

**SYNTHESIS AND CHARACTERIZATION OF VARIOUS
MACROMOLECULAR ARCHITECTURES BY USING COMBINED
CONTROLLED AND PHOTOINITIATED POLYMERIZATION METHODS**

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**KONTROLLÜ VE FOTOKİMYASAL POLİMERİZASYON YÖNTEMLERİ
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LIST of ABBREVIATIONS

ATRP	: Atom Transfer Radical Polymerization
ROP	: Ring-opening Polymerization
PSt	: Polystyrene
MMA	: Methyl Methacrylate
CHO	: Cyclohexene Oxide
¹H-NMR	: Hydrogen Nuclear Magnetic Resonance Spectroscopy
IR	: Infrared Spectrophotometer
GPC	: Gel Permeation Chromatography
AIBN	: α,α' -Azobisisobutyronitrile
AFM	: Atomic Force Microscopy
PCL	: Poly(ϵ -Caprolactone)
PMMA	: Poly(methyl Methacrylate)
DSC	: Differential Scanning Calorimetry
CL	: Epsilon Caprolactone
NMP	: Nitroxide Mediated Polymerization
RAFT	: Reversible Addition-Fragmentation Chain Transfer Polymerization
Sn(Oct)₂	: Stannous Octoate
UV	: Ultra Violet
MW	: Molecular Weight
MWD	: Molecular Weight Distribution
CRP	: Controlled Radical Polymerization
RP	: Radical Polymerization
PDI	: Polydispersity Index
SFRP	: Stable Free Radical Polymerization
4-VP	: 4-Vinyl Pyridine
Bipy	: Bipyridine
dTBipy, dHBipy	
dNBipy	: Substituted Bipyridines
TMEDA	: <i>N,N,N',N'</i> -Tetramethylethylenediamine
PMDETA	: <i>N,N,N',N'',N'''</i> -Pentamethyldiethylenetriamine
HMTETA	: <i>N,N,N',N'',N''',N''''</i> -Hexamethyltriethylenetetraamine
Me₆-TREN	: Tris[2-(dimethylamino)ethyl]amine
DMF	: Dimethyl Formamide
M	: Monomer
TEMPO	: 2,2,6,6-Tetramethyl-piperidinyloxy
ESR	: Electron Spin Resonance
DXO	: 1,5-Dioxepan-2-one
MALDI-TOF	: Matrix-assisted Laser Desorption/Ionization Time-of-flight
D	: Dye Molecule
COI	: Coinitiator
PS	: Photosensitizer

D	: Electron Donor
A	: Electron Acceptor
CT	: Charge-transfer
SCE	: Standard Calomel Electrode
PI	: Polyisoprene
AFA	: Addition-fragmentation Agent
ETM	: Ethyl Thiophene Methacrylate
TPE	: Thermoplastic Elastomers
RIM	: Reaction Injection Moulding
PTHF	: Polytetrahydrofuran
PEO	: Polyethylene Oxide
AN	: Acrylonitrile
St	: Styrene
PtBuA	: Poly(tert-butylacrylate)
MA	: Methyl Acrylate
TBMA	: Tert-butyl Methacrylate
VL	: σ -Valerolactone
PBd	: Polybutadiene
LRP	: Living Radical Polymerization
PIB	: Polyisobutylene
SEC	: Size-exclusion Chromatography
SCVP	: Self-condensing Vinyl Polymerization
PI	: Photoinitiator
PTA	: <i>N,N</i> -Dimethyl-4-vinylphenethylamine
HPLC	: High Performance Liquid Chromatography
TEA	: Triethylamine
HTEMPO	: 4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinyl-1-oxy
NBS	: <i>N</i> -bromosuccinimide

