İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF NOVEL WELL-DEFINED MACROPHOTOINITIATORS PREPARED BY ATRP AND ROP METHODS AND THEIR USE IN BLOCK COPOLYMERIZATION

Ph.D. Thesis by
Mustafa DEĞİRMENCİ
(515992005)

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Supervisor (Chairman): **Prof. Dr. Yusuf YAĞCI**
Members of the Examining Committee: **Prof. Dr. Niyazi BIÇAK (İ.T.Ü.)**
Prof. Dr. Gürkan HIZAL (İ.T.Ü.)
Prof. Dr. İskender YILGÖR (Koç Ü.)
Assoc. Prof. Dr. Nihan NUGAY (B.Ü.)

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ATRP VE ROP METODLARI İLE TASARLANMIŞ YENİ MAKROFOTOBAŞLATICILARIN SENTEZİ, KARAKTERİZASYONU VE BLOK KOPOLİMERİZASYONDA KULLANILMALARI

DOKTORA TEZİ
Mustafa DEĞİRMENCİ
(515992005)

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Tez Danışmanı : **Prof. Dr. Yusuf YAĞCI**

Diğer Jüri Üyeleri: **Prof. Dr. Niyazi BIÇAK (İ.T.Ü.)**
Prof. Dr. Gürkan HIZAL (İ.T.Ü.)
Prof. Dr. İskender YILGÖR (Koç Ü.)
Doç. Dr. Nihan NUGAY (B.Ü.)

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TABLE of CONTENTS

LIST of ABBREVIATIONS

CRP : Controlled Radical Polymerization
ATRP : Atom Transfer Radical Polymerization
NMP : Nitroxide Mediated Polymerization
SFRP : Stable Free Radical Polymerization
RAFT : Reversible Addition-Fragmentation Chain Transfer Polymerization
ROP : Ring-Opening Polymerization
PI : Photoinitiator
CTA : Chain Transfer Agent
PPI : Polymeric Photoinitiator
GPC : Gel Permeation Chromatography
IR : Infrared spectrophotometer
NMR : Nuclear Magnetic Resonance Spectroscopy
UV : Ultra Violet
M : Monomer
St : Styrene
MMA : Methyl Methacrylate
ε-CL : Epsilon Caprolactone
CHO : Cyclohexene Oxide
PSt : Polystyrene
PMMA : Poly(methyl Methacrylate)
PLC : Poly(ε-Caprolactone)
PCHO : Poly(cyclohexene Oxide)
COI : Coinitiator
bpy : Bipyridine
THF : Tetrahydrofuran
HMPP : 2-Hydroxy-2-Methyl-1-Phenyl Propan-1-One, Darocure 1173, (Monofunctional ROP Initiator)
B : Benzoin (Monofunctional ATRP Initiator)
HE-HMPP : 2-Hydroxy-1-[4-(2-Hydroxyethoxy)phenyl]-2-Methyl Propan-1-One, Irgagure 2959, (Bifunctional ROP initiator)
On^+ : Onium Salt
$Ph_2I^+PF_6$: Diphenyliodonium Hexafluorophosphate
$Ph_3S^+PF_6^-$: Triphenylsulfonium Hexafluorophosphate
$EMP^+PF_6^-$: *N*-Ethoxy-2-Methylpyridinium Hexafluorophosphate
HMPP-Br : 1,1-Dimethyl-2-Oxo-2-Phenylethyl-2-bromopropanoate (Monofunctional ATRP Initiator)
B-Br : 2-Oxo-1,2-diphenylethyl-2-Bromo Propionate (Monofunctional ATRP Initiator)
Br-HE-HMPP-Br : 2-(4-{[(2-Bromopropanoyl)oxy]methoxy}phenyl)-1,1-dimethyl-2-Oxoethyl-2-Bromopropanoate (Bifunctional ATRP Initiator)

HMPP-PSt	: Photoactive Polystyrene with Darocure 1173 End Chain Units
B-PSt	: Photoactive Polystyrene with Benzoin End Chain Units
HE-HMPP-PSt	: Photoactive Polystyrene with Irgacure 2959 Mid-Chain Units
HMPP-PCL	: Photoactive Poly(ε-Caprolactone) with Darocure 1173 End Chain Units
B-PCL	: Photoactive Poly(ε-Caprolactone) with Benzoin End Chain Units
HE-HMPP-PCL	: Photoactive Poly(ε-Caprolactone) with Irgacure 2959 Mid-Chain Units

LIST of TABLES

LIST of FIGURES

Page No

LIST of SYMBOLS

$\Phi_{R\cdot}$	: Quantum Yield of Radical Formation
Φ_P	: Quantum Yield of Photoinitiation
f	: Initiator Efficiency
λ	: Wavelength
ε	: Molar absorption Coefficient
$h\upsilon$	: Radiation
$R^{\cdot}$	: Radical
I	: Initiator
COI	: Coinitiator
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

SYNTHESIS AND CHARACTERIZATION OF NOVEL WELL-DEFINED MACROPHOTOINITIATORS PREPARED BY ATRP AND ROP METHODS AND THEIR USE IN BLOCK COPOLYMERIZATION

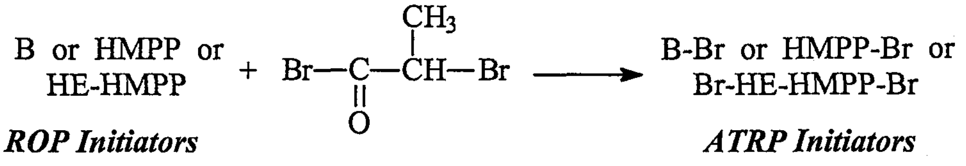
SUMMARY

Macrophotoinitiator is the abbreviation of macromolecular photoinitiator. A macrophotoinitiator is generally referred to a linear macromolecule possessing side- or main- chain photo reactive groups capable of initiating polymerization reaction. These materials are of great scientific and technological interest because of their application in UV-curable coatings and as precursors for graft and block copolymers depending on the position of the photoinitiator moiety incorporated into the polymer chain. The advantages expected from the polymeric photoinitiators include good compatibility, low migration, and low volatility which reduces odor problems associated with the low molar-mass photoinitiators

The present work describes the synthesis and characterization of novel well-defined end- and mid-chain functional macrophotoinitiators of polystyrene (PSt) and poly(ε-caprolactone) (ε-CL) prepared by two different controlled/living polymerization methods namely, Atom Transfer Radical Polymerization (ATRP) and Ring-Opening Polymerization (ROP) and their subsequent use in block copolymerization.

For this purpose, mono- and dihydroxy functional photoinitiators namely, benzoin (B), 2-hydroxy-2-methyl-1-phenyl propan-1-one (HMPP), Darocure 1173, and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl propan-1-one (HE-HMPP), Irgacure 2959, respectively were used as initiators.

New mono and bifunctional ATRP initiators were synthesized by the condensation of 2-bromopropanoyl bromide with B, HMPP and HE-HMPP, respectively and characterized (reaction 1).

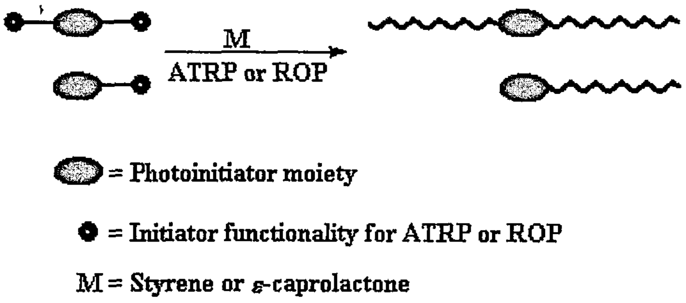


$$\begin{array}{c}\text{B or HMPP or}\\ \text{HE-HMPP}\end{array} + \mathrm{Br{-}\underset{\underset{O}{\|}}{C}{-}\overset{\overset{CH_3}{|}}{CH}{-}Br} \longrightarrow \begin{array}{c}\text{B-Br or HMPP-Br or}\\ \text{Br-HE-HMPP-Br}\end{array} \qquad (1)$$

ROP Initiators ***ATRP Initiators***

The ATRP of styrene (St) in bulk at 110 °C by means of ATRP initiators in conjunction with a cuprous complex Cu(I)Br/bipyridine and the ROP of (ε-caprolactone) (ε-CL) in bulk at 110 °C by means of ROP initiators in conjunction with the stannous-2-ethylhexanoate ($Sn(Oct)_2$) catalyst yielded well-defined

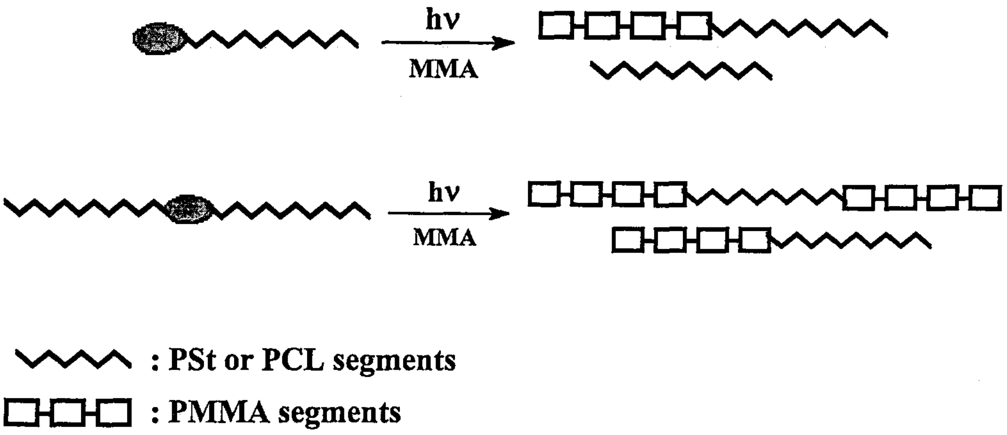
macrophotoinitiators of polystyrenes and poly(ε-caprolactone)s with photoactive alkoxy phenylketone groups. The GPC, IR, H-NMR, UV and fluorescence spectroscopic studies revealed that low-polydispersity polystyrene and poly(ε-caprolactone) with desired photoinitiator functionality at the end or in the middle of the chain were obtained. The synthetic strategy followed for the preparation of macrophotoinitiators is described in Scheme 1.



(2)

Scheme 1. Schematic representation for preparation of macrophotoinitiators

These prepolymers (macrophotoinitiators) were used to induce radical polymerization of methyl methacrylate (MMA) upon irradiation via α-cleavage of the incorporated phenyl ketone groups. The type of macrophotoiniator influences the polymerization products. While end-chain functional macrophotoinitiators led to the formation of both homo and block copolymers, only block copolymers of St or ε-CL and MMA were formed with mid-chain functional macrophotoinitiator (reactions 3, 4). Successful blocking has been confirmed by a strong change in the molecular weight of the prepolymer and the block copolymer as well as by NMR spectral measurements.



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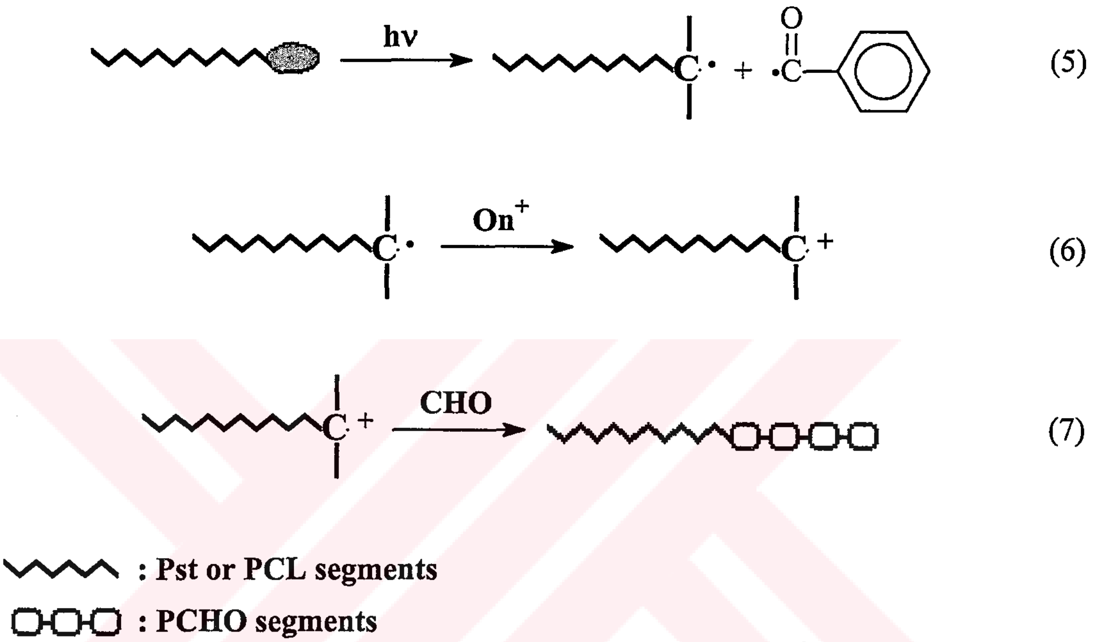
Scheme 2. Schematic representation for preparation of block copolymers via photoinduced free radical polymerization

As an alternative usage of the macrophotoinitiators, transformation polymerization approach was also applied. For this purpose, transformation reaction was carried out in order to convert the polymeric radicals into initiating cations with the aid of oxidizing agents such as iodonium and pyridinium salts. With this method block copolymers of monomers which do not polymerize with the same mechanism were prepared. For transformation reactions, macrophotoinitiators with benzoin end chain units (B-PSt and B-PCL) were used to induce free radical promoted cationic polymerization of cyclohexene oxide (CHO) in the presence of an onium salt. The reason for using benzoin containing macrophotoinitiators is the strong electron donating efficiency of hydroxybenzyl radicals stemming from such prepolymers. Schematic representation for the preparation of PSt (or PCL)-PCHO block copolymers is depicted in Scheme 3.



Scheme 3. Schematic representation for preparation of block copolymers via photoinduced free radical promoted cationic polymerization

It should be pointed out that the benzoyl radicals formed instantaneously do not participate in the redox process, due to their electronic structure, i.e. possessing electron withdrawing carbonyl group. This way selected redox process is achieved.

ATRP VE ROP METODLARI İLE TASARLANMIŞ YENİ MAKROFOTOBAŞLATICILARIN SENTEZİ, KARAKTERİZASYONU VE BLOK KOPOLİMERİZAYONDA KULLANILMALARI

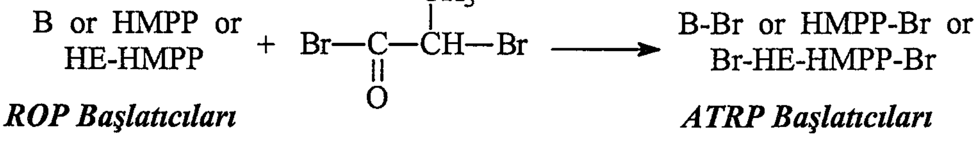
ÖZET

Makrofotobaşlatıcı kavramı makromoleküler ve fotobaşlatıcı kelimelerinin kısaltılmış şeklidir. Genellikle bir makrofotobaşlatıcı, ana zincir veya zincir ucunda polimerizasyon reaksiyonlarının başlatılmasını sağlayan bir fotoaktif grup içeren makromolekülü ifade etmektedir. Macrofotobaşlatıcılar UV-sertleştirme uygulamalarında kullanılmaları ve aynı zamanda fotoaktif grubun konumuna bağlı olarak graft ve blok kopolimerlerin sentezinde başlatıcı fonksiyunu görmelerinden dolayı bilimsel ve teknolojik olarak büyük bir öneme sahiptirler. Polimerik fotobaşlatıcılardan beklenilen avantajlar iyi uyumluluk, göçme olaylarının az olması ve istenmeyen kokulara neden olan düşük mol ağırlıklı analoglarına göre az uçucu olmalarıdır.

Bu çalışmada, iki ayrı kontrollü/yaşayan polimerizasyon sistemi olan Atom Transfer Radikal Polimerizasyon (ATRP) ve Halka Açılması Polimerizasyonu (ROP) yöntemleri ile ana zincir ve zincir ucunda fotoaktif grup içeren tasarlanmış yeni polistiren (PSt) ve poli(ε-kaprolakton) (PCL) marofotobaşlatıcılarının sentezi, karakterizasyonu ve blok kopolimerizasyonda kullanılmaları incelenmiştir.

Bu amaçla, bir ve iki hidroksil fonksiyonuna sahip fotobaşlatıcılar, benzoin (B), 2-hidroksi-2-metil-1-fenil propan-1-on (HMPP), Darocure 1173 ve 2- hidroksi-1-[4-(2-hidroksietoksi)fenil]-2-metil propan-1-on) (HE-HMPP), Irgacure 2959, başlatıcı olarak kullanıldı.

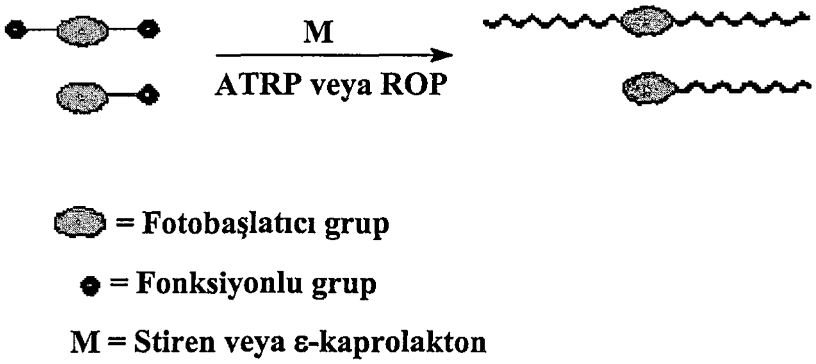
Yeni tek ve çift fonksiyonlu ATRP başlatıcıları, 2-brompropanoil bromür'ün B, HMPP ve HE-HMPP fotobaşlatıcıları ile kondensasyonu sonucu elde edildi karakterizasyonu yapıldı (tepkime 1).



$$\text{B or HMPP or HE-HMPP} + \text{Br}-\underset{\underset{\text{O}}{\|}}{\text{C}}-\overset{\overset{\text{CH}_3}{|}}{\text{CH}}-\text{Br} \longrightarrow \text{B-Br or HMPP-Br or Br-HE-HMPP-Br} \qquad (1)$$

Stirenin (St) Atom Transfer Radikal Polimerizasyonu, ATRP başlatıcıları ve bakır(I) kompleksi Cu(I)Br/bipiridin varlığında çözücüsüz ortamda, 110 ^{0}C'de, ε-kaprolakton'un Halka Açılması Polimerizasyonu ise ROP başlatıcıları ve kalay oktoat, Sn(Oct)$_2$, katalizörü varlığında çözücüsüz ortamda, 110 ^{0}C'de gerçekleştirildi.

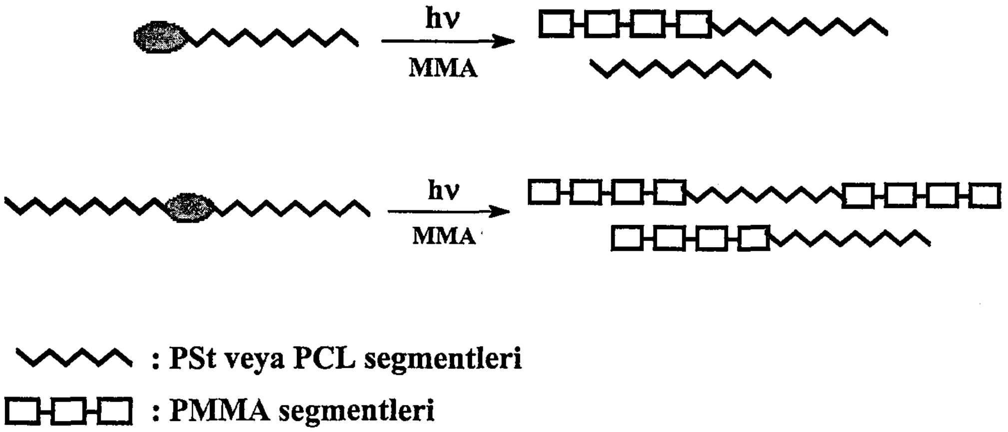
Bu polimerizasyonların sonucunda fotoaktif alkoksi fenil keton gruplarını içeren tasarlanmış polistiren ve poli(ε-kaprolakton) macrofotobaşlatıcıları sentezlendi. Ucunda ve ortasında istenilen fotobaşlatıcı fonksiyonuna ve dar molekül ağırlığı dağılımına sahip polistiren ve poli(ε-kaprolakton) polimerlerinin sentezlenmiş olduğu, GPC ve IR, H-NMR, UV ve floresans spectroskopik çalışmaları ile ispatlandı. Makrofotobaşlatıcıların sentetik olarak hazırlanışı Şekil 1. de gösterilmiştir.



(2)

Şekil 1. Macrofotobaşlatıcıların hazırlanışının şematik olarak gösterimi

Metil metakrilatın (MMA) fotokimyasal yolla radikalik olarak polimerleşmesinde, UV ışığına maruz bırakıldıklarında fenil keton grubunun bulunduğu kısımdan α–bölünmesine uğrayan bu önpolimerler (macrofotobaşlatıcılar) kullanıdı. Kullanılan makrofotobaşlatıcı tipi oluşan polimerizasyon ürününü üzerinde etkin bir rol oynamaktadır. Zincir ucunda fotoaktif grup içeren makrofotobaşlatıcıların kullanılması ile hem homo, hem de blok kopolimerler elde edilirken, zincir ortasında fotoaktif grup içeren makrofotobaşlatıcıların kullanılmasından St veya ε-CL ile MMA'nın sadece blok kopolimerleri ele geçer (tepkime 3 ve 4). Başarılı bir şekilde bloklaşmanın gerçekleştiği, önpolimer ve blok kopolimerlerin molekül ağırlıklarındaki büyük farklılığın yanısıra, NMR spektral ölçümleri ile de ispatlandı.

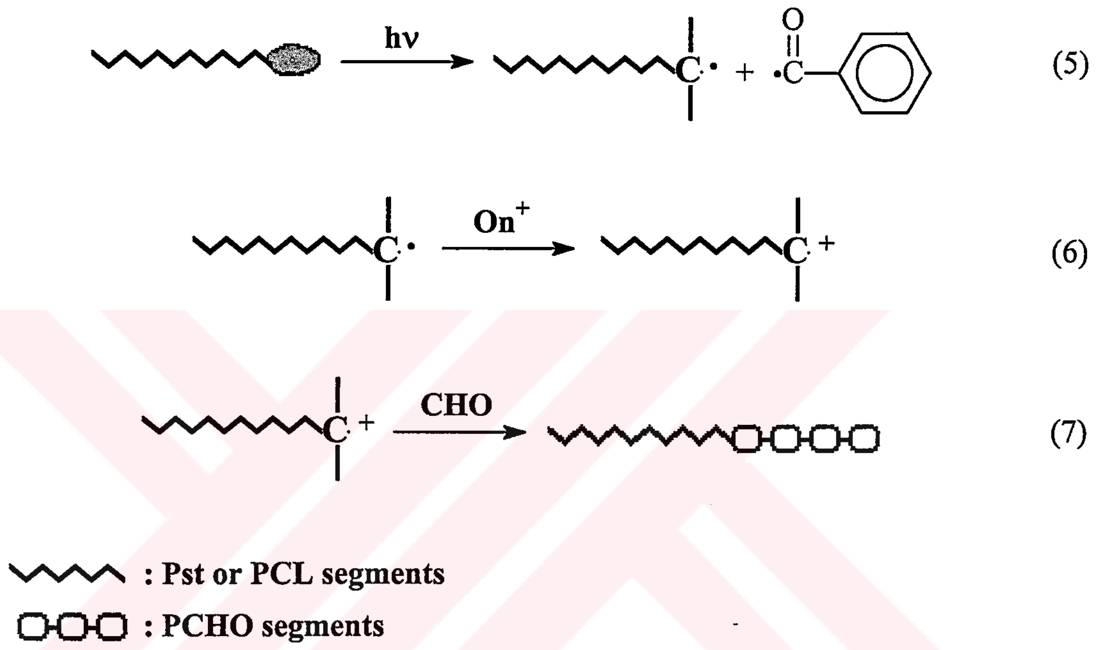


(3)

(4)

Şekil 2. Blok kopolimerlerin fotokimyasal serbest radikalik polimerizasyon yöntemiyle elde edilmelerinin şematik olarak gösterilişi

Bir alternatif olarak, aynı zamanda dönüşüm polimerizasyonu yöntemi makrofotobaşlatıcılara uygulandı. Bu amaçla, piridinyum ve iyodonyum tuzları gibi oksitleme vasıtaları yardımıyla polimerik radikalleri katyona çevirmek için dönüşüm reaksiyonu gerçekleştirildi. Bu yolla aynı mekanizma ile polimerleşmeyen monomerlerden blok kolpolimer hazırlamak mümkündür. Dönüşüm reaksiyonları için, bir onyum tuzu varlığında siklohezenoksit'in katyonik olarak polimerleşmesinde radikal kaynağı olarak kullanılan ve zincir uç grubunda benzoin bulunduran makrofotobaşlatıcılardan (B-PSt ve B-PCL) yararlanıldı. Benzoin içeren makrofotobaşlatıcıların kullanılmasının nedeni bu tür önpolimerlerden elde edilen hidroksibenzil radikallerinin güçlü elektron verebilme özelliğine sahip olmalarıdır. Şekil 3. de PSt (veya PCL)-PCHO blok kopolimerlerinin sentezlerinin şematik olarak gösterilişi verilmiştir.



Şekil 3. Blok kopolimerlerin radikal kaynaklarıyla fotokimyasal katyonik polimerizasyon yöntemiyle elde edilmelerinin şematik olarak gösterilişi

Aynı sistemde meydana gelen benzoil radikalleri (tepkime 5), yapısındaki karbonil grubunun elektron çekici özelliğinden dolayı redoks prosesine katılmadığını belirtmekte yarar vardır. Bu şekilde seçimli redoks prosesi başarılmıştır.

1. INTRODUCTION

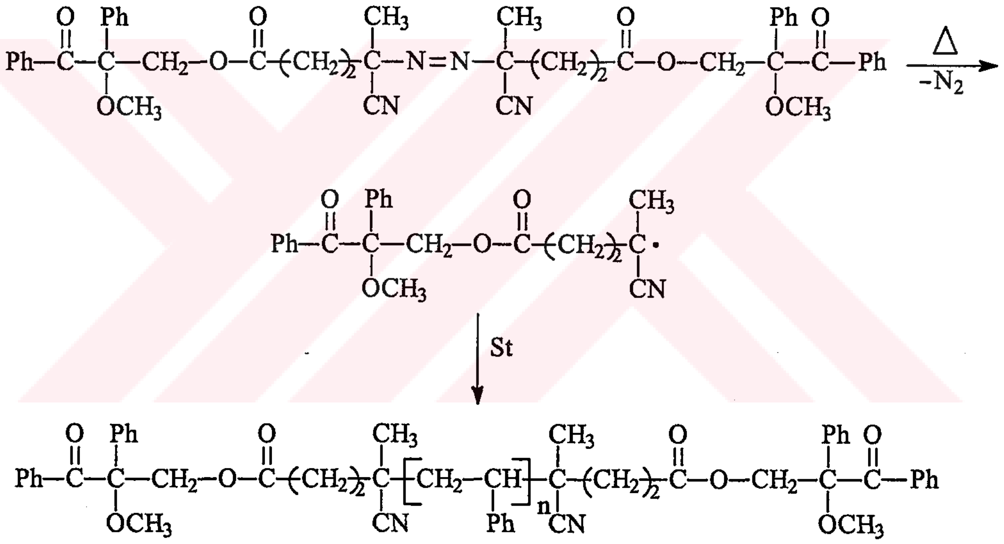
The synthesis of polymers with well-defined compositions, architectures, and functionalities has long been of great interest in polymer chemistry. Typically, living polymerization techniques are employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination [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. The development during the last decade of various processes for the control of free radical polymerizations (CRP) has lead to new ways of synthesizing polymers with new architectures. 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 predetermined molecular weights and narrow molecular weight distributions and block copolymers and other well-defined structures can be obtained.

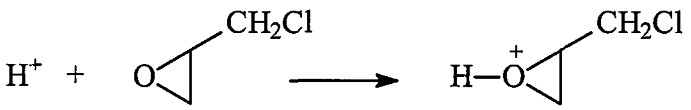
Polymers possessing side- or main-chain photo reactive groups capable of initiating polymerization reaction receive continuous interest due to their application in various fields of UV curing and in polymer synthesis [8,9]. In UV curing applications, the advantages expected from the polymeric photoinitiators include good compatibility, low migration, and low volatility which reduces odor problems associated with the low molar-mass photoinitiators [10,11]. Polymeric photoinitators are also precursors for block or graft copolymers depending on the position of the photoinitiator moiety incorporated into the polymer chain. Many side- and main-chain photoinitiators have been synthesized and their photochemistry and utilization in both applications have been reviewed extensively [8-12].

Polymers containing terminal photoactive benzoin groups were synthesized using azo-benzoin initiators [13,14]. The thermal treatment of these initiators in the presence of styrene (St) leads to benzoin groups at both ends of polystyrene chain, as polystyryl radicals tend to terminate via recombination.



(1.1)

Such photoactive polymers can be used in the preparation of block copolymers of monomers with different chemical nature such as those with liquid crystalline properties [15]. Similarly, activated monomer (AM) polymerization was used to produce polymers with terminal benzoin groups [16,17]. The process was easily adapted so that benzoin type photoinitiators containing hydroxyl group were used as initiators in the activated monomer polymerization.



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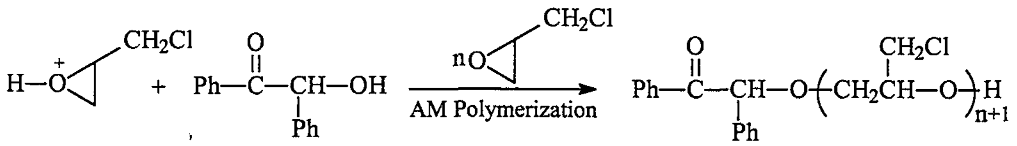


(1.3)

Aliphatic polyesters are an attractive class of polymer that can be used in biomedical and pharmaceutical applications. Because of such applications homo- and copolymers of polylactones such as poly(ε-caprolactone) receive interest. Tin octoate, $Sn(O(O)CCH(C_2H_5)C_4H_9)_2$, in short $Sn(Oct)_2$, is the most widely used [18] initiator to synthesize designed polymers based on poly(ε-caprolactone). In particular when used in conjunction with hydroxyl functional compounds or prepolymers, telecehelics, linear and star-shaped block copolymers or networks can be obtained [19-27] via corresponding alkyl octoate formation.

This study describes the preparation of novel macrophotoinitiators of polystyrene and poly(ε-caprolactone) by two controlled/living polymerization methods namely, ATRP and ROP, and subsequently their use in block copolymerization.

2. THEORETICAL PART

2.1. 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 [28].

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

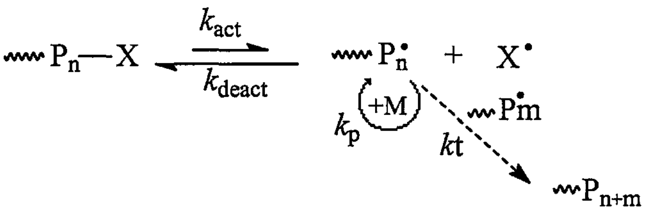
-the rate of depropagation is low in comparison with propagation and the system is sufficiently homogeneous, in the sense of availability of active centers and mixing.

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

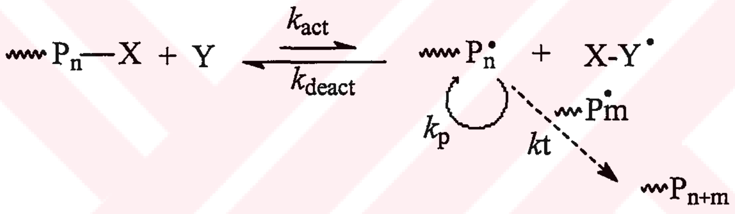
1. polymerization proceeds until all the monomer has been consumed - further addition of monomer results in continued polymerization
2. the number average molecular weight, M_n (or X_n, the number average degree of polymerization), is a linear function of conversion
3. the number of polymer molecules (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.[28,29] 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) [30], **nitroxide mediated polymerization** (NMP) or **stable free radical polymerization** (SFRP) [31] and **reversible addition-fragmentation chain transfer polymerization** (RAFT) [32].

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.



(2.1)



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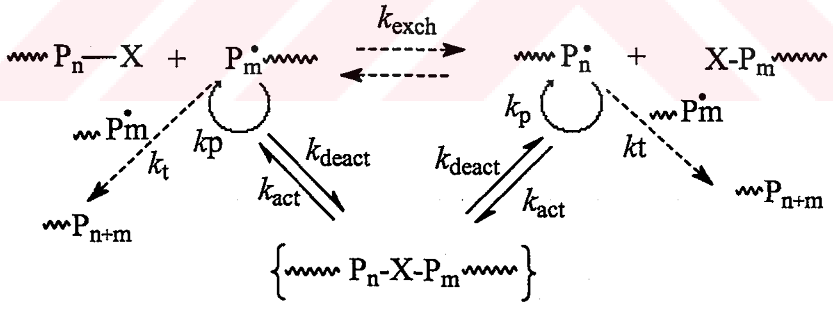


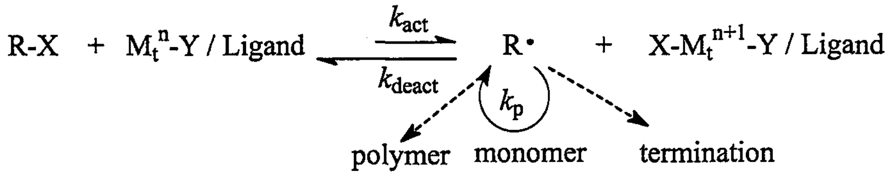
(2.3)

2.1.1 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 [28,30].

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 [28,30,33].

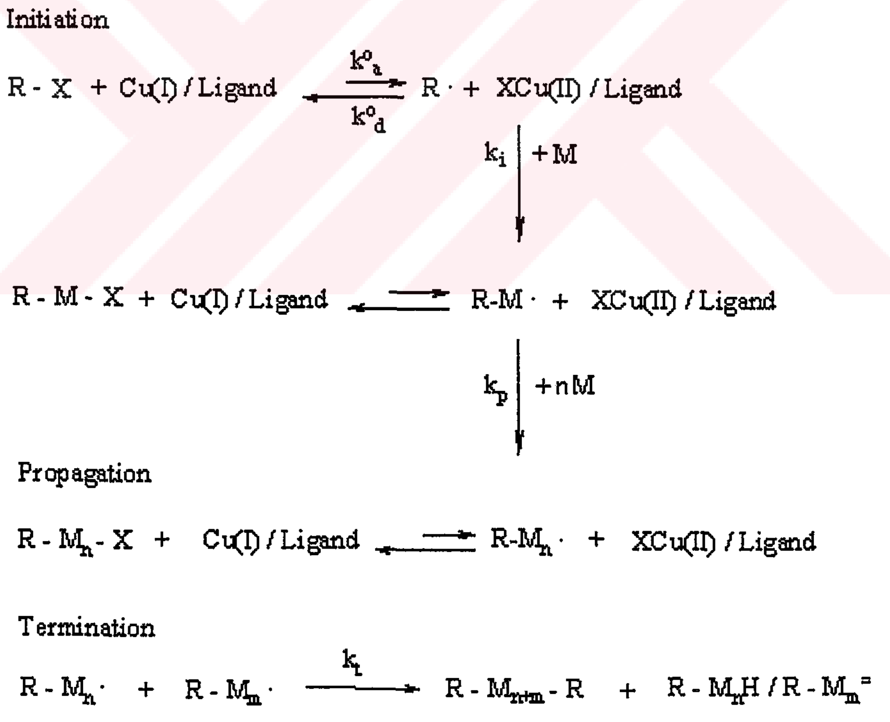
Atom transfer radical addition can be extended to ATRP if the conditions can be modified such that more than one addition step is possible. An ATRP system consists of an initiator, a copper (I) halide complexed with some ligand (s), and of course, monomer. ATRP occurs as a repetitive addition of a monomer 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 (2.4) [30,33].



