$ , and the solvent was removed by rotary evaporatory. The solid product was diluted with  $\text{CH}_2\text{Cl}_2$  and poured into ten-fold excess of cold methanol. Epoxy end chain functionalized poly( $\epsilon$ -caprolactone) macromonomer was collected after filtration and drying at room temperature in a vacuum for three days.

Yield: 100 %  $M_n$  GPC = 2950,  $M_w/M_n$  = 1.3  $M_n$ , NMR = 1592

### 3.3.3 General Polymerization Procedure for Atom Transfer Radical Polymerization (ATRP)

A round bottom-flask equipped with magnetic stirrer and a lateral neck with tap was used. The system was vacuumed and back-filled with dry nitrogen several times. Catalyst (CuBr), ligand 2, 2'-dipyridyl (dpy), initiator ((3-cyclohexene oxide -1-methylol)-2-bromopropanoate) and styrene were introduced under inert atmosphere. The flask was placed in an oil bath warmed at 110°C and stirred at that temperature. After a given time, the mixture was diluted with THF and poured into ten-fold methanol. The solid was collected after filtration and drying at 40°C in vacuum overnight.

In order to remove the complex salts from the polymers they were redissolved in THF and passed through a silica gel column followed by precipitation in methanol.

### 3.3.4 General Photochemical Cationic Copolymerization Using Macromonomers Prepared by ATRP and ROP Methods

Appropriate solutions of epoxy end functionalized macromonomers ( PSt or PCL) and monomer (CHO) when indicated in CH<sub>2</sub>Cl<sub>2</sub> containing onium salt (Ph<sub>2</sub>I<sup>+</sup>) in Quartz tubes were degassed with nitrogen prior to irradiation. At the end of irradiation in "Rayonet" photoreactor equipped with 15 Philips lamps and emitting light nominally at 300 nm at room temperature, the solutions were poured into cold methanol. The precipitated copolymers were filtered off and dried in vacuum. Conversion of CHO was determined gravimetrically after subtracting the weight of the precursor polymers.

The detailed polymerization conditions are given in the Results & Discussion section.

### 3.3.5 Characterizations

<sup>1</sup>H-NMR spectra were recorded on a Bruker 250 MHz spectrometer with CDCl<sub>3</sub> as the solvent and tetramethylsilane as the internal standard. Gel permeation chromatography (GPC) analyses were performed with a set up consisting of an Waters 996 apparatus equipped with three Waters ultrastyrigel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min and a

refractive index detector. Molecular weights of polymers were calculated with the aid of polystyrene standards.





## 4. RESULTS AND DISCUSSION

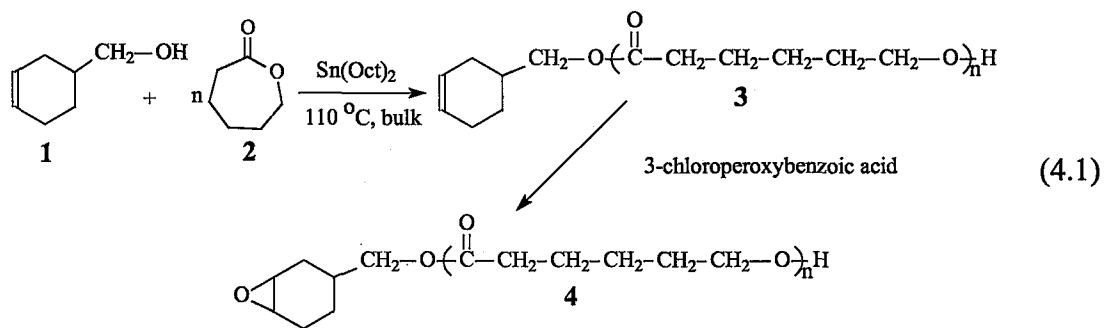
Our target was to synthesize cyclohexene oxide type macromonomers by using controlled polymerization methods. We have selected two different methods namely, Atom Transfer Radical Polymerization (ATRP) and Controlled Ring Opening polymerization (CROP), because of their versatility to prepare well-defined macromolecular structures. Cyclohexene oxide functionality was deliberately chosen since it readily undergoes photoinitiated cationic polymerization.

Moreover, structural similarity of the functional group with the cyclohexene oxide itself allow variations with number of branched units when it is used together in the photoinitiated cationic polymerization. Obviously, the use of bicyclohexene oxide monomers would lead to the formation of cross-linked networks possessing dangling polymer chains prepared by the controlled polymerization.

### 4.1. Synthesis of Macromonomers

#### 4.1.1 Synthesis of Poly( $\epsilon$ -caprolactone) Macromonomer by Controlled Ring Opening Polymerization (CROP)

It is well known that Tin(II) 2-ethylhexanoate, commonly referred to as stannous octoate [ $\text{Sn}(\text{Oct})_2$ ], is a frequently used catalyst in the ROP of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) via coordination insertion mechanism [116, 114, 144]. The synthesis of macromonomers of poly( $\epsilon$ -caprolactone) with cyclohexene (3) and epoxy (4) end chain group were depicted in reactions. First, we have performed the reaction of 3-cyclohexene-1-methanol (initiator) (1) with  $\epsilon$ -caprolactone ( $\epsilon$ -CL) (2) in the presence of stannous octoate catalyst. In view of the reported role of hydroxyl groups as initiators in ring-opening polymerization, this reaction was expected to produce a polymer containing a cyclohexene group on one chain end (3) derived from initiator. Then, cyclohexene oxide end functionalized poly ( $\epsilon$ -caprolactone) (4) was prepared by epoxidation of this precursor using 3-chloroperoxybenzoic acid under inert atmosphere at 0 °C (Reaction 4.1)



As can be seen from Figure 4.1, in the  $^1\text{H-NMR}$  spectra of the precursors can be found not only the specific signals of poly( $\epsilon$ -caprolactone) (PCL), but also absorptions belonging to the rests of initiators.

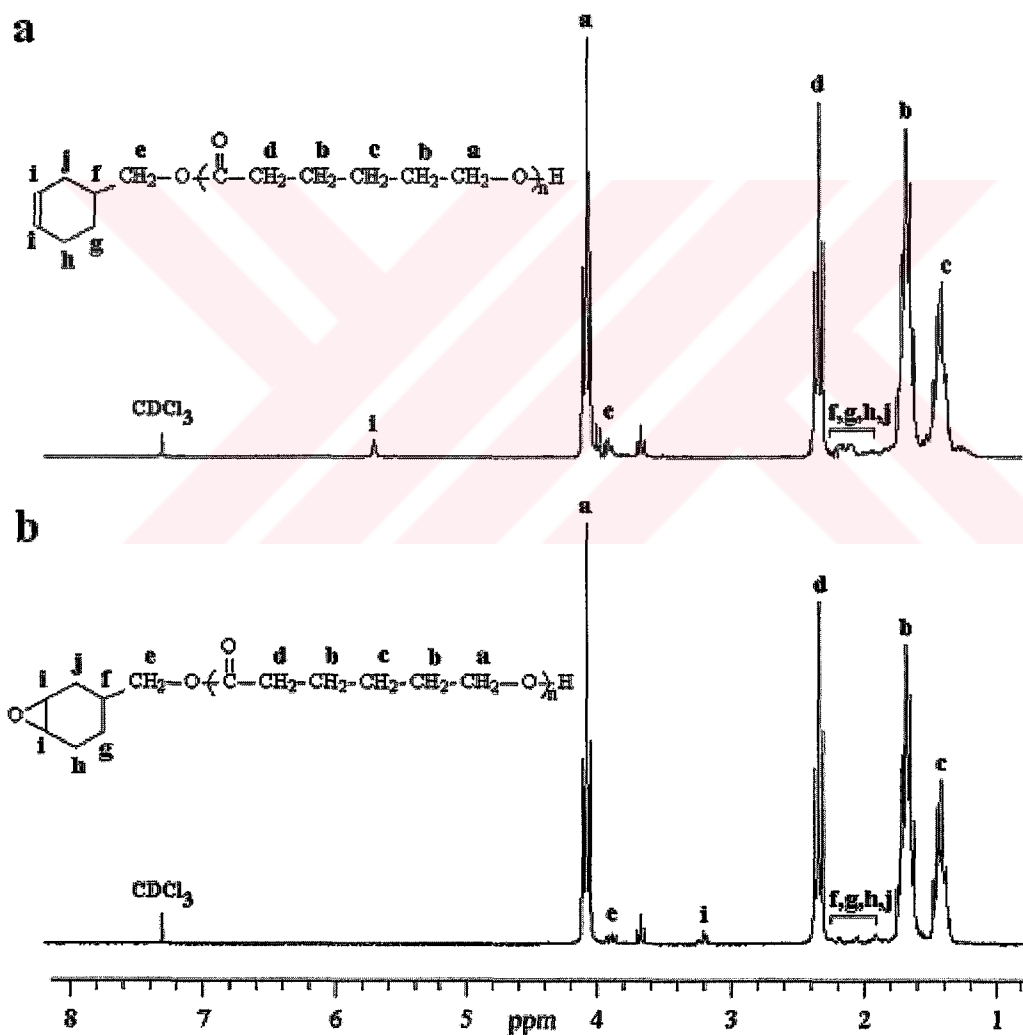


Figure 4.1.  $^1\text{H-NMR}$  spectra of macromonomers.