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LIST of SYMBOLS

λ	: Wavelength
$h\nu$	: Radiation
$R^\cdot$	: Radical
I	: Initiator
COI	: Coinitiator
M	: Monomer
C^+	: Cation
$C^{+\cdot}$	: Radical cation
C^-	: Anion
S	: Sensitizers
M_n	: The number average molecular weight
M_w	: The weight average molecular weight
M_w/M_n	: The molecular weight distribution
P_n^*	: Propagating species
M_t^n	: Transition metal
$P_n^=$	: Polymer having a double bond at the chain end due to termination by disproportionation
P_{n+m}	: Polymer terminated by chain combination
X	: Halide group
k_a	: Rate constant of activation
k_{da}	: Rate constant of deactivation
k_p	: Rate constant of propagation
k_t	: Rate constant of termination
Z	: Activating group in the structure of RAFT agent
R	: Homolytically leaving group in the structure of RAFT agent
$P_n^\cdot, P_m^\cdot$	: Active propagating species
S_N2	: Bimolecular Nucleophilic Substitution
PI^*	: Excited photoinitiator
I_a	: Intensity of radiation absorbed by the system
I_o	: Intensity of radiation falling on the system
l	: Optical path length in Beer Lambert law
$[S]$	: Concentration of the absorbing molecule in Beer Lambert law
ϵ	: Molar extinction coefficient
$\Phi_{R^\cdot}$	: Quantum yield of radical formation
f_p	: Initiation efficiency of photogenerated radicals
E_T	: Triplet energy
F	: Faraday constant
$E_{1/2}^{ox} (D/D^+)$	: Oxidation potential of donor
$E_{1/2}^{red} (A/A^-)$	: Reduction potential of acceptor
E_{PS}	: Singlet state energy of the photosensitizer

ΔE_c	: Coulombic stabilization energy
ΔG	: Gibbs Energy Change
On^+	: Onium salt cation
f	: Functionality
L	: Phosphine ligand
λ_{inc}	: Wavelength of incident light
T_g	: Glass-transition temperature



SYNTHESIS AND CHARACTERIZATION OF VARIOUS MACROMOLECULAR ARCHITECTURES BY USING COMBINED CONTROLLED AND PHOTOINITIATED POLYMERIZATION METHODS

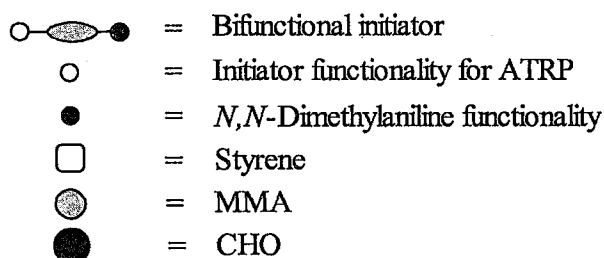
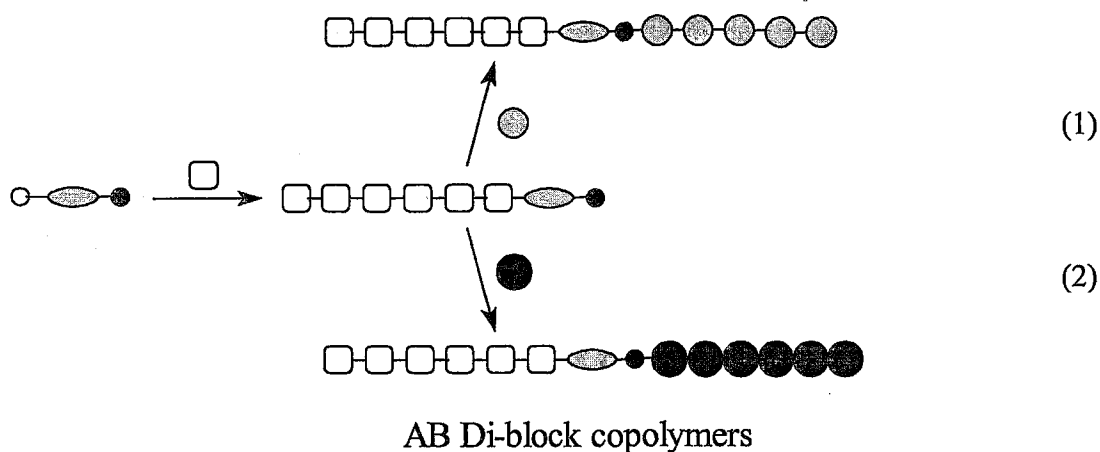
SUMMARY

Advanced polymeric materials with specialized properties are of great interest. Block and graft copolymers are the most demanded advanced materials since they display combined physical and mechanical properties. Because of their diverse macromolecular structures, they may possess novel characteristics required for many high-tech applications. Therefore, engineering macromolecular architectures is one of the major goals in polymer chemistry. Controlled polymerization methods appear to be the most powerful and versatile tools in achieving this goal.