(2.4)

2.1.1.1 Mechanism and Kinetics of ATRP

The general mechanism of ATRP which is schematically represented in (2.5a-d), involves the abstraction of a halogen from the dormant chain by a metal center, such as complexes of Cu^1, in a redox process [28]. Upon halogen abstraction, the free radical formed (the active species) can undergo propagation. However, the free-radical is also able to abstract the halogen back from the metal, reproducing the dormant species. These processes are rapid, and the equilibrium that is established favors the dormant species. By this way, all chains can begin growth at the same time, and the concentration of free radicals is quite low, resulting in a reduced amount of irreversible radical-radical termination. The final result is that degrees of polymerization (DP) can be predetermined (DP=Δ [M]/ $[I]_o$) and M_w/M_n is quite low (1, 05-1,5), and good control of functionalities is achieved [34].



Initiation

$$R\text{-}X + Cu(I)/Ligand \underset{k^o_d}{\overset{k^o_a}{\rightleftharpoons}} R\cdot + XCu(II)/Ligand \quad (2.5a)$$

$$\downarrow k_i \; +M$$

$$R\text{-}M\text{-}X + Cu(I)/Ligand \rightleftharpoons R\text{-}M\cdot + XCu(II)/Ligand \quad (2.5b)$$

$$\downarrow k_p \; +nM$$

Propagation

$$R\text{-}M_n\text{-}X + Cu(I)/Ligand \rightleftharpoons R\text{-}M_n\cdot + XCu(II)/Ligand \quad (2.5c)$$

Termination

$$R\text{-}M_n\cdot + R\text{-}M_m\cdot \xrightarrow{k_t} R\text{-}M_{n+m}\text{-}R + R\text{-}M_nH / R\text{-}M_m^{=} \quad (2.5d)$$

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).

$$R_P = k_{app}[M] = k_p\,[P\bullet]\,[M] = k_p\,K_{eq}\,[I]_o\,\frac{[Cu(I)]\,[M]}{[Cu(II)X]} \qquad \text{(Eq:2.1)}$$

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 $K_{eq} = k_{act}/k_{deact} = 4 \times 10^{-8}$ [35,36].

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 [28].

2.1.1.2 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 [30] . The currently used catalyst systems are not sufficient to polymerize less reactive monomers that produce non–stabilized, reactive radicals such as ethylene, α–olefins, vinyl chloride and vinyl acetate, though copolymerization is sometimes successful [28].

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

(i) Styrene: Styrene ATRP is usually conducted at 110 °C for bromide–mediated polymerizaiton and 130 °C for the chloride–mediated polymerization [37]. 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 [28].

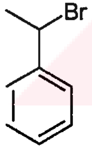
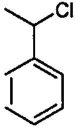
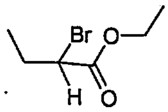
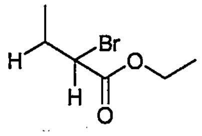
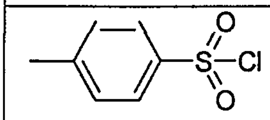
(ii) Methyl Methacrylate: The standard conditions for MMA ATRP are similar to those of styrene ATRP except that less copper(I) catalyst is needed and the polymerizations are conducted in 50% solution in diphenyl ether or dimethoxy benzene at 90 °C. The use of copper bromide instead of copper chloride 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 [28].

b) Initiators

The most frequently used initiator types in ATRP systems are given in Table 2.1.

Table 2.1. 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 α–carbon, such as aryl, carbonyl and allyl groups, potentially can be used as ATRP initiators.

Polyhalogenated compounds (CCl_4 and $CHCl_3$) 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 [33].

c) Transition Metals

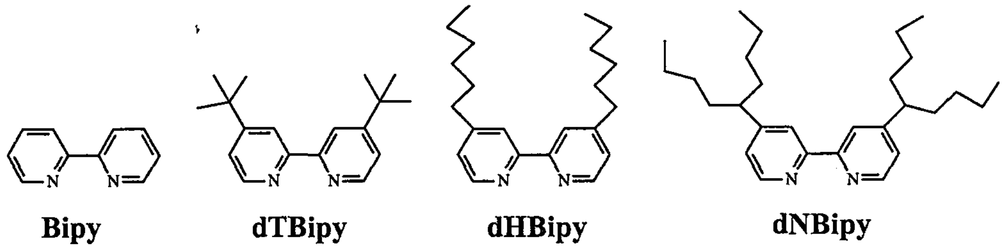
Basic requirements for good catalyst are high selectivity towards atom transfer process and high labiality of the resulting $X\text{-}M_t^{n+1}$ species (higher oxidation state of metal). The metal should participate in a one-electron process which would result in oxidative addition/reductive elimination but not in atom transfer process. Additionally, the metal should have a high affinity for atom/group X, but a low affinity for hydrogens and alkyl radicals. Otherwise, transfer reactions (β-hydrogen elimination) and the formation of organometallic derivatives may be observed reducing selectivity of propagation and control (livingness) of process. The most important factors in selecting good ATRP catalyst are the equilibrium position, dynamics of exchange between dormant and active species. These parameters are related to the redox cycle M_t^n/M_t^{n+1} but it must be remembered that ATRP is not an electron transfer process but an atom transfer process. Thus, the inner coordination sphere of M_t^n must expand to accommodate a new X (halide) ligand. Expansion from tetra to pentacoordinated structure Cu(I)/2 ligand → X-Cu(II)/2 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), $Ru(II)/Al(OR)_3$ and $Fe(II)/3\ PR_3$ [35,36].

d) Ligands

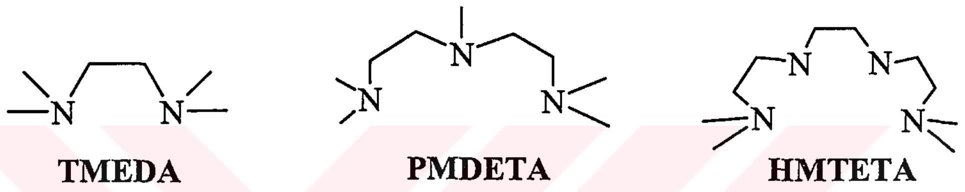
The position of the atom transfer equilibrium depends upon the nature of the metal and ligands. Generally, more electron donating ligands stabilize better the higher oxidation state of the metal and accelerate the polymerization [33]. Ligands that sterically crowd the metal center prevent the approach of the alkyl halide initiator or end group and therefore are poor ligands for ATRP [28].

The most widely used ligands for ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as N,N,N ,N ,N pentamethyldiethylenetriamine

(PMDETA), Tetramethylethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetraamine (HMTETA), tris[2-(dimethylamino) ethyl]amine (Me$_6$-TREN) and Alkylpyridylmethaneimines are also used. Examples of ligands used in copper-mediated ATRP are shown in below [38,39].



(2.6)



(2.7)

e) Deactivators

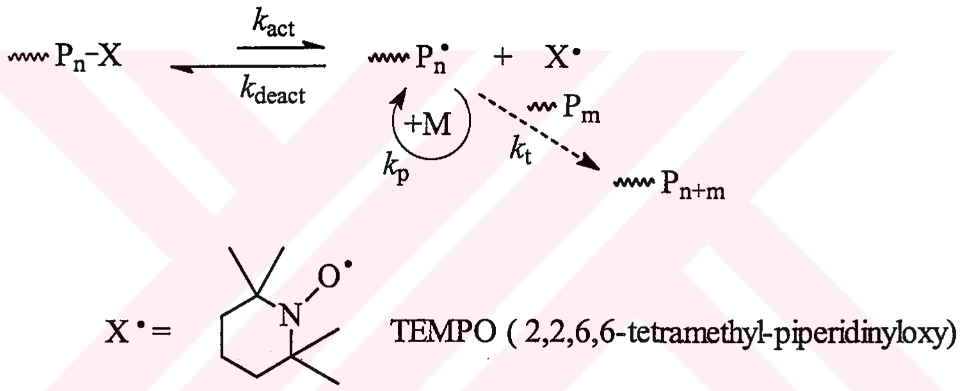
The deactivator plays a vital role in ATRP in reducing the polymerization rate and the polydispersity of the final polymer. In the limit that the rate of deactivation is too slow or does not occur, and then ATRP simply becomes a redox initiated polymerization. For copper–catalyzed ATRP, the deactivator is the corresponding copper (II) halide complex (e.g. 2dNbpy/CuX$_2$) [33].

In most systems the concentration of deactivator continuously, but slowly, increases due to slow termination by radical coupling [33].

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 [33].

2.1.2 Stable Free Radical Polymerization (SFRP)

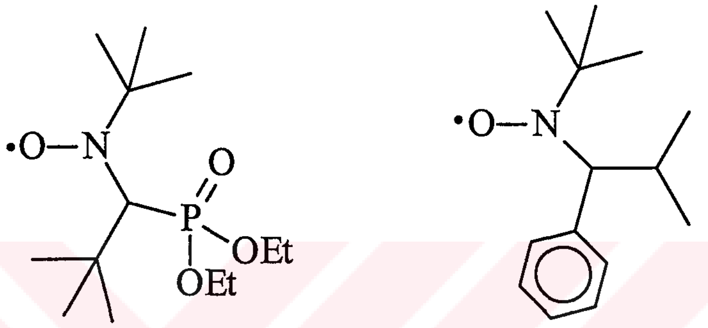
Nitroxide mediated living free radical polymerization (NMP) belongs to a much larger family of processes called stable free radical polymerizations (SFRP). In this type of process, the propagating species ($P_n^{\cdot}$) reacts with a stable radical ($X^{\cdot}$) as seen in reaction 2.7 [40]. The resulting dormant species (Pn-X) can then reversibly cleave to regenerate the free radicals once again. Once $P_n^{\cdot}$ forms it can then react with a monomer, M, and propagate further. The most commonly used stable radicals have been nitroxides, especially 2,2,6,6-tetramethylpiperidinyloxy (TEMPO). The general mechanism for nitroxide-mediated polymerization is shown in reaction 2.7.



(2.7)

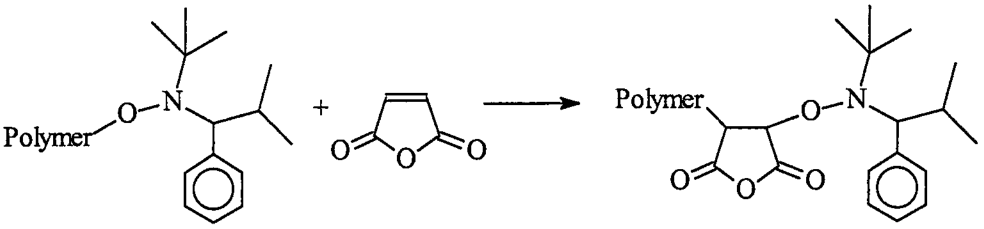
Although NMP is one of the simplest methods of controlled free radical polymerization (CRP), it has many disadvantages. Many monomers will not polymerize because of the stability of the dormant alkoxyamine that forms. Also, since the reaction is kinetically slow, high temperatures and bulk solutions are often required. Also, the alkoxyamine end groups are difficult to transform and require radical chemistry.

Recent work in NMP has revolved around the synthesis and evaluation of new nitroxide radicals, chain end functionalization, and the exploration of the synthesis of block, random, star, and graft copolymers. A review has recently been published which covers these topics in detail [31]. The most popular nitroxide used for NMP in the past has been TEMPO. However, TEMPO is limited in the range of monomers which are compatible to polymerize by NMP, mostly due to the stability of the radical. Hawker *et. al.* recently discovered that by replacing the α-tertiary carbon atom with a secondary carbon atom, the stability of the nitroxide radical decreased which leads to an increased effectiveness in polymerization for many monomers in which TEMPO was uneffective [41] (formulas 2.8). While TEMPO and TEMPO derivatives are only useful for styrene polymerizations, the new derivatives permit the polymerization of acrylates, acrylamides, 1,3-dienes, and acrylonitrile based monomers with very accurate control of molecular weights and low polydispersities. Another family of nitroxides that have shown to have the same success is phosphonate derivatives designed by Gnanou *et.al* [42].

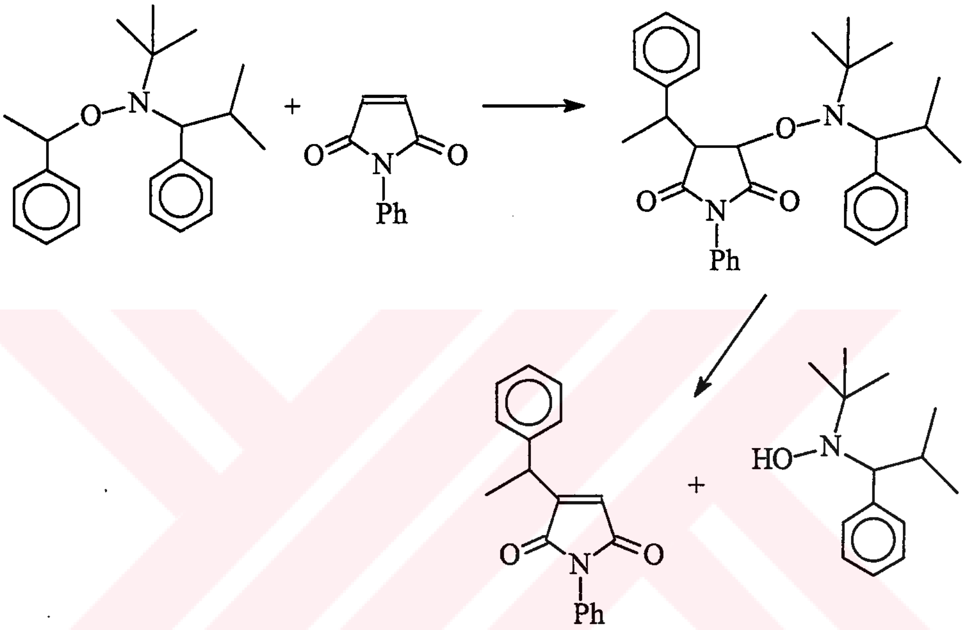


(2.8)

The chain end functionalization of polymers synthesized by NMP is a significant problem because dormant chains containing alkoxyamines can regenerate terminal radicals which can depolymerize at high temperatures. A very interesting chain end functionalization process has also been discovered by Hawker *et. al.* which involves the controlled monoaddition of maleic anhydride or maleimide derivatives to the alkoxyamine chain end [43]. The alkoxyamine can then easily be eliminated and other functional groups can be introduced. This process relies on the resistance of maleic anhydride or maleimide derivatives to homopolymerize and the ability of the precursor to reform the olefin by elimination of the hydroxylamine.

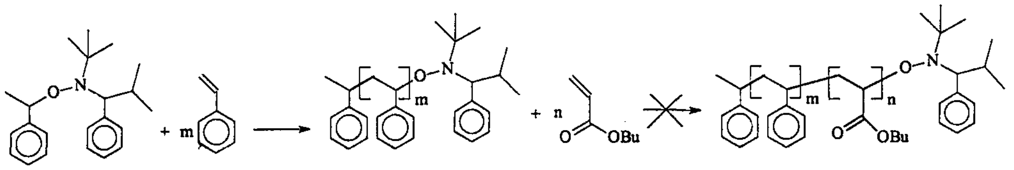


(2.9)

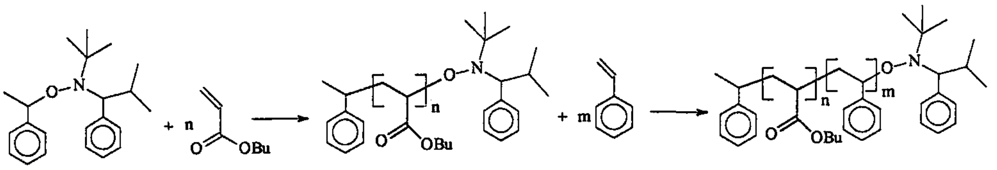


(2.10)

NMP is an excellent method for synthesizing diverse and well defined macromolecular structures. Block copolymers can be synthesized in many varying ways. Amphiphilic materials were synthesized by Frechet *et al* by first reacting a polyether with chlorinated alkoxyamine derivative to form a macroinitiator [44]. The Macroinitiator then underwent polymerization with styrene to produce amphiphillic block copolymer with very low polydispersities and accurately controlled molecular weights. Other block copolymerizations have combined NMP with other polymerization methods such as transition metal mediated [45] anionic [46] ring opening [47] or even radical [48]. Also, block copolymers can be constructed by the polymerization of one monomer followed by another. This can be realized due to the living nature of the polymerization which allows the chain ends at 100 % conversion to be reactive. Using the alkoxyamines designed by Hawker *et al*, a block copolymer of styrene and n-butyl acrylate was synthesized [41] (reactions 2.11 and 2.12). The polymerization only proceeded by first forming a polymer of n-butyl acrylate and then reacting this macroinitiator with styrene.



(2.11)



(2.12)

Also, through NMP, star, graft, and dendritic polymers are realized. Graft polymers were synthesized by Frechet *et. al.* by reacting an alkoxyamine with both styrene and p-chloromethylstyrene [47]. Then the halide is displaced with a hydroxy functionalized alkoxyamine initiator which can further polymerize with monomer to form a graft polymer. This method has been expanded to synthesize dendritic structures by Pispas *et. al* [45]. A random copolymer of styrene and p-chloromethylstyrene is produced and the halides are transformed into alkoxyamines. Then a further polymerization is performed on both styrene and p-chloromethylstyrene. The graft polymer now consists of random copolymer pendant groups.

2.1.3 Reversible Addition–Fragmentation Chain Transfer Polymerization (RAFT)

As elucidated by Rizzardo [49,50] , the elementary reaction of RAFT involves a reversible chain transfer in which a dithioester behaves as a chain transfer agent (CTA). The CTA reacts with either the primary radical or a propagating chain, forming a new CTA and eliminating R , which re-initiated polymerization. The dithioester is transferred between the active and dormant chains, thus maintaining the living character of the polymerization. As seen from scheme 1, RAFT mechanism differs from normal free radical polymerization mechanism by having a chain transfer agent, which leads to addition-fragmentation, re-initiation/propagation and chain equilibrium between chain radical and a new CTA. Because the addition-fragmentation chain transfer process is reversible, so the process is called reversible addition-fragmentation chain transfer polymerization (RAFT).

Initiation

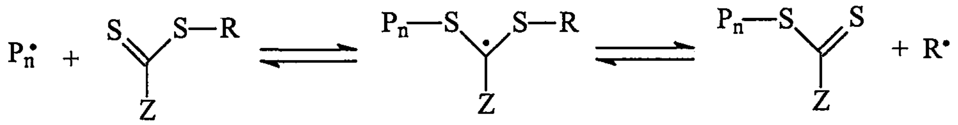
$$I{-}I \longrightarrow 2I\bullet \qquad (2.13)$$

$$I\bullet + M \longrightarrow I{-}M\bullet$$

Propagation

$$I{-}M\bullet + M_n \longrightarrow P_n^{\bullet} \qquad (2.14)$$

Addition-Fragmentation (Chain tarnsfer)

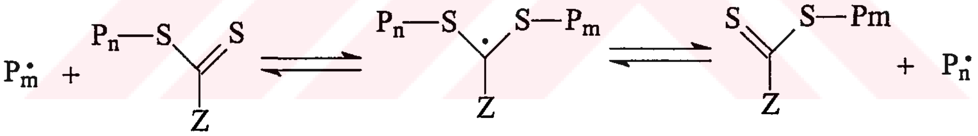


(2.15)

Reinitiation/ Propagation

$$R^{\bullet} \xrightarrow{\text{Monomer}} \longrightarrow P_m^{\bullet} \qquad (2.16)$$

Chain Equilibration



(2.17)

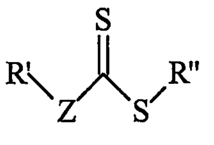
Termination

$$P_n^{\bullet} + P_m^{\bullet} \longrightarrow \text{Dead polymer} \qquad (2.18)$$

In RAFT, the CTA acts as so-called "trapping agent" because it is transferred between the active and the trapped chain. These trapped chain, usually called dormant chains, are unable to propagate but also unable to terminate. Because chain termination is bimolecular reaction, so the termination rate is second order with respect to the radical concentration [$M_m^{\cdot}$]. While chain propagation is first order to the radical concentration [$M_m^{\cdot}$] and proportional to the monomer concentration [M]. So we can see the termination rate is far less than propagation rate. Therefore, the probability of termination is largely reduced with respect to that of chain growth. So this leads to a negligible amount of terminated chains at the end of process. This is why RAFT has a living character. However, since terminations are definitely present, so this polymerization is also referred to as pseudo-living radical polymerization. The resultant polymer has a controlled molecular weight and narrow molecular weight distribution.

2.1.3.1 Keys to Successful RAFT

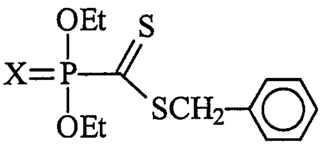
As seen from 2.19, the elementary difference between normal free radical polymerization and RAFT is the presence of a special kind of chain transfer agent (CTA). A RAFT process is actually a kind of degenerative chain transfer reaction, in which activation and deactivation occur at the same time or an active site migrates from one chain to another. So the key to successful RAFT polymerization is to select highly efficient CTA. In the structure of commonly used chain transfer agent, dithioester. The polymerization is carried out in the presence of thiocarbonylthio of general structure Z-C(=S)S-R and results in the formation of end-functionalized polymers. Z should activate the C=S double bonds. So the rate of addition and fragmentation must be fast relative to the rate of propagation which leads to rapid consumption of the RAFT agent and fast equilibrium of the dormant and active chain. On the other hand, the leaving group R must easily be leave and be able to re-initiate polymerization for the chain reaction to proceed. Generally, R should be a good homolytic leaving group when compared to polymer chain.



$R' = CH_3$; $R'' = C(CH_3)_2CN$
$R' = CH_3$; $R'' = CH(Ph)COOH$
R' and $R'' = CH_2Ph$
R' and $R'' = CH(CH_3)Ph$

(2.19)

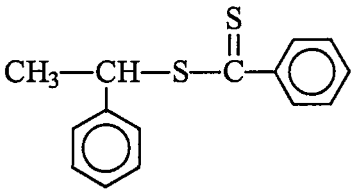
As shown above, Z can be aryl, alkyl, NR`$_2$, OR` or SR` and R can be $(CH_3)_2CN$, CH(Ph)COOH and so on. For example, in year 2001 Sparnacci [51] had used Benzyl (diethoxyphosphoryl) **(1)** dithioformate and benzyl(diethoxythiophosphoryl) dithioformate **(2)** as CTA. Their formulas are as follows:



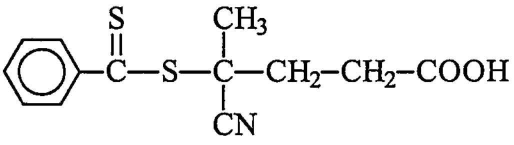
X = O, **(1)**
S, **(2)**

(2.20)

Fukuda [52] had used 1-phyenylehtyl dithiobenzoate **(3)** and Mccormick [53] had used 4-Cyanopentanoic acid dithiobenzoate **(4)** as CTA,



PDB **(3)**



(4)

(2.21)

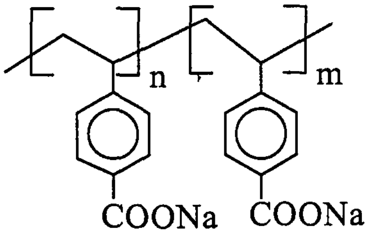
2.1.3.2 RAFT Experimental Process.

RAFT reactions differ from traditional free radical polymerization by adding a special chain transfer agent. Like traditional free radical polymerization, it can be thermally or initiator (AIBN) initiated. The process can be in bulk, solution or in emulsion [54-56] . On the other hand, RAFT polymerization can be well controlled relative to normal free radical polymerization. On the other hand, when compared to controlled living ionic polymerization or ATRP, RAFT can be conducted in a variety of mild experimental conditions. While the former only be realized for limited monomers at critical conditions.

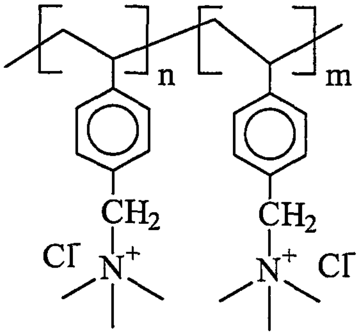
Till now, many of the polymers synthesized by RAFT are styrene, methyl acrylate(MA), and methyl methacrylate (MMA) based. Moreover, copolymer had also been synthesized using this method. For example, McCormick [57] synthesized poly(sodium 4-styrenesulfonate) by using **(4)** as a CTA. The reaction is fast and the resulting homopolymers are almost monodisperse, with a narrow molecular weight polydispersity index in the range of 1.12-1.25, well below the theoretical lower limit of 1.5 for classical free radial polymerization.

Using a dithioester-capped sodium 4-styrenesulfonate homopolymer as a macro chain transfer agent, a block copolymer with sodium 4-vinylbenzoate **(5)** had been synthesized. Additionally, a block copolymer of (ar-vinylbenzyl)-

trimethylammonium chloride with N,N-dimethylvinylbenzylamine **(6)** has been synthesized, using the same method. This presents the first examples of AB diblock copolymers prepared in aqueous media via RAFT.



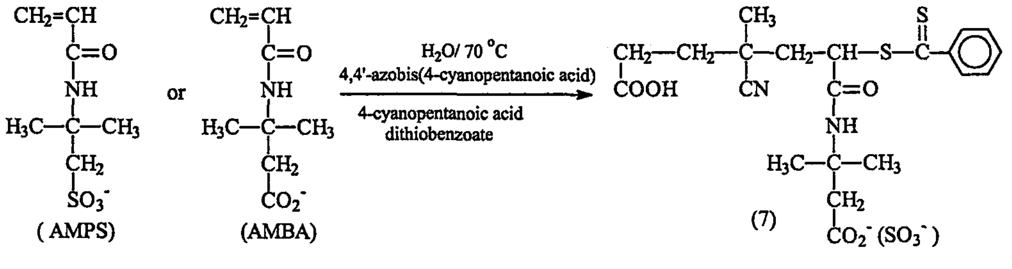
(5)



(6)

(2.22)

Similarly, they also reported the first RAFT polymerizations of two **anionic** acrylamido-monomers [58] : sodium 2-acrylamido-2-methylpropane-sulfonate (AMPS) and sodium 3-acrylamido-3-methylbutanoate (AMBA). The Poly(AMPS) and poly (AMBA)homopolymers **(7)** were subsequently employed as macro-CTAs for the block co-polymerization of the opposite monomer (i.e., RAFT-mediated Poly(AMPS) was used as the macro-CTAs for RAFT polymerization of AMBA, yielding a di-block copolymer of poly (AMPS-block-AMBA), and vice versa). Clearly the ability to polymerize these anionic monomers in a controlled fashion in aqueous media via RAFT is a great breakthrough.



(2.23)

Moreover, Thang and coworkers [49] used a trithiocarbonate as CTA to prepare polymers with symmetrical trithiocarbonate function located in his middle of polymer chain. So it allows insertion of monomers at the middle site of polymer chain. Thus a triblcok ABA copolymer can be formed. They have synthesized polystyrene-block-poly(n-butyl acrylate)-block-polystyrene.

Fukuda [50] had studied RAFT-mediated graft polymerization of styrene initiated on a silica particle. It was proved that the RAFT-mediated graft polymerization is a kind of reaction-diffusion process. This reports the first application of RAFT mediated polymerization to surface-initiated graft copolymerization.

RAFT is a new and robust method to synthesize well-controlled water-soluble polymers and copolymers with low polydispersity index. The process can be conducted in mild conditions with a broad range of monomers. Clearly this method is highly beneficial and should facilitate the synthesis more water-soluble polymers with complex structure which is unattainable by other methods. Compared to normal free radical polymerization and controlled polymerization (NMP, ATRP or living ionic polymerization), RAFT offers the following advantages of synthesis of water-soluble polymer:

1. Mild conditions, reaction is fast.
2. Reaction can be conducted in aqueous media as well as in organic solvents.
3. A more broad range of monomers can be chosen. For example anionic monomer like AMBA can be used.
4. RAFT is a controlled polymerization. The resultant polymer has low polydispersity index (~1-1.25).
5. Di-block copolymers, tri-block copolymers, star polymers have been synthesized.

Because RAFT has the above advantages to synthesize water-soluble polymers, the author believes it will be come widely used in industry. Future work will focus on the the following aspects:

1. Find more kinds of highly efficient RAFT chain transfer agents (CTAs)
2. Application of RAFT to more monomers other than currently used styrene, MMA and MA based ones.
3. Water-soluble polymer of more complex structure should be synthesized and found use in industries.

2.2 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 macromolecular architecture techniques. 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.

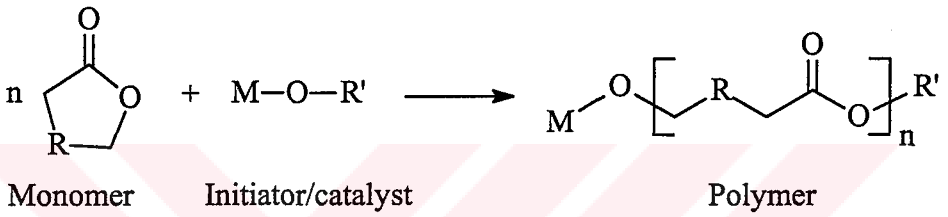
2.2.1 Ring-Opening Polymerization (ROP)

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/property relationship. The third reason for studying these kinds of systems is that they are valuable models for the examination of the kinetics [59] mechanisms [60] of elementary reactions in polymerization.

2.2.2 Ring-Opening Polymerization of Cyclic Esters

Polylactones and polylactides 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 2.24 presents the reaction pathway for the ROP of a cyclic ester.



(2.24)

R= $(CH_2)_{0\text{-}3}$, M= Metal

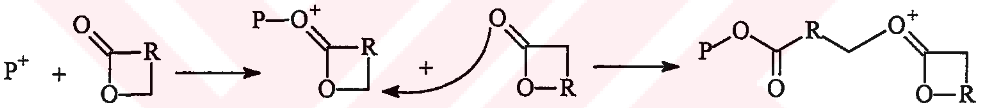
Each macromolecule formed generally contains one chain end terminated with a functional group originating from the termination reaction and one terminus end capped with a functional group originating from the initiator. By altering the catalyst or initiator and the termination reaction, the nature of 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 [61]. 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 [62], *viz.*, cationic, anionic, or "coordination-insertion" mechanisms [63-65]. In addition, radical, zwitterionic [66], or active hydrogen [62] 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.

2.2.2.1 Cationic Ring-Opening Polymerization

Among the cyclic esters, 4-, 6-, and 7- membered rings form polyesters when reacted with cationic catalysts [62] . The cationic ROP involves the formation of a positively charged species which is subsequently attacked by a monomer (reaction 2.25). The attack results in a ring-opening of the positively charged species through an S_N^2-type process.



(2.25)

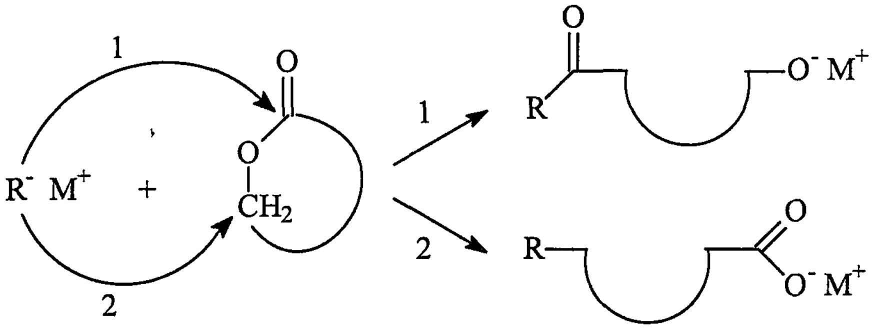
P= Polymer

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 [67,68].

2.2.2.2 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 2.26 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 [69]. 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.

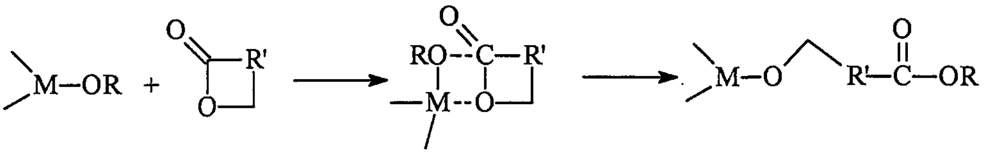


(2.26)

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 [70]. The anionic ring-opening of four-membered rings (b -lactones) occurs through alkyl-oxygen or acyl-oxygen cleavage giving a carboxylate or alkoxide. Larger lactones, such as ε-caprolactone (ε-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.

2.2.2.3 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 [63,64]. Reaction 2.27 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.



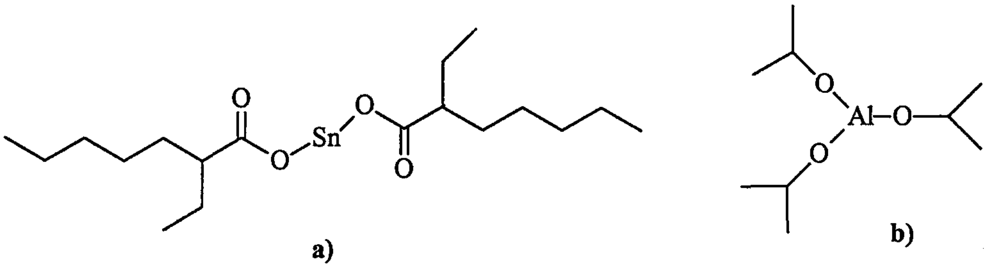
(2.27)

The coordination-insertion type of polymerization has been thoroughly investigated since it may yield well-defined polyesters through living polymerization [64]. When two monomers of similar reactivity are used, block copolymers can be formed by sequential addition to the "living" system.

2.2.3 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.