The <sup>1</sup>H-NMR spectra of the poly(ε-caprolactone) (1) with cyclohexene (2) and epoxy end chain groups (3 and 4) display the signals characteristic of the corresponding segments (Figure 4.1). For example, the  $\alpha$  protons of double bond 5.63 ppm observed in the spectrum of 3 [Figure 4.1(a)] completely disappeared in the spectrum of 4 [Figure 4.1(b)]. Moreover, the new signals at 3.12-3.17 ppm were assigned to the protons of the CHO moiety, indicating successful epoxidation.

Table 4.1 shows details of the conditions for the preparation of the PCL macromonomers. Previously, we used PCL<sub>1</sub> as macromonomer for the synthesis of homo and graft copolymers of PCL and CHO.

Table 4.1 Synthesis of Epoxy End Functionalized Poly(ε-caprolactone) Macromonomers.

Polymer <sup>a</sup>	Conversion <sup>b</sup> %	Mn <sup>c</sup> (theo.)	Mn <sup>d</sup> (NMR)	Mn <sup>e</sup> (GPC)	Mw/Mn
PCL <sub>1</sub>	>99	2350	2150	<b>1800</b>	<b>1,2</b>
PCL <sub>2</sub>	>99	2350	1692	<b>2950</b>	<b>1,3</b>

a: 1.Step: Controlled Ring Opening Polymerization (CROP) carried out at 110 °C, 5 days,  $[n_{(\epsilon\text{-Caprolactone})} / n_{\text{ROH}} = 20, n_{\text{ROH}}/n_{\text{Sn(Oct)2}} = 400]$ , in CH<sub>2</sub>Cl<sub>2</sub> 2.Step: Epoxidation was done after synthesis of cyclohexene end functionalized macromonomer at 0 °C time = 120 minute in CH<sub>2</sub>Cl<sub>2</sub>, [Macromonomer] = 5 g [NaHCO<sub>3</sub>] = 5,70 mmol.

b: Conversion was calculated gravimetrically.

c: The theoretical molecular weight calculated by using the following equation.

$$M_{n,th} = [M]_0 / [I]_0 \times M_w \times \text{Conversion} + M_I$$

d: Molecular weight was calculated by using ratio between epoxy and aliphatic hydrogen peak.

e: Molecular weight of PCL macromonomer was calculated by using following conversion formula  $M_{\text{PCL}} = 0,259 M_{\text{PSt}}^{1,073}$

Figure 4.2 shows the GPC trace of epoxy end chain functionalized macromonomer (4). It is unimodal and narrow indicating that no side reactions occurred and prepared in a controlled manner.

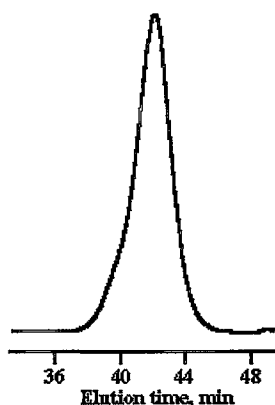
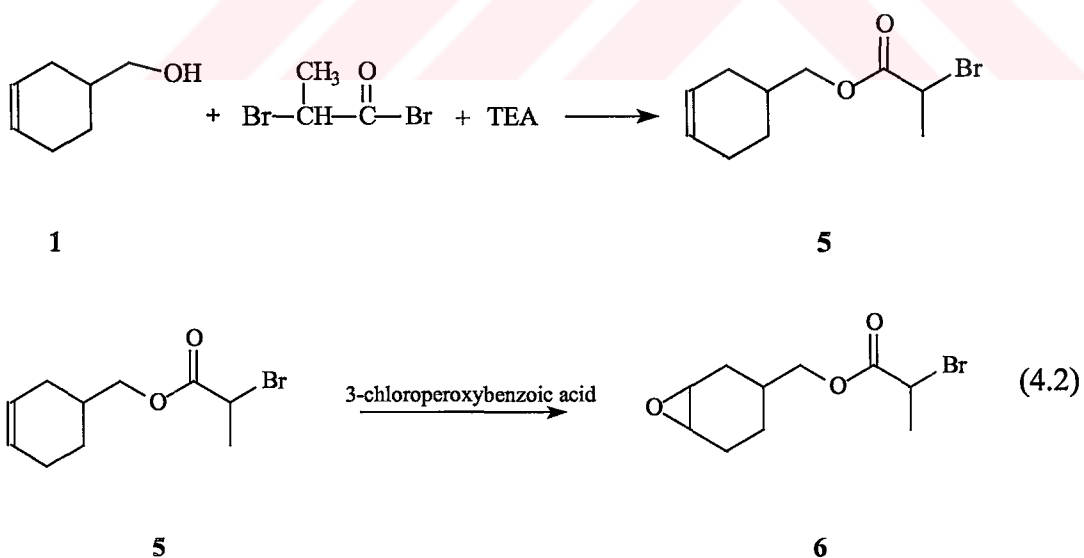


Figure 4.2. GPC trace of epoxy chain end functionalized macromonomer (4)

## 4.1.2 Synthesis of Polystyrene Macromonomer by Atom Transfer Radical Polymerization (ATRP)

### 4.1.2.1. Synthesis of ATRP Initiator

The initiator was synthesized in two steps; condensation and epoxidation. Firstly, we have performed the reaction of 3-cyclohexene-1-methanol with triethylamine by mixing and refluxing under nitrogen for 8 hours. The intermediate (3-cyclohexene-1-methylol)-2-bromopropanoate (CHMBP) (5) was obtained after several purification processes, as described in the experimental part.



The sample was purified by applying column chromatography and TLC additionally. The condensation was extracted out. Following this step, epoxidation procedure using 3-chloroperoxybenzoic acid was applied [148]. The final initiator was purified

with column chromatography. The overall synthesis of the initiator (6) and related intermediate (5) were depicted in reaction 4.2.

The  $^1\text{H-NMR}$  spectra of the olefinic intermediate and epoxide are presented in Figure 4.3. The characteristic peak of cyclohexene adjacent to double bond, in the compound (5), at  $\delta$  5.6 ppm completely disappeared after epoxidation [Figure 4.3(a)]. Moreover, the new signals appeared at  $\delta$  2.95 ppm of epoxide, clearly confirm the successful epoxidation [Figure 4.3 (b)]. The signal adjacent to aromatic peak, which comes from peroxybenzoic acid disappeared.

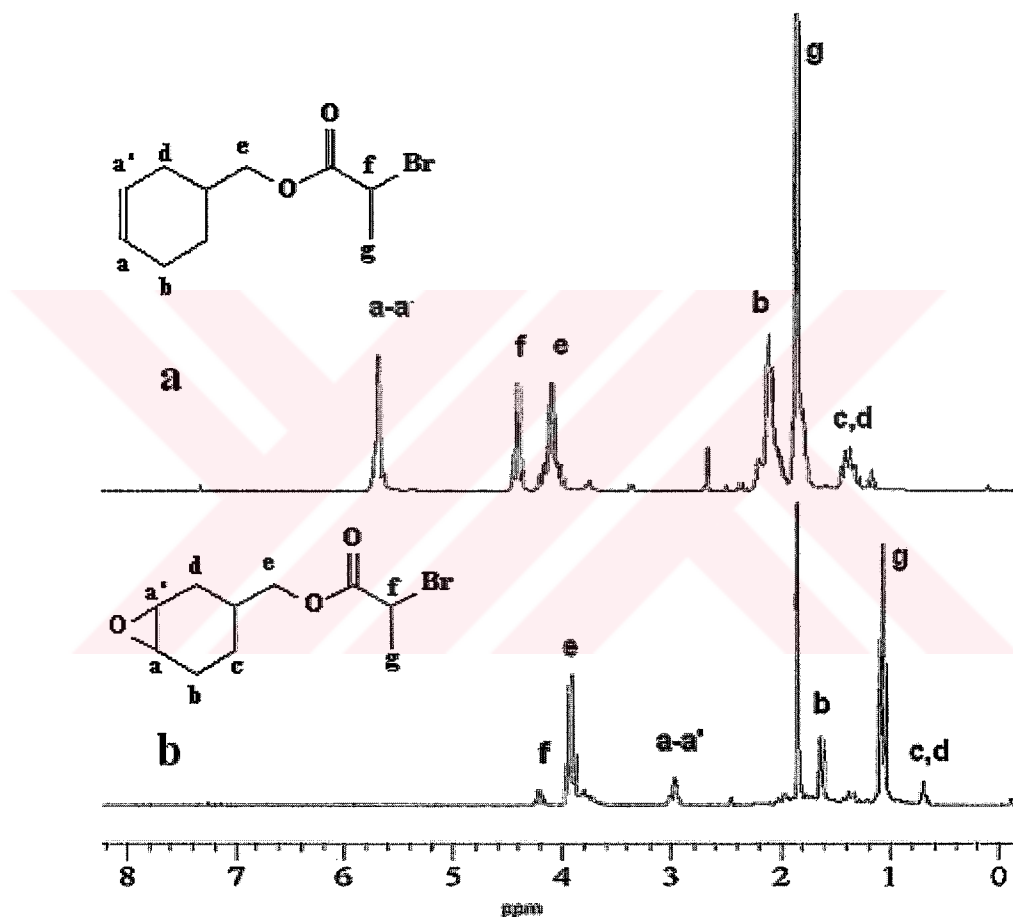
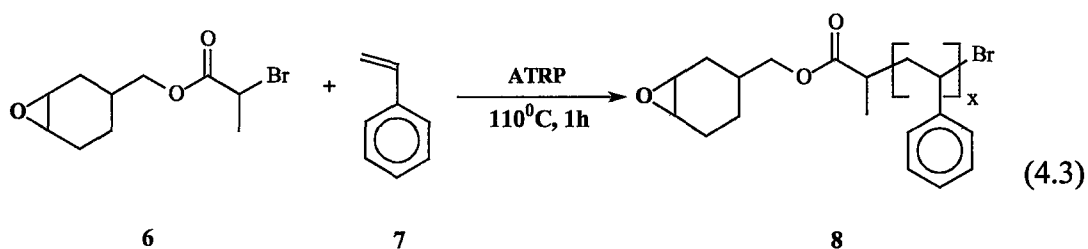