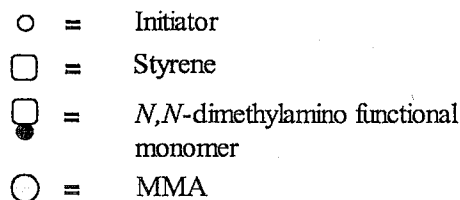
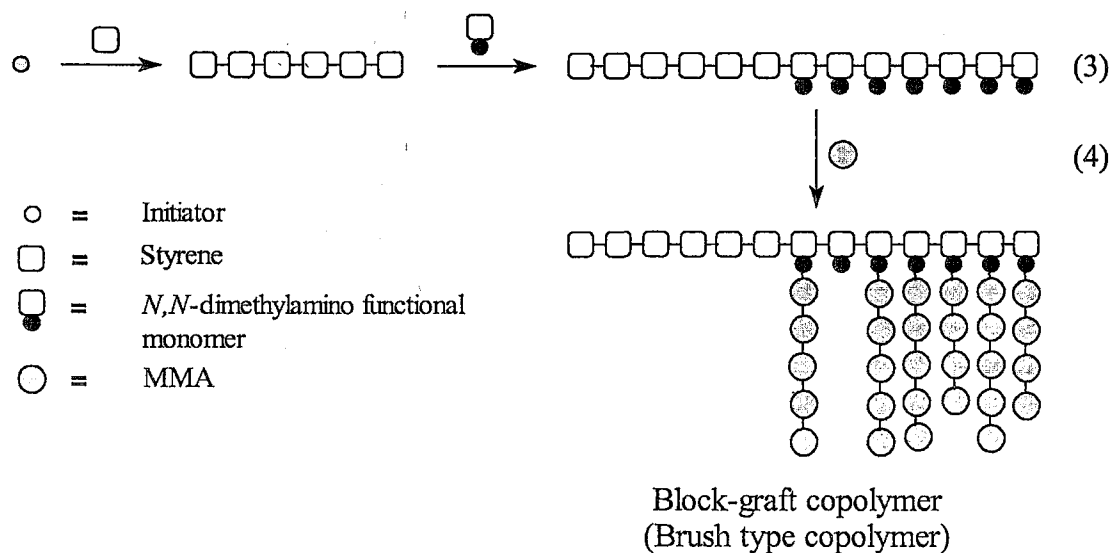
In the present work, macromolecular chains of various chemical compositions were assembled in original topologies by combination of Atom Transfer Radical Polymerization (ATRP) or Ring-opening Polymerization (ROP) with photoinduced radical or radical promoted cationic polymerizations. These macromolecular architectures involve block, graft, block-graft, and brush type copolymers as well as miktoarm star copolymers and hyper-branched polymers.

For this purpose, end-chain, mid-chain or side-chain mono- or bi- amino- or *N,N*-dimethylamino-functional precursor polymers were prepared either by ATRP or ROP. Subsequently, these prepolymers served as macromolecular co-initiators in photoinduced radical or promoted cationic polymerizations.