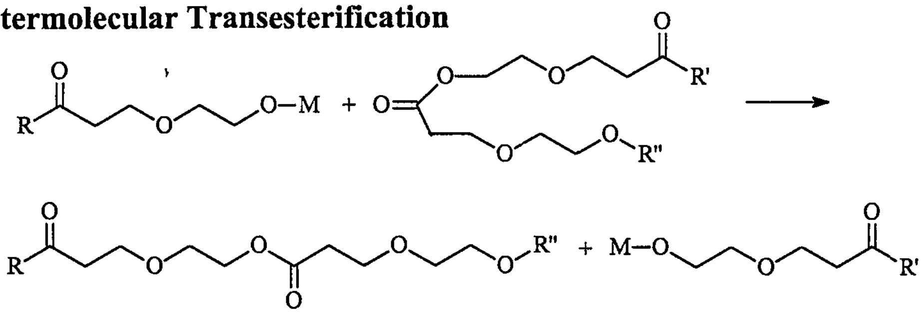
A large variety of organometallic compounds, e.g., metal alkoxides and metal carboxylates, has been studied as initiators or catalysts in order to achieve effective polymer synthesis [71]. Many reactions catalyzed by metal complexes are highly specific and, by careful selection of metal and ligands, 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. Formulas in 2.28 show some of the most frequently used initiators and catalysts in ROP of lactones. **a)** stannous octoate and **b)** aluminum isopropoxide



(2.28)

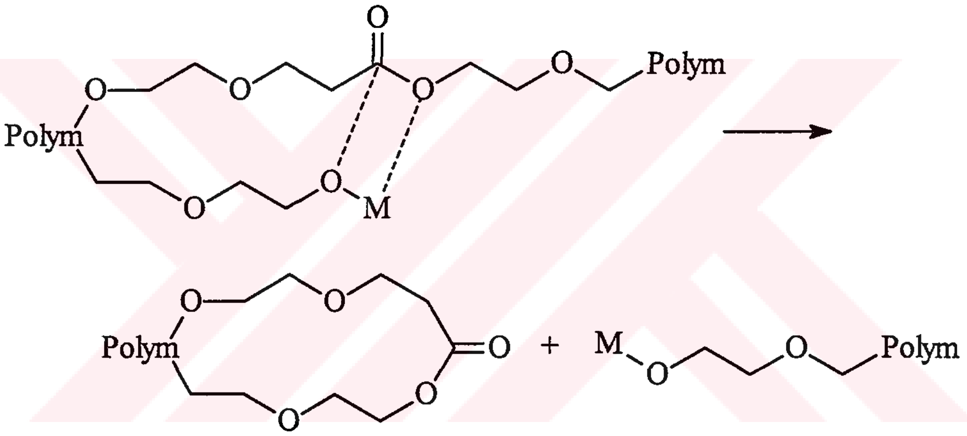
It is well known from the ROP of lactones and lactides that the catalyst or initiator causes transesterification reactions at elevated temperatures [72], or at long reaction times (reactions 2.29 and 2.30) [73].

Intermolecular Transesterification



(2.29)

Intramolecular Transesterification (back-biting)



(2.30)

Intermolecular transesterification reactions modify the sequences of copolylactones 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).

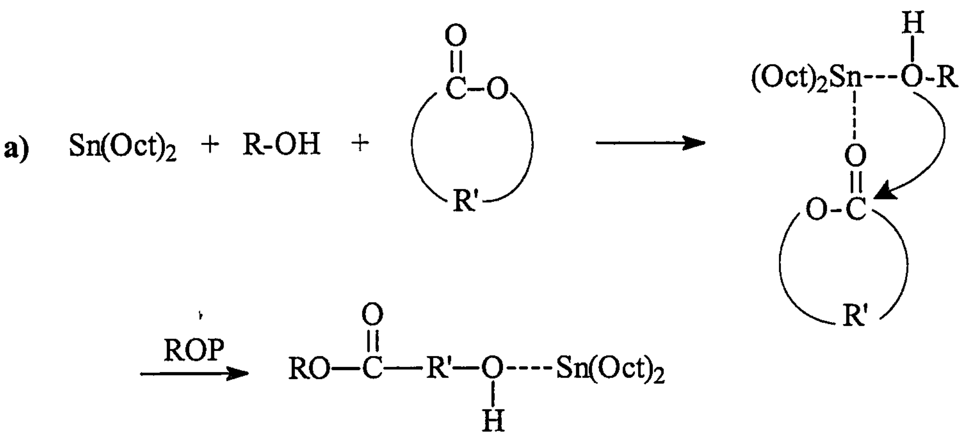
As displayed in the proposed scheme, each intramolecular transesterification randomly breaks the polymer chain. In this way, an attack on the polymer chain leads to a free residual polymer and a new randomized, modified polymer. Consequently, an original copolymer with a block-like structure would be 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 [74]. Depending on the metal used, the initiator is more or less active towards side-reactions such as transesterification reactions [74]. The relative reactivity of different metal alkoxide initiators towards chains already formed has been reported to be:
$Bu_2Sn(OR)_2 > Bu_3SnOR > Ti(OR)_4 > Zn(OR)_2 > Al(OR)_3$ [74].

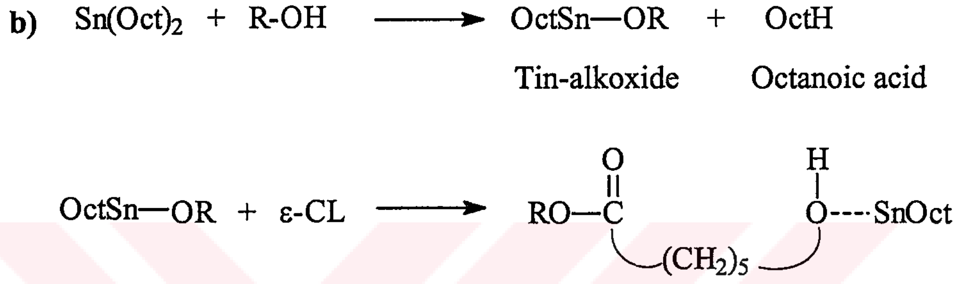
a) Tin(II) 2-Ethylhexanoate

Tin(II) 2-ethylhexanoate, commonly referred to as stannous octoate [$Sn(Oct)_2$], is a frequently used catalyst in the ROP of lactones and lactides [75]. $Sn(Oct)_2$ 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 [76] over a long period of time, it is not until now that the ROP mechanism is about to be elucidated [77,78]. The $Sn(Oct)_2$ is not thought to be the actual initiator since the molecular weight does not depend on the monomer-to-$Sn(Oct)_2$ molar ratio. The most promising mechanism is a "coordination-insertion" mechanism where a hydroxy functional group is thought to coordinate to $Sn(Oct)_2$, 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 [78] where the co-initiating alcohol functionality and the monomer are both coordinated to the $Sn(Oct)_2$ complex during propagation. Penczek and coworkers have presented a mechanism [77] where the $Sn(Oct)_2$ 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 [77] and ε-CL polymerization. Reactions 2.31 and 2.32 show the two different proposals. The main ROP mechanism proposals with $Sn(Oct)_2$ as catalyst, **a)** complexation of a monomer and alcohol prior to ROP and **b)** formation of a tin-alkoxide before ROP of CL



(2.31)



(2.32)

The $Sn(Oct)_2$ catalyst is a strong transesterification agent, and the resulting copolymers normally have a randomized microstructure [73]. An increase in reaction temperature or reaction time increases the amount of transesterification reactions.

The ROP of lactide with $Sn(Oct)_2$ 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

ROP initiated with aluminum tri-isopropoxide has been extensively investigated by several research groups since it yields well-defined polymers through living polymerization [79]. A living polymerization is a chain polymerization which proceeds in the absence of the kinetic steps of termination or chain transfer [79].

Polymerization with aluminum tri-isopropoxide is assumed to proceed through a "coordination-insertion" mechanism, which consists of monomer complexation to the active species and insertion by rearrangement of the covalent bonds. The mechanism leads to cleavage of the acyl-oxygen bond of the monomer and of the metal-oxygen bond of the propagating species. The propagation is characterized by the almost total absence of side-reactions such as transesterification reactions, at least until complete monomer conversion has occurred. The initiator is active at low temperatures (reaction temperatures of 0 –25 °C are often reported) and the initiator is preferentially used in solution polymerization.

c) Tin(IV) Alkoxides

Monotin alkoxides, tin dialkoxides and cyclic tin alkoxides have been utilized as initiators in the ROP of cyclic esters. The tin alkoxides are known to form cyclic species during synthesis and the dibutyltin alkoxides are known to exist as monomers and dimers. The cyclic tin alkoxides were originally studied because of their resistance towards hydrolysis. The tin alkoxides have been reported to be effective transesterification catalysts initiating polymerization at moderate temperatures [80].

The tributyl derivatives have been thoroughly studied since they are easily synthesized by nucleophilic substitution of commercial tributyltin chloride, they are easy to handle due to their moisture resistance, and they are relatively soluble in lactones.

The polymerization of lactones with tin alkoxides is thought to follow the "coordination-insertion" mechanism. The ring-opening of the monomer proceeds through acyl-oxygen cleavage with retention of the configuration. Tin(IV) complexes have been used to produce predominantly syndiotactic poly(b-hydroxybutyrate), macrocyclic poly(b-hydroxybutyrate), poly(ε-CL), and polylactide [80]. The cyclic tin alkoxides have the additional advantage of offering a convenient synthetic pathway for the synthesis of macromers, triblock, and multiblock copolymers.

d) Tin(II) Alkoxides

Recently, tin(II) butoxide was used in the polymerization of L,L-lactide [81]. The initiation is fast and quantitative and no transesterification or back-biting reactions are observed. The reaction proceeds with acyl-oxygen bond scission with retention of the configuration, and can be used both in bulk and solution (THF, 20–80 °C) polymerization. It is possible to control the molecular weight in the range of 10^3 to

10^6 with a MWD of 1.15 –1.85. The polymerization is very fast, $k_p = 5 \times 10^{-1}$ mol^{-1} L s^{-1}, with only the rare earth alkoxides being faster.

e) Lanthanide Alkoxides

ROP of lactones and lactides using lanthanide alkoxide-based initiators is a relatively recent discovery. The first example of lactones polymerization by lanthanide alkoxide complexes was reported in a DuPont patent written by McLain and Drysdale in 1991 [82]. In general, the activity of these catalysts is much higher than that determined for aluminum alkoxides, especially in lactide polymerization. Polymers of relatively high molecular weight and narrow MWD are formed. The negative side-reactions such as macrocycle formation, transesterification, and racemization are absent.

Yttrium isopropoxide and yttrium 3-oxapentoxide initiators were the first lanthanide alkoxides described in the literature for the ROP of ε-CL [83]. The discovery of lanthanide-based initiator systems allowed the block copolymerization of ε-CL with compounds such as ethylene, tetrahydrofuran [141], L-LA, trimethylene carbonate, and methyl methacrylate. This type of initiator has also been used to prepare poly(b - butyrolactone)s.

2.2.4 Kinetics of Ring-Opening Polymerization

The kinetics of polymerization has been investigated in order to study the mechanism of controlled ROP. The results of the kinetic experiments have been utilized to understand the action of the initiator in more detail.

ROP reactions initiated with a metal alkoxide initiator are generally characterized by an equilibrium between the free and the aggregated metal alkoxide [84]:

$$\left(P_n^*\right)_m \overset{K_{da}}{\rightleftharpoons} mP_n^* \tag{2.33}$$

$$P_n^* + M \xrightarrow{k_p} P_{n+1}^* \tag{2.34}$$

where P_n^* and M denote respectively non-aggregated active centers, aggregated active centers, and monomer, K_{da} is the aggregation equilibrium constant, k_p the propagation rate constant, and m the degree of aggregation. The aggregation causes a temporarily termination of the growing species, since the chains propagate only if they are non-aggregated. Due to the difference in reactivities between the aggregated compounds, the kinetics of polymerization is influenced.

In order to solve the kinetic equations corresponding to this system, Penczek and coworkers have recently proposed a method to determine the degree of aggregation from the curved plots of $\ln(k_{app})$ versus $\ln [I]_0$. The solution for the general case of the m -aggregate formation is:

$$(k_{app})^{1-m} = -m/K_{da}\,(k_p)^{m-1} + k_p\,[I]_o\,(k_{app})^{-m} \qquad \text{(Eq:2.2)}$$

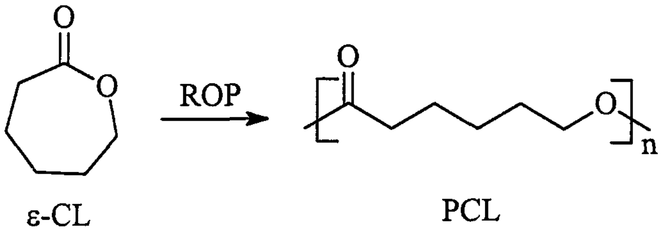
and in the logarithmic form:

$$\ln(k_{app}) = 1/m\,\ln[I]_o + C \qquad \text{(Eq:2.3)}$$

This equation allows a straight linear interpretation of the experimental data. When the logarithm of the apparent rate constant is plotted versus the logarithm of the initial initiator concentration, the slope of the line gives the external order in the initiator. The equation is valid for polymerization in which a fast reversible aggregation of the active centers takes place.

2.2.5 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 2.34 shows the monomer (ε-CL) structure and the resulting repeating unit.



(2.35)

The poly(ε-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(ε-CL) chain cleavage under the same conditions [85]. Different approaches have been used to copolymerize ε-CL to increase the degradation rate. Copolymers of ε-CL and D-LA of all compositions degraded much more rapidly than their component homopolymers [85] .This observation has been attributed to morphological differences, specifically a reduction in crystallinity and a lowering of the glass transition temperature.

Random copolymers of ε-CL with 1,5-dioxepan-2-one (DXO) have been investigated [86]. The copolymers were crystalline up to a DXO content of 40%, and it was concluded that the DXO units were incorporated into the poly(ε-CL) crystals. The block copolymerization has also been investigated and the resulting material was shown to exhibit thermoplastic elastomeric properties [87].

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. $Sn(Oct)_2$ 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 (triblock, 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.

2.3 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 [88,89].

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 [90] 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.

2.3.1 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 2.36.

$$\left.\begin{array}{lll} PI \xrightarrow{h\nu} PI^{*} & & \text{Absorption} \\ PI^{*} \longrightarrow R_1^{\bullet} + R_2^{\bullet} & & \text{Radical Generation} \\ R_1^{\bullet} + M \longrightarrow R_1{-}M^{\bullet} & & \end{array}\right\} \text{Photoinitiation}$$

$$\left.\begin{array}{l} R_1{-}M^{\bullet} + M \longrightarrow R_1{-}MM^{\bullet} \\ R_1{-}MM^{\bullet} + (n\text{-}2)\,M \longrightarrow R_1{-}M_n^{\bullet} \end{array}\right\} \text{Propagation} \qquad (2.36)$$

$$\left.\begin{array}{l} R_1{-}M_n^{\bullet} + R\text{-}H \longrightarrow R_1{-}M_n{-}H + R^{\bullet} \\ R^{\bullet} + M \longrightarrow R{-}M^{\bullet} \end{array}\right\} \text{Transfer}$$

$$\left.\begin{array}{l} R_1{-}M_n^{\bullet} + R_1{-}M_m^{\bullet} \longrightarrow R_1{-}M_{n+m}{-}R_1 \\ R_1{-}M_n^{\bullet} + R_2^{\bullet} \longrightarrow R_1{-}M_n{-}R_2 \\ R_1{-}M_n^{\bullet} + R_1{-}M_m^{\bullet} \longrightarrow R_1{-}M_n + R_1{-}M_m \\ R_1{-}M_n^{\bullet} + R_2^{\bullet} \longrightarrow R_1{-}M_n + R_2 \end{array}\right\} \text{Termination}$$

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 effected by light. Since in this part 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, as seen, e.g., in Scheme 1.

2.3.1.1 Absorption of Light

The absorption of light excites the electrons of a molecule, what lessens the stability of a bond and can, under favorable circumstances, lead to its dissociation. Functional groups that have high absorbency, like phenyl rings or carbonyl groups, are referred to as chromophoric groups. Naturally, photoinduced bond dissociations do often take place in the proximity of the light absorbing chromophoric groups. In some examples, however, electronic excitation energy may be transferred intramolecularly to fairly distant, but easily cleavable bonds to cause their rupture.

The intensity I_a of radiation absorbed by the system is governed by the Beer Lambert law, where I_0 is the intensity of light falling on the system, l is the optical path length and [S] is the concentration of the absorbing molecule having the molar extinction coefficient ε.

$$I_a = I_0 \left(1 - e^{-\varepsilon l [S]}\right) \qquad \text{(Eq:2.4)}$$

If the monomer possesses chromophoric groups and is sensitive towards light (i.e., it undergoes photoinduced chemical reactions with high quantum yields) one can carry out photopolymerizations by just irradiating the monomer. In many cases, however, monomers are not efficiently decomposed into radicals upon irradiation. Furthermore, monomers are often transparent to light at λ>320 nm, where commercial lamps emit. In these cases, photoinitiators are used. These compounds absorb light and bring about the generation of initiating radicals.

2.3.1.2 Radical Generation

2.3.1.2a Radical Generation by Monomer Irradiation

Some monomers are able to produce radical species upon absorption of light. Studies on various vinyl compounds show that a monomer biradical is formed.

$$M \xrightarrow{h\nu} \boxed{\cdot M \cdot} \tag{2.37}$$

These species are able to react with intact monomer molecules thus leading to growing chains. Readily available monomers which to some extent undergo polymerization and copolymerization upon UV irradiation are listed in Table 2.2.

Table 2.2. Photosensitive Monomers

Allyl methacrylate
Barium acrylate
Cinnamyl methacrylate
Diallyl phthatlate
Diallyl isophtalate
Diallyl terephthalate
2-Ethylhexyl acrylate
2-Hydroxyethyl methacrylate
2-Hydroxypropyl acrylate
N,N'-Methylenebisacrylamide
Methyl methacrylate
Pentaerythritol tetramethacrylate
Styrene
Tetraethylene glycol dimethacrylate
Tetrafluoroethylene
N-Vinylcarbazole
Vinyl cinnamate
Vinyl 2-fuorate
Vinyl 2-furylacrylate

However, regarding technical applications radical generation by irradiation of vinyl monomer does not play a role due to the very low efficiency of radical formation and the usually unsatisfactory absorption characteristics.

2.3.1.2b Radical Generation by Initiators

In the photoinduced polymerization applications, initiators are usually used to generate radicals. Photoinitiators are generally divided into two classes according to the process by which initiating radicals are formed [91].

Compounds which undergo **unimolecular** bond cleavage upon irradiation as shown in reaction 2.38 are termed **type I photoinitiators** or **PI_1- type initiators.**

$$\underset{\text{photoinitiator}}{PI} \xrightarrow{h\nu} \underset{\substack{\text{excited}\\ \text{photoinintiator}}}{PI^*} \xrightarrow{\substack{\text{unimolecular reaction}\\ \text{(fragmentation)}}} \underset{\text{free radicals}}{R^{1\bullet} + {}^{\bullet}R^2} \qquad (2.38)$$

If the excited state photoinitiator interacts with a second molecule (a coinitiator) to generate radicals in a bimolecular reaction as shown in reaction 2.39, the initiating system is termed a **type II Photoinitiator** or **PI_2-type initiator.**

$$\underset{\text{photoinitiator}}{PI} \xrightarrow{h\nu} \underset{\substack{\text{excited}\\ \text{photoinintiator}}}{PI^*} + \underset{\text{coinitiator}}{COI} \xrightarrow{\text{bimolecular reaction}} \underset{\text{free radicals}}{R^{1\bullet} + {}^{\bullet}R^2} \qquad (2.39)$$

Efficient photoinitiators of both classes are known and find everyday usage. Type I photoinitiators are highly reactive UV photoinitiators, but are less frequently used in visible light curing systems. Type II photoinitiators are versatile initiators for UV curing system and visible light photoinitiators belong almost exclusively to this class of photoinitiators.

Type I Photoinitiators: *Unimolecular Photoinitiators*. These substances undergo a homolytic bond cleavage upon absorption of light. The fragmentation that leads to the formation of radicals is, from the point of view of chemical kinetics, a unimolecular reaction.

$$PI \xrightarrow{h\nu} PI^{*} \xrightarrow{k} \dot{R}_1 + \dot{R}_2 \qquad (2.40)$$

$$\frac{d[\dot{R}_1]}{dt} = \frac{d[\dot{R}_2]}{dt} = k \ [PI^{*}] \qquad (Eq:2.5)$$

The number of initiating radicals formed upon absorption of one photon is termed as quantum yield of radical formation ($\phi_{R\bullet}$)

$$\Phi_{R\bullet} = \frac{\text{Number of initiating radicals formed}}{\text{Number of photons absorbed by the photoinitiator}} \qquad (Eq:2.6)$$

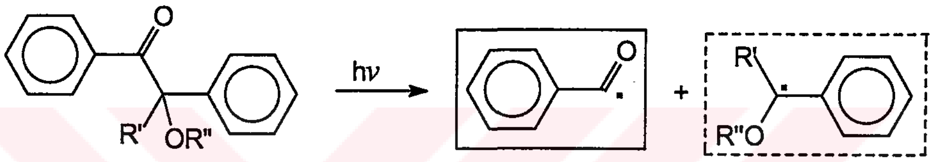
Theoretically, cleavage type photoinitiators should have a $\Phi_{R\bullet}$ value of two since two radicals are formed by the photochemical reaction. The values observed, however, are much lower because of various deactivation routes of the photoexcited initiator other than radical generation. These routes include physical deactivation such as fluorescence or non-radiative decay and energy transfer from the exited state to other, ground state molecules, a process referred to as quenching. The reactivity of photogenerated radicals with polymerizable monomers is also to be taken into consideration. In most initiating systems, only one in two radicals formed adds to monomer thus initiating polymerization. The other radical usually undergoes either combination or disproportionation. The initiation efficiency of photogenerated radicals (f_P) can be calculated by the following formula

$$f_P = \frac{\text{number of chain radicals formed}}{\text{number of primary radicals formed}} \qquad (Eq:2.7)$$

The overall photoinitiation efficiency is expressed by the quantum yield of photoinitiation (Φ_P) according to the following equation:

$$\Phi_P = \Phi_{R\bullet}\ \mathrm{x}\ f_P \qquad \text{(Eq:2.8)}$$

Regarding the energy necessary, it has to be said that the excitation energy of the photoinitiator has to be higher than the dissociation energy of the bond to be ruptured. The bond dissociation energy, on the other hand, has to be high enough in order to ensure long term storage stability. The majority of Type I photoinitiators are aromatic carbonyl compounds with appropriate substituents, which spontaneously undergo *α-cleavage* generating free radicals according to reaction 2.41. The benzoyl radical formed by the reaction depicted is very reactive towards the unsaturations of vinyl monomers [92].



(2.41)

R' = H, Alkyl, subst. Alkyl
R" = H, Alkyl, subst. Alkyl

The α-cleavage often referred to as Norrish Type I reaction [93] of carbonyl compounds starts from the initiator's triplet state, which is populated via intersystem crossing. Notably, the excited triplet states are usually relatively short lived that prevents excited molecules to undergo side reactions with constituents of the polymerization mixture. While triplet quenching by oxygen can, in most cases, be neglected due to the short lifetime of the triplet states, quenching by monomer sometimes plays a role. However, this refers exclusively to monomers with low triplet energies, like, e.g., styrene ($E_T = 259\ \mathrm{kJ\ mol^{-1}}$ [94]).

If the absorption characteristics of a cleavable compound are not meeting the requirements, i.e., the compound absorbs at too low wavelengths, the use of sensitizers (S) with matching absorption spectra is recommendable. Sensitizers absorb the incident light and are excited to their triplet state. The triplet excitation energy is subsequently transferred to the photoinitiator which forms initiating radicals. This process has to be exothermic, i.e., the sensitizers triplet energy has to be higher than the triplet energy level of the initiator. Through energy transfer, the initiator is excited and undergoes the same reactions of radical formation as if it were excited by direct absorption of light. The sensitizer molecules return to their ground state upon energy transfer; they are therefore not consumed in the process of initiation.

$$S \xrightarrow{h\nu} {}^3S^* \qquad (2.42)$$

$${}^3S^* + PI \longrightarrow S + {}^3PI^* \qquad (2.43)$$

Type II Photoinitiators: *Bimolecular Photoinitiators*. The excited states of certain compounds do not undergo Type I reactions because their excitation energy is not high enough for fragmentation, i.e., their excitation energy is lower than the bond dissociation energy. The excited molecule can, however, react with another constituent of the polymerization mixture, the so-called coinitiator (COI), to produce initiating radicals. In this case, radical generation follows 2nd order kinetics.

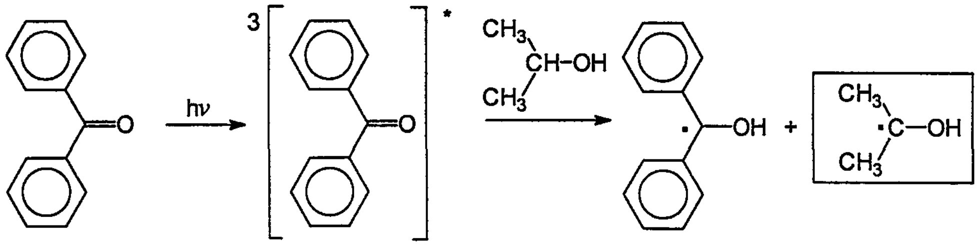
$$PI \xrightarrow{h\nu} PI^* \qquad (2.44)$$

$$PI^* + COI \xrightarrow{k} R_1^{\bullet} + R_2^{\bullet} \qquad (2.45)$$

$$\frac{d[\dot{R}_1]}{dt} = \frac{d[\dot{R}_2]}{dt} = k\ [PI^*]\ [COI] \qquad (Eq:2.9)$$

There are two distinct pathways of radical generation by Type II initiating systems:

(I) ***Hydrogen abstraction*** from a suitable hydrogen donor. As a typical example, the photoreduction of benzophenone by isopropanol is depicted. Bimolecular hydrogen abstraction is limited to diaryl ketones [93]. From the point of view of thermodynamics, hydrogen abstraction is to be expected if the diaryl ketone's triplet energy is higher than the bond dissociation energy of the hydrogen atom to be abstracted.


(2.46)

(II) photoinduced *electron transfer reactions* and subsequent fragmentation. In electron transfer reactions, the photoexcited molecule, termed as sensitizer for the convenience, can act either as electron donor or electron acceptor according to the nature of the sensitizer and coinitiator. Fragmentation yields radical anions and radical cations, which are often not directly acting as initiating species themselves but undergo further reactions, by which initiating free radicals are produced.

$$S \xrightarrow{h\nu} S^* \qquad (2.47)$$

$$S^* + A \longrightarrow S^{+\bullet} + A^{-\bullet} \dashrightarrow \text{further reactions} \qquad (2.48)$$

$$S^* + D \longrightarrow S^{-\bullet} + D^{+\bullet} \dashrightarrow \text{further reactions} \qquad (2.49)$$

The electron transfer is thermodynamically allowed, if ΔG calculated by the Rehm-Weller equation (18) [95] is negative.

$$\Delta G = F\ [\, E_{1/2}^{ox}\,(D/D^{+\bullet}) - E_{1/2}^{red}\,(A/A^{-\bullet})\,] - E_S + \Delta E_c \qquad \text{(Eq.2.10)}$$

F... Faraday constant

$E_{1/2}^{ox}$ $(D/D^{+\bullet})$, $E_{1/2}^{red}$ $(A/A^{-\bullet})$...oxidation and reduction potential of donor and acceptor, respectively

E_S...Singlet state energy of the sensitizer

ΔE_c...Coulombic stabilization energy

Electron transfer is often observed for aromatic ketone/amine pairs and always with dye/coinitiator systems.

2.3.2 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 coating, microelectronics and printing plates [89,91,96-99]. 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.

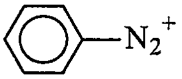
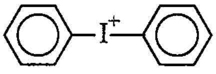
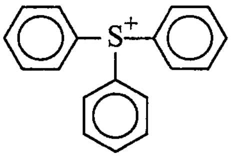
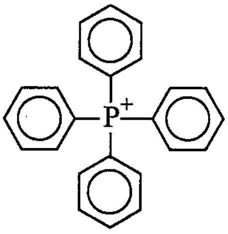
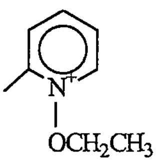
Much effort has been devoted to free radical systems [89,98] mainly due to the availability of a wide range of photoinitiators and the great reactivity of acrylate-based monomers. Despite the most popular industrial application based on the photoinitiated free radical photopolymerization there are some 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 SbF_6^- and AsF_6^- has been utilized [100].

Since the photoinitiator is one of the most important part of a UV initiated polymerization, many attempts 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 photoresist 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

				
Aryldiazonium 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 [101].

The photochemistry of these novel classes of photoinitiators is well documented [89,91,96-99]. Onium salts used in cationic photopolymerization mainly absorb the wavelengths of light between 225 and 350 nm [96,100,102,103]. UV characteristic of selected onium salts are given in Table 2.4. 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).

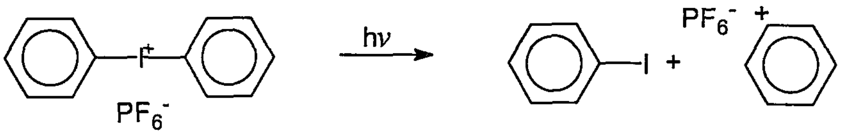
2.3.2.1 Direct Photolysis

If onium salt initiators I absorb light, electronically excited initiator I* species are produced. The latter undergo a heterolytic or homolytic bond rupture leading to cations C^+ or radical cations $C^{+\cdot}$, respectively.

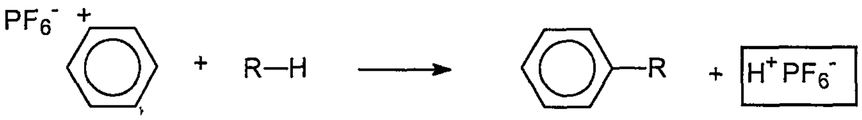
$$\mathrm{I} \xrightarrow{h\nu} \mathrm{I}^* \begin{array}{l} \nearrow \; C^+ \; + \; R \\ \searrow \; C^{+\cdot} \; + \; R^{\cdot} \end{array} \tag{2.50}$$

In some cases, these entities are able to react directly with monomer molecules starting a cationic polymerization. Frequently, C^+ or $C^{+\cdot}$ 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.

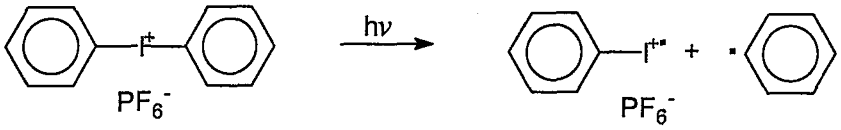
The mechanism of onium salt initiation is depicted on the example of diphenyliodonium hexafluorophosphate.



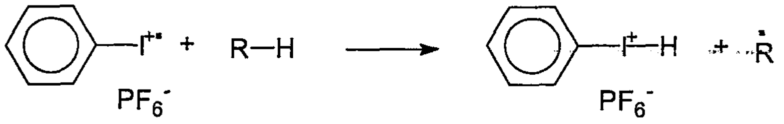
(2.51)



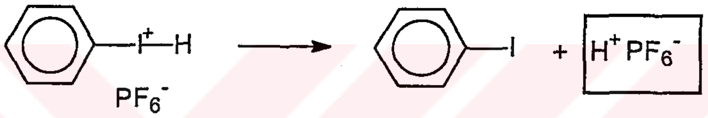
(2.52)



(2.53)



(2.54)

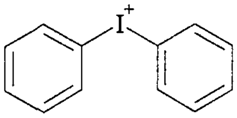
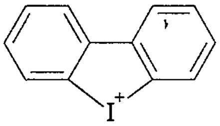
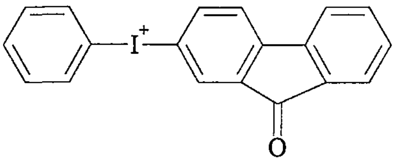
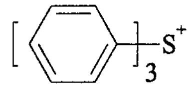
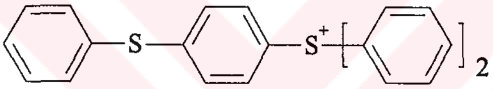
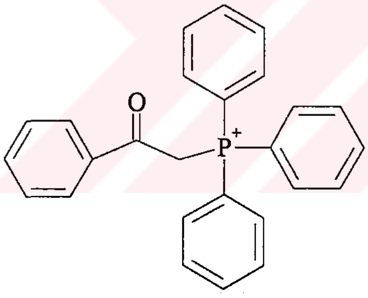
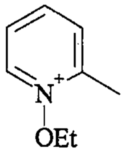
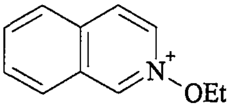
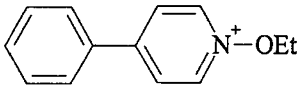


(2.55)

2.3.2.2 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. 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 four modes of indirect initiation will be discussed.

Table 2.4. UV Absorption Characteristics of Selected Onium Salts

Cation	Anion	λ_{max} (nm)	ε_{max} (l mol^{-1} cm^{-1})
	BF_4^-	227	17800
	AsF_6^-	264	17300
	AsF_6^-	366	745
	AsF_6^-	227	21000
	PF_6^-	230 300	24330 19500
	SbF_6^-	257	32000
	PF_6^-	266	5925
	PF_6^-	337	4220
	PF_6^-	310	21440

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.

$$PS \xrightarrow{h\nu} (PS^*) \qquad (2.56)$$

$$(PS^*) + PI \xrightarrow{\text{energy transfer}} PS + (PI^*) \qquad (2.57)$$

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.

$$(PS^*) + On^+X^- \longrightarrow (PS^{+\bullet})X^- + On^\bullet \qquad (2.58)$$

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* (PS) should be higher than that of excited onium salt $E^*(On^+)$. On the other hand the electron transfer (reaction 2.58) is energetically allowed, if ΔG calculated by (equation 2.11) (extended Rehm- Weller equation) [104] is negative.

$$\Delta G = F\,[\,E_{ox}^{1/2}(PS) - E_{red}^{1/2}(On^+)\,] - E^*(PS) \qquad (Eq:2.11)$$

where $E_{ox}^{1/2}$ and $E_{red}^{1/2}$ are half wave oxidation and reduction potential of photosensitizer and photoinitiator respectively, F=97 kJ mol^{-1} V^{-1}, is the conversion factor and E*(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 [105]. 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^{-1}.

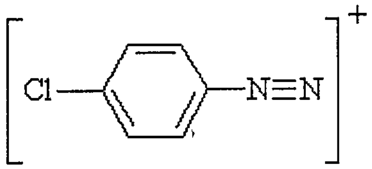
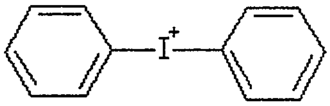
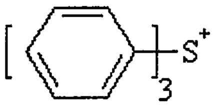
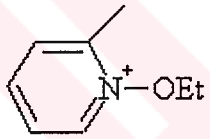
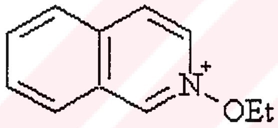
Table 2.5. Halfwave Oxidation Potentials $E^{ox}_{1/2}(PS)$ (vs Standard Calomel Electrode (SCE)) and Triplet or Singlet energies E*(PS) of Commonly Used Photoinitiators

Photosensitizer	**$E^{ox}_{1/2}$ (PS) (V)**	**E*(PS) (kJ mol^{-1})**
Acetophenone	2.9	308 (E_t)
Benzophenone	2.7	290 (E_t)
Thioxantone	1.7	277 (E_t)
Anthracene	1.1	319 (E_s)
Perylene	0.9	277 (E_s)
Phenothiazine	0.6	239 (E_t)
m-Trifluoromethyl acetophenone	2.7	305 (E_t)
Xantone	-	311 (E_t)

It has been shown that photosensitized decomposition of onium salt follows different route from that observed for direct photolysis of the onium salts [106,107]. 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	**$E^{red}_{1/2}$ (V) (vs SCE)**	**E^*_t(kJ mol^{-1})**
	0.35	-
	-0.2	268
	-1.1	314
	-0.7	-
	-0.5	-

2) ***Electron Transfer Via Exciplex***

Many aromatic hydrocarbons such as anthracene, phenothiazine, and 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;

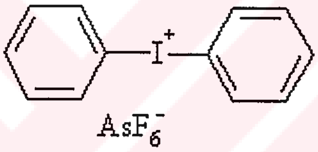
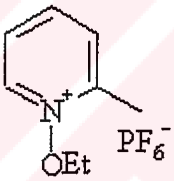
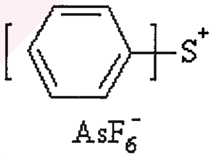
$$PS \longrightarrow PS^* \xrightarrow{On^+X^-} [PS^* \ldots\ldots On^+X^-] \longrightarrow PS^{+\cdot}X^- + On^\cdot \qquad (2.59)$$

$$PS^{+\cdot}X^- + R\text{-}H \longrightarrow HPS^+X^- + R^\cdot \qquad (2.60)$$

$$HPS^+X^- \longrightarrow H^+X^- + PS \qquad (2.61)$$

Since the oxidation potentials of sensitizers $E^{ox}_{1/2}$ are easy to determine, the calculation of ΔG 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.