Figure 4.3.  $^1\text{H}$  NMR spectra of olefinic intermediate (a) and initiator (b).

#### 4.1.2.2. Synthesis of Polystyrene (PSt) Macromonomer

Polystyrene (PSt) macromonomer was prepared by Atom Transfer Radical Polymerization (ATRP) in bulk at  $110^\circ\text{C}$  in the presence of epoxy end-functionalized initiator (6). Molecular weights of macromonomers were determined by GPC. The reaction proceeds in one step, as shown in reaction 4.3.



Among the macromonomers,  $2^b$  was chosen as the prepolymer ( $PS_{t_1}$ ) for photoinitiated cationic polymerization, since the molecular weights obtained by  $^1H$  NMR and GPC calculation were in closer agreement, as can be seen in Table 4.2.

Table 4.2. Synthesis of Macromonomer by ATRP Reaction.

Run	$[M]_0$ (molxL <sup>-1</sup> )	$[M]_0$ /[I] <sub>0</sub>	Time (min)	Conv. <sup>c</sup> %	$Mn^d$ (theo.)	$Mn^e$ (NMR)	$Mn^f$ (GPC)	Mw /Mn
1 <sup>a</sup>	17,5	175	60	7	1538	878	1894	1,2
2 <sup>b</sup>	8,8	43,8	60	26	1461	1380	1955	1,2

T= 110 ° C Monomer: Styrene (Mw = 104.15 g/mol)

Initiator: CHOP (Mw = 264g/mol)

a: (Initiator : CuBr: dPy =0,5:1: 3)

b: (Initiator : CuBr: dPy =1:1: 3)c: Conversions were calculated gravimetrically

d:  $Mn_{theo} = ([M]_0/[I]_0 \times \text{conversion \%} \times (104.15) + 264$

e: Molecular weights were calculated according to the PS aromatic protons (5H), Initiator hydrogens in  $\beta$ -position (3H)

f: Molecular weights were calculated according to the linear PS standards.

The macromonomer structure was assigned by means of  $^1H$  NMR spectral measurement. The  $^1H$  NMR spectrum of the macromonomer displays typical signals at 3.12 ppm CH-O-CH, 3.69 ppm CH-CH<sub>2</sub>-O, and 6.61-7.1 ppm Ar-H as shown in Figure 4.4.

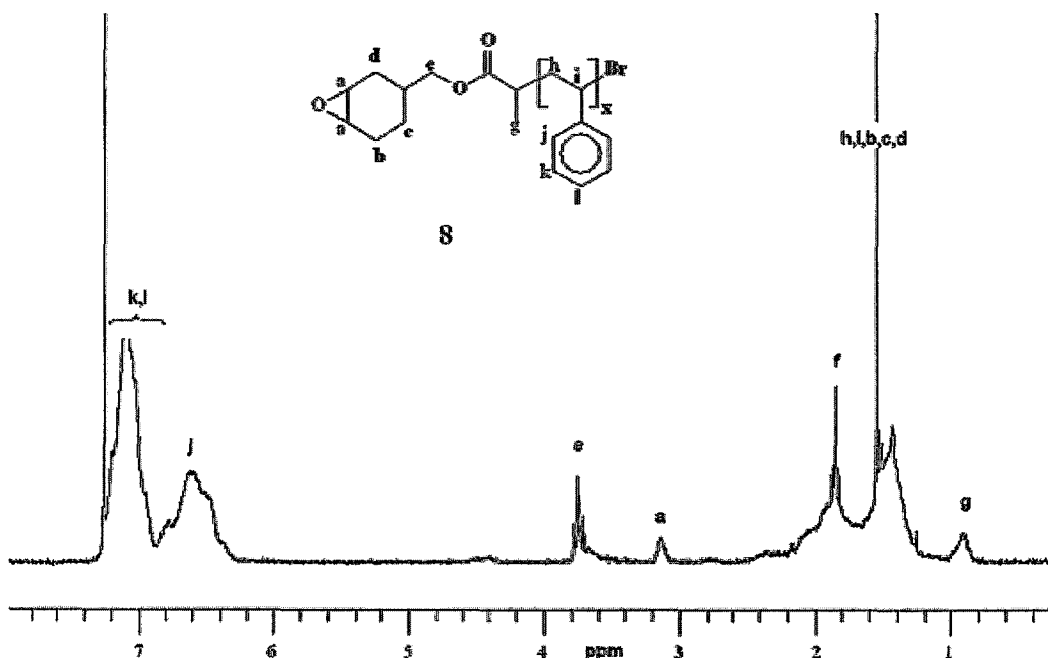
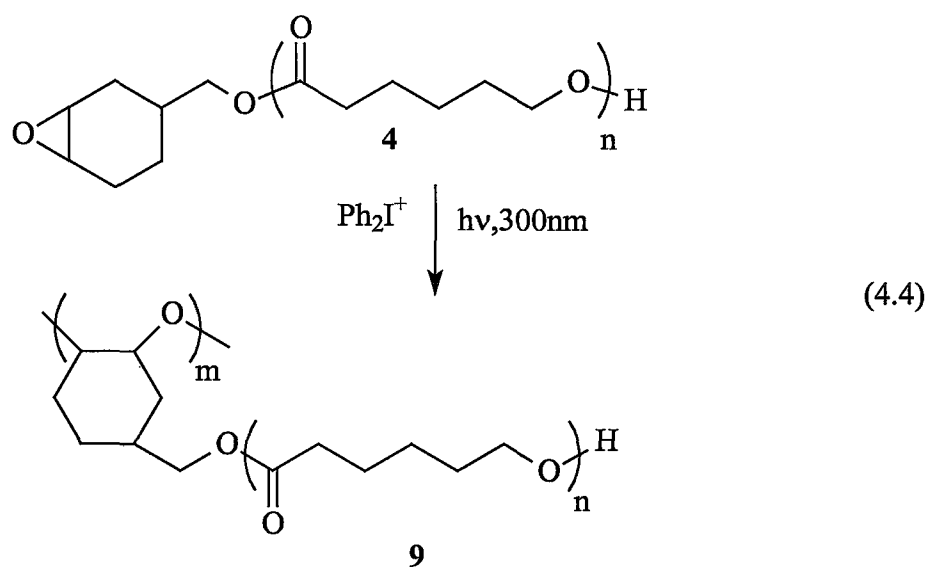


Figure 4.4. The  $^1\text{H}$  NMR spectrum of Polystyrene Macromonomer ( $\text{PSt}_1$ ).