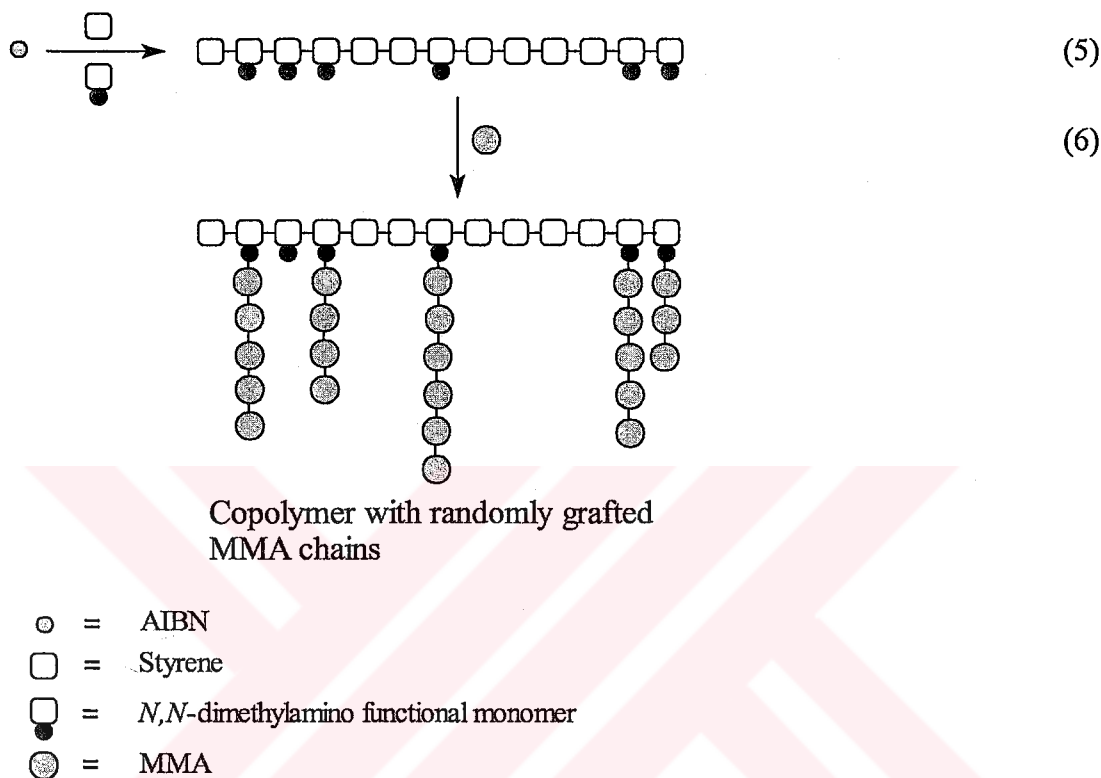
For the preparation of diblock copolymers, *N,N*-dimethylaniline end-functional polystyrenes (PSt) with well-defined structures and low polydispersities were synthesized by ATRP of styrene in bulk at 110°C using 4-(dimethylamino)benzyl 4-(bromomethyl) benzoate as initiator in conjunction with a cuprous complex, Cu(I)Br/bipyridine. These polymers were further used in block copolymerization with methyl methacrylate (MMA) and cyclohexene oxide (CHO) via photoinduced radical and radical promoted cationic polymerization routes, respectively, as represented by (1) and (2). In the former case, macroradical generation was achieved with benzophenone sensitizer by photoexcitation followed by hydrogen abstraction from amino end groups. A visible light initiating system has been utilized in the radical promoted cationic polymerization of CHO. The system involves a xanthene dye (Erythrosin B) as the sensitizer, an aromatic *N,N*-dimethylamino group and diphenyl iodonium hexafluorophosphate as the radical source and radical oxidizer, respectively. While pure block copolymers were obtained in the free radical route, the free radical promoted cationic polymerization yielded both block and homopolymers.



In the next part of the thesis, the preparation of a brush type block-graft copolymer is described. Firstly, monodisperse poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene was synthesized via anionic living polymerization carried out at -78°C under a pressure of 10^{-6} torr using cumyl potassium as the initiator. Subsequent photoinduced radical polymerization of MMA through side chain-functional *N,N*-dimethyl amino groups yielded both crosslinked polymer and a brush type block-graft copolymer to a lesser extent as illustrated by (3) and (4). Upon irradiation at a wavelength of 350 nm, macroradicals were generated via hydrogen abstraction from amino side-chain groups by the excited benzophenone. The block-graft copolymer was characterized by $^1\text{H-NMR}$, IR, and GPC analysis.