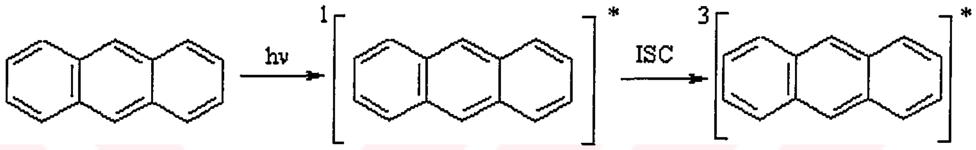
Table 2.7. Sensitization of Onium Salts; ΔG in kJ mol^{-1}

						
Sensitizer	ΔG	Sens[a]	ΔG	Sens[b]	ΔG	Sens[a]
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	+

[a] Polymerization of the diepoxide, 3,4-epoxycyclohexylmethyl-3,4- epoxy cyclohexane carboxylate[108].
[b] Polymerization of cyclohexene oxide [109].

However not all sensitizers are suitable in conjunction with onium salts. According to equation 2.11, 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 (Ar_2I^+ and Ar_3S^+) by anthracene has been investigated in detail in a number of papers [110-112]. Exciplex formation is followed by a partly loss of anthracene's aromatic system as concluded from the decrease in the sensitizer fluorescence. These reactions are illustrated in equations 2,62-2,66 on the example of diphenyliodonium salt. Notably, similar coupling reactions of radical cations with the radicals formed from the salts were also observed with alkoxy pyridinium salts [113].



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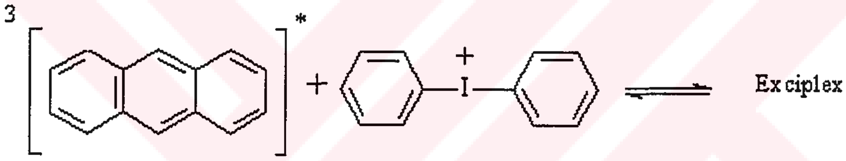

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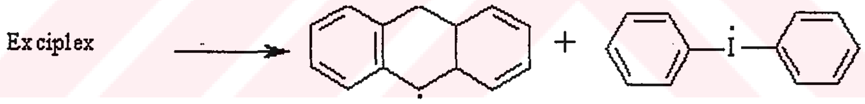

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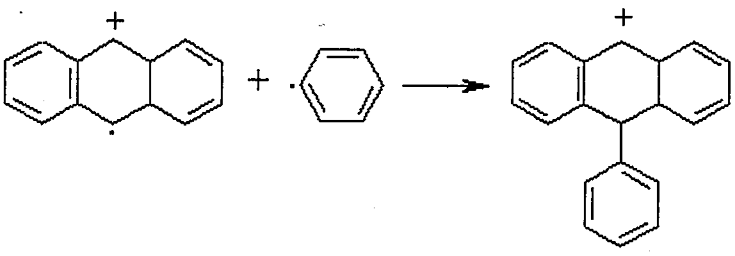
(2.65)



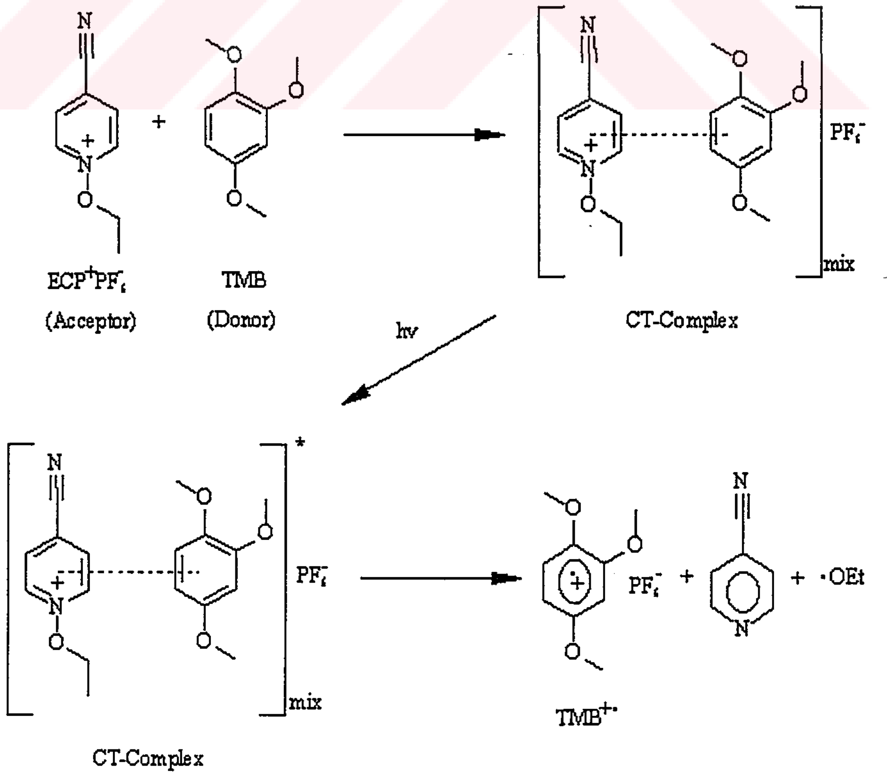
(2.66)

counter ion is omitted.

The sensitization of thioxhanthone follows only partly the general mechanism described for the exciplex formation [113]. 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 [114]. 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 equations 2.67 and 2.68 for the initiation of the cationic polymerization has been suggested [114].



(2.67)

(2.68)

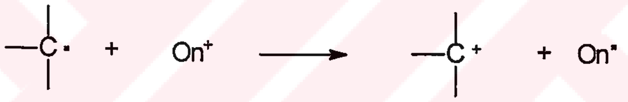
Since the proton scavenger 2,6-di-tert-butylpyridine did not noticeably influence the polymerization, the initiation by Brønsted acid that could be formed after an interaction with hydrogen donor components can be excluded. Notably, the CT complexes described above are applicable for the photoinitiation 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

4) ***Sensitization by free radical photoinitiators***

Free radicals can also induce decomposition of onium salts. Two types of free radical induced initiation are currently available.

a) *Oxidation of radicals*

Many photochemically formed radicals can be oxidized by onium salts according to the following reaction:



$$-\overset{|}{\underset{|}{C}}\cdot \;+\; \mathrm{On}^{+} \longrightarrow -\overset{|}{\underset{|}{C}}^{+} \;+\; \mathrm{On}^{\cdot} \qquad (2.69)$$

The cations thus generated are used as initiating species for cationic polymerization. This process is usually termed as the free radical promoted cationic polymerization.

This so-called free radical promoted cationic polymerization is an elegant and fairly flexible type of sensitized cationic polymerization [115,116]. Free radicals may be produced not only by photochemically but also thermally or by irradiating the system with high energy rays. Table 2.8 shows free radical photoinitiator and onium salt combinations generally used in free radical promoted cationic polymerization.

Table 2.8. Initiating Systems for Free Radical Promoted Cationic Polymerization

Free Radical Source	**Onium Salt**
Benzoin derivatives	Iodonium /pyridinium salts
Benzophenone	Iodonium /pyridinium salts
Acylphosphine oxides	Iodonium /pyridinium salts
Dye-amine	Iodonium salt
Vinyl halides	Sulphonium/pyridinium salts
o-Phtaldehyde	Pyridinium salts
Azo compounds	Iodonium /pyridinium salts
Polysilanes	Iodonium /pyridinium salts

The efficiency of onium salts as oxidizing agents is related to their electron affinity. The higher the oxidation power of the onium salt, the higher (more positive) is the reduction potential $E_{red}^{1/2}$ (On$^+$).

The efficiency of onium salts in this mode of polymerization rises in the order of trialkyl sulphonium salts < alkoxy pyridinium salts < diaryliodonium salts < aryldiazonium salts (see Table 2.6). Aryldiazonium salts are the most suitable for the oxidation of radicals. However, their practical application is hampered by the lack of thermal stability. Diphenyliodonium salts have also a relatively high reduction potential. Being very suitable for the oxidation of free radicals, these salts have been most frequently used for the oxidation of photogenerated free radicals. On the other hand, triphenylsulphonium salts have only limited potential for radical induced cationic polymerizations due to their low reduction potential. However, some highly nucleophilic radicals could be oxidized with sulphonium salts.

Provided the oxidation and reduction potentials of the free radical and the onium ion, respectively, are known, it can be estimated on the bases of the Rehm-Weller (equation 2.12) whether a radical can be oxidized by a given onium salt or not.

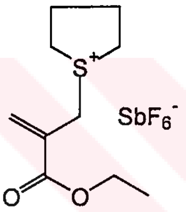
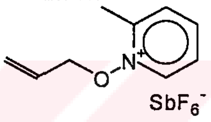
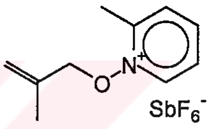
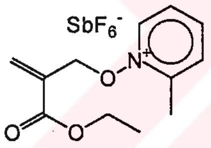
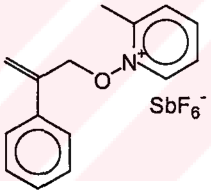
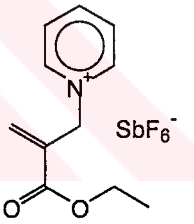
$$\Delta G = F\,[E_{ox}^{1/2}(R^{\cdot}) - E_{red}^{1/2}(On^{+})] \qquad \text{(Eq:2.12)}$$

However, the calculation of ΔG is usually not feasible since the exact oxidation potentials $E_{ox}^{1/2}$ ($R^{\cdot}$) of most radicals involved in radical promoted polymerizations are unknown.

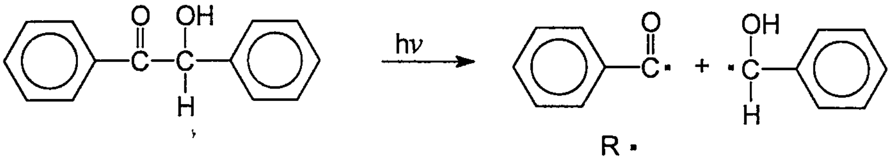
b) *Addition-fragmentation reactions*

The advantage of allylic salts that can undergo addition fragmentation reactions derives from the fact that virtually all sorts of thermal and light-sensitive radical initiators may be utilized for cationic polymerization, which enables an adaptation to most initiation conditions. In contrast to radical promoted cationic polymerization based on the oxidation of radicals, one is not limited to oxidizable radicals.

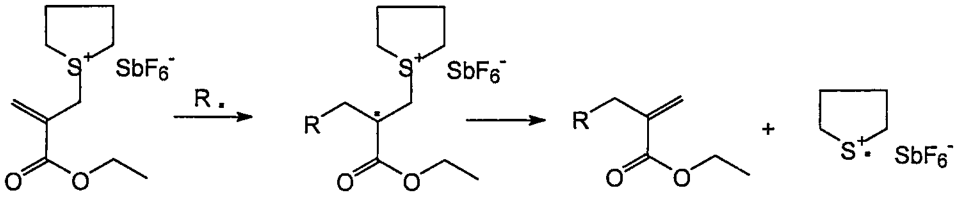
Table 2.9. Addition Fragmentation Agents (AFAs) for Cationic Polymerization

The mechanism of the addition fragmentation type initiation is depicted below on the example of ETM salt and benzoin photoiniator.



(2.70)



(2.71)

The first step consists in the photogeneration of free radicals. Virtually any photolabile compound undergoing homolytic bond rupture may be used as a radical source. The radicals add to the double bond of the allylonium salt thus producing a radical in β position to the heteroatom of the onium salt cation. Consequently, the molecule undergoes fragmentation yielding initiating cations. The proposed mechanism was evidenced by analysis of the photolysis products. The initiating efficiency has been demonstrated on a number of cationically polymerizable monomers, such as cyclohexene oxide, butylvinyl ether and N-vinylcarbazol.

2.4 Macrophotoinitiators

There has been much interest in molecules containing covalently bonded photoinitiating groups (macrophotoinitiators). Macrophotoinitiators may offer various advantages over the low molecular weight photoinitiators such as greater reactivity, low volatility and low migration. From the practical point of view, macrophotoinitiators are used as either photocrosslinking agents or precursors for block and graft copolymers. Macrophotoinitiators as curing agents have already been surveyed in two recent review articles [117,118] and summarized in table 2.10 [119].

Table 2.10. Polymeric Photoinitiators (PPI) For UV Curing Applications

PPI	**Photosensitive group**	**Type**
Polybenzoin	Benzyl	a, c
Poly(benzylketal)	Benzylketal	a, c
Poly(tricholoroacetophenone)	Acetophenone derivative	a, b, c
Poly(benzoinacrylates)	Benzoin or benzionmethylether	b, c
Poly(hydroxyalkylphenones)	Hydroxyalkylphenone	b, c
Poly(vinyl or acrloylbenzophenone	Benzophenone	c, d
Poly(acroylthioxanthone)	Thioxanthone	c, d
Polysiloxanes	Benzoin ether, benzilketal acetophenone derivative	b, c
Polysilanes	Si-Si bond	a, c, e
Polymeric iodonium salt	iodonium salt	b, e

a = Main chain photoinitiator
b = Side chain photoinitiator
c = Cleavage-type photoinitiator
d = H-Abstraction-type photoinitiator
e = Also cationic photoinitiator

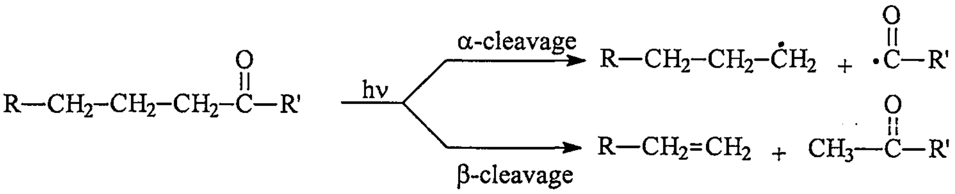
The principal focus of this part will be to describe the synthesis of novel well defined block and graft copolymers by using macrophotoinitiators. Compared with most of the thermally induced macroinitiators, the radiation sensitive macroinitiators have the advantage of being applicable at low temperatures especially at room temperature. This is of prime importance with regard to the probability of occurrence of side reactions such as homopolymerization which proceeds in parallel with block or graft copolymerization, if macroinitiators promoted thermally. Moreover, because of the selective absorptivity of certain groups (chromophores), it is possible to produce reactive sites at definite positions in the macromolecule.

Macrophotoinitiators possessing chromophoric groups either in the main chain or as pendant groups can be prepared in two ways;

- by synthesis and polymerization of monomers with photoactive groups
- by introduction of photoactive group into a polymer.

The latter case may be achieved in initiation or termination steps of particular polymerization or reacting functional groups of a performed polymer with functional groups of low molecular weight compounds possessing also photoactive groups.

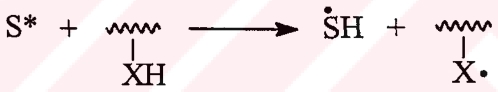
Macrophotoinitiators, analogous to the low molecular weight photoinitiators, are divided into two classes, according to their radical generation mechanism namely cleavage-type (type I), (reaction 2.72) and hydrogen abstraction-type (type II) (reactions 2.73, 2.74 and 2.75) macrophotoinitiator.



$$R{-}CH_2{-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}R' \xrightarrow[h\nu]{\alpha\text{-cleavage}} R{-}CH_2{-}CH_2{-}\dot{C}H_2 + \cdot\overset{O}{\overset{\|}{C}}{-}R'$$

$$R{-}CH_2{-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}R' \xrightarrow[\beta\text{-cleavage}]{h\nu} R{-}CH_2{=}CH_2 + CH_3{-}\overset{O}{\overset{\|}{C}}{-}R' \qquad (2.72)$$

$$S \xrightarrow{h\nu} S^* \qquad (2.73)$$



$$S^* + \underset{XH}{\sim\sim} \longrightarrow \dot{S}H + \underset{X\cdot}{\sim\sim} \qquad (2.74)$$

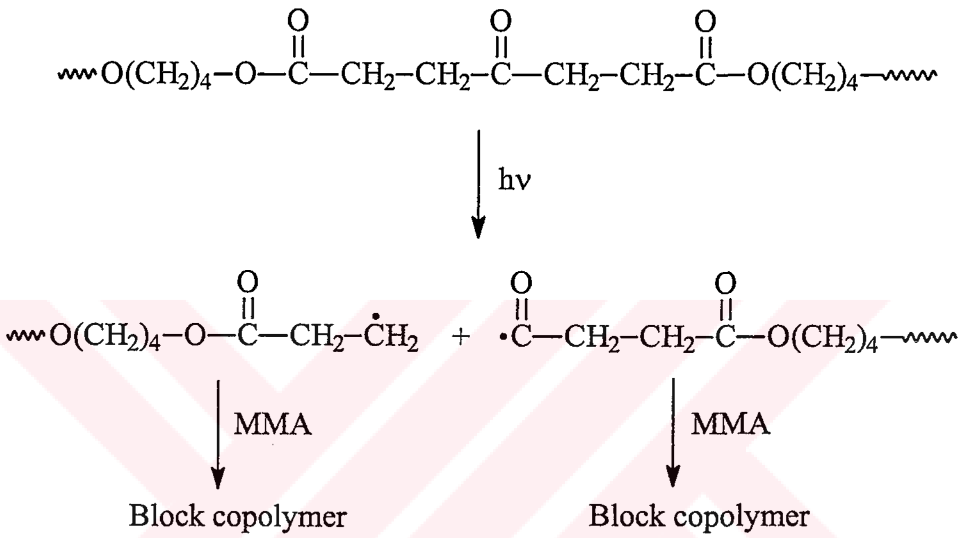
$$\underset{X\cdot}{\sim\sim} + M \longrightarrow \underset{X-(M)_n^-}{\sim\sim} \qquad (2.75)$$

α-Cleavage is the most important reaction and leads to free radicals which are capable of initiating polymerization of appropriate monomers.

Type II macrophotoinitiators function in initiating process indirectly, as result of hydrogen abstraction by electronically excited sensitizer molecules S* from lateral functional groups present in the macrophotoinitiator (reactions 2.73-2.75). Obviously, when the hydrogen releasing groups are located at the chain ends, the resulting polymer will be a block copolymer.

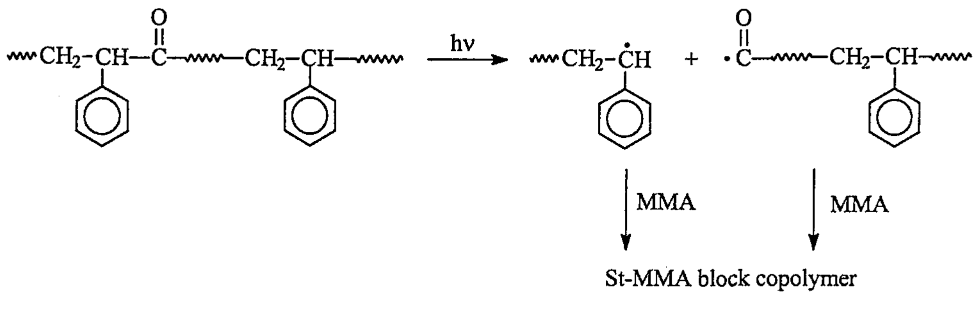
2.4.1 Cleavage –type Macrophotoinitiators

On the basis of α-Cleavage, Dhanras and Guillet [120] used poly(tetramethylene sebacate co-γ-ketopimalate) as a macroinitiator according to the following reactions (reaction 2.76). However, the resulting product was a mixture of unreacted polyester and block copolymer.



(2.76)

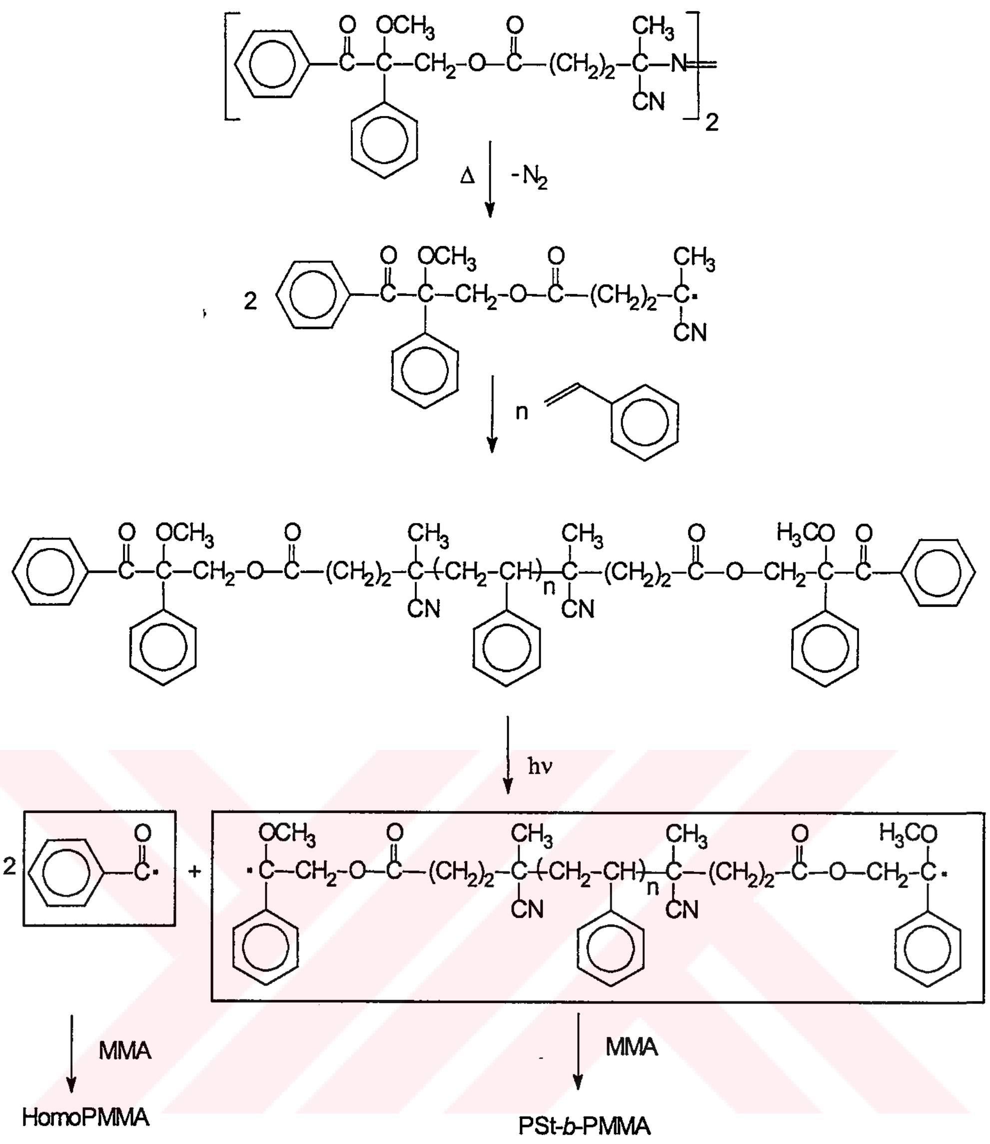
Kawai and coworkers [121] prepared similar carbonyl containing photoactive polystyrene and polyvinylchloride by copolymerizing CO with corresponding monomers. Irradiation of poly(styrene-co-carbonmonoxide) in the presence of methylmethacrylate resulted in a mixture containing up to 70 % by weight block copolymer according to fractionation, turbidity and elemental analysis (reactions 2.77)



(2.77)

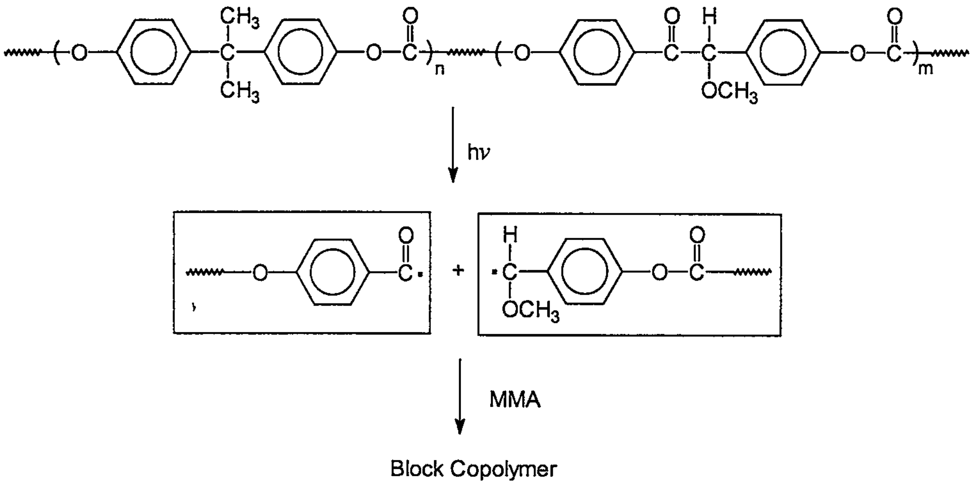
When acrylic acid was used as the second monomer, the block copolymer yield was lower (50 % by weight). Carefully purified block copolymer after extraction with methanol was successfully tested as membranes in reverse osmosis experiments with aqueous NaCl solutions.

Polymers containing terminal photoactive benzoin groups have been synthesized using azo-benzoin initiators [13,14]. The thermal treatment of these initiators in the presence of styrene leads to benzoin groups at both ends of the polystyrene chain, since polystyryl radicals tend to terminate via recombination. Upon irradiation of the styrene based photoinitiators, benzoyl and alkoxy-benzyl radicals are produced, both capable of initiating polymerizations to give mixtures of homopolymers and block copolymers. Obviously, one could also use the benzoin site of the azo benzoin initiator for a photopolymerization in the first step and activate the azo sites in a subsequent, thermal reaction. However, regarding homopolymer formation the method depicted in (2.78) has to be given priority to since benzoin groups are thermally stable whereas azo groups may be photolytically ruptured. Benzoin azo initiators are, furthermore, suitable for the synthesis of block copolymers with one of two monomers being cationically polymerizable [122,123].



(2.78)

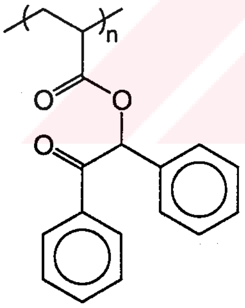
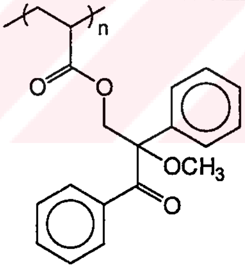
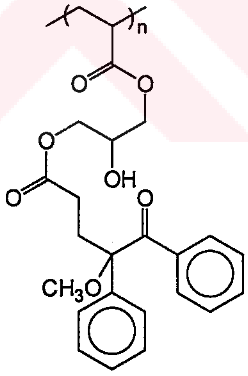
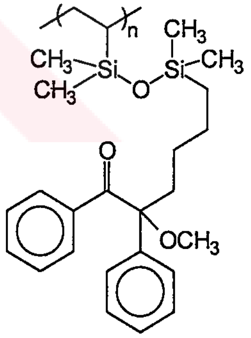
Benzoin methyl ethers have been incorporated into a polycarbonate chain. The synthesis was achieved by polycondensing bisphenol A with phosgene in the presence of 4,4'-dihydrobenzoin methylether [124]. Irradiation of the resulting polycondensate in the presence of methyl methacrylate resulted in block copolymer formation, as illustrated in (2.79). Apart from methyl methacrylate, other vinyl monomers, such as ethyl methacrylate and acrylonitrile have been polymerized by the macroinitiator [125].



(2.79)

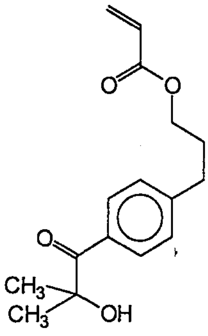
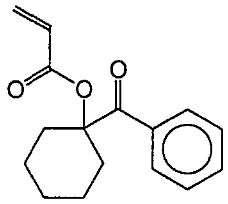
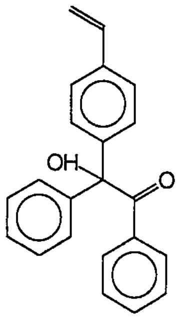
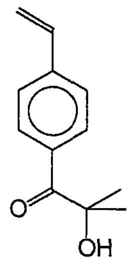
Macroinitiators containing groups of benzoin type in the side chain were synthesized by several authors [126-129]. Some examples are summarized in Table 2.11. Notably, a spacer between the polymer backbone and the benzoin moiety enhances the activity of the initiator in vinyl polymerization considerably. This phenomenon is attributed to an easier accessibility of reactive benzoin sites.

Table 2.11. Side-Chain Benzoin Type Macroinitiators

			
[126]	[127]	[128]	[129]

Several polymerizable monomers based on either acrylic acid or styrene containing photodissociable groups have been developed [130-132].

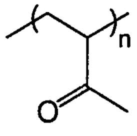
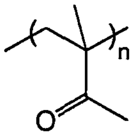
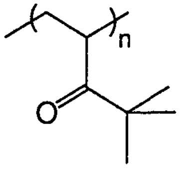
Table 2.12. Monomers Containing Photolable Groups

			
[130]	[131]	[132]	[132]

These monomers may be radically homopolymerized or copolymerized with various vinyl monomers. Macrophotoinitiators prepared from the two styrene based monomers depicted were found to possess an activity comparable to that of efficient low molecular weight photoinitiators.

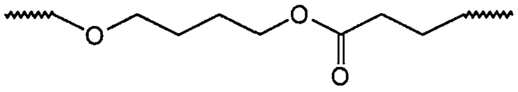
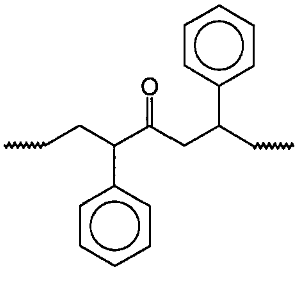
Polymers that possess carbonyl groups in the side chains are able to generate lateral macroradicals upon UV irradiation. The polymers depicted in Table 2.13 have been used as photoinitiators. Photolysis of these initiators in the presence of vinyl monomers gives both graft copolymer and homopolymer, since polymeric and low molecular weight carbonyl radicals are formed.

Table 2.13. Polymers With Side- chain Carbonyl Groups

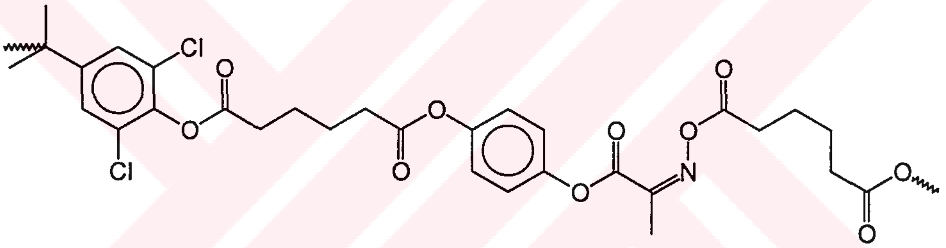
		
[133]	[134]	[134]

Copolymers containing carbonyl groups in the main chain have been used in early works as photoinitiators. These copolymers undergo main chain scission upon irradiation. In the presence of vinyl monomer, the terminal radicals react with monomer initiating its polymerization. Following this method, various block copolymers (second comonomer in the block copolymer: methyl methacrylate) have been obtained.

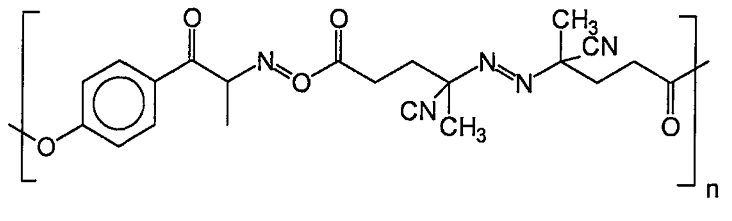
Table 2.14. Photoinitiators With In-chain Carbonyl Groups

	
[120]	[121]

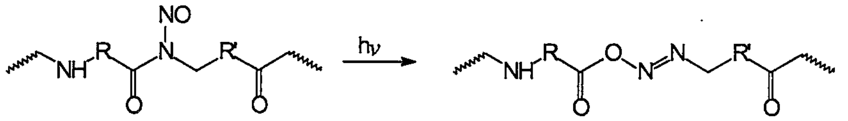
Polymer bound acyl oxime esters have also been reported to be suitable radical sources [124]. Polyesters containing acyl oxime oxides were prepared by a polycondensation reaction [135]. Irradiation of these compounds with light of 365 nm in the presence of vinyl monomers (styrene) gave block copolymers.


(2.80)

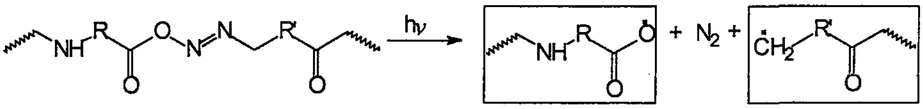
Polystyrene containing acyl oxime ester groups was synthesized using an azo-acyloxime ester bifunctional initiator (2.81) [136]. In the first stage, the azo-acyloxime ester initiator was heated in the presence of styrene, whereby styrene polymerization is initiated by the azo sites. In a second step, the acyloxime ester sites were photochemically activated to start the polymerization of a second monomer. The striking advantage of acyloxime ester groups in macrophotoinitiators derives from the fact that upon photolysis apart from the macroradicals two low molecular weight products (CH_3CN and CO_2) are formed. These photolysis products prevent the macroradicals from recombining, what leads to relatively high initiation efficiencies.


(2.81)

A similar effect is observed for polymeric initiators containing nitroso groups in their main chain [137]. Upon absorption of two photons, nitrogen is released and initiating macroradicals are formed, as depicted in (2.82 and 2.83). Notably, care must be taken while working with nitroso containing macroinitiators for they may decompose violently under the influence of UV light or heat.