## 4.2. Photoinitiated Cationic Polymerization

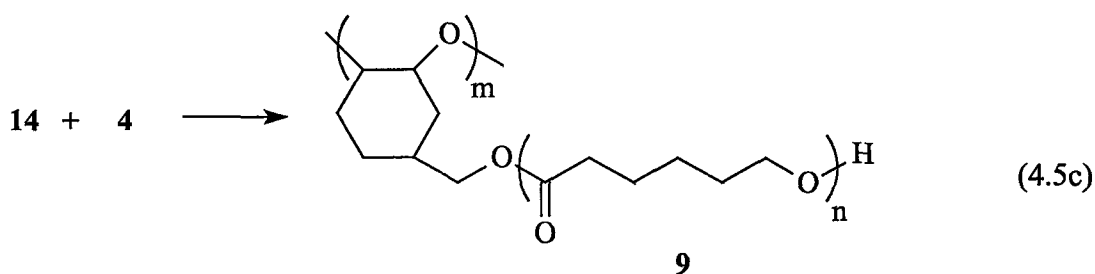
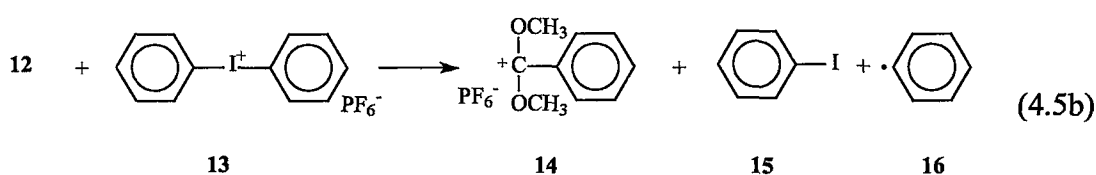
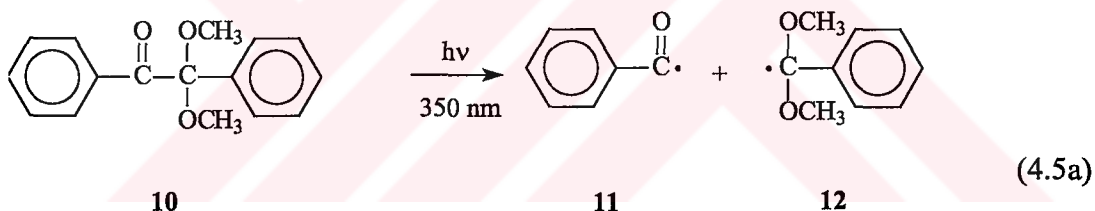
### 4.2.1. Homopolymerization of Poly( $\epsilon$ -caprolactone) Macromonomer

Table 4.3 shows photoinitiation types used in our work. Homopolymerization of macromonomers provide regular star- or comb-shaped polymers with a very high branch density [145,149] All types of photoinitiation systems yielded polymers with high conversion (< 99 %) and basically the same structure (Reaction 4.4).



Expectedly, molecular weight distributions of obtained polymers were slightly higher than that of the macromonomer. Photoinitiated cationic polymerization by direct irradiation of the iodonium salt at 300 nm can bring some limitations on the potential use of PCL macromonomers because of their overlapping tail absorptions.

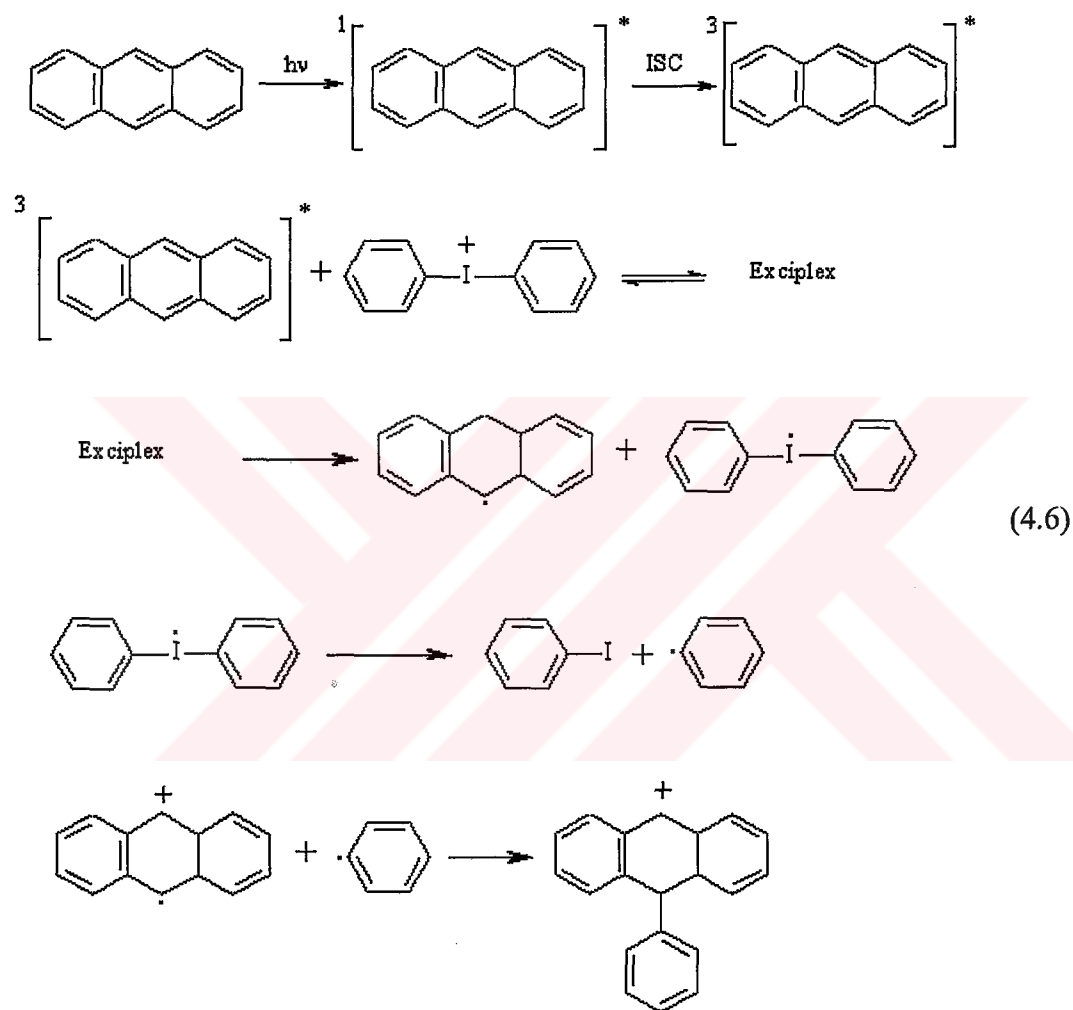
Therefore, we have also employed indirect ways, namely free radical promoted electron transfer photosensitization for providing working conditions for photoinitiated cationic polymerization at a broad wavelength range. In radical promoted cationic polymerization DMPA was used as radical source. The photolysis of DMPA results in  $\alpha$ -cleavage and 2, 2-dimethoxy benzyl (strong electron donor) and benzoyl (electron withdrawing) radicals are formed, according to the reaction 4.5. When irradiated in the presence of an onium salts such as diphenyl iodonium at 350 nm, wavelengths where onium salt is transparent, the light is absorbed only by DMPA. The photochemically generated 2,2-dimethoxy benzyl radicals reduce the iodonium salt to yield corresponding carbocations [146] capable of initiating cationic polymerization of epoxy end chain functionalized macromonomer (Reaction 4.5 (a), 4.5(b), 4.5(c)).



In earlier studies on photoinitiated cationic polymerization using anthracene as a sensitizer it was shown that the electron transfer, governed by energetic and



thermodynamic considerations, was the dominant process. The magnitude of the free  $\Delta G$  energy for the electron transfer should have been  $10 \text{ kJ mol}^{-1}$ . The  $\Delta G$  value ( $-193 \text{ kJ mol}^{-1}$ ) suggests that the electron transfer from singlet anthracene to iodonium ions is quite favorable [146]. Anthracene radical cation or Bronsted acid formed from hydrogen abstraction reaction may initiate the polymerization (Reaction 4.6) (Table 4.3).



counter ion is omitted.

Table 4.3 Photoinitiated Cationic Polymerization of Poly( $\epsilon$ -caprolactone) Macromonomer, PCL<sub>1</sub> (200 g L<sup>-1</sup>, M<sub>n</sub> = 1800) in the Presence of Ph<sub>2</sub>I<sup>+</sup>PF<sub>6</sub><sup>-</sup> (5x10<sup>-3</sup> mol L<sup>-1</sup>) at Room Temperature in CH<sub>2</sub>Cl<sub>2</sub>.

Photoinitiation Type	Activator (mol L <sup>-1</sup> )	Wavelength ( $\lambda$ , nm)	Time (h)	Conversion (%)	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>
Direct	---	300	5	> 99	8650	1.60
Promoted	DMPA	350	5	> 99	10600	1.39
Sensitized	Anthracene	300	5	> 99	12500	1.71

GPC traces of homopolymers are unimodal indicated that no homopolymer formation observed. For instance, Figure 4.5 shows the GPC chromatogram of 9 graft copolymer formed from anthracene sensitized polymerization which is typical of this series of compounds.