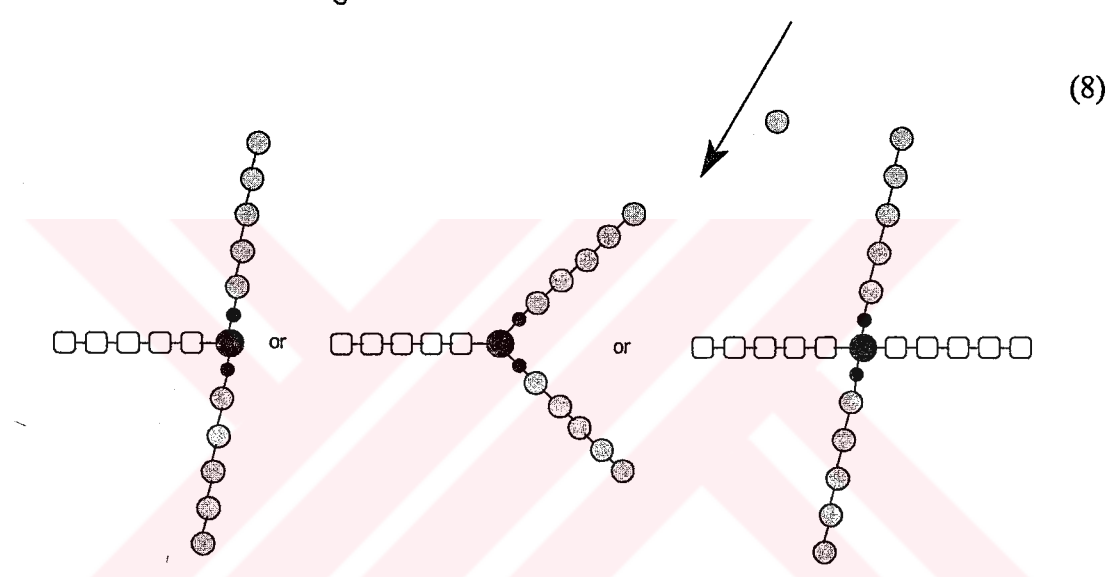
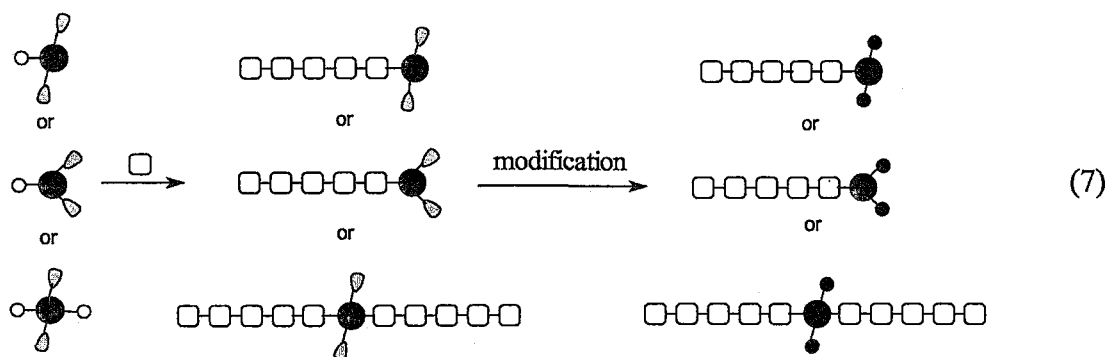
Furthermore, random copolymers possessing H-donating sites for photoinduced grafting were synthesized and characterized. Styrene and 2-(dimethylamino)ethyl methacrylate with varying compositions were copolymerized by classical radical polymerization with the use of AIBN as initiator. Grafting from *N,N*-dimethyl amino functions by the photoinduced radical polymerization of methyl methacrylate (MMA) was successfully achieved by using benzophenone as photosensitizer. The mechanism is depicted below (5 and 6).