(2.82)

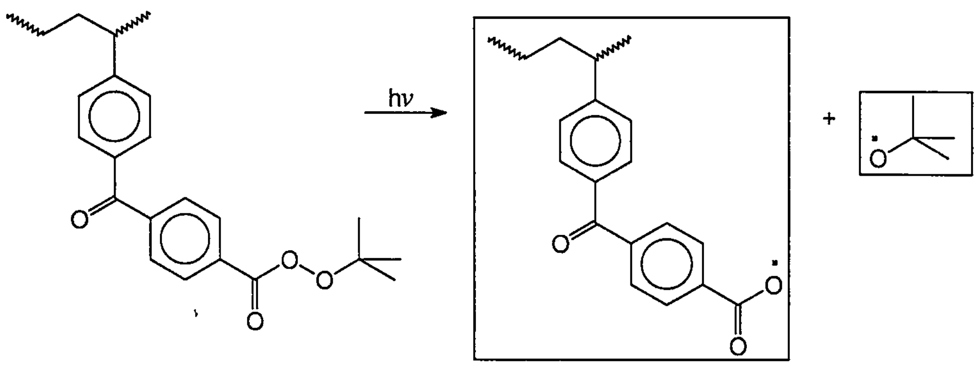


(2.83)

Photosensitive polymers containing azo groups [138] or triazene groups [139] in the main chain also undergo main chain scission and evolve nitrogen upon UV irradiation. With respect to photochemistry, alkylaryl initiators are of special interest, since they have better absorption characteristics than dialkyl initiators and are, on the other hand, more reactive than the respective diaryl substituted compounds.

Various organic disulfides including thioram disulfides are also capable of acting as thermal and photochemical initiators for free radical polymerization. For example, when the polymerization of styrene was initiated by tetraethylthioram disulfide, the polymer was found to contain terminal Et_2N-CS-S groups. Photolyzed in the presence of vinyl monomer these photosensitive polymers give block copolymers.

Peroxyesters with triplet photosensitizer functionalities are efficient initiators for free radical polymerization of monomer provided the monomers do not quench the polymer's excited triplet state. For example, methyl methacrylate was photografted onto polystyrene containing a low fraction of peroxybenzoate (2.84). Upon irradiation in the presence of methyl methacrylate both homopolymer and graft copolymer was formed, as can be easily understood on the basis of (reaction 2.84).

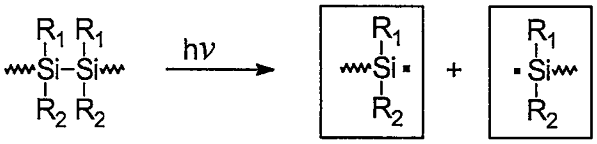


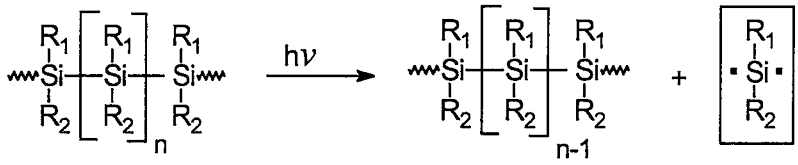
(2.84)

Polymers containing halogen atoms, especially brominated polymers, have also shown some potential in free radical polymerization. Since the bond energy of C-X is relatively low for X being chlorine or bromine, these bonds are easily photolytically ruptured. Thus, brominated polystyrene was used to initiate the polymerization of methyl methacrylate [140]. Furthermore, brominated polyacrylamide and polyacrylonitrile served as radical generating photoactive polymer for the grafting of acrylamide and ethyleneglycol oligomers.

The curing of polysiloxane formulations by chemically attached groups of initiating Type I is of great interest. Since the cured coatings possess interesting features, such as high stability towards heat and chemicals and good flexibility, they are attractive for a number of applications [141,142]. Prepared by various synthetic strategies, polysilanes containing benzoin ether, benzoin acrylate, benzilketals, α,α-dialkoxyacetophenones, α-hydroxyalkylphenones and α,α-dialkylacethophenone were used as macrophotoinitiators.

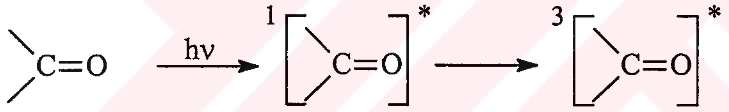
Due to their high photosensitivity polysilanes are suitable sources of free radicals. These silicon based polymers decompose upon absorption of UV light with quantum yields ranging between 0.2-0.97 [143] producing silyl radicals and silylene biradicals (reactions 2.85 and 2.86). Polysilanes absorb usually light of wavelengths below 350 nm; changes of the organic substituents R_1 and R_2 as well as the number of silica atoms per chain however cause considerable alterations in the absorption characteristics [143]. Although radicals are formed with high yields, the initiation efficiency of polysilanes is not very high owing presumably to disproportionation reactions between the two kinds of radicals formed. However, polysilanes showed good performance in photocuring of vinyl functionalized polysiloxanes and in the polymerization of several vinyl monomers [144,145]. In the latter study, upon irradiation of polysilane - vinyl copolymers in the presence of a further monomer block copolymers were synthesized [145].


(2.85)


(2.86)

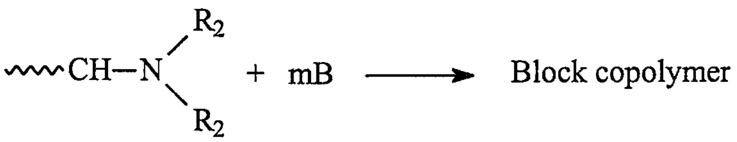
2.4.2 H-Abstraction-type macrophotoinitiators

Block and graft copolymerization of vinyl monomers can be achieved by taking advantage of the fact that triplet states of aromatic ketones readily react with amines according to following reactions.


(2.87)

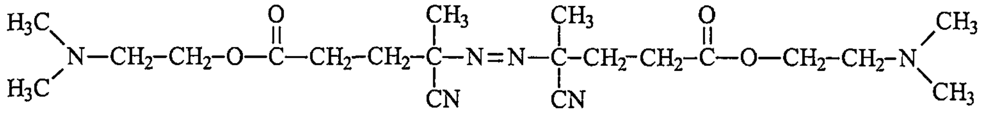

(2.88)

Radicals formed by the reactions in above can initiate the polymerization of vinyl compounds, and if the amine group is attached to a macromolecule, a block copolymer is formed (reaction 2.89).



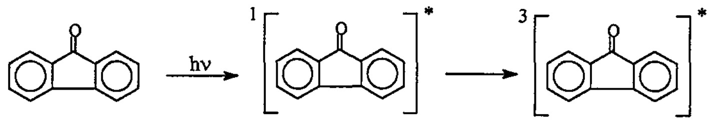
$$\sim\!\sim CH{-}N(R_2)_2 + mB \longrightarrow \text{Block copolymer} \qquad (2.89)$$

Formation of homopolymer is expected to be negligible since the amine derived radicals are a better initiator than the semipinacol radical. The preparation of polystyrene with N,N -dimethyl amino end groups from an azo-initiator is described by Yagci at al. [146]

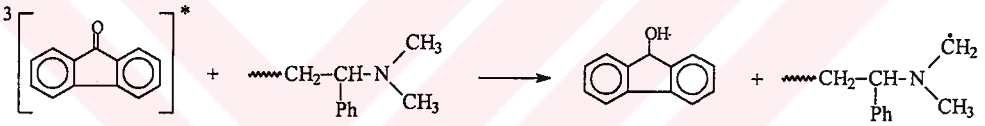


$$(H_3C)_2N-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-N(CH_3)_2 \quad (2.90)$$

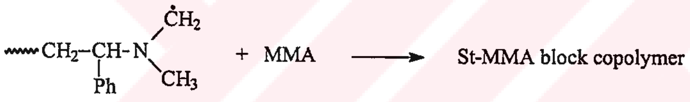
Polymers functionalized by this method were irradiated at λ=350 nm in the presence of 9-flurenone and MMA to yield block copolymers (reactions 2.91, 2.92 and 2.93).



(2.91)

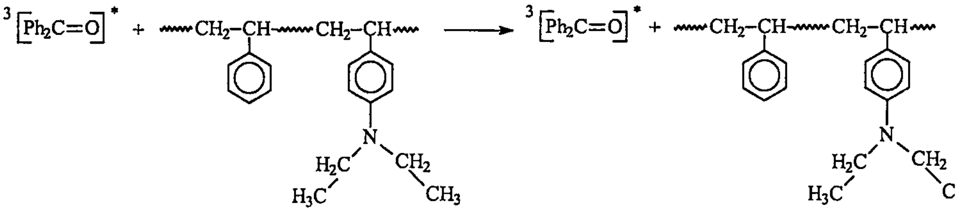


(2.92)



(2.93)

Kinstle and Watson [147] achieved the grafting of viniyl monomers using the same H-abstraction mechanism. They irradiated poly(styrene-co-p-N,N'–diethylaminostyrene) in the presence of 2-ethylhexyl methacrylate (EHMA) and benzophenone at λ=350 nm. In this case lateral macroradicals were formed by hydrogen abstraction from diethyl amino groups by benzophenone triplets (reaction 2.94).



(2.94)

Low monomer concentration and short irradiation time were chosen so that selectivity of reactions could be enhanced. Apart from graft copolymer, homo-PEHMA was also formed. However, the grafting efficiency was high: about 77 % of the converted monomer was grafted onto the backbone polymer. The rather low homopolymer yield was attributed again to the relatively inefficient initiating power of benzophenone ketyl radical.

2.4.3 Macrophotoinitiators with Halogen-containing Groups

When polymers with functional groups like $-CX_3$, $-CHX_2$ or $-CH_2X$ are irradiated ($\lambda = 350...450$ nm) in the presence of $Mn_2(CO)_{10}$, terminal carbon centered macroradicals are formed [148]. Upon absorption of light, $Mn_2(CO)_{10}$ decomposes yielding $Mn(CO)_5$, a compound that reacts with terminal halogen groups according to (59).

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2\ Mn(CO)_5 \tag{2.95}$$

$$-(A)_n-CCl_3 + Mn(CO)_5 \longrightarrow \boxed{-(A)_n-\dot{C}Cl_2} + Mn(CO)_5Cl \tag{2.96}$$

These terminal radicals may be used to initiate the polymerization of a second monomer, whereby block copolymers are formed. Notably, homopolymerization is not observed in this process since any low molecular weight radicals are generated upon the reaction of $Mn(CO)_5$ with the macroinitiator.

Naturally, this polymerization procedure may only be applied, if the polymer end functionalized with halogen containing groups is available. There are methods for converting terminal -OH, $-NH_2$ and -COOH groups into $-CCl_3$ groups [149]. Furthermore, polymers containing terminal $-CCl_3$ functionalities may be obtained using a bifunctional azo initiator [150].

Besides for block copolymers, the reaction of $Mn_2(CO)_{10}$ with halogen groups attached to polymer backbones has been utilized for the synthesis of graft copolymers [151,152]. A drawback of this method is that in many cases combination of macroradicals is observed giving rise to crosslinking rather than grafting. Network formation *vs*. grafting has been studied for a number of trunk polymer/monomer combinations.

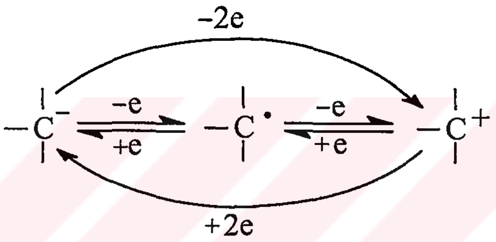
2.5 Synthesis of Block Copolymers by Combination of Different Polymerization Routes

Advanced polymeric materials with special properties are of great interest. Block and graft copolymers are the most demanded advanced materials because of their diverse copolymer structures [153-155]. In most cases, the corresponding homopolymers do not form homogeneous phase. However, linear arrangement of the blocks by chemical bonds results in the realization of a stable structure with two phases separated. Each segment exerts its character or function to the bulk of the copolymers. This way various properties are improved or combined to give possibility of using block copolymers as comptabilizers, impact modifiers, surface modifiers, coating materials, antistatic agents and adhesives. Block copolymerization has also aroused a great deal of interest in biomaterials science. For instance, combination of synthetic polymers and constituent units of biopolymers via block copolymerization generates widely applicable functional materials. Furthermore, block and graft copolymers possessing a liquid crystalline and amorphous or crystalline components can have advance applications, e.g. in electro-optics [156,157].

A number of techniques for the preparation of block copolymers have been developed [1,158,159]. Living ionic polymerization is elegant method for the controlled synthesis of block copolymers. However, besides high purity requirements this technique is limited to ionically polymerizable monomers and excludes monomers that polymerize by other mechanisms. In fact there exist some limitations even for the ionically polymerizable monomers. Whether the block copolymerization of two ionically polimerizable monomers can or can not be carried out is critically dependent on the structure and relative reactivity of the ionic species and the monomers. For example only a few monomers are suitable for the preparation of block copolymers by anionic polymerization. A similar situation is valid for cationic polymerization. Furthermore, the synthesis of block copolymers between structurally different polymers i.e. condensation and vinyl polymers, by a single polymerization method is rather difficult due to the nature the respective polymerization mechanisms.

In order to extend the range of monomers for synthesis of block copolymers, transformation approach was postulated by which the polymerization mechanism could be changed from one to another which is suitable for the respective monomers [160,161]. All the research works performed in the area of polymerization transformation mechanism could be outlined in two categories:

(1) *Direct transformation reactions*: The transformation of a polymerization mechanism is carried out at the end of the first block segment in the polymerization mixture that means the species which initiated the polymerization mechanism of the first monomer by one mechanism was transformed to another mechanism by a redox process without termination and isolation.



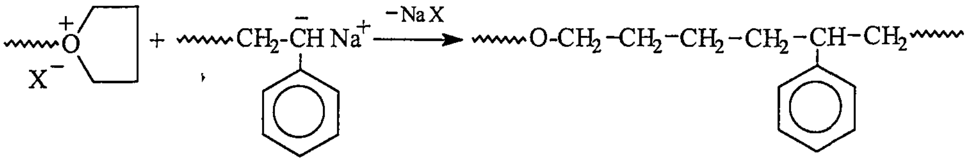
(2.97)

(2) *Indirect Transformation*: This type of transformation usually requires multistep reactions. The stable but potentially reactive functional group for the second polymerization mode is introduced to the chain ends either in the initiation or the termination steps of the polymerization the first monomer. The polymer is isolated and purified, and finally the functional groups are converted to another kind of species by external stimulation such as photoirradiation, heating or chemical reaction.

$$I + nM_1 \xrightarrow{\text{mechanism A}} I\left[M_1\right]_{n-1}M_1^{*} \xrightarrow{\text{termination}} I\left[M_1\right]_{n}F \tag{2.98}$$

$$I\left[M_1\right]_{n}F + mM_2 \xrightarrow{\text{mechanism B}} I\left[M_1\right]_{n}\textit{block}\left[M_2\right]_{m} \tag{2.99}$$

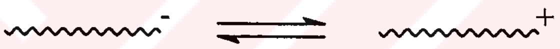
The coupling reactions in which the mutually reactive polymerizing ends are terminated with each other, i.e., cationic and anionic polymerization (2.100) are not considered as transformation reactions since the polarity of the propagating sites remains the same for the individual steps and transformation is not involved. In this connection it should be pointed out that the coupling reactions also yield block copolymers of monomers polymerizable with different modes.[162]



(2.100)

2.5.1 Direct Transformations

In this case, propagating active centers are transformed directly to another active center with different polarity. This transfer occurs through an electron transfer as shown in following (2.101) for the transformation involving anionic and cationic systems.

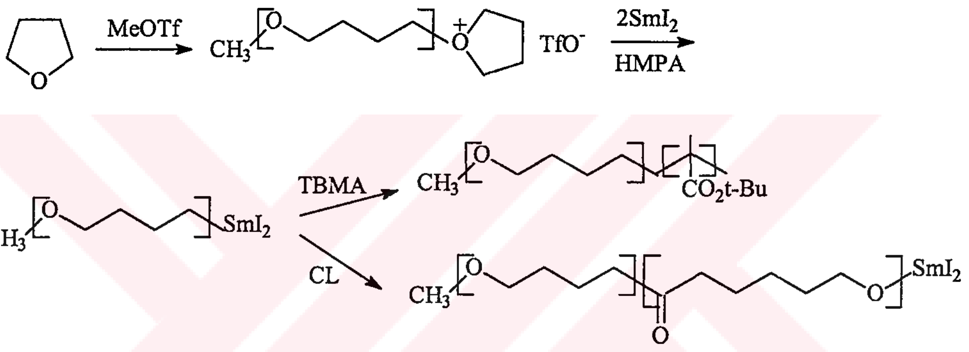


(2.101)

There has been a lack of interest in the direct transformation, mainly because of the short life time of propagating sites, particularly radicals. The active center must have a lifetime sufficient to permit transformation. Furthermore, a thermodynamic limitation for a successful redo process may result from unsuitable redo potentials of the propagating species and oxidant and reductant.

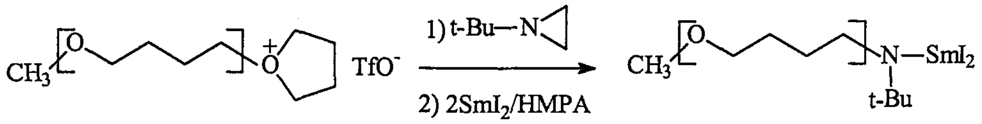
2.5.1.1 Cation to Anion Direct Transformation

The first reported development for the direct transformation was by Endo and co-workers [163]. This process involves the reduction of the cationic propagating end of polytetrahydrofuran (PTHF) to the anionic one by SmI_2 / HMPA. The two electron reductions of propagating oxonium ion proceeded quantitatively to give PTHF with terminal organosamarium moieties. The transformed anionic species reacted with *tert*-butyl methacrylate (TBMA) [164] ε-caprolactone (CL) [165] and σ-valerolactone (VL) [166] to yield a block copolymers of THF with respective monomers, as shown in reactions 2.102.



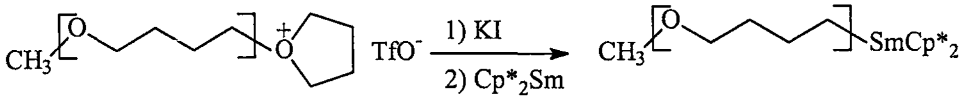
(2.102)

In early studies it was reported that methacrylates possessing a small ester groups can not be polymerized by means of samarium iodide which limits the synthetic utility of the samarium iodide induced transformation. This restriction is due to the exclusive attack of the terminal carbanion to carbonyl carbon of the monomer. However, this restriction was overcome by three modification methods. First method involves the conversion of propagating cation of polytetrahydrofuran into terminal samarium amide by reaction of the living end with N-tert-butylaziridine and subsequent reduction with samarium iodide [167] (reaction 2.103).



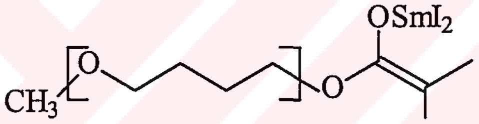
(2.103)

Alternatively, bis(pentamethylcyclopentadienyl)samarium (Cp^*_2Sm) instead of samarium iodide was used in the reduction step (reaction 2.104).



(2.104)

Although the availability of second monomers were expanded, the block efficiency was still unsatisfactory in both cases i.e. the contamination of the homopolytetrahydrofuran was unavoidable. It was recently reported that polytetrahydrofuran with terminal samarium enolates initiates polymerization of methyl methacrylates with quantitative initiation efficiency. Polytetrahydrofuran with terminal samarium enolates of the following structure (2.105) is obtained by the treatment of living ends with sodium 2-bromoisobutyrate followed by the reduction of carbon-bromine bond with samarium iodide.

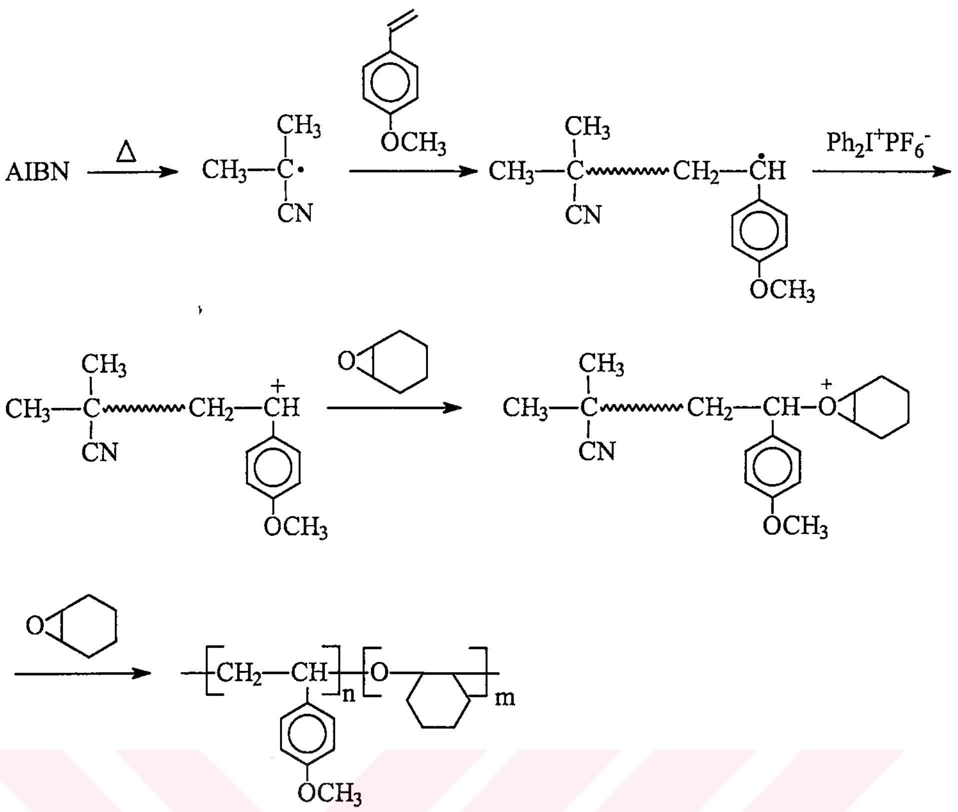


(2.105)

This synthetic procedure offers novel block copolymers of cationically and anionically polymerizable monomers.

2.5.1.2 Radical to Cation Direct Transformation

In another approach, the direct transformation of propagating radical into propagating cation took place. The transformation of the radicals to corresponding cations was achieved in the presence of electron transfer agents such as onium salts [168]. This transformation reaction was confirmed by ESR study of model radicals and by the preparation of block copolymers of *p*-methoxystyrene and cyclohexeneoxide according to the following reactions (reactions 2.106).



(2.106)

2.5.2 Indirect transformations

The most popular and best documented method is indirect transformation which uses various polymerization modes. Although indirect transformation involves several multistep paths leading to the transformation of active centers, it is much more convenient to achieve than direct transformation. In the following table, the methods will be classified according to the nature of the propagating centers involved in the transformation polymerization.

Table 2.15. Transformation Reactions Used for Block Copolymer Synthesis

TYPES OF TRANSFORMATION REACTION	REFERENCE
1- Transformations Involving Condensation Polymerization	[169]
- Transformation of Condensation Polymerization to Radical polymerization	[161,170]
• *Transformations Through Azo Initiators*	[171,172]
• *Transformations Through Photoinitiators*	[124,149,161]
- Transformation of Condensation Polymerization to Living Radical Polymerization	[173,174]
- Transformation of Macrocyclic Polymerization to Condensation Polymerization	[175,176]
2- Transformation of Anionic Polymerization to Radical Polymerization	[177-179]
- Anionic to Photoinduced Radical Transformation	[180]
- Anionic to "Living" Radical Transformation	[181,182]
3-Transformation of Cationic Polymerization to Radical Polymerization	[114,183,184]
- Cationic to "Living" Radical Transformation	[185,186]
4- Transformation of Radical Polymerization to Anionic Polymerization	[187,188]
5- Transformation of Radical Polymerization to Cationic Polymerization	[13,14,122]
6- Transformations Involving Anionic and Cationic Polymerizations	[189,190]
7- Transformations Involving Activated Monomer Polymerization	[16,17,191]
8- Transformations Involving Metathesis Polymerization	[192,193]
9- Transformations Involving Ziegler-Natta Polymerization	[194,195]
10- Transformations Involving Group Transfer Polymerization	[196,197]

In conclusion, using transformation reactions, i.e., combining different polymerization mechanisms, novel polymeric materials may be synthesized from new and existing monomers. As shown in this part, a full range of possible block and graft copolymers builds from monomers with different chemical structure are accessible through transformation reactions. It is clear that the transformation reactions will continue to attract interest in the near future because of the possibility of the various newly developed “living”/controlled polymerization mechanisms. It would be possible to design and synthesize materials having precise structures with desired properties by combination of such mechanisms.

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_2 several hours and distilled under reduced pressure (50 °C/25 mm Hg). Middle fraction was collected and immediately used.

Methyl Methacrylate (MMA) (Aldrich)

It was washed with 5% aq. NaOH solution, dried over $CaCl_2$ and vacuum distilled from CaH_2 prior to use.

Epsilon Caprolactone (ε-CL)

It was vacuum distilled over calcium hydride just before use.

Cyclohexene Oxide (CHO) (Fluka)

It was vacuum distilled from calcium hydride (CaH_2) before use.

3.1.2 Solvents

Dichloromethane (CH_2Cl_2) (Lab-scan)

methylene chloride was used as solvent for dissolving bulky polymer formations, also in UV measurements. It was first washed with conc. H_2SO_4 until the acid layer remained colourless, then washed with water, aq. %5 NaOH and then water again. It was pre-dried with $CaCl_2$ and distilled from CaH_2.

n- Hexane (Aldrich)

It was used without further purification.

Tetrahydrofuran (THF) (J.T. Baker)

It was used as eluent for chromatography as received (HPLC grade).

Methanol (Technical)

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

3.1.3 Initiators and Other Chemicals

2-Hydroxy-2-methyl-1-phenyl propan-1-one (HMPP), Darocure 1173

It was used as a photoinitiator, received from Ciba Specialty Chemicals and used without further purification.

Benzoin (B) (Aldrich)

It was recrystalized from ethanol prior to use, and used as a photoinitiator.

2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl propan-1-one (HE-HMPP), Irgacure 2959

It was used as a photoinitiator, received from Ciba Specialty Chemicals and used without further purification.

Diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) (Fluka)

It was used as received.

***N*-ethoxy-2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$)**

It was prepared as described previously [103,109].

2 – Bromopropionyl bromide (Aldrich)

It was used without further purification.

Copper (I) Bromide (CuBr) (Aldrich)

It was used as received.

2, 2'-Bipyridine (bpy) (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

A merry-go-round type photoreactor equipped with 16 Philips 8W / O6 lamps emitting light nominally at 350 nm was used.

3.2.2 UV Spectrophotometer

UV-Visible spectra were recorded on a Perkin Elmer Lambda 2 spectrometer.

3.2.3 Elemental Analysis

Elemental analysis measurements were performed by a CHNS-932 (LECO) instrument.

3.2.4 Infrared Spectrophotometer (IR)

IR spectra were recorded on a Shimadzu IR-470 infrared spectrophotometer.

3.2.5 Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H-NMR analyses were recorded on a Bruker 250 MHz NMR Spectrometer.

3.2.6 Gel Permeation Chromatography (G.P.C)

Gel permeation chromatography (GPC) analyses were performed with a set up consisting of an Agilent 1100 RI apparatus equipped with three Waters ultrastyragel 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 were calculated by using monodisperse polystyrene standards. For macrophotoinitiators of ε-caprolactone the following conversion formula was used [27] $M_{\mathrm{PCL}} = 0.259 M_{\mathrm{PSt}}{}^{1.073}$

3.3 Preparation Methods

3.3.1 Synthesis of Atom Transfer Radical Polymerization (ATRP) Initiators

3.3.1.1 Synthesis of 1,1-dimethyl-2-oxo-2-phenylethyl-2-bromopropanoate (Monofunctional Photonitiator) (HMPP-Br);

2-Hydroxy-2-methyl-1-phenyl propan-1-one (**HMPP**) (2.2717 g, 13.85 mmol), 30 mL CH_2Cl_2 and pyridine (1.21 g, 15.3 mmol) were added into a 100 mL three-necked round bottom flask fitted with a condenser, a magnetic stirrer, nitrogen inlet-outlet, and an addition funnel containing 2-bromopropanoyl bromide (3.30 g, 15.3 mmol) and 5-7 mL CH_2Cl_2 mixture. The flask was placed in an ice-water bath. The solution of 2-bromopropanoyl bromide was added dropwise over a period of 0.5 h under nitrogen. Then the mixture was allowed to reach room temperature, and stirred at that temperature over the night. The white precipitate was filtered, and the solution was washed three times with 1M HCl and twice with water. Finally, the solution was dried with $MgSO_4$, and the solvent was removed by vacuum distillation. An orange viscous liquid product (**HMPP-Br**) was obtained. Yield: 3.62 g, 86%.

$C_{13}H_{15}O_3Br$ (299.163)	Calc. :	C 52.80	H 5.16
	Found:	C 52.19	H 5.05

^{1}H-NMR in $CDCl_3$ (δ ppm): 8.0-7.92 (d, 2H, *o*-aromatic); 7.56-7.37 (m, 3H, *m, p* –aromatic); 4.29-4.2 (m, 1H, C<u>H</u>-Br); 1.75 (s, 6H, C<u>H</u>$_3$-C-C<u>H</u>$_3$); 1.63-1.62 (d, 3H, C<u>H</u>$_3$-CH-)

UV in CH_2Cl_2, nm (ε, L mol^{-1} cm^{-1}): 280 (1460.34); 350 (175.86)

3.3.1.2 Synthesis of 2-oxo-1,2-diphenylethyl-2-bromopropanoate (Monofunctional Photoinitiator) (B-Br)

Benzoin (**B**) (5.8793 g, 27.7 mmol), nearly 100 mL CH_2Cl_2 and pyridine (2.4204 g, 30.6 mmol) 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 2-bromopropanoyl bromide (6.6059 g, 30.6 mmol) and 5-7 mL CH_2Cl_2 mixture. The flask was placed in an ice-water bath. The solution of 2-bromopropanoyl bromide was added dropwise over a period of 35-40 min. under nitrogen. Then the mixture was allowed to reach room temperature, and stirred at that temperature over the night. The white precipitate was filtered, and the solution was washed three times with 1M HCl and twice with water. Finally, the solution was dried with $MgSO_4$, and the solvent was removed by vacuum distillation. The product was redissolved in CH_2Cl_2 and crystallized from ethanol. A white solid product was obtained. Yield: 7.77 g, 81%, m.p.: 62 °C

$C_{17}H_{15}O_3Br$ (347.218)	Calc. :	C 58.80	H 4.35
	Found:	C 58.10	H 4.44

^{1}H-NMR in $CDCl_3$ (δ ppm): 7.93-7.89 (d, 2H, *o*-aromatic); 7.54-7.24 (m, 8H, o,*m, p* –aromatic); 6.86 (s, 1H, -C<u>H</u>-O); 4.56-4.45 (m, 1H, -C<u>H</u>-Br); 1.90-1.87 (d, 3H, C<u>H</u>$_3$-CH-)

UV in CH_2Cl_2, nm (ε, L mol^{-1} cm^{-1}): 322 (278.58)

3.3.1.3 Synthesis of 2-(4-{[(2-bromopropanoyl)oxy]methoxy}phenyl)-1,1-dimethyl-2-oxoethyl-2-bromopropanoate (Bifunctional Photoinitiator) (Br-HE-HMPP-Br);

Br-HE-HMPP-Br was synthesized according to a procedure similar to that used for the monofunctional initiator (**HMPP-Br**). An orange oily product was obtained. Yield: 3.63 g, 80 %

$C_{18}H_{22}O_6Br_2$ (494.174): Calc. C 43.89 H 4.66
Found: C 43.75 H 4.49

^{1}H-NMR, in $CDCl_3$,(δ ppm): 8.08-8.01 (d, 2H, CO-*aromatic*); 6.98-6.89 (d, 2H, O-*aromatic*); 4.57-4.51 (m, 2H, $C\underline{H}_2$-O-aromatic) ; 4.47-4.23 (m, 4H, $C\underline{H}$-Br + $C\underline{H}_2$-O-CO); 1.84-1.63 (m, 12H, $C\underline{H}_3$)
UV in CH_2Cl_2, nm (ε, L mol^{-1} cm^{-1}): 272 (17149.63); 320 (288.06)

3.3.2 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 bipyridine (bpy), initiator (**HMPP-Br** or **B-Br** or **Br-HE-HMPP-Br**) and St 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.

3.3.3 General procedure for Ring-Opening Polymerization (ROP)

Calculated amounts of monomer (ε-caprolactone), stannous octoate and photoinitiators (**B**, **HMPP** or **HE-HMPP**) were added under nitrogen in previously flamed and nitrogen- purged schlenk tubes equipped with magnetic stirrer. The detailed polymerization conditions are given in Table 4.2. The ε-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_2Cl_2 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.

3.3.4 Synthesis of Macrophotoinitiators by ATRP of Styrene

3.3.4.1 Preparation of Well-defined Photoactive Polystyrene with Darocure 1173 End Chain Units by ATRP (HMPP-PSt)

Photoactive polystyrene with Darocure 1173 end chain units, **HMPP-PSt,** was synthesized according to procedure that used for ATRP.

3.3.4.2 Preparation of Well-defined Photoactive Polystyrene with Benzoin End Chain Units by ATRP (B-PSt)

Photoactive polystyrene with Benzoin end chain units, **B-PSt,** was synthesized according to procedure that used for ATRP.

3.3.4.3 Preparation of Well-defined Photoactive Polystyrene with Irgacure 2959 Mid-Chain Units by ATRP (HE-HMPP-PSt)

Photoactive polystyrene with Irgagure 2959 mid-chain units, **HE-HMPP-PSt,** was synthesized according to procedure that used for ATRP.

3.3.4.3a Photolysis of Photoactive Polystyrene with Irgacure 2959 Mid-Chain Units (HE-HMPP-PSt) in the presence of a radical scavenger

Photolysis reaction was carried out under nitrogen atmosphere. Prior to irradiation, He-HMPP-PSt (0.3 g, 1.67×10^{-5} mol), hydroquinone (radical scavenger) (0.6 g, 5.45×10^{-3} mol) and 1-2 ml dichloromethane (solvent) was placed in a pyrex tube previously heated with a heat gun and flushed with dry nitrogen and irradiated in a merry-go-round type photoreactor equipped with 15 Philips 8 W/06 lamps emitting light nominally at λ >300 nm and a cooling system. After 120 min irradiation the solution was poured into methanol. The precipitated polymer was then filtered off and dried in vacou.

3.3.5 Synthesis of Macrophotoinitiators by ROP of ε-Caprolactone

3.3.5.1 Preparation of Well-defined Photoactive Poly (ε-Caprolactone) with Darocure 1173 End Chain Units by ROP (HMPP-PCL)

Photoactive poly (ε-caprolactone) with Darocure 1173 end chain units, **HMPP-PCL,** was synthesized according to procedure that used for ROP.

3.3.5.2 Preparation of Well-defined Photoactive Poly (ε-Caprolactone) with Benzoin End Chain Units by ROP (B-PCL)

Photoactive poly (ε-caprolactone) with Benzoin end chain units, **B-PCL,** was synthesized according to procedure that used for ROP.

3.3.5.3 Preparation of Well-defined Photoactive Poly (ε-Caprolactone) with Irgacure 2959 Mid-Chain Units by ROP (HE-HMPP-PCL)

Photoactive poly (ε-caprolactone) with Irgagure 2959 mid-chain units, **HE-HMPP-PCL** was synthesized according to procedure that used for ROP.