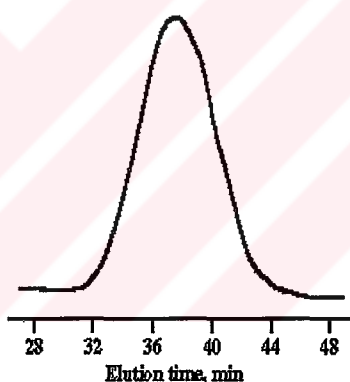


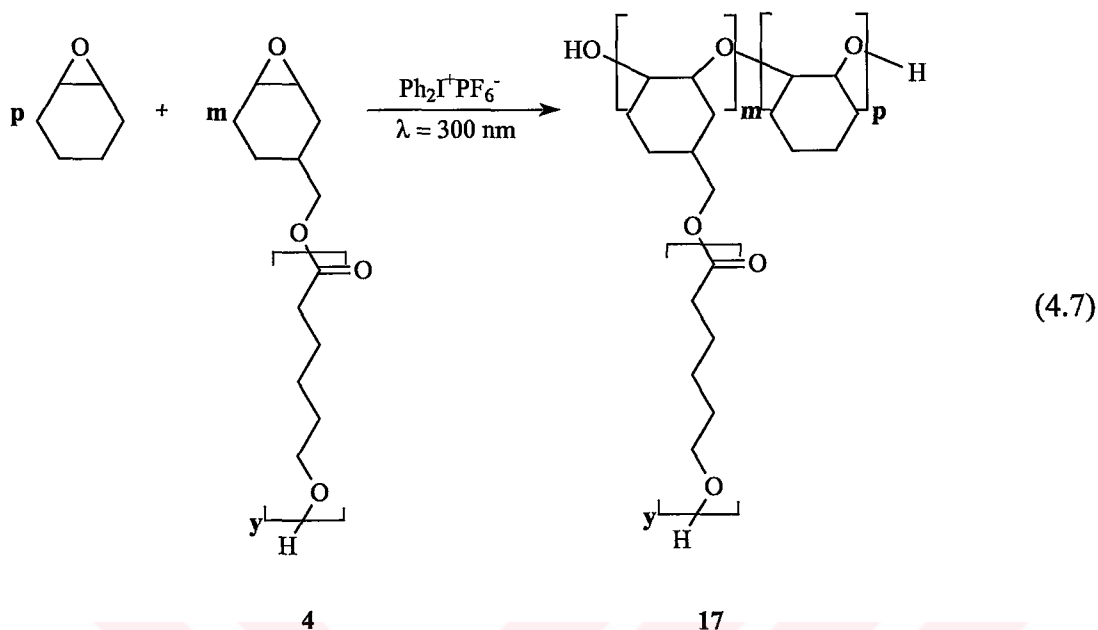
Figure 4.5. GPC trace of graft copolymer prepared via anthracene sensitization polymerization

The polymer structures were also assigned by means of NMR spectral measurements. Although typical signals for CL units were detected, signals for CHO units were not detected due to the probably high molecular weight of graft polymer and covering of CHO units by long chains of CL segments.

#### 4.2.2 Copolymerization of Poly( $\epsilon$ -caprolactone) with Cyclohexene Oxide (CHO)

PCL macromonomer was used as a comonomer in the copolymerization with CHO under similar conditions that applied for the polymerization of PCL macromonomer itself. Typical results concerning photochemically induced cationic polymerization of

CHO with PCL macromonomer at room temperature are shown in Table 4.4 (Reaction 4.7)



Typical results concerning photochemically induced cationic polymerization of cyclohexene oxide (CHO) at room temperature by using PCL macromonomer (4) are shown in Table 4.4.

Table 4.4. Photoinitiated Cationic Polymerization of Poly( $\epsilon$ -caprolactone) Macromonomer, PCL<sub>1</sub> (200 g L<sup>-1</sup>, M<sub>n</sub> = 1800) with Cyclohexene Oxide (CHO) at Room Temperature in CH<sub>2</sub>Cl<sub>2</sub> by Using Ph<sub>2</sub>I<sup>+</sup>PF<sub>6</sub><sup>-</sup> (5 × 10<sup>-3</sup> mol L<sup>-1</sup>).

Run	CHO (mol L <sup>-1</sup> )	Wavelength (λ, nm)	Time (min)	Con. <sup>a</sup> (%)	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	Comp. (mol, %) <sup>b</sup>	
							PCL	PCHO
A <sup>c</sup>	0.89	350	300	40	10700	1.51	58	42
B	0.89	300	20	40	7300	1.42	67	33
C	3.09	300	20	42	6500	2.14	26	74
D	4.94	300	20	50	4600	2.70	18	82
E <sup>d</sup>	9.89	300	20	36	5200	1.85	22	78

<sup>a</sup> CHO conversion, <sup>b</sup> Calculated from <sup>1</sup>H-NMR spectra of samples

<sup>c</sup> DMPA was used as a free radical source.

<sup>d</sup> Bulk

As can be seen, the concentration of CHO macromonomer influences the composition of the graft copolymer. PCL macromonomer as the comonomer allowed for a rather simple incorporation of PCL side chains into poly(cyclohexene oxide) backbone. This way poly(cyclohexene oxide)-*g*-poly( $\epsilon$ -caprolactone) graft copolymer with random sequences of the following structure (17) In solution polymerization (run B, C and D), with the increasing of CHO concentration while conversion and MWD decreased,  $M_n$  of polymer and the percentage of PCHO in copolymer substantially increased at the same irradiation time under UV at  $\lambda=300\text{nm}$ . This is expected to occur since higher amount of CHO can contribute to the further polymerization. For comparison we have performed polymerization in bulk (Run E). As can be seen from Table 4.4, photopolymerization performed in bulk (run E) gave lower conversion, lower MWD and higher  $M_n$  than photopolymerization performed in solution (Run D) at the same conditions, this is likely due to the less termination reactions.

Figure 4.4 shows the GPC chromatograms of 4 and graft copolymer formed therefrom. The new peak at lower elution volume is ascribed to the block copolymer. Notably, no peak pertaining to residual homopolymer was detected.

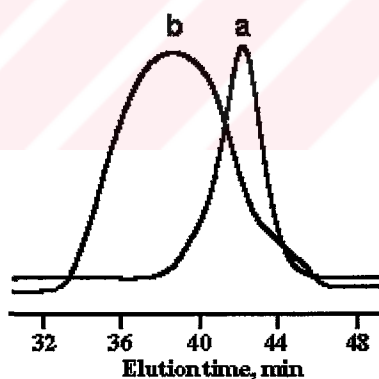


Figure 4.6. GPC trace of PCL<sub>1</sub> (4) (a) and PCL<sub>1</sub> – *g* - PCHO graft copolymer (17) (Table 4.4, run C) (b).

The graft copolymer structures were also assigned by means of NMR spectral measurements. The NMR spectrum of the block copolymer display typical signals at 3.36 ppm OCHCHO (PCHO) and 4.03 ppm OCH<sub>2</sub> (PCL<sub>1</sub>) (Figure 4.7).