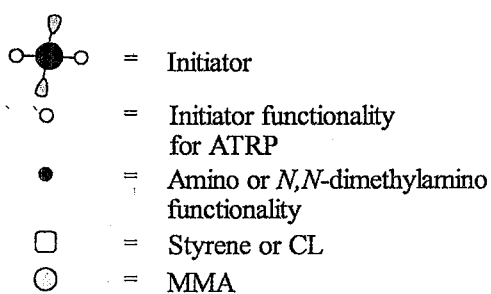
Additionally, it was shown that 2-(dimethylamino)ethyl methacrylate could be employed in the preparation of a hyper-branched polymer. The monomer was photopolymerized in the presence of benzophenone. Surface morphology of the hyper-branched structure was examined by atomic force microscopy (AFM) images.

The final part of the work involves preparation of miktoarm star copolymers. Well-defined polystyrene (PSt) or poly(ϵ -caprolactone) (PCL) precursor polymers possessing central or end 2,5-dibromo-1,4-phenylene, 2,5-dibromo-benzene or 3,5-dibromobenzene moieties were synthesized by ATRP or ROP. Further modification of these polymers in one or two reaction steps at the aromatic bromine atoms afforded bi-functionalized prepolymers. First reaction step employed a Suzuki coupling reaction between aromatic bromine functional polymers and 3-aminophenylboronic acid, when di-amino-containing intermediates were obtained. The second step was a condensation reaction between the di-amino functional intermediates and 4-(dimethylamino)-benzaldehyde. Thus, dimethyl-amino functional prepolymers were synthesized, as well. The presence of amino or *N,N*-dimethyl amino functional groups in the structure of intermediate polymers permitted copolymerization with methyl methacrylate (MMA) by photoinduced radical polymerization by using benzophenone or Erythrosin B as photosensitizer and 4- or 3-armed star copolymers (PSt-PMMA or PCL-PMMA) were obtained. The

mechanism is represented schematically by (7) and (8) below. The structures of all the starting polymers, intermediate polymers and final copolymers were analyzed by spectral methods ($^1\text{H-NMR}$, IR), as well as by GPC measurements. DSC analyses were performed for prepolymers and copolymers and compared.



A_2B and A_2B_2 type miktoarm star copolymers



KONTROLLÜ VE FOTOKİMYASAL POLİMERİZASYON YÖNTEMLERİ BİRLİKTE KULLANILARAK ÇEŞİTLİ MAKROMOLEKÜLER YAPILARIN SENTEZİ VE KARAKTERİZASYONU