3.3.6 General Block Copolymerization Procedure Using Macrophotoinitiators Prepared by ATRP and ROP Methods

Photopolymerizations were carried out in bulk. Appropriate solutions of monomer (MMA) containing given amounts of macrophotoinitiators (**HMPP-PSt** or **B-PSt** or **HE-HMPP-PSt** or **HMPP-PCL** or **B-PCL** or **HE-HMPP-PCL**) were placed in pyrex tubes and degassed with nitrogen prior to irradiation by a merry-go-round type photoreactor equipped with 15 Philips 8 W/06 lamps emitting light nominally at λ >300 nm and a cooling system. At the end of given time, polymers were poured into methanol, filtered, dried and weighted. Conversions were determined gravimetrically. The detailed polymerization conditions are given in the Results & Discussion section.

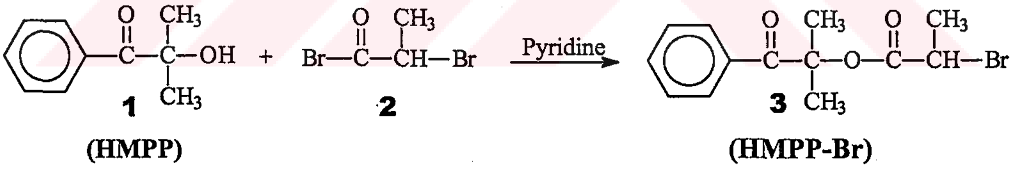
3.3.7 General Photoinduced Free Radical Promoted Cationic Block Copolymerization Procedure Using Macrophotoinitiators Prepared by ATRP and ROP Methods

Appropriate solutions of polymeric photoinitiators (**HMPP-PSt** or **B-PSt** or **HE-HMPP-PSt** or **HMPP-PCL** or **B-PCL** or **HE-HMPP-PCL**) and monomer (CHO) in bulk containing onium salt (Ph_2I^+ or EMP^+ or Ph_3S^+) in Pyrex tubes were degassed with nitrogen prior to irradiation. At the end of irradiation in a merry-go-round type photoreactor equipped with 15 Philips lamps and emitting light nominally at 350 nm at room temperature, the solutions were poured into cold methanol. The precipitated copolymers were filtered off and dried in vacuo. The detailed polymerization conditions are given in the Results & Discussion section.

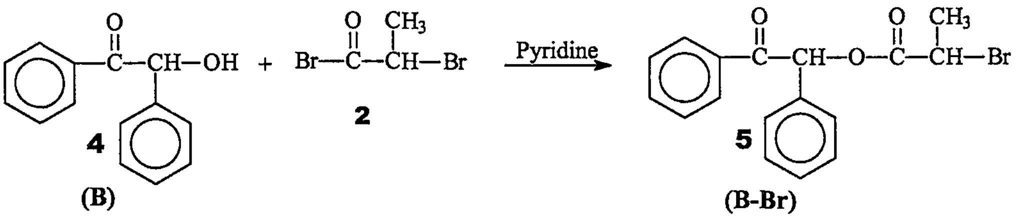
4. RESULTS and DISCUSSION

4.1 Preparation of End- and Mid-chain Functional Photoinitiators for ATRP

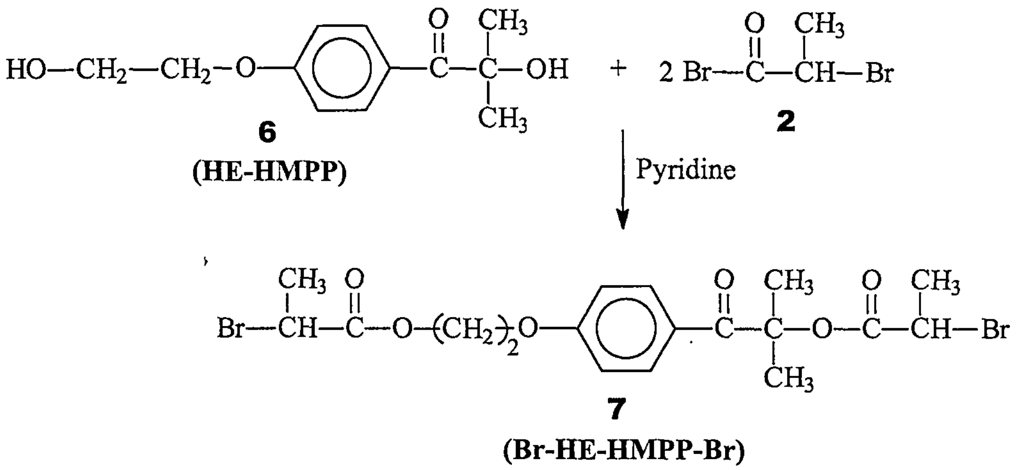
It has been shown that CuBr/bipyridine complex is very effective for ATRP in conjunction with alkyl halides [198]. The objective of this work was to design initiators, with alkoxy phenyl ketone containing alkyl bromide(s) so as to produce photo-functionalized polymers. Mono and bifunctional initiators (**HMPP-Br (3)**, **B-Br** (5) and **Br-HE-HMPP-Br** (7)) were prepared by reactions of 2-bromopropanoyl bromide (2) with 2-hydroxy-2-methyl-1-phenyl-propane-1-one, **HMPP** (1), 2-hydroxy-1,2-diphenyl-1-ethanone (Benzoin), **B** (4) and 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-propane-1-one, **HE-HMPP** (6), respectively, as shown in following reactions.



(4.1)



(4.2)



(4.3)

The structures of the new ATRP initiators were confirmed by elemental analysis as well as spectroscopic investigations. The IR spectra contain the characteristic C=O ester band and the C=O keto group of the photoinitiator moiety at 1735 and 1686 cm^{-1}, respectively (Figure 4.1). The ^{1}H-NMR (Figure 4.2, 4.3 and 4.4) and ^{13}C-NMR spectra (Figure 4.5), also contain the expected peaks, confirming the structure of the initiators (vide infra).

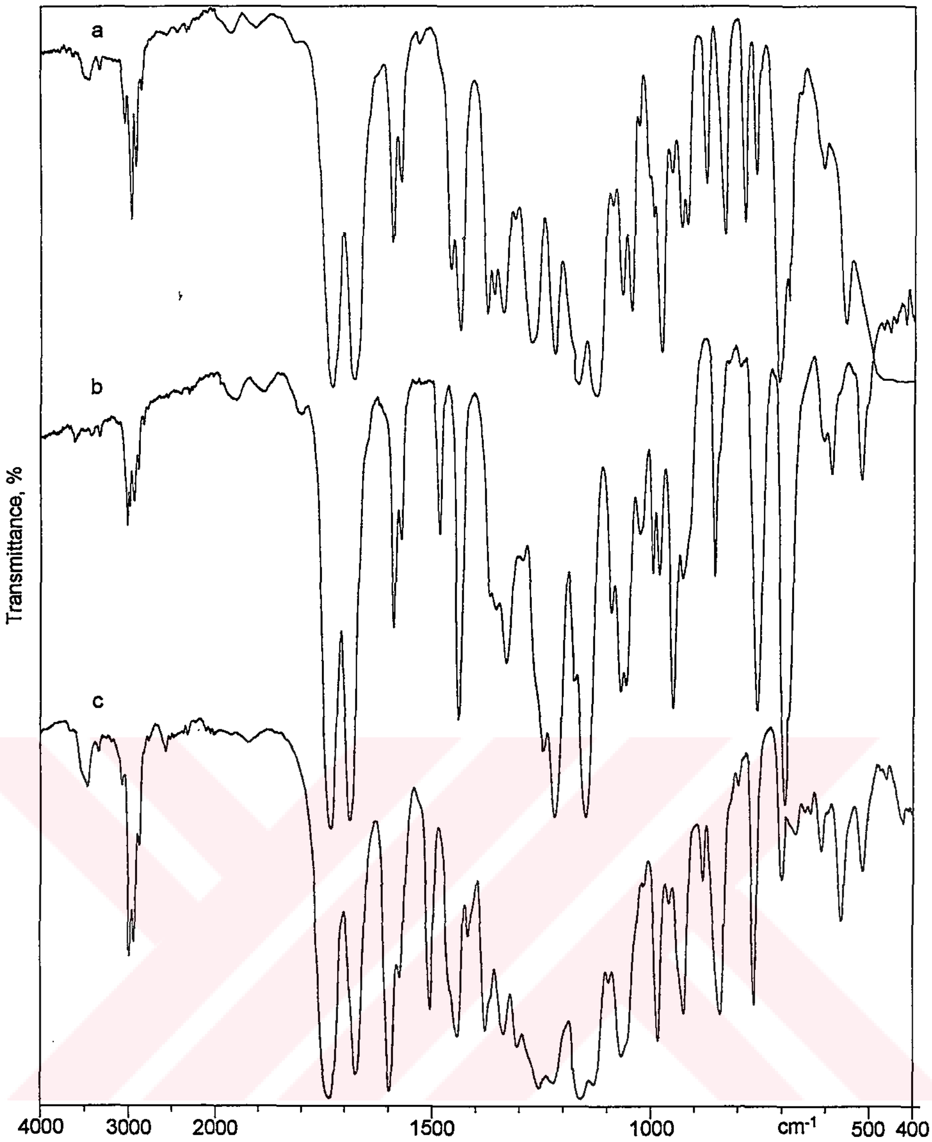
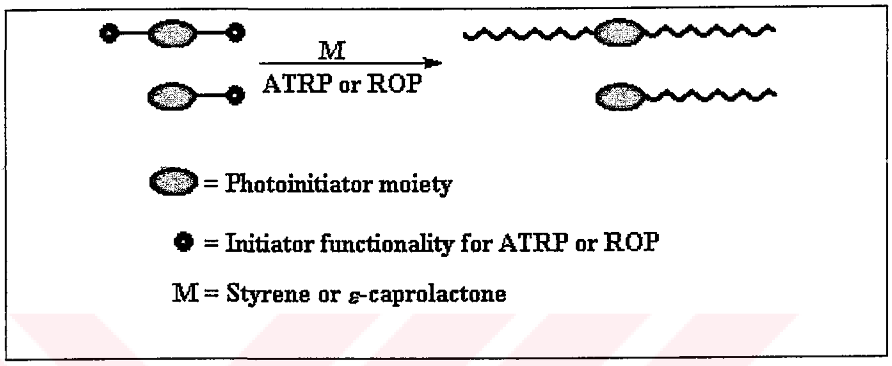


Figure 4.1. IR spectra of ATRP initiators: **HMPP-Br (a)**, **B-Br (b)** and **Br-HE-HMPP-Br (c)**

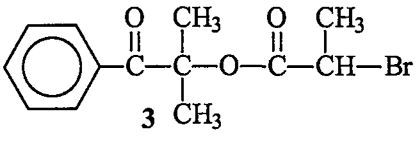
4.2 Preparation of Macrophotoinitiators

Macrophotoinitiators are polymers with photoinitiator functionality at side chains or in the end or middle of the chain [10]. These materials are of great scientific and technological interest because of their application in UV-curable coatings [91] and as precursors for graft and block copolymers depending on the position of the photoinitiator moiety incorporated [8]. Many macrophotoinitiators have been synthesized and their utilization in both applications has been studied. The major concern for their uses particularly in the latter application was related to the efficiency of functionalization, well-defined and predetermined structures, and low polydispersities. Obviously, if all chains are not functionalized, upon irradiation non-functionalized chains will not be activated and consequently remain as homopolymers in the system. Since the perfect fictionalization is not achieved by conventional polymerization methods, controlled/living polymerization techniques are of interest for the preparation of macrophotoinitiators. The synthetic strategy for the preparation of macrophotoinitiators is described in following.

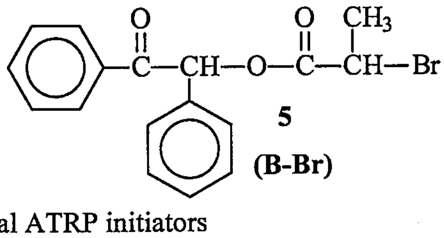


4.2.1. Macrophotoiniators Prepared by Atom Transfer Radical Polymerization (ATRP)

Among the newly developed controlled/living radical polymerization methods [28], atom transfer radical polymerization (ATRP) is the most versatile technique providing a variety of adjustable options [30]. A series of photoinitiators possessing initiating sites i.e., alkyl halide for ATRP were prepared and listed below. The synthetic strategy for their preparation was described above.

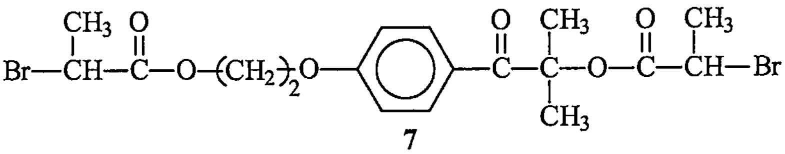


3
(HMPP-Br)



5
(B-Br)

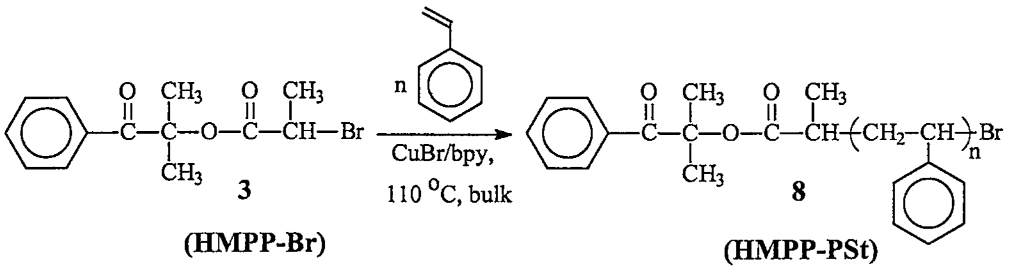
Monofunctional ATRP initiators



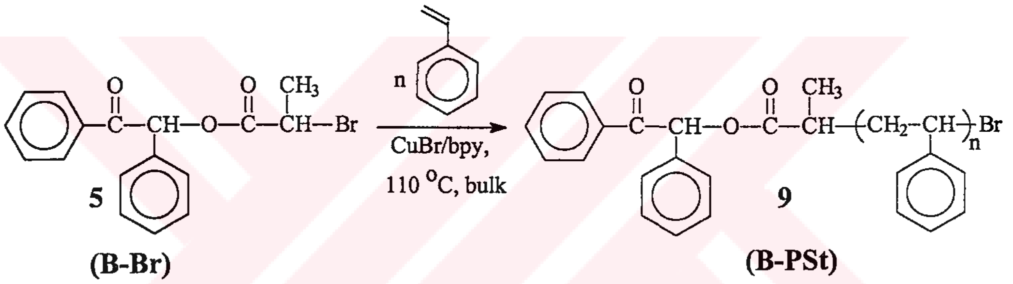
7
(Br-HE-HMPP-Br)

Bifunctional ATRP initiator

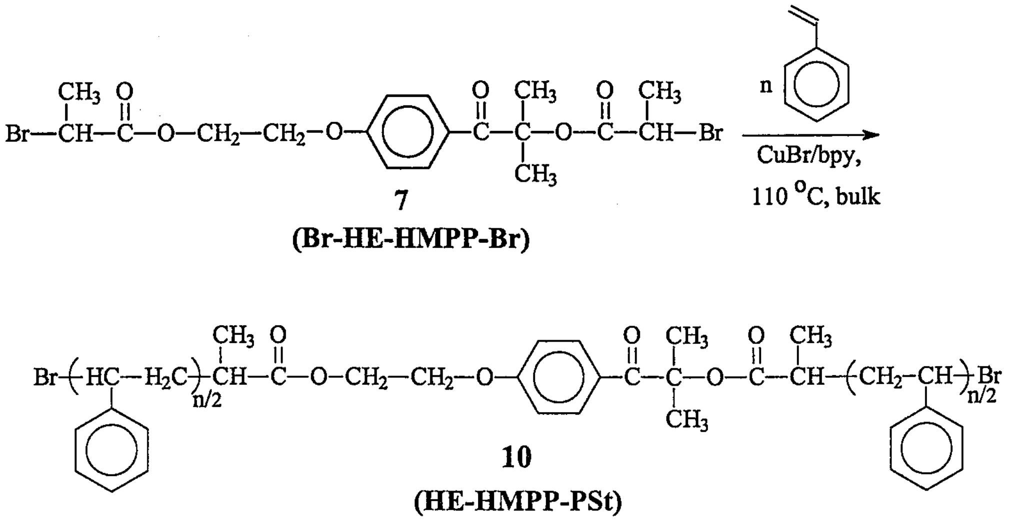
The ATRP of styrene (St) in bulk at 110 °C by means of monofunctional initiators **HMPP-Br** (3) and **B-Br** (5) and bifunctional initiator **Br-HE-HMPP-Br** (7) in conjunction with a Cu(I)Br/bipyridine yield end-chain and mid-chain functional macrophotoinitiators. The detailed polymerization conditions and results are given in Table 4.1.



(4.4)



(4.5)



(4.6)

As can be seen from Table 4.1, the measured and calculated M_n values are in good agreement indicating that each initiator added to the solution generates one or two growing ends depending on the initiator functionality. By modifying the initiator concentration and polymerization time, macroinitiators with various molecular weights and low polydispersities were obtained. The GPC traces are unimodal and narrow indicating that no side reactions occurred.

Table 4.1. Synthesis of Macrophotoinitiators by ATRP[a] of Styrene

Run	**Initiator**	[I]x10^{-2} (mol.L^{-1})	Time (hr)	**Polymer**	Conversion (%)	M_n[b] (theo.)	M_n (GPC)	M_w/M_n	M_n (H-NMR)
A	**HMPP-Br**	39	7	**HMPP-PSt-1**	70	2100	2450	1.12	2500
B	**HMPP-Br**	7.0	3	**HMPP-PSt-2**	53	7150	7700	1.20	8200
C	**HMPP-Br**	7.0	4	**HMPP-PSt-3**	68	9200	9700	1.12	10500
D	**HMPP-Br**	8.5	6	**HMPP-PSt-4**	82	8950	9600	1.17	10350
E	**HMPP-Br**	3.5	7	**HMPP-PSt-5**	57	14700	16200	1.14	nd[c]
F	**B-Br**	17.7	3	**B-PSt-1**	89	4950	4700	1.18	4450
G	**B-Br**	8.7	5	**B-PSt-2**	77	8500	8550	1.17	8950
H[d]	**B-Br**	1.17	7	**B-PSt-3**	17	9300	8800	1.19	10900
I	**Br-HE-HMPP-Br**	4.4	5	**HE-HMPP-PSt-1**	25	5700	5650	1.14	6000
J	**Br-HE-HMPP-Br**	4.4	6	**HE-HMPP-PSt-2**	80	17200	18000	1.15	nd[c]

[a] Temp.110°C, $[St]_o$=8,75 mol L^{-1}(in bulk),
[b] Calculated by $[M_0]/[I_0]$ x Conv. x $MW_{monomer} + MW_{initiator}$
$[I_0]$/[CuBr]/[Bpy]: 1/1/3 for the initiator **HMPP-Br** and **B-Br**
$[I_0]$/[CuBr]/[Bpy]: 1/2/6 the initiator **Br-HE-HMPP-Br**
[c] nd: not determined
[d] $[I_0]$/[CuBr]/[Bpy]: 1/0.5/1.5

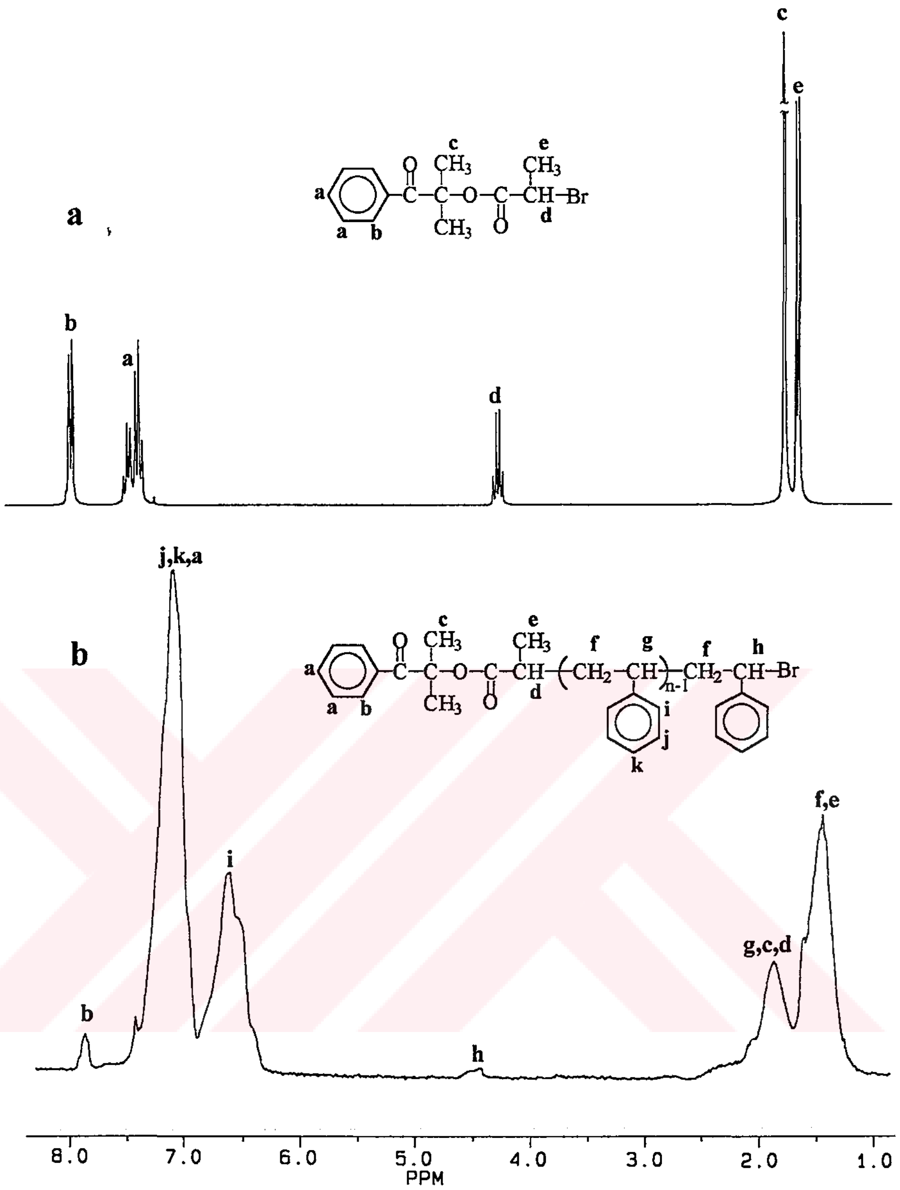


Figure 4.2. ^{1}H-NMR spectra of ATRP initiator **HMPP-Br** (**a**) and monofunctional polystyrene macrophotoinitiator **HMPP-PSt-1** (**b**) in $CDCl_3$

The number average molecular weight calculated by comparison of the integration ratio of aromatic proton resonances of **HMPP-Br** (Figure 4.2), **B-Br** (Figure 4.3) and **HE-HMPP-Br** group (Figure 4.4) compare favorably with the molecular weight calculated by the monomer-to-initiator ratio and the one measured by GPC. This confirms that the chains are quantitatively functionalized to generate the desired polystyrene (PSt) macrophotoinitiators.

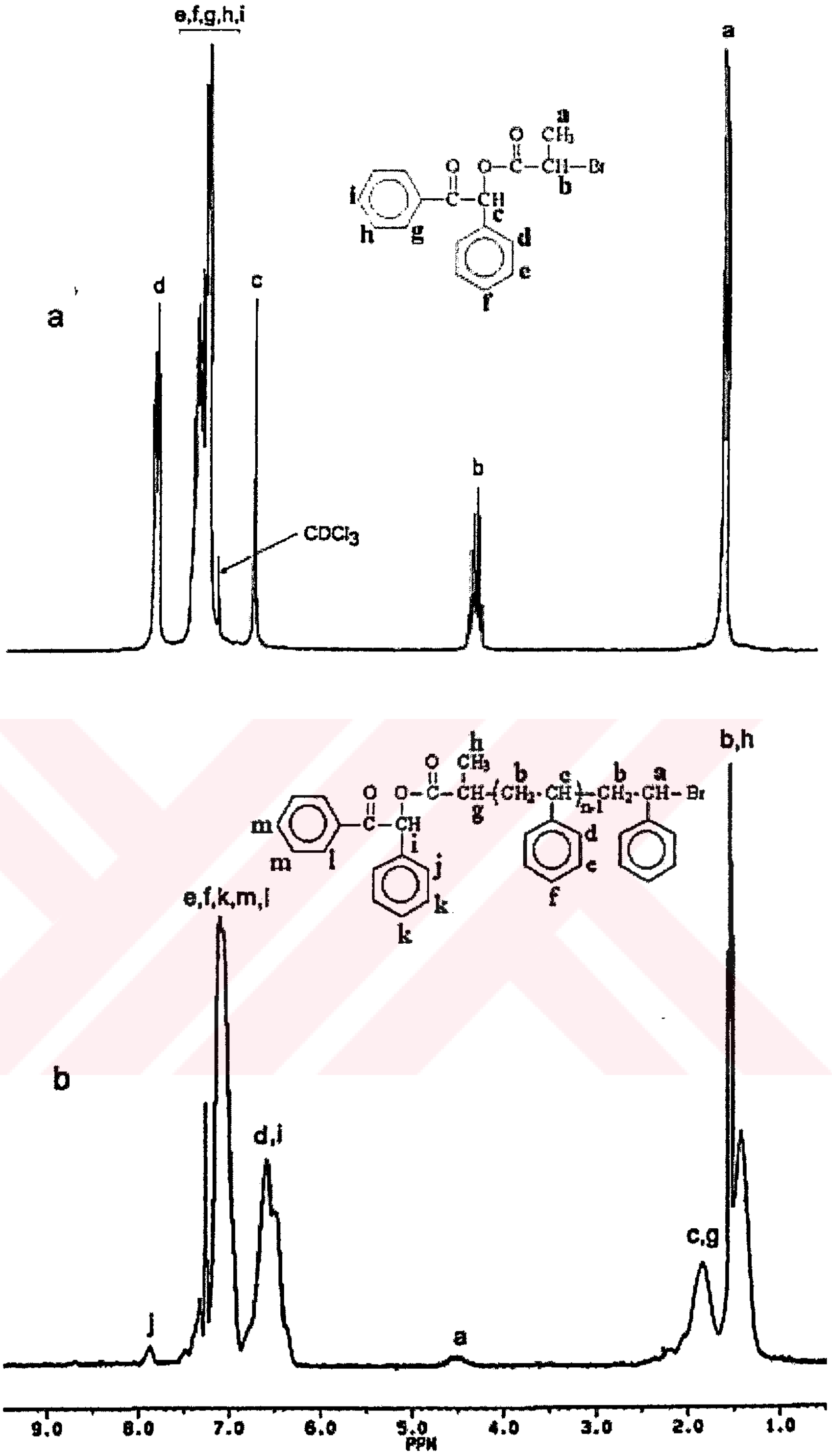


Figure 4.3. ^{1}H-NMR spectra of ATRP initiator **B-Br** (**a**) and monofunctional polystyrene macrophotoinitiator **B-PSt-1** (**b**) in $CDCl_3$

As can be seen from Figure 4.2, 4.3 and 4.4 in the ^{1}H-NMR spectra of the low molecular samples can be found not only the specific signals of polystyrene, but also absorptions belonging to the rests of initiators. For example, in the case of the sample **HMPP-PSt-1**, the **b** protons appear very clear at about 7.9 ppm, while the ones are covered by the aromatic protons of polystyrene (Figure 4.2 **b**). The **d** protons of the initiator (Figure 4.2 **a**) from 4.2-4.29 ppm appear in the polymer spectrum together with the aliphatic protons of polystyrene, but the final CH-Br proton (**h**) from the end of macromolecule are found at 4.5 ppm. Peaks corresponding to the rest of the initiator can also be found in the ^{1}H-NMR spectra of the other monofunctional and bifunctional macroinitiator. In the ^{1}H-NMR spectrum of **HE-HMPP-PSt-1**: **f** at 7.86 ppm, **c** and **d** near the new CH-Br (**m**) in the range 3.95-4.45 ppm. So, the molecular weights can be calculated also from ^{1}H-NMR data, taking into account the intensities of integrals belonging to polystyrene in aromatic region and those specific to the rests of initiators. For monofunctional macroinitiators; **HMPP-PSt-1** and **B-PSt-1** the obtained values ($M_{n,\ HNMR} = 2500$) and ($M_{n,\ HNMR} = 4450$) fit exactly with that found from GPC measurements (Table 4.1). For bifunctional macroinitiator **HE-HMPP-PSt-1** the value of molecular weight calculated from ^{1}H-NMR spectrum ($M_{n,\ HNMR} = 6000$) is also very close to that obtained by GPC ($M_{n,\ GPC} = 5650$).

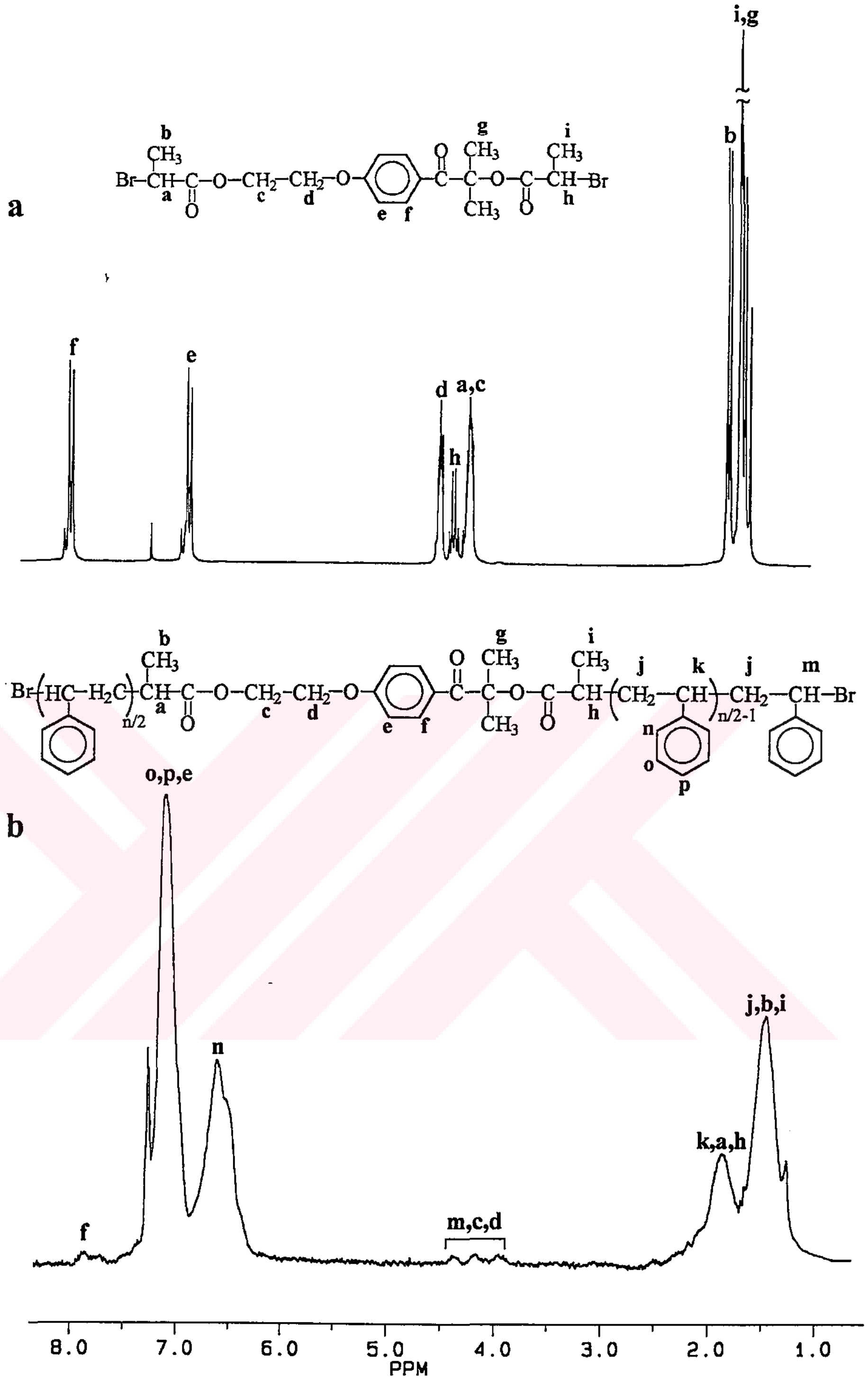


Figure 4.4. ^{1}H-NMR spectra of ATRP initiator **Br-HE-HMPP-Br** (**a**) and bifunctional polystyrene macrophotoinitiator **HE-HMPP-PSt-1** (**b**) in $CDCl_3$

The ^{13}C-NMR spectra (Figure 4.5) also contain the expected peaks, confirming the structure of the initiators.

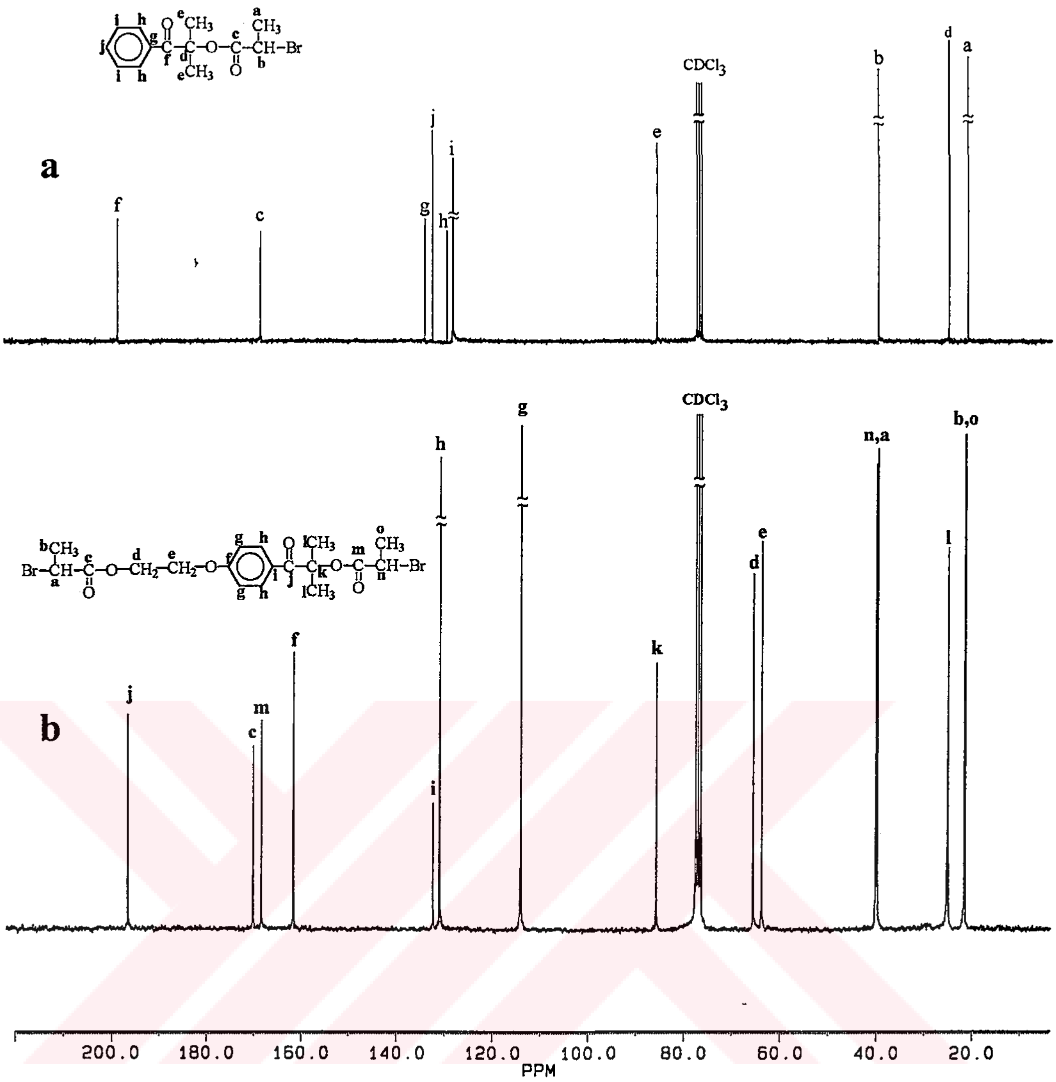


Figure 4.5. ^{13}C-NMR spectra of ATRP initiator **HMPP-Br** (**a**) and monofunctional polystyrene macrophotoinitiator **HMPP-PSt-1** (**b**) in CDCl$_3$

The incorporation of alkoxyphenyl ketone groups into polymers was also evidenced by UV absorption measurements. Figures 4.6, 4.7 and 4.8 show the absorption spectra of precursors **HMPP-Br**, **B-Br** and **Br-HE-HMPP-Br** together with the polystyrenes obtained. It can be seen that each spectrum contains a characteristic absorption band of the precursor α-hydroxy phenyl ketone photoinitiators.