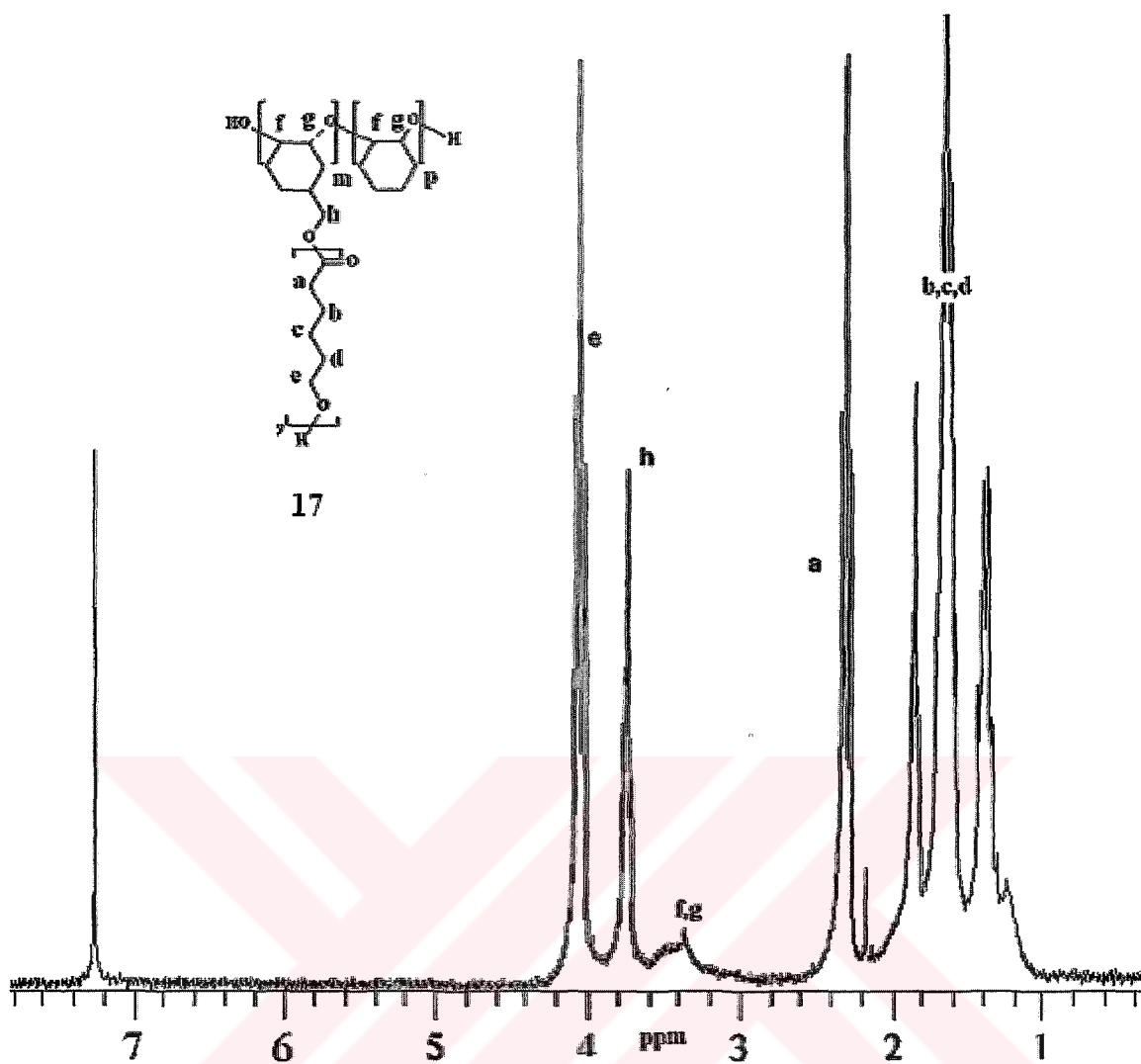


Figure 4.7.  $^1\text{H-NMR}$  spectra of  $\text{PCL}_1\text{-g-PCHO}$  graft copolymer (17)  
(Table 4.4, Run C)

Apart from CHO, bifunctional monomer, 3,4-epoxycyclohexyl-3',4'-epoxycyclohexene carboxylate (EEC) was used for this system. In the case of EEC, after 5 h irradiation a crosslinked polymer containing soft segments of linear PCL was obtained. The crosslinked polymer exhibited interesting swelling behaviour. At the same conditions in the presence of  $\text{Ph}_2\text{I}^+\text{PF}_6^-$ , while the swelling values for crosslinked polymer of EEC prepared by using only EEC bifunctional monomer was 600 %, for the crosslinked polymer obtained by using macromonomer (4) was 800 % in dichloromethane as a solvent. This is due to the soft segments of linear PCL in crosslinked network. The PCL segments increase the free volume of obtained crosslinked polymer and caused uptaking higher amount of solvent.

### 4.2.3. Copolymerization of Polystyrene Macromonomer with Cyclohexene Oxide (CHO)

We have also used Polystyrene macromonomer (**8**) in photoinitiated cationic polymerization in a similar manner as described for PCL macromonomer. Thus PSt macromonomer was polymerized cationically itself, with CHO monomer and also with PCL macromonomer (Reaction 4.8). The overall results are shown in Table 4.5 (Run2).

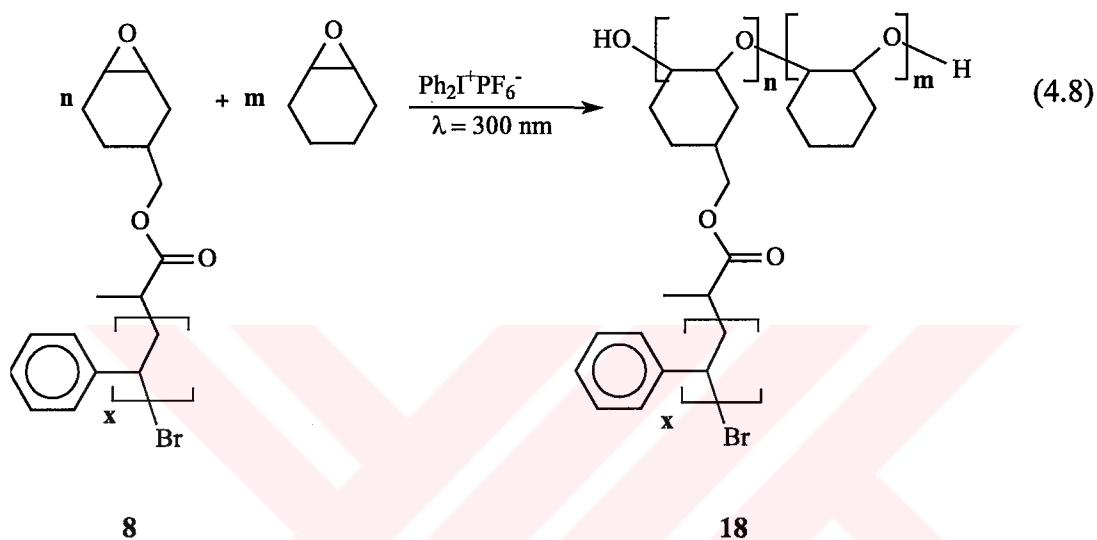


Figure 4.8 shows the GPC chromatograms of **8** and the graft copolymer formed there. The new peak at lower elution volume is ascribed to the graft copolymer. No peak was detected pertaining to residual homopolymer.

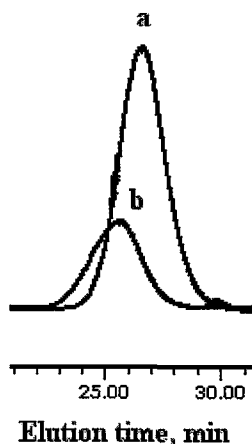


Figure 4.8. GPC trace of PSt (**8**) (a) and PSt-g-PCHO graft copolymer (**18**) (b) (Table 4.5, Run 3).

The graft copolymer structures were assigned by means of NMR spectral measurement. The NMR spectrum of the graft copolymer displays typical signals at 7.08-6.58 ppm (PSt) and 3.39 ppm (PCHO) (Figure 4.9).

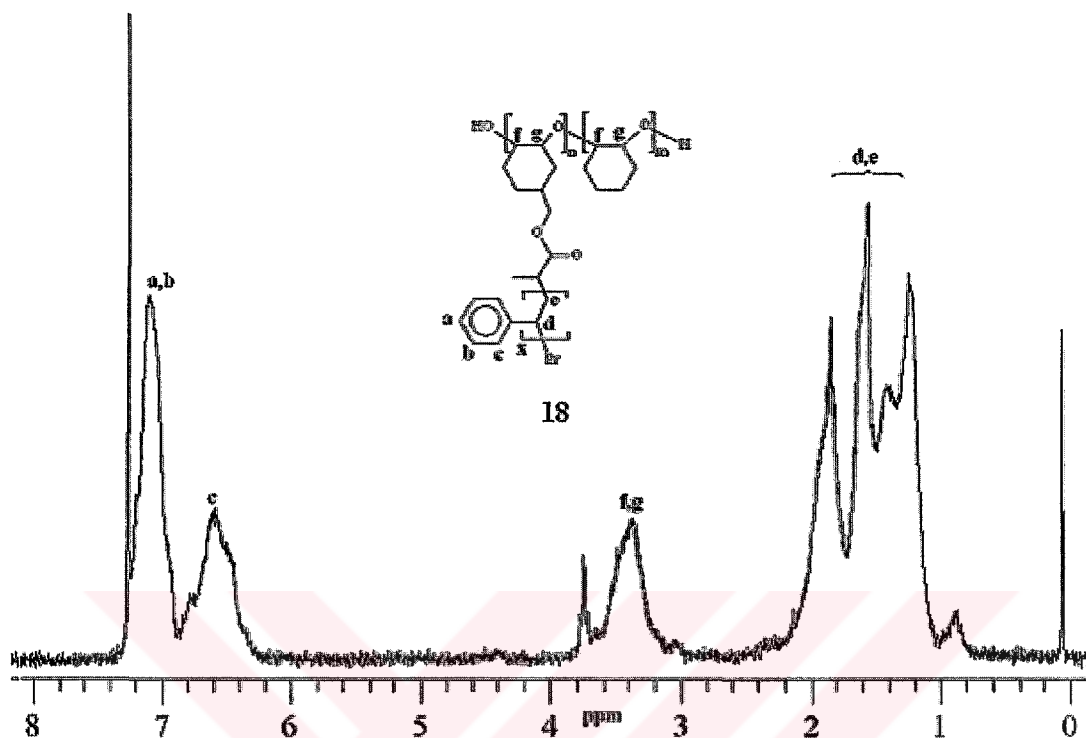


Figure 4. 9. <sup>1</sup>H NMR spectrum of PSt-g-PCHO graft copolymer.