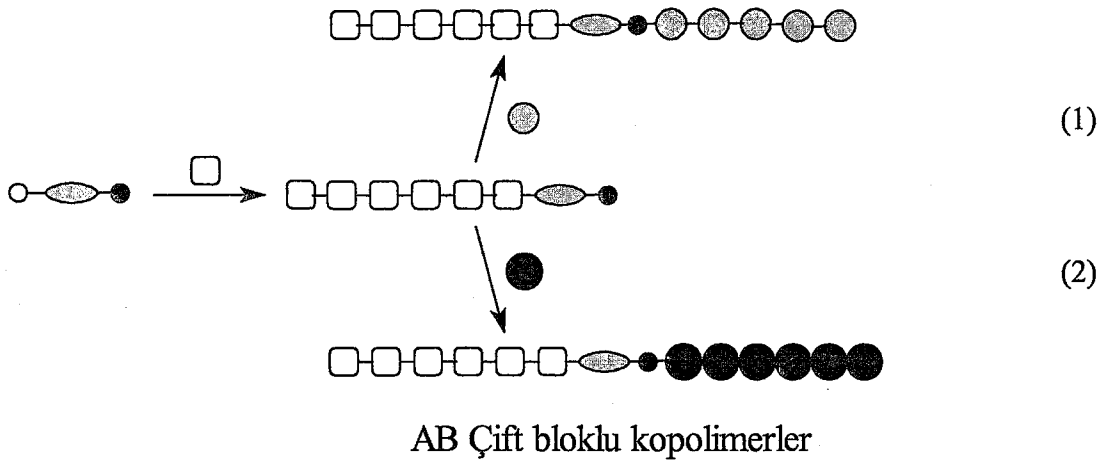
ÖZET

Üstün özellikler gösteren ileri polimerik malzemeler büyük ilgi görmektedir. Farklı fiziksel ve mekanik özellikleri birarada bulunduran blok ve aşırı kopolimerler en çok rağbet gören ileri malzemeler arasındadır. Çeşitli makromoleküler yapılara sahip olmaları bu polimerlere ileri teknoloji uygulamaları için gereken özgün özellikler kazandırmıştır. Bu sebeple, makromoleküler yapıların tasarlanması polimer kimyasındaki ana hedeflerden biridir. Bu hedefe ulaşmada kontrollü polimerizasyon yöntemleri en güçlü ve kullanışlı vasıtalarlardır.

Bu çalışmada, çeşitli kimyasal kompozisyonlardaki makromoleküler zincirlerden Atom Transfer Radikal Polimerizasyonu (ATRP) veya Halka-açılması Polimerizasyonu (ROP) ile fotokimyasal radikal veya katyona yükseltgenmiş radikal polimerizasyonu yöntemlerinin birlikte kullanılmasıyla orijinal yapılar inşa edilmiştir. Bu makromoleküler yapılar arasında blok, aşırı, blok-aşırı ve fırça tipli kopolimerlerin yanı sıra farklı kollu yıldız kopolimerler ve hiper-dallanmış polimerler sayılabilir.

Bu amaçla, ATRP veya ROP yöntemleri ile zinciri sonunda, ortasında ya da yan zincirinde tek veya çift amino veya *N,N*-dimetil amino fonksiyonları bulunduran başlangıç polimerleri hazırlandı. Daha sonra, bu başlangıç polimerleri fotokimyasal radikal veya katyona yükseltgenmiş radikal polimerizasyonlarında makromoleküler ko-başlatıcılar olarak kullanıldılar.

Çift bloklu kopolimerlerin hazırlanması için ilk olarak 110°C de 4-(dimetilamino)benzil 4-(bromometil) benzoat başlatıcısıyla birlikte Cu(I)Br/bipridin kompleksi kullanılarak, çözeltisiz ortamda stirenin ATRP'nu ile istenilen zincir uzunluklarında ve düşük molekül ağırlığı dağılımına sahip *N,N*-dimetil anilin sonlu polistirenler sentezlendi. Bu polimerler bir sonraki aşamada metil metakrilatın (MMA) ve siklohekzen oksitin (CHO) sırasıyla fotokimyasal radikal ve katyona yükseltgenmiş radikal polimerizasyonlarında şekil (1) ve (2) de gösterildiği gibi blok kopolimer eldesinde kullanıldılar. Fotokimyasal radikal polimerizasyonunda makroradikal üretimi, benzofenonun ışıkla uyarılmasının ardından amino uç gruplarından hidrojen koparmasıyla gerçekleştirilmiştir. CHO'in katyona yükseltgenmiş fotopolimerizasyonunda ise görünür dalga boylu ışıkla başlatılan bir polimerizasyon sisteminden yararlanılmıştır. Bu sistemde uyarıcı olarak bir ksanten boyar madde (Eritrosin B), radikal kaynağı olarak aromatik *N,N*-dimetil amino grubu ve radikal yükseltgeyici olarak da difenil iyodonyum hekzaflorofosfat yer alır. Radikalik yöntemle saf blok kopolimerler elde edilmiş ancak katyona yükseltgenmiş radikal polimerizasyonu ile blok kopolimerin yanı sıra homopolimer oluşumu da gözlenmiştir.