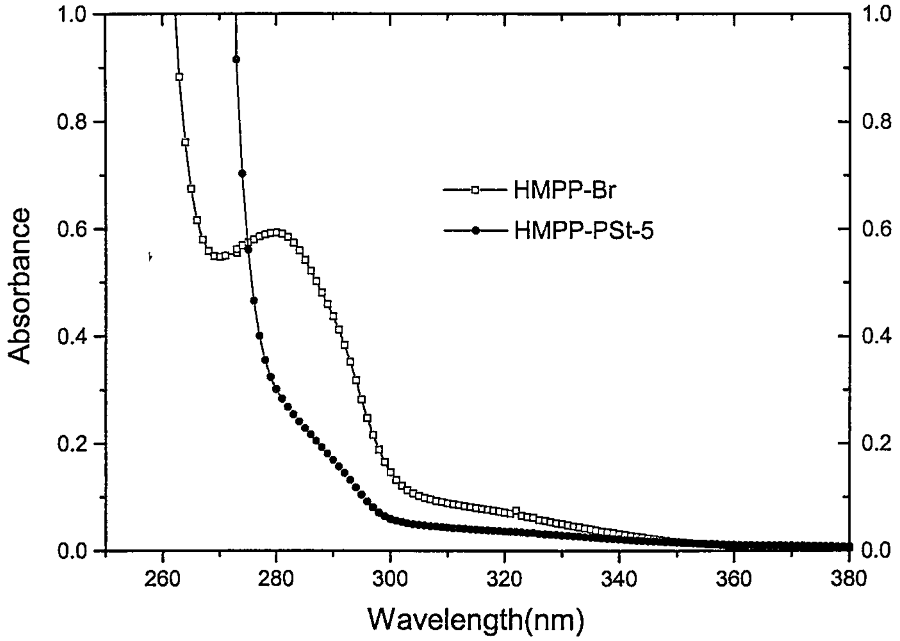


Figure 4.6. Absorption spectra of **HMPP-Br** ($4x10^{-4}$ mol L^{-1}) and **HMPP-PST-5** (2.64 g L^{-1}) in CH_2Cl_2

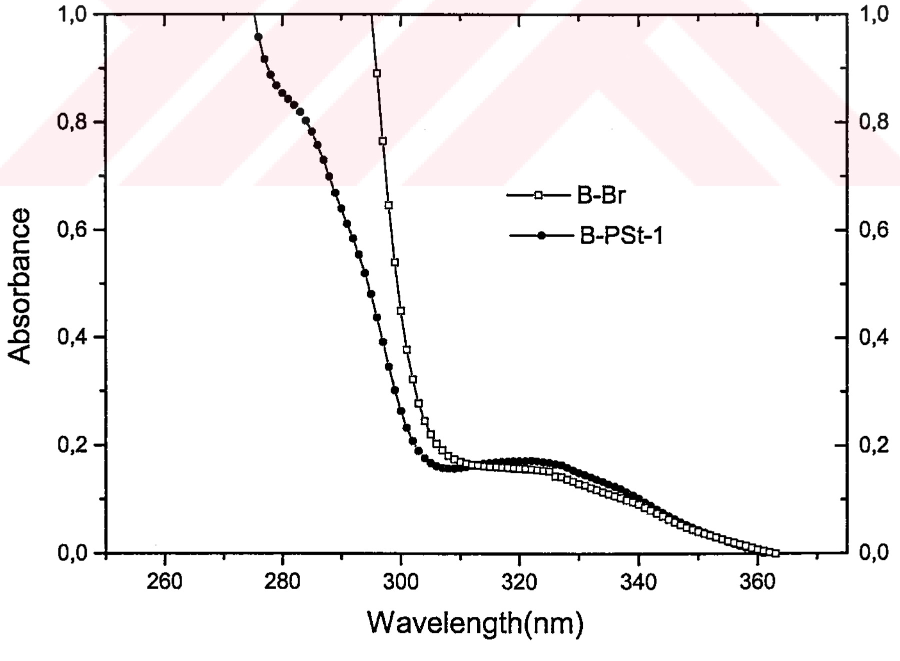


Figure 4.7. Absorption spectra of **B-Br** ($6.16x10^{-4}$ mol L^{-1}) and **B-PSt-1** (2.68 g L^{-1}) in CH_2Cl_2

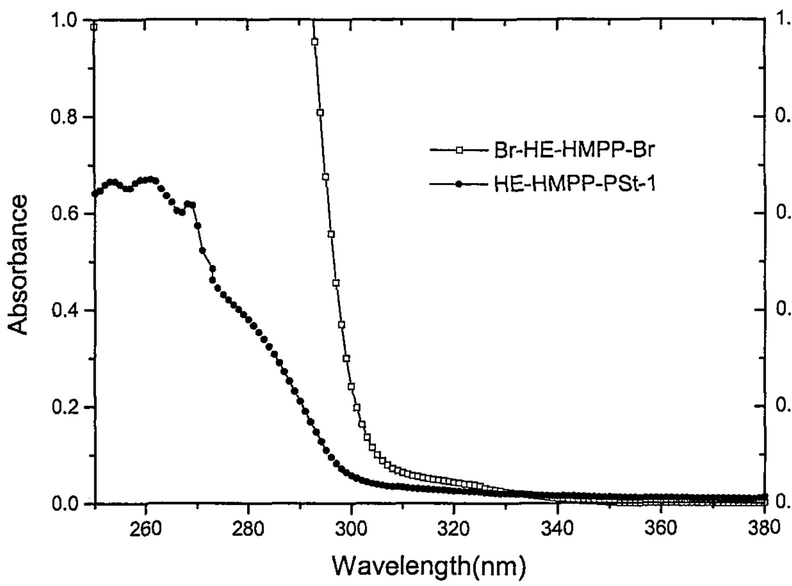


Figure 4.8. Absorption spectra of **Br-HE-HMPP-Br** ($1.5x10^{-4}$ mol L^{-1}) and **HE-HMPP-PSt-1** (0.54 g L^{-1}) in CH_2Cl_2

Figure 4.9 shows the fluorescence emission of the related molecules (**Br-HE-HMPP-Br** and **HE-HMPP-PSt-2**) in Methylene chloride at room temperature. Both spectra show the vibrational structures of the phenyl ketone chromophore. These spectroscopic investigations suggest that the photochromophoric phenyl ketone groups were conserved under the polymerization conditions.

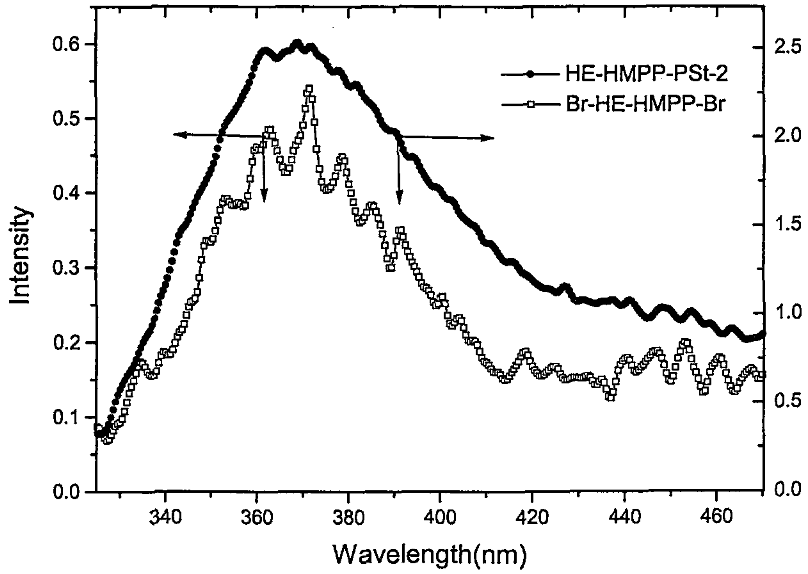


Figure 4.9. Fluorescence spectra of **Br-HE-HMPP-Br** (10^{-3} mol L^{-1}) and **HE-HMPP-PSt-2** (50 g L^{-1}), in CH_2Cl_2, λ_{exc}=320nm

Even more convincing evidence for the presence of the alkoxy phenyl ketone group was obtained from the photo degradation of polymers produced by means of ATRP. As can be seen from the GPC traces in Figure 4.10, after photolysis of Pest (**HE-HMPP-PSt-2**) in Methylene chloride in the presence of hydroquinone as the radical scavenger, a significant reduction in the molecular weight was observed. The number of chain scission per macromolecule, $N_s = (M_{n0}/M_{nt})-1$, is found to be 0.80, where M_{n0} (18000) and M_{nt} (10000) denotes the number average molecular weight before and after photolysis.

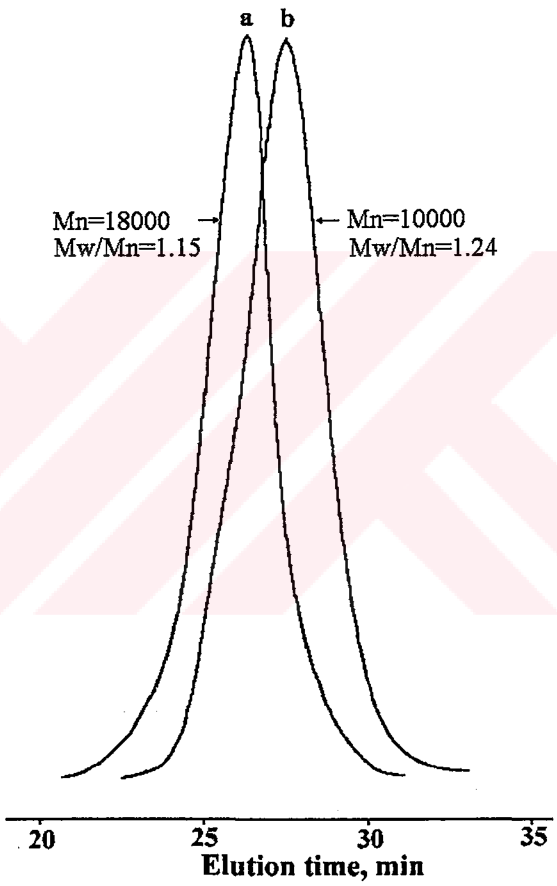
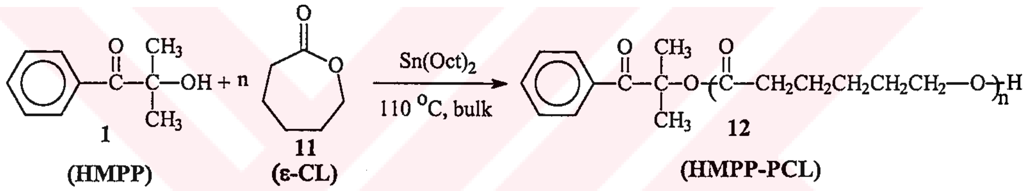


Figure 4.10. GPC traces of **HE-HMPP-PSt-2** before (**a**) and after photolysis (**b**)

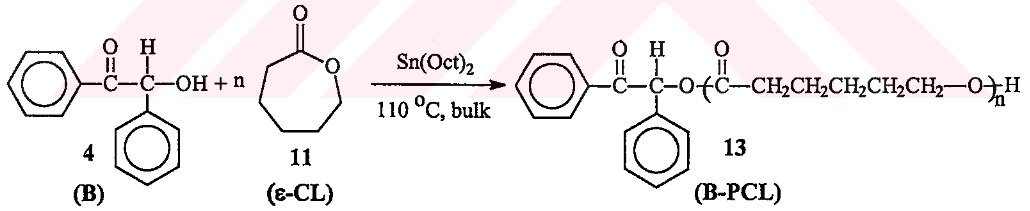
We have also tested the photoinitiation capability of these polymers. A typical photochemically induced polymerization of bulk methyl methacrylate (2 ml) at 25 °C with **HE-HMPP-PSt-1** (0.2030g, 3.6×10^{-5} mol) produced 14.5 % conversion of MMA after 90 min of irradiation time. A control experiment without the polymeric initiator gave only negligible amount of polymer after the same irradiation time.

4.2.2 Macrophotoiniators Prepared by Ring-opening Polymerization (ROP)

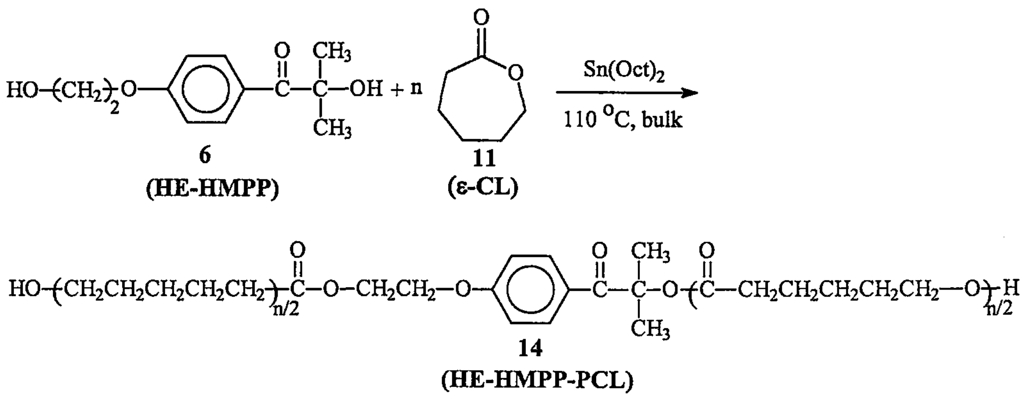
The synthesis of macrophotoinitiators of poly(ε-caprolactone) depicted in following reactions involved the reaction of photoinitiators, namely 2-hydroxy-2-methyl-1-phenyl propan-1-one, **HMPP** (**1**), benzoin **B** (**4**), and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl propan-1-one, **HE-HMPP** (**6**), with ε-caprolactone (**ε-CL**) in the presence of stannous 2-ethyl-hexanoate (stannous octoate) in short $Sn(Oct)_2$ catalyst. In view of the reported role of hydroxyl groups as initiators in ring-opening polymerization, this reaction was expected to produce polymers containing a photoiniator group on one end or on the middle of the chain, derived from a single or two terminal units of the photoinitiators, respectively.



(4.7)



(4.8)



(4.9)

As can be seen from Table 4.2, the measured and calculated M_n values are in good agreement indicating that each photoinitiator added to the solution generates one or two growing ends depending on the initiator functionality. Some discrepancy observed with the values calculated by spectral methods may be due to the inaccuracy of the molecular weight determination by end-group analysis.

Table 4.2. Synthesis of Macrophotoinitiators by ROP[a] of ε-Caprolactone

Run	**Initiator**	$[I]x10^2$ $(mol.L^{-1})$	Time (hour)	**Polymer**	Conversion (%)	$M_{ntheo.}$	M_{nGPC}[b]	M_w/M_n	$M_{nH\text{-}NMR}$	M_{nUV}
K	**HMPP**	41	48	**HMPP-PCL**	90	2450	2600	1.08	3650	2560
L	**B**	45	72	**B-PCL-1**	84	2150	2500	1.13	4200	3050
M	**B**	45	96	**B-PCL-2**	100	2500	3300	1.57	4170	4000
N	**HE-HMPP**	22	90	**HE-HMPP-PCL**	100	4800	4400	1.56	5100	5300

[a] Temp.110 °C, $[\varepsilon\text{-CL}]_o = 9.02$ mol L^{-1}(in bulk),
$[I_0]/[\varepsilon\text{-CL}]$: 1/20 and $[Sn(Oct)_2]/[I]$: 1/400 for the initiator **HMPP** and **B**
$[I_0]/[\varepsilon\text{-CL}]$: 1/40 and $[Sn(Oct)_2]/[I]$: 1/200 for the initiator **HE-HMPP**

[b] Calculated by $M_{PCL} = 0.259M_{PSt}^{1.073}$ conversion formula [27]

The GPC traces are unimodal and narrow indicating that no side reactions occurred. Moreover, dual detection by refractive index and UV measurements provides clear evidence for the complete functionalization. As can be seen from Figure 4.11, GPC trace of poly(ε-caprolactone) prepared from benzoin measured by UV (λ=330 nm) and refractive index appear at the same elution volume.

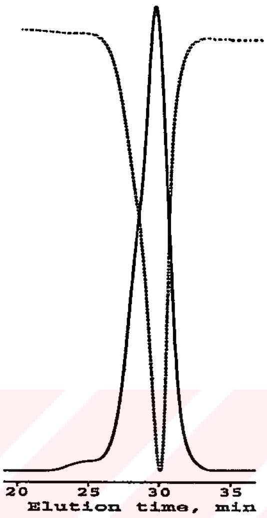


Figure 4.11. GPC trace of **B-PCL**; refractive index signal (—) and UV signal at λ=330 nm (----)

The IR spectra of polymers contain the characteristic carbonyl (C=O) group of the photoinitiator moiety at 1720 cm^{-1}. For example, Figure 4.12 shows the IR spectrum of polymeric photoinitiator, **B-PCL (13)** which is typical of this series of compounds.

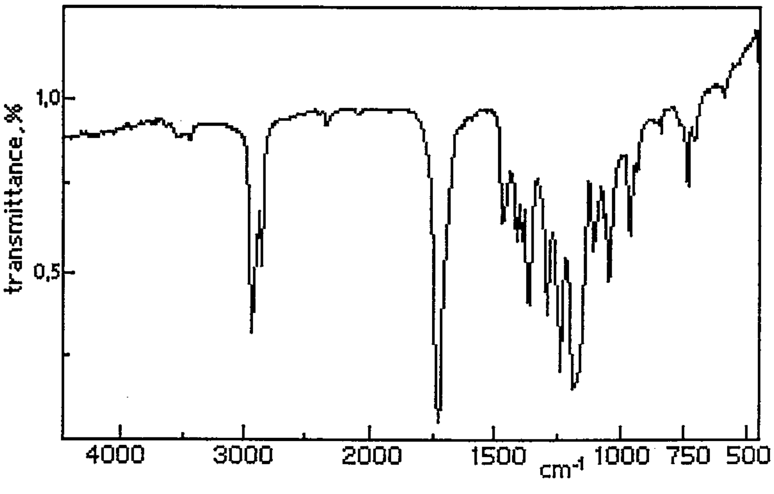


Figure 4.12. IR spectrum of **B-PCL**

In the ^{1}H-NMR spectra of the polymer samples can be found not only the specific signals of poly(ε-caprolactone) (PCL), but also absorptions belonging to the rests of initiators. In Figure 4.13, 4.14 and 4.15 are shown the ^{1}H-NMR spectra of polymeric photoinitiators, **HMPP-PCL (12), B-PCL (13)** and **HE-HMPP-PCL (14)** in $CDCl_3$.

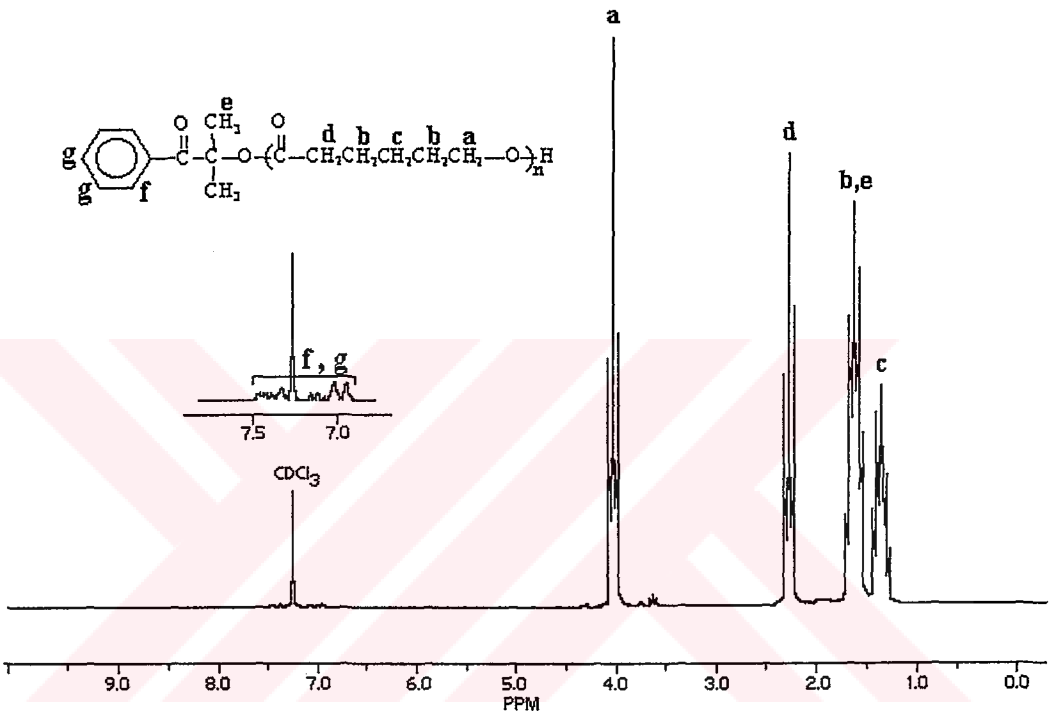


Figure 4.13. The ^{1}HNMR spectrum of **HMPP-PCL** in $CDCl_3$

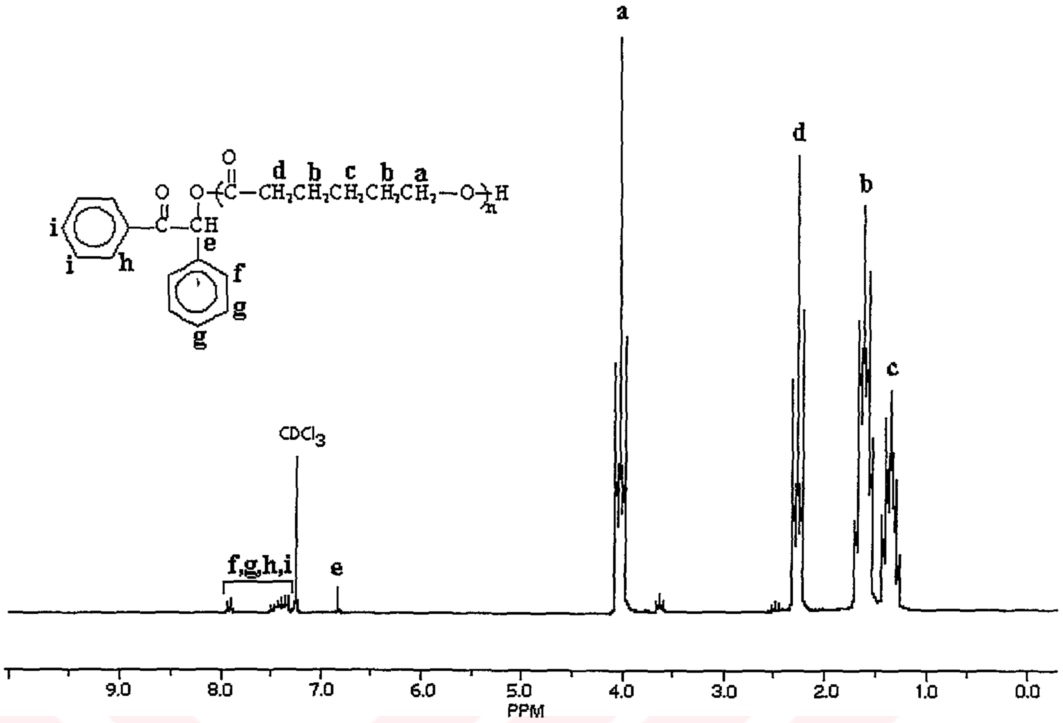


Figure 4.14. The ^{1}HNMR spectrum of **B-PCL** in $CDCl_3$

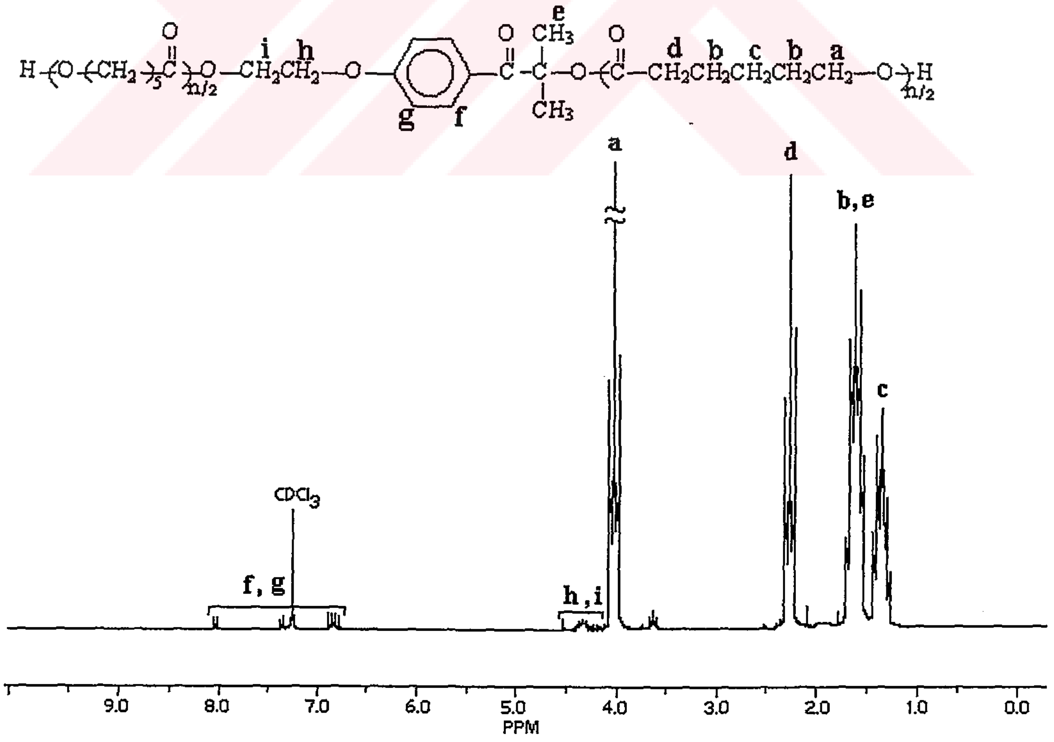


Figure 4.15. ^{1}H-NMR spectrum of **HE-HMPP-PCL** in $CDCl_3$.

A summary of the ^{1}H-NMR chemical shifts for these photoinitiators is given in Table 4.3. The incorporation of alkoxyphenyl ketone groups into polymers was also evidenced by UV absorption measurements. Figures 4.16, 4.17 and 4.18 show the UV absorption spectra of precursors, **HMPP (1), B** (4) and **HE-HMPP (6)**, together with the PCL's, **HMPP-PCL** (12), **B-PCL** (13) and **HE-HMPP-PCL** (14), obtained. It can be seen that all spectra contain a characteristic absorption band of the precursor photoinitiators.

Table 4.3. Spectral Characterization of Macrophotoinitiators of ε-Caprolactone

	^{1}H-NMR		UV	
Macrophoto-initiator	Group	δ (in ppm)	λ_{max} (nm)	ε (L mol^{-1}cm^{-1})
HMPP-PCL	$C\mathit{H}_2$-O CH_2-$C\mathit{H}_2$-CH_2-$C\mathit{H}_2$-CH_2-O and CO-C($C\mathit{H}_3$)$_2$-O CH_2-CH_2-$C\mathit{H}_2$-CH_2-CH_2-O CO-$C\mathit{H}_2$ Ar-H	4.00-4.06 (t, 2H) 1.56-1.68 (m, 10H) 1.29-1.41 (m, 2H) 2.25-2.31 (t, 2H) 6.80-7.48 (m, 5H)	320	96 (104)[a]
B-PCL	$C\mathit{H}_2$-O CH_2-$C\mathit{H}_2$-CH_2-$C\mathit{H}_2$-CH_2-O CH_2-CH_2-$C\mathit{H}_2$-CH_2-CH_2-O CO-$C\mathit{H}_2$ Ar-CH Ar-H	4.01-4.06 (t, 2H) 1.56-1.73 (m, 4H) 1.29-1.41 (m, 2H) 2.25-2.31 (t, 2H) 6.83 (s, 1H) 7.32-7.92 (m, 10H)	320	201 (217)[a]
HE-HMPP-PCL	$C\mathit{H}_2$-O CH_2-$C\mathit{H}_2$-CH_2-$C\mathit{H}_2$-CH_2-O and CO-C($C\mathit{H}_3$)$_2$-O CH_2-CH_2-$C\mathit{H}_2$-CH_2-CH_2-O CO-$C\mathit{H}_2$ Ar-H O-$C\mathit{H}_2$-$C\mathit{H}_2$-O	4.00-4.05 (t, 2H) 1.56-1.73 (m, 10H) 1.28-1.41 (m, 2H) 2.25-2.37 (t, 2H) 6.86-8.06 (m, 4H) 4.12-4.54 (m, 4H)	320	117 (286)[a]

[a] Values in parentheses indicate the molar extinction coefficients of the precursor low molar mass photoinitiators.

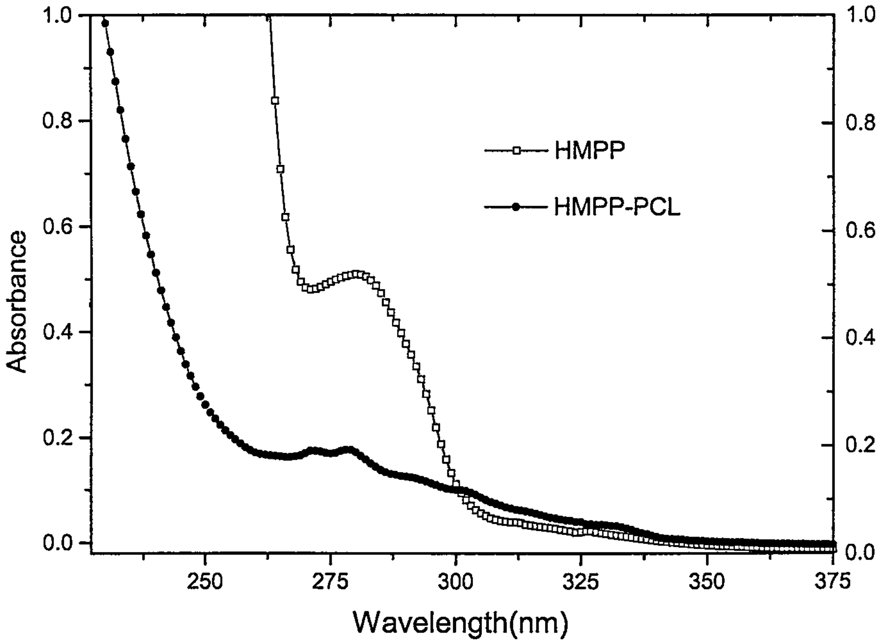


Figure 4.16. Absorption spectra of **HMPP** (2.92 x 10^{-4} mol L^{-1}) and **HMPP-PCL** (1.62 g L^{-1}) in CH_2Cl_2.

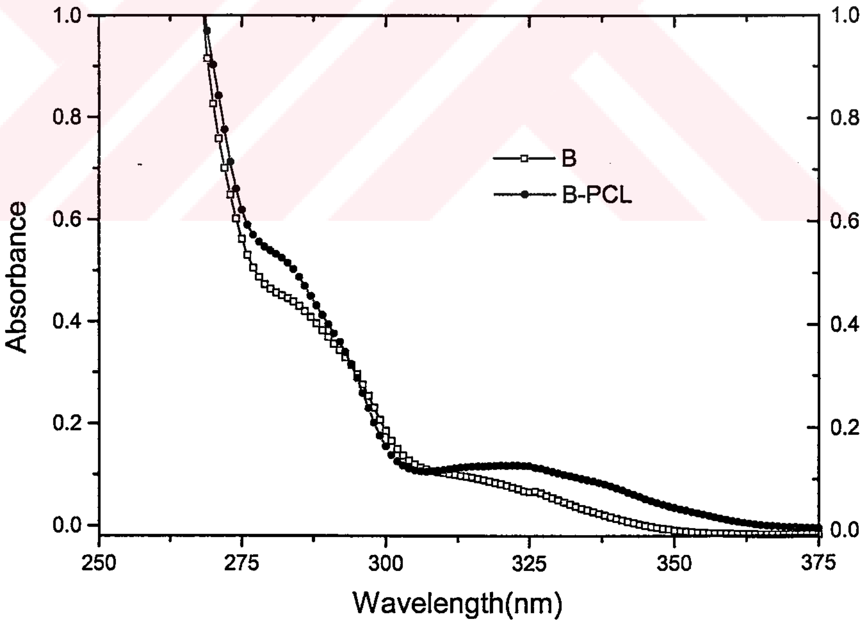


Figure 4.17. Absorption spectra of **B** (3.77 x 10^{-4} mol L^{-1}) and **B-PCL** (2.08 g L^{-1}) in CH_2Cl_2.

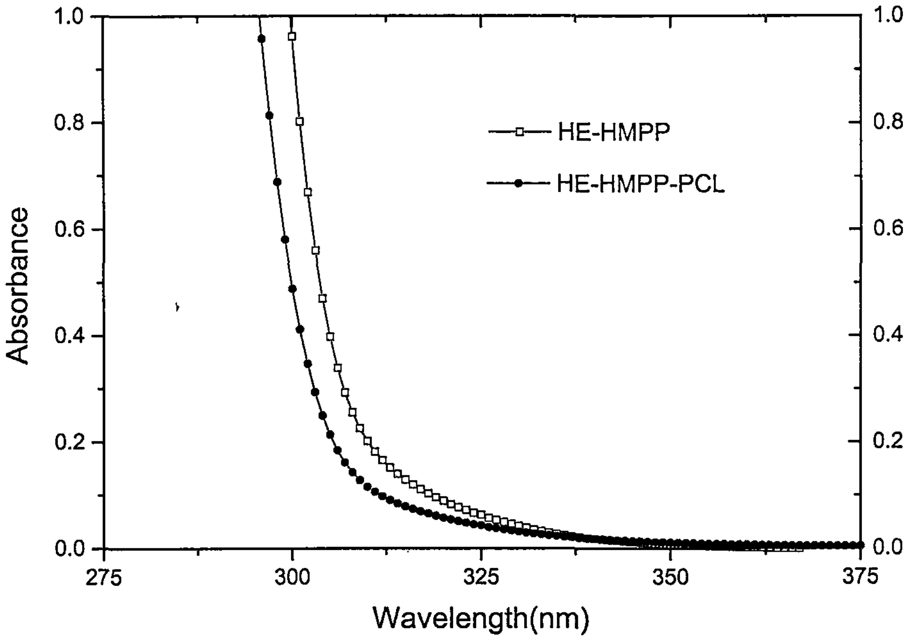


Figure 4.18. Absorption spectra of **HE-HMPP** (3.12×10^{-4} mol L^{-1}) and **HE-HMPP-PCL** (2.16 g L^{-1}) in CH_2Cl_2.