#### 4.2.4. Copolymerization of Polystyrene and Poly(ε-caprolactone) Macromonomers

Photoinitiated cationic polymerization of polystyrene (8) and poly(ε-caprolactone) (4) in the presence of  $\text{Ph}_2\text{I}^+\text{PF}_6^-$  yielded copolymers of PCL and PSt macromonomers. The overall process is represented in reaction 4.9. Notably, both PSt and PCL side chains take part in the structure.

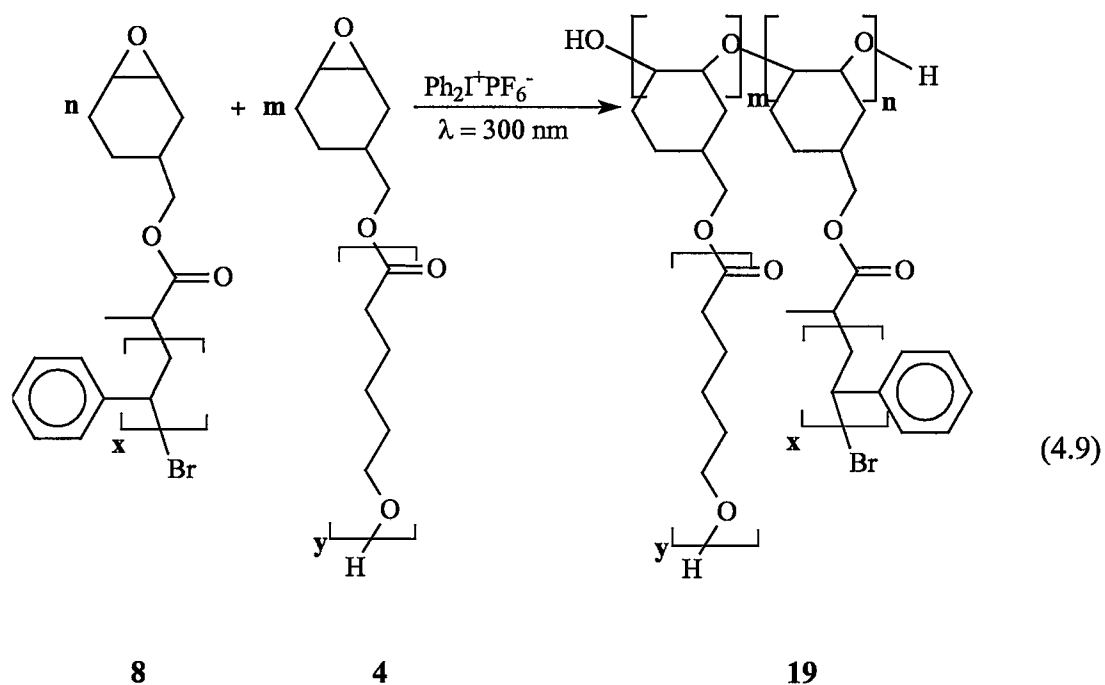


Figure 4.10 shows the GPC chromatograms of **8** and **4** and their copolymer. Although not very significant, some shift to the lower elution volume was observed.

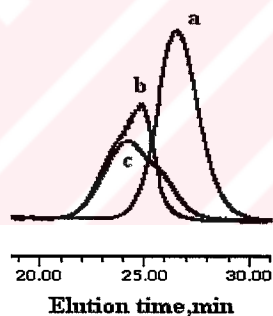


Figure 4.10. GPC traces of PSt (**8**) (a), PCL (**4**) (b) and PSt-*g*-PCL graft copolymer (**19**) (c) (Table 4.5, Run 4).

The copolymer structure were also assigned by means of NMR spectral measurements. The spectrum of the graft copolymer displays typical signals at 7.08-6.57 ppm aromatic peaks (PSt) and 4.06 ppm (PCL) (Figure 4.11) indicating both structural units.



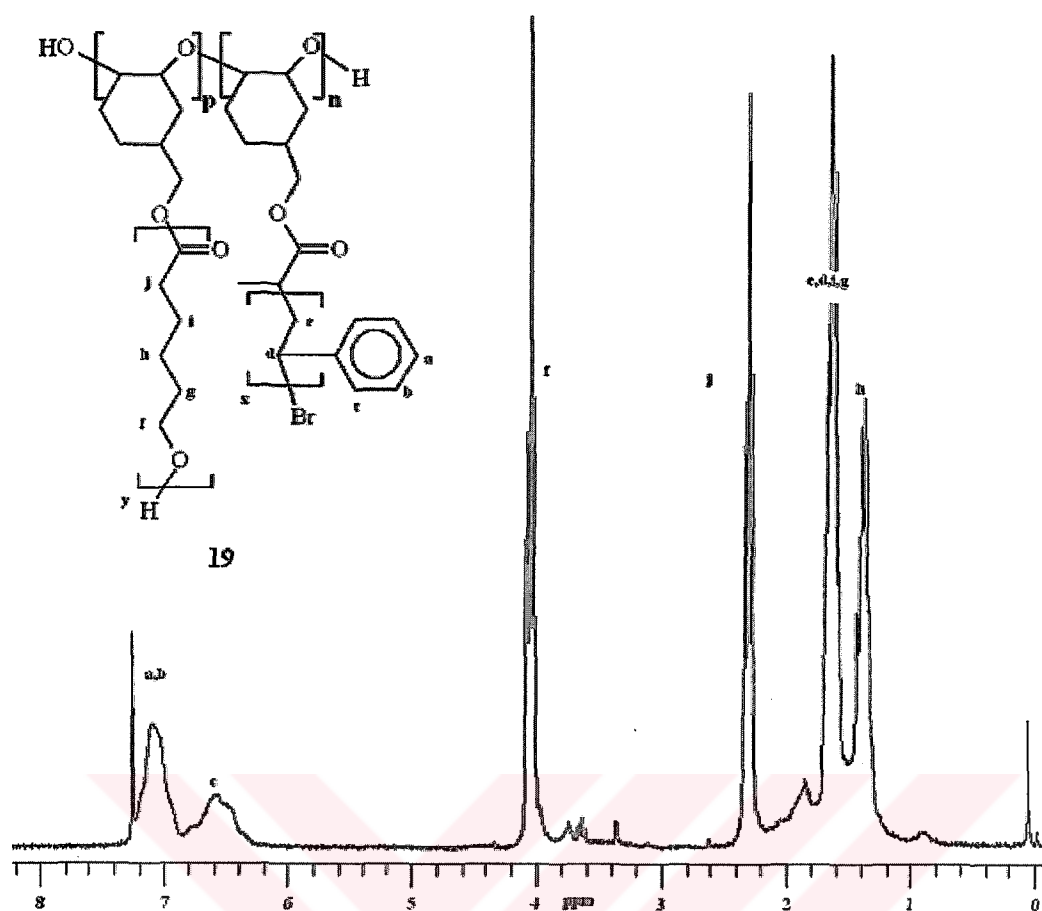


Figure 4.11.  $^1\text{H}$  NMR spectrum of PSSt-g-PCL graft copolymer.

#### 4.2.5. Copolymerization of Polystyrene and Poly( $\epsilon$ -caprolactone) Macromonomers with Cyclohexene Oxide (CHO)

Photoinitiated cationic polymerization of polystyrene macromonomer (**8**) and poly( $\epsilon$ -caprolactone) macromonomer (**4**) with CHO in the presence of  $\text{Ph}_2\text{I}^+\text{PF}_6^-$  yielded PCHO-g-PCL-PSSt (**20**) according to the following reaction 4.10.

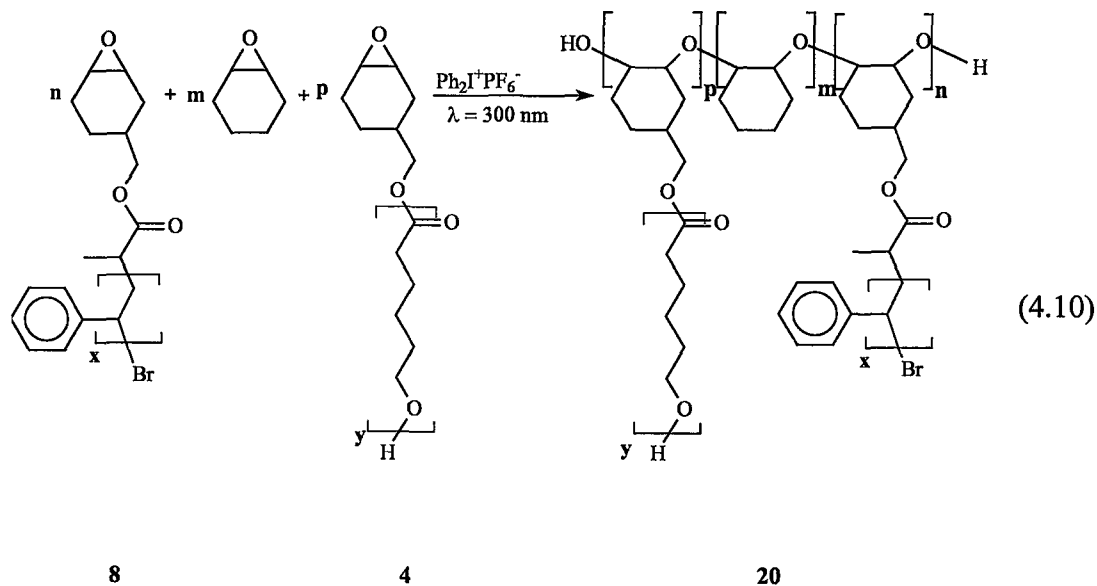


Figure 4.12 shows the GPC chromatogram of **8**, **4** and their graft copolymer (**20**) formed there. The new peak at lower elution volume is ascribed to the graft copolymer. No peak was detected pertaining to residual homopolymer.