- = Çift fonksiyonlu başlatıcı
- = ATRP için başlatıcı fonksiyonallitesi
- = *N,N*-Dimetilanilin fonksiyonallitesi
- = Stiren
- = MMA
- = CHO

Tezin diğer bölümünde fırça tipli blok-aşı kopolimer eldesi anlatılmaktadır. İlk olarak, kümül potasyum başlatıcısı varlığında, -78°C de ve 10^{-6} torr basınç altında gerçekleştirilen anyonik yaşayan polimerizasyonla düşük molekül ağırlığı dağılımlı poli(*N,N*-dimetil-4-vinilfenetilamin)-*blok*-polistiren sentezlendi. *N,N*-dimetil amino yan zincir fonksiyonlu bu polimerden MMA'ın fotokimyasal radikal polimerizasyonu sonucu çapraz bağlı polimer ve daha az oranda fırça tipli blok-aşı kopolimer elde edildi. Polimerizasyon mekanizması (3) ve (4) de şematik olarak gösterilmiştir. 350 nm dalgaboylu ışıkla uyarılan benzofenonun yan zincirdeki amino gruplarından hidrojen koparmasıyla makroradikal oluşumu sağlanmıştır. Blok-aşı kopolimerin karakterizasyonu $^1\text{H-NMR}$, IR ve GPC analizleriyle yapıldı.

Ayrıca, fotokimyasal aşılamaya uygun H-verici gruplar taşıyan rastgele kopolimerler sentezlenip, karakterizasyonu yapıldı. Stiren ve 2-(dimetilamino)etil metakrilatın AIBN başlatıcısı varlığında klasik radikal polimerizasyonla çeşitli kompozisyonlardaki kopolimerleri hazırlandı. Benzofenon varlığında metil metakrilatın (MMA) fotokimyasal radikal polimerizasyonu ile oluşturulan PMMA zincirleri *N,N*-Dimetil amino fonksiyonel grupları üzerinden başarıyla aşılandığı görüldü. İlgili mekanizma aşağıda gösterilmiştir (5 ve 6).



- = Başlatıcı
- = Stiren
- ◻ = *N,N*-dimetilamino fonksiyonlu monomer
- = MMA

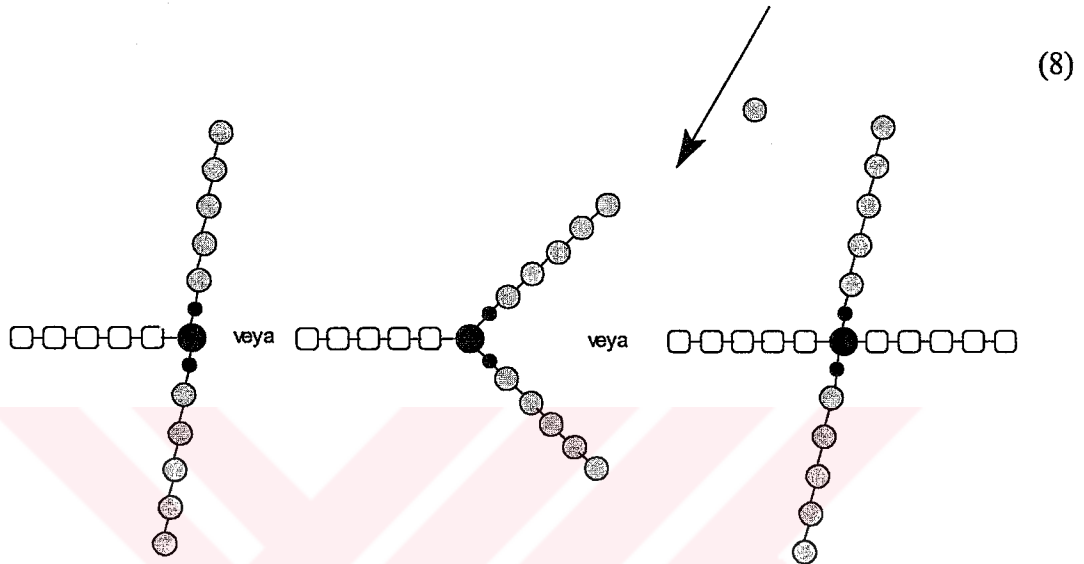