It can be seen that polymeric photoinitiators have spectra which are typical for benzoyl chromophores absorbing strongly in far UV and possessing an absorption maximum of the n π^* transitions around 320 nm (λ_{max} 320 nm, ε 100-200 L mol^{-1} cm^{-1}) [199]. Thus they are suitable for use in formulations which do not absorb strongly in this region. Notably, the extinction coefficients of the polymeric photoinitiators, particularly the mid-chain initiator, **HE-HMPP-PCL (14)**, are lower than those of the precursors. This behavior may be due to the restricted mobility of the chromophoric groups in tethered to polycaprolactone.

Figure 4.19 shows the fluorescence emission of the related compounds, **B (4)** and **B-PCL (13),** in chloroform at room temperature. Both spectra show the vibrational structures of the benzoin chromophore. Notably, the fluorescence intensity is higher in the case of polymer indicating limited self quenching [200,201] due to the low mobility. Similar behavior was noted in the fluorescence emission studies of the other photoiniators, **HMPP (1)** and **HE-HMPP (6)**, and the corresponding polymers, **HMPP-PCL (12)** and **HE-HMPP-PCL (14)**. These spectroscopic investigations suggest that the photochromophoric phenyl ketone groups were conserved under the polymerization conditions.

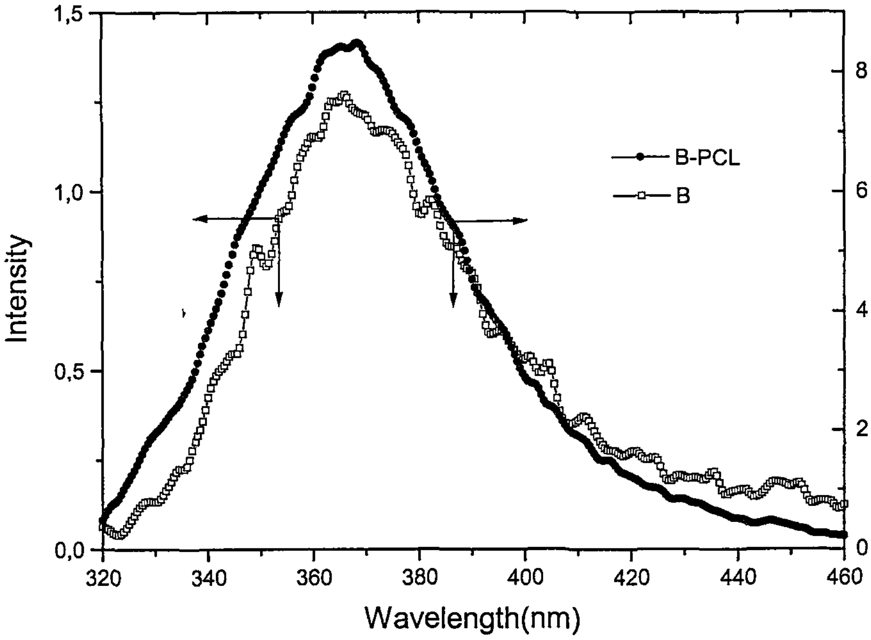


Figure 4.19. Fluorescence spectra of **B** (1.41×10^{-3} mol L^{-1}) and **B-PCL** (10.67 g L^{-1}), in $CHCl_3$, $\lambda_{exc} = 310$ nm.

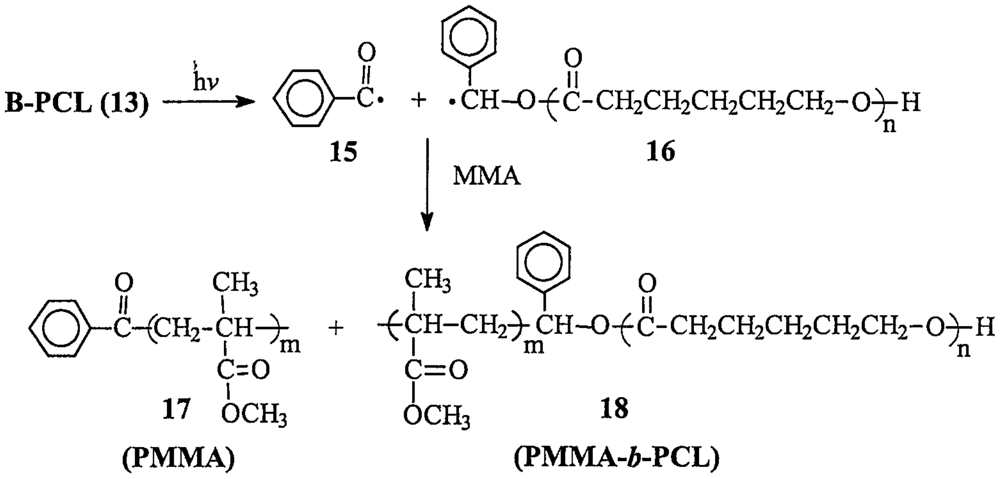
We have also tested the photoinitiation capability of these polymers. Typical results concerning photochemically induced polymerization of bulk methyl methacrylate (MMA) at 25 °C by using PCL photoinitiators are shown in Table 4.4. It should be pointed out that a control experiment without a polymeric initiator gave only negligible amount of polymer after the same irradiation time.

Table 4.4. Photoinduced Polymerization of bulk MMA (9.42 mol L^{-1}) by using poly(ε-Caprolactone) (100 g L^{-1}) photoinitiators. λ_{inc}>300nm

Run	Initiator	Irradiation time (min)	Yield[a] (%)	HomoPMMA (%)	HomoPMMA ($M_n \times 10^{-3}$)[b]	PCL-*b*-PMMA (%)	PCL-*b*-PMMA ($M_n \times 10^{-3}$)[b]
O	**HMPP-PCL**	150	9	54	6	46	130
P	**B-PCL-1**	105	14	36	6.8	64	93
Q	**B-PCL-2**	105	14	28	10	72	93
R	**HE-HMPP-PCL**	75	21	0	-	100	79
S[c]	**HE-HMPP**	35	17	100	56	-	-

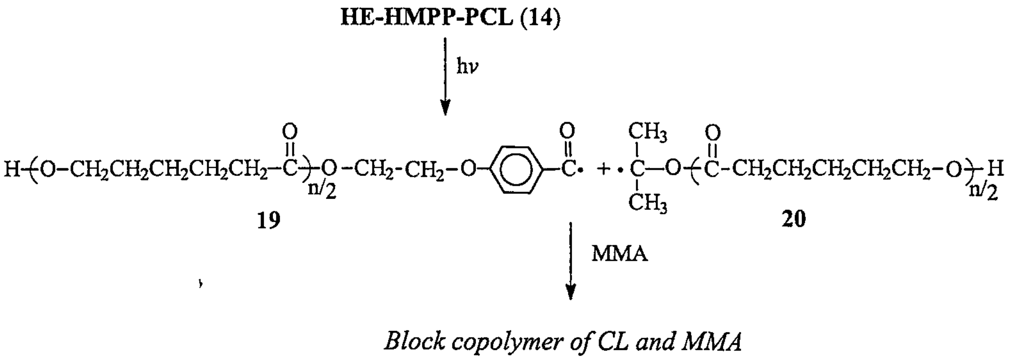
[a] MMA conversion
[b] Determined by GPC according PMMA standards
[c] [H-HMPP] = 2.3×10^{-2} mol L^{-1}.

UV irradiation of the polymeric photoiniators caused α-scission and yielded benzoyl, **15**, and polymer bound radicals, **16**, according to the following reaction as shown for the case of benzoin linked polymer, **13**.



(4.10)

Either or both of these radicals may then initiate the polymerization of MMA. In this connection we refer to the work of Pappas [202,203] who demonstrated that both radicals are equally effective as initiators in the polymerization of MMA. In our case it would appear necessary for the polymer-bound radical to initiate polymerization for successful block copolymerization. However, homo poly(methyl methacrylate), **PMMA (17)**, formation is inevitable when end-chain functional macrophotoinitiators, **HMPP-PCL (12)** and **B-PCL (13)**, were employed. Macroinitiator **B-PCL (13)** gave a lower percent of homopolymerization relative to **HMPP-PCL (12)**. This is probably due to the difference in the reactivity of the polymer bound radicals, namely substituted benzyl and alkoxy propyl radicals, towards olefinic compounds since benzoyl radicals are formed in each case. Although the bimolecular rate constant for the reaction of hydroxy propyl radicals with MMA was found [204] to be $k = 5.4 \times 10^5$ L mol^{-1} s^{-1}, the corresponding value for substituted benzyl radicals is not known. A different situation was encountered in the case of **HE-HMPP-PCL (14)**. Upon irradiation of this initiator in the presence of MMA, radical sites are formed only at macromolecules. No additional free radicals, which can initiate homopolymerization, are produced in this reaction.



(4.11)

This is the great advantage of **HE-HMPP-PCL (14)** over the other initiators, **HMPP-PCL (12)** and **B-PCL (13)**, where the decomposition of functional molecules leads, apart from macroradicals, also isolated small radicals capable of initiating homopolymerization. Figure 4.20 shows the GPC chromatograms of **HE-HMPP-PCL (14)** and block copolymer formed there from. The new peak at lower elution volume is ascribed to the block copolymer. Notably, no peak pertaining to residual homopolymer was detected.

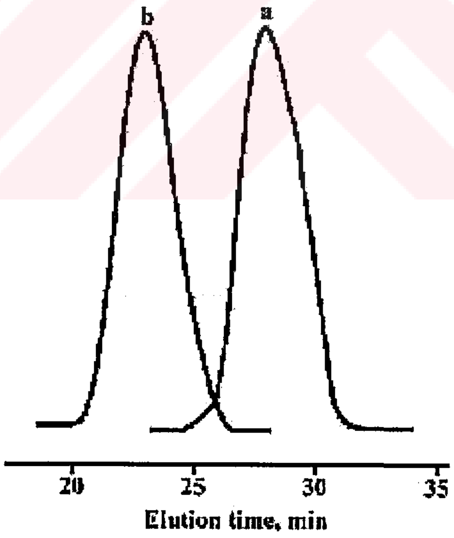


Figure 4.20. GPC traces of **HE-HMPP-PCL**, (**a**) and PCL-PMMA block copolymer (Table 4.4, Run R) (**b**).

The block copolymer structure was also assigned by means of NMR spectral measurements. Typical signals for both MMA and CL units were detected (Figure 4.21). Aromatic protons corresponding to the photoinitiator moieties were not detected due to the relatively high molecular weight of the block copolymer. For comparison, photopolymerization initiated by low-molar mass photoinitiator,

HE-HMPP was also included in Table 4.4. Notably, initiation efficiency is rather low in the case of polymeric photoinitiator which is in agreement with the observations made on Para substituted hydroxy acetophenone derivatives [205]. The overall efficiency of radical generation process was found to be lower for both oligomer and the dodecyl substituted derivatives.

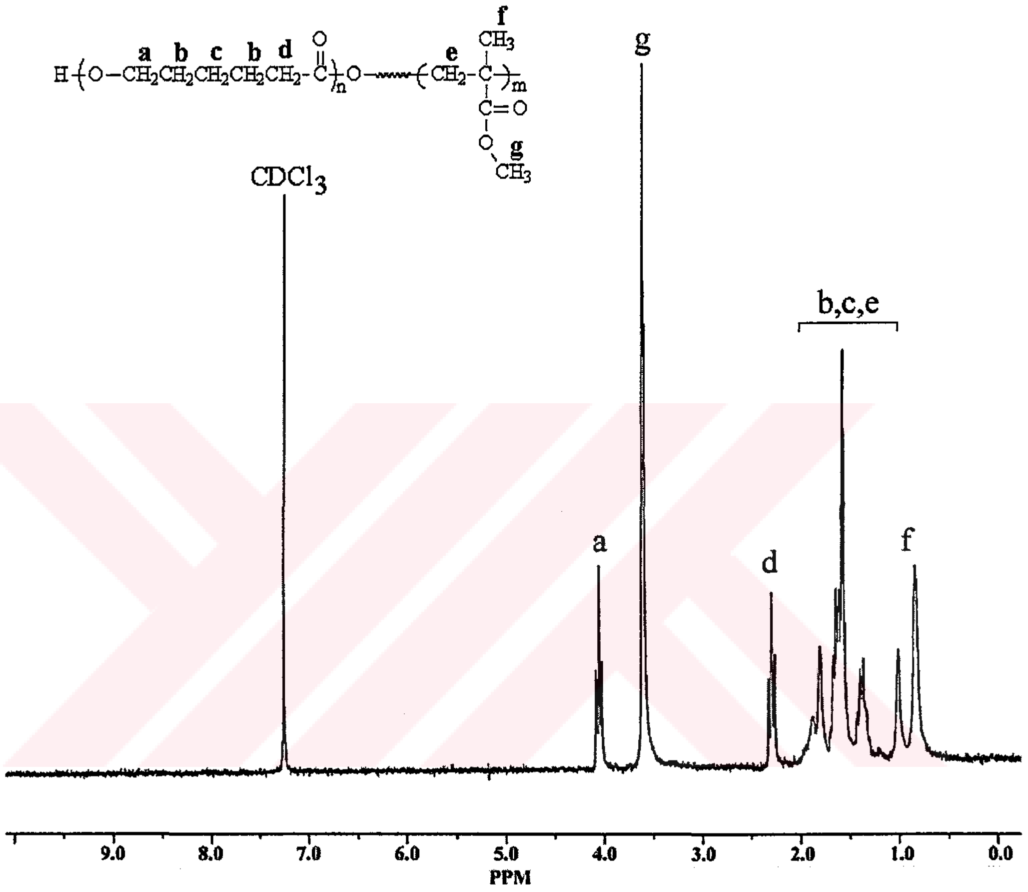
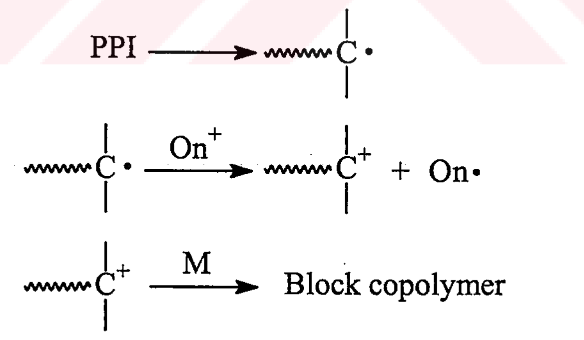


Figure 4.21. ^{1}H-NMR spectrum of PCL-PMMA block copolymer (Table 4.7, Run R) in $CDCl_3$.

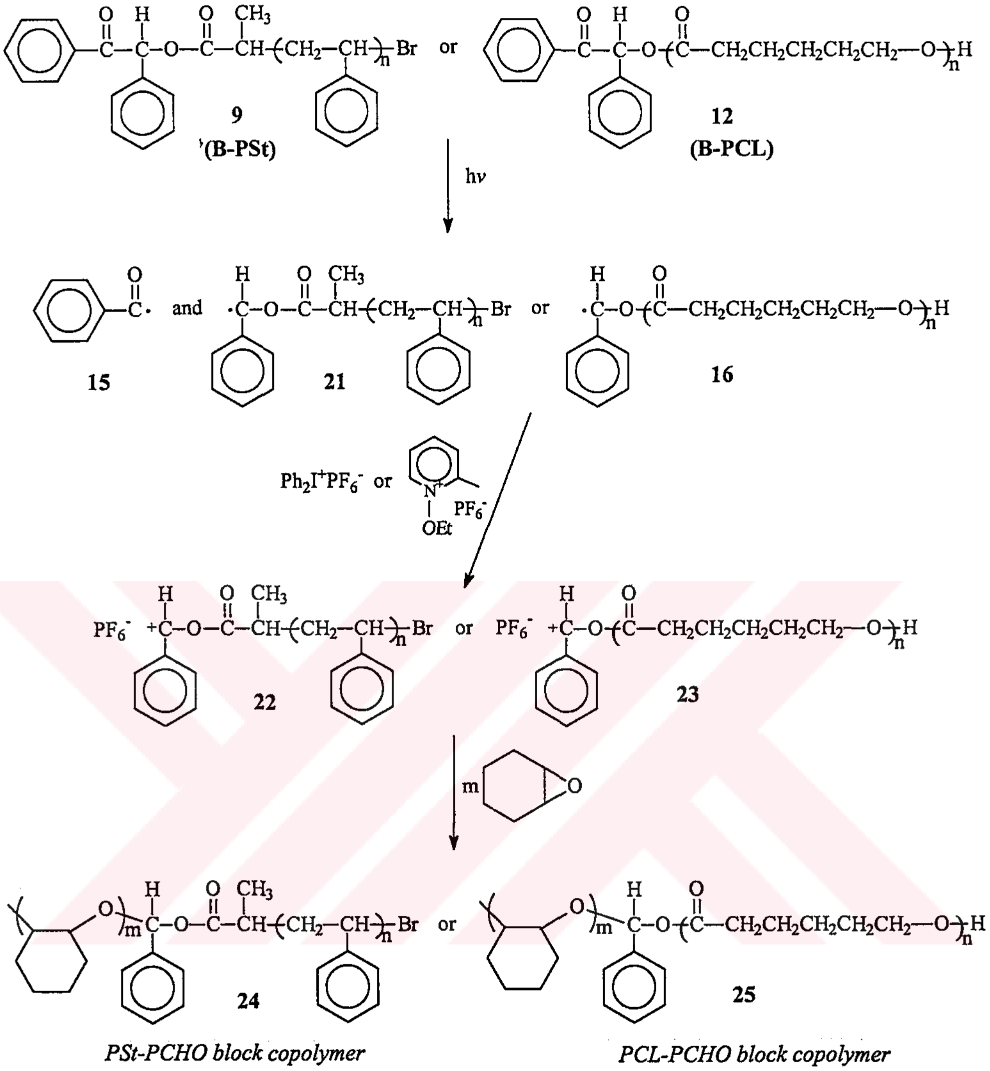
4.3. Photoinduced Free Radical Promoted Cationic Block Copolymerization by Using Macrophotoinitiators

It was previously shown that macrophotoinitiators can be used in photoinduced radical polymerization to yield block copolymers [8,13]. But, in the case of macrophotoinitiators prepared by ATRP, the resulting copolymers are eventually formed from radically polymerizable monomers. Obviously, this type of block copolymers can be synthesized directly by applying ATRP itself with the benefit of better control of polydispersity [206]. However, the use of macrophotoinitiators in blocking reactions is not limited to free radical process. They can also be used in photoinduced free radical-promoted cationic polymerization to yield block copolymers of monomers polymerizable with different mechanisms. The initial stage of the process is also radicalic. It is known that certain onium salts such as $Ph_2I^+PF_6^-$ and $EMP^+PF_6^-$ can efficiently oxidize photochemically generated electron donating free radicals [99,100]. If the photolysis is carried out in the presence of cationicly polymerizable monomer such as cyclohexene oxide (CHO) the polymer attached radical is converted to initiating cations to generate block copolymers.



PPI : *Polymeric photoinitiator*
M : *Cationic polymerizable monomer*

For the photoinduced free radical promoted cationic block copolymerization benzoin linked polystyrene and poly(ε-caprolactone) prepared by ATRP and ROP methods respectively were used as macrophotoinitiators. Upon irradiation benzoyl radicals and polymer bound radicals are formed via α-cleavage of the benzoin moiety incorporated to the polymer chains. In the presence of Ph_2I^+ or EMP^+ the polymer attached radical is converted to initiating cations. The cations thus generated are used as initiating species for cationic polymerization of CHO to get block copolymers according to the following reactions.



(4.9)

It should be pointed out that benzoyl radicals formed concomitantly do not participate in the oxidation process [207]. Typical results concerning block copolymerization by using polystyrene and poly(ε-caprolactone) macrophotiniatitors are presented in Tables 4.5 and 4.6, respectively.

Table 4.5. Photoinduced Free Radical Promoted Cationic Block Copolymerization[a] of CHO by Using PSt Macrophotoinitiator

	Onium	Time	Yield[b]	HomoPCHO	Pst-*b*-PCHO		
Run	salt	(min)	(%)	(%)	(%)	M_{nGPC}^{c}	M_w/M_n
T	Ph_2I^+	35	42	5	95	6100	2.76
U	EMP^+	60	37	4	96	7900	2.34

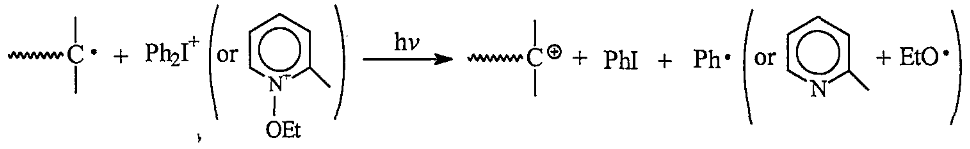
[a][CHO]= 9.91 mol L^{-1}, [PSt]=100 g L^{-1} (B-PSt-1, $M_n = 4700$)
[Onium salt] = $5x10^{-3}$ mol L^{-1} $\lambda_{inc} = 350$ nm
[b]CHO conversion
[c]Determined by GPC according PSt standards

Table 4.6. Photoinduced Free Radical Promoted Cationic Block Copolymerization[a] of CHO Using PCL Macrophotoinitiator

	Onium	Time	Yield[b]	HomoPCHO	PCL-*b*-PCHO		
Run	salt	(min)	(%)	(%)	(%)	M_{nGPC}^{c}	M_w/M_n
V	Ph_2I^+	15	56	7	93	6000	1.83
W	EMP^+	30	27	11	89	5500	1.64

[a][CHO] = 9.91 mol L^{-1}, [PCL] = 100 g L^{-1} (B-PCL-1, $M_n = 2500$)
[Onium salt] = 5×10^{-3} mol L^{-1}, $\lambda_{inc} = 350$ nm
[b]CHO conversion
[c]Determined by GPC according PSt standards

Different reactivity of dipenyliodonium (Ph_2I^+) and N-ethoxy-2-methylpyrdinium (EMP^+) salts in initiating the free radical promoted cationic polymerization may be explained in terms of different redox potentials (relative to SCE) of the salts: -0.2 V (Ph_2I^+) [208] and -0.7 V (EMP^+) [209]. Homopolymer formation, although at low rate, observed with both PSt and PCL macrophotoinitiators are due to the participation of the radicals formed from the decomposition of onium salts (reactions 4.10 and 4.11) in further redox reactions (reaction 4.12). Homopolymer formation via direct decomposition of onium salts can be disregarded, since selective irradiation is applied. At the irradiation wavelength ($\lambda = 350$ nm) the emitted light is absorbed only by the macrophotoinitiator and onium salts are transparent. The extraction of homopoly(cyclohexene oxide) was performed by using n-hexane, since n-hexane is a solvent for homoPCHO.



(4.10)

$$\mathrm{Ph}^{\bullet}\ (\text{or EtO}^{\bullet}) + \mathrm{R{-}H} \longrightarrow \mathrm{R}^{\bullet} + \mathrm{Ph{-}H}\ (\text{or EtOH}) \qquad (4.11)$$

$$\mathrm{R}^{\bullet} \xrightarrow{-\,e^{-}} \mathrm{R}^{+} \qquad (4.12)$$

The block copolymer structures were assigned by ^{1}H-NMR spectral measurements. The ^{1}H-NMR spectra of the polystyrene-*b*-poly(cyclohexene oxide) and polycaprolactone-*b*-poly(cyclohexene oxide) display the signals characteristic of the corresponding segments (Figures 4.22 and 4.24).

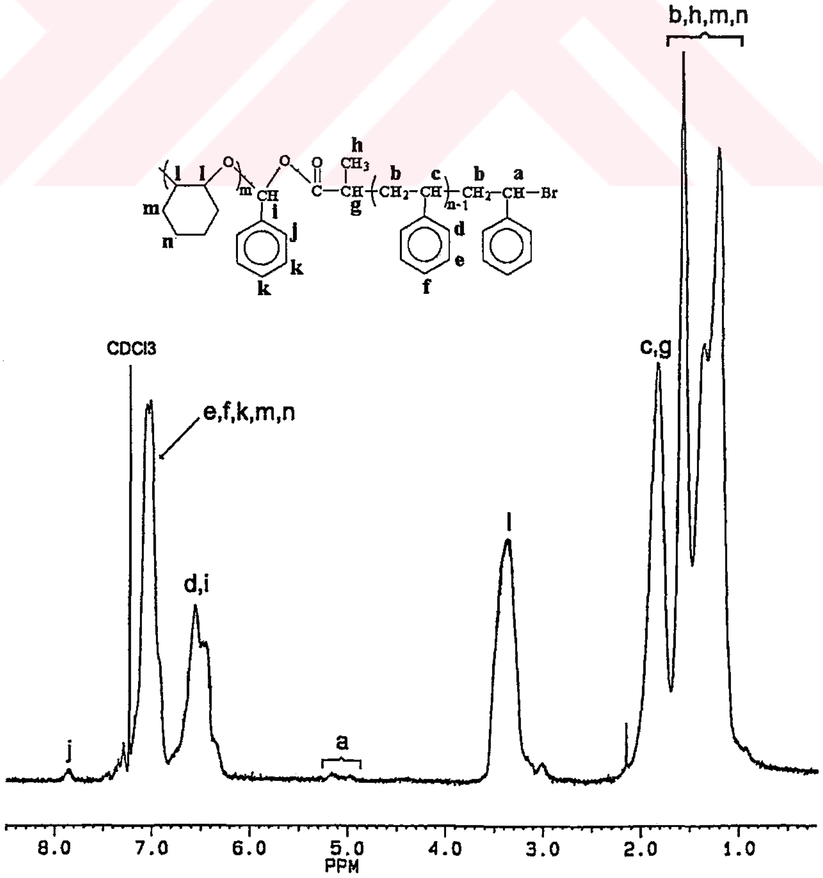


Figure 4.22. ^{1}H-NMR spectra of PSt-*b*-PCHO block copolymer (Table 4.5, Run T.)

Figure 4.23 shows the GPC chromatograms of PSt ($M_n = 4700$) and block copolymer formed therefrom. The new peak at lower elution volume is ascribed to the block copolymer.

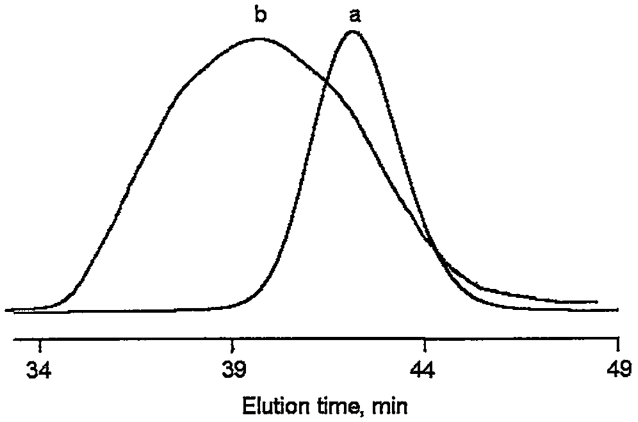


Figure 4.23. GPC traces of PSt, (**a**) and PSt-*b*-PCHO block copolymer (Table 4.5, Run T) (**b**).

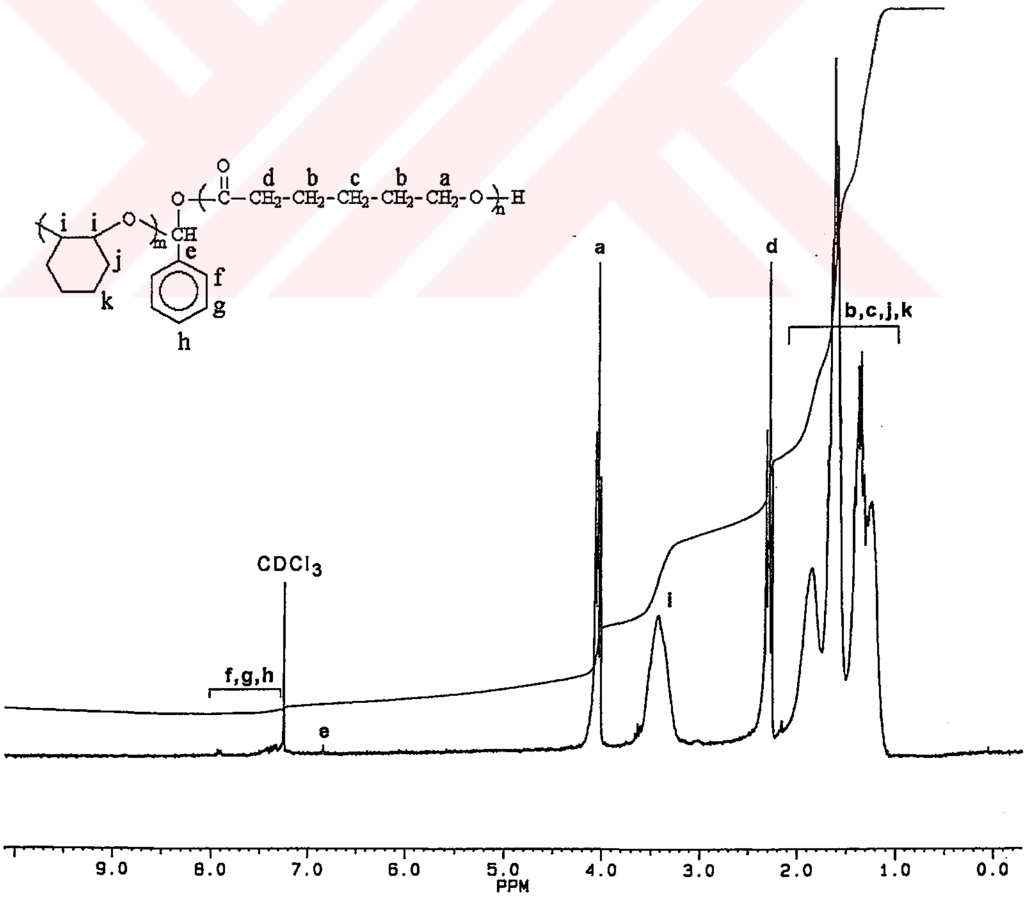


Figure 4.24. The ^{1}HNMR spectrum of PCL-b-PCHO block copolymer (Table 4.6, Run W)

5. CONCLUSIONS

In this thesis, the synthesis and characterization of novel well-defined polymeric photoinitiators prepared by controlled/living polymerizations such as ATRP and ROP and their use in block copolymerization were described.

New mono and bifunctional ATRP initiators (**HMPP-Br**, **B-Br** and **Br-HE-HMPP-Br**) were synthesized by the condensation of 2-bromopropanoyl bromide with **HMPP**, **B** and **HE-HMPP** photoinitiators. Their structures were characterized by spectral methods.

Using mono and bifunctional ATRP initiators, macrophotoinitiators of styrene (**HMPP-PSt**, **B-PSt** and **HE-HMPP-PSt**) with well-defined structure were synthesized by atom transfer radical polymerization method. Using mono- and dihydroxy functional free radical photoinitiators (**HMPP**, **B** and **HE-HMPP**), we successfully prepared polymeric photoinitiators (**HMPP-PCL**, **B-PCL** and **HE-HMPP-PCL**) by ring-opening polymerization of ε-CL using $Sn(Oct)_2$ through corresponding alkyl octoate formation. UV absorption characteristics and the fluorescence emission of the macrophotoinitiators are similar to that of the precursor low-molar-mass photoinitiator.

In addition, polymeric photoinitiators of ε-CL represent a class of potentially useful materials in biomedical applications due to their potential benefits of biocompatibility and non-toxicity of PCL backbone and polymeric nature of the photoinitiator.

Such prepared narrowly distributed polymeric photoinitiators can be used in photopolymerization of vinyl monomers such as MMA. Under UV irradiation, these photosensitive polymers generate polymeric radicals. In the presence of a radical polymerizable monomer block copolymers were formed. The type of macrophotoinitiator influences the polymerization products. While both homo and block copolymers are formed with the end-chain functional photoinitiators, the mid-chain functional photoinitiators yield purely block copolymers.

On the other hand, transformation reaction was also carried out in order to convert the polymeric radicals into initiating cations with the aid of oxidizing agents such as iodonium and pyridinium salts. These way block copolymers of monomers which do not polymerize with the same mechanism were prepared.

For photoinduced free radical promoted reactions polymeric photoinitiators with benzoin end units (**B-PSt and B-PCL**) were deliberately chosen and used. Being photolized with fairly high quantum yields, benzoin and derivatives are so far the most effective photoinitiators [210]. The photolysis of benzoin containing polymeric photoinitiator results in α-cleavage and hydroxybenzyl (strong electron donor) and benzoyl (electron withdrawing) radicals are formed. Because of structural reasons the electron donating efficiency of hydroxybenzyl radicals are much higher comparing with the other electron donating polymeric radicals formed from **HMPP-PSt** or **HMPP-PCL** and **HE-HMPP-PSt** or **HE-HMPP-PCL**. In the presence of an onium salt (oxidant) such as $Ph_2I^+PF_6^-$ and $EMP^+PF_6^-$ hydroxybenzyl polymeric radicals can easily be converted to the corresponding polymeric carbocations which are ready to start cationic polymerization of cationic polymerizable monomers such as CHO.

The polymeric photoinitiators with well-defined structures can be used in variety of applications. Photoinitiators with fairly high molecular weight avoids the problems associated with the volatility. Thus, the formulations containing polymeric photoinitiators can be exposed to high temperatures because of their non-volatility. Solubility and miscibility problems, often observed with coatings containing low-molecular weight photoinitiators do not occur with the macromolecular ones, as polymers are easily miscible with the resin to be cured and as well as the final, cured film [98]. The low migration tendency of polymeric photoinitiators brings about a reduced proneness to yellowing of the cured films. Their value in UV curing in food packing applications will be more important since future legislation will require photoinitiation systems with zero migration. Besides, they can be used to prepare tailor-made block copolymers. Thus this work has broadened the practical synthetic route to well-defined polymers with photoinitiator functionality.

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AUTOBIOGRAPHY

Mustafa Değirmenci was born in Çelikhan/Adıyaman in 1970. He graduated from Çelikhan Lisesi in 1987. In the same year he was admitted to Fırat University Science and Arts Faculty Chemistry Department. He graduated with honorary degree from there in 1991.

He worked as a Chemistry Teacher at Yeniçağa 60. Yıl Lisesi in Yeniçağa/Bolu between 1991-1994, he was appointed as a Research Assistant at Harran University Science and Arts Faculty Chemistry Department in 1994.

He was accepted as a M.Sc. student to Fırat University, Institute of Science in 1995 and completed his studies in 1997.

He was registered as a Ph.D. student to Istanbul Technical University Polymer Science and Technology Program in 1998 through a post graduate program for developing Universities (35. Madde) organized by Higher Education Constitution (YÖK). After completing English preparation course, he started his Ph.D. studies in 1999.

He is married and has two children.

He is co-author of the following 11 scientific papers published in international journals.

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    C. Dursun, **M.Degirmenci,** Y.Yagci, S.Jockush, N.J.Turro
    Polymer, submitted