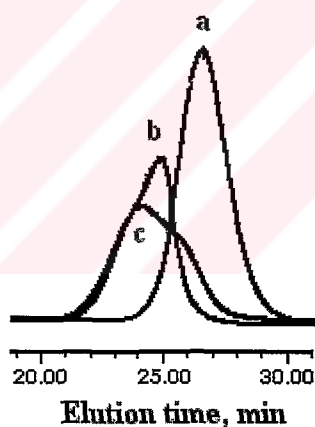


Figure 4.12. GPC traces of PSt (**8**) (**a**) PCL (**4**) (**b**) and PCHO-*g*-PCL-PSt graft copolymer (**20**) (**c**) (Table 4.5, Run 5).

The graft copolymer of PSt (**8**), PCL (**4**) and CHO was analyzed by NMR spectral measurements. The NMR spectrum displays typical signals at 7.08-6.58 ppm Ar-H (PSt), 3.35 ppm OCHCHO (PCHO) and 2.32-2.26 ppm OCH<sub>2</sub> (PCL) (Figure 4.13).

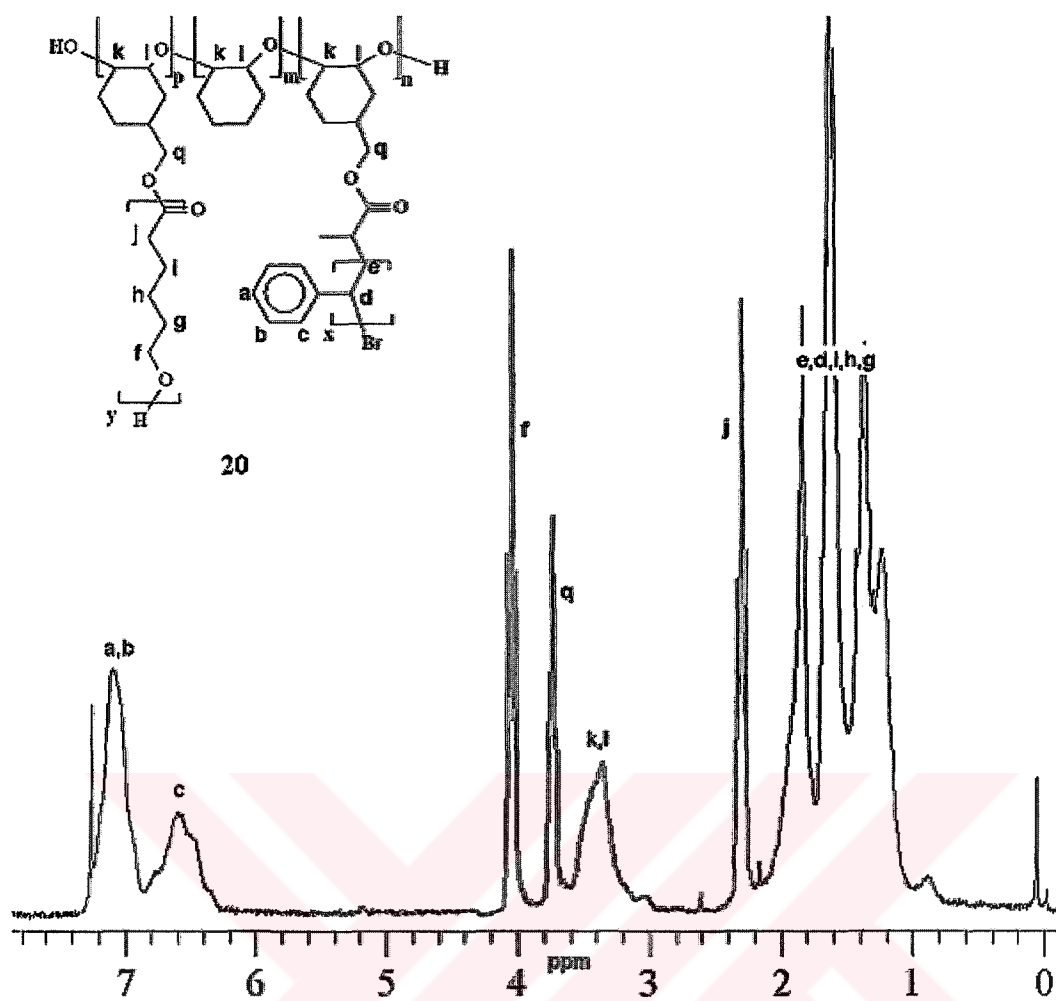


Figure 4.13. <sup>1</sup>H NMR spectrum of PCHO-g-PCL-PSSt graft copolymer.

**Table 4.5. Photoinitiated Cationic Polymerization Polystyrene and Poly( $\epsilon$ -caprolactone) macromonomers in the Absence and in the Presence of Cyclohexene Oxide (CHO) at Room Temperature in  $\text{CH}_2\text{Cl}_2$  by Using  $\text{Ph}_3\text{I}^+\text{PF}_6^-$  ( $5 \times 10^{-3} \text{ M}$ ), Irradiation wavelength ( $\lambda = 300 \text{ nm}$ ) [ $P_1 = \text{PSt} = 1950 \text{ g/mol}$ ],  $P_2 = \text{PCL}_2 = 2950 \text{ g/mol}$ ]**

Run	Macromonomer		Monomer (CHO) $\text{molL}^{-1}$	Irradiation Time (min.)	Conv. <sup>a</sup> %	Mn (GPC)	Mw/Mn	Copolymer Composition <sup>b</sup> (mol, %)		
	$P_1$ ( $\text{g.L}^{-1}$ )	$P_2$ ( $\text{g.L}^{-1}$ )						Pst	PCL	PCHO
1	---	200	0,89	45	13	7900	1,22	---	29	71
2	---	200	3,09	45	24	3100	1,7	---	3	97
3	40	---	0,45	30	28	3200	1,36	11	---	89
4	40	40	---	300	---	4850	1,56	40	60	---
5	80	80	0,89	360	3	4900	1,6	7	5	88

a)

a: CHO conversion  
b: Calculated from  $^1\text{H-NMR}$  spectra of samples.

From these results, it obvious that the polymerizability of the macromonomers, PSt is rather low. This behaviour is particularly observed when both macromonomers were used together in the system. The use of CHO monomer improves the polymerizability to some extend. But, in this case the major component of the copolymer is the CHO units having very small amount of PSt and PCL side chains. The lower reactivity of the macromonomers may be attributed to the limited mobility of the macromonomers compare to bare monomer CHO.



## 5. CONCLUSIONS

In conclusion, novel PCL and PSt macromonomers possessing CHO end group were synthesized and employed in photoinitiated cationic (co)polymerization using diphenyliodonium salt. Syntheses were facilitated by using ring opening polymerization of CL or ATRP of St and their subsequent epoxidation processes.

The photoinitiated polymerizations were carried out by taking advantage of onium salt decomposition under UV irradiation at various wavelengths. While high wavelength irradiation was utilized for the radical promoted and sensitized polymerization, the direct irradiation at lower wavelengths gave the structurally same polymers. The process is useful to obtain side chain copolymers of the macromonomers and also graft copolymer depending on the monomer composition in the polymerization.

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1. Synthesis and Characterization of Cyclohexene Oxide Functional Poly ( $\epsilon$ -caprolactone) Macromonomers and Their Use in Photoinitiated Cationic Homo- and Copolymerization.

Degirmenci M., **Izgin O.** and Yagci, Y., 2004.  
*J. Polym. Sci. Polym. Chem.Ed.*, (42), 3365

### Scientific Activities

2003- 17<sup>th</sup>. National Chemistry Congress – Poster Presentation.  
(Istanbul University, Istanbul, Turkey)

2004- 18<sup>th</sup>. National Chemistry Congress – Oral Presentation.  
(Kafkas University, Kars, Turkey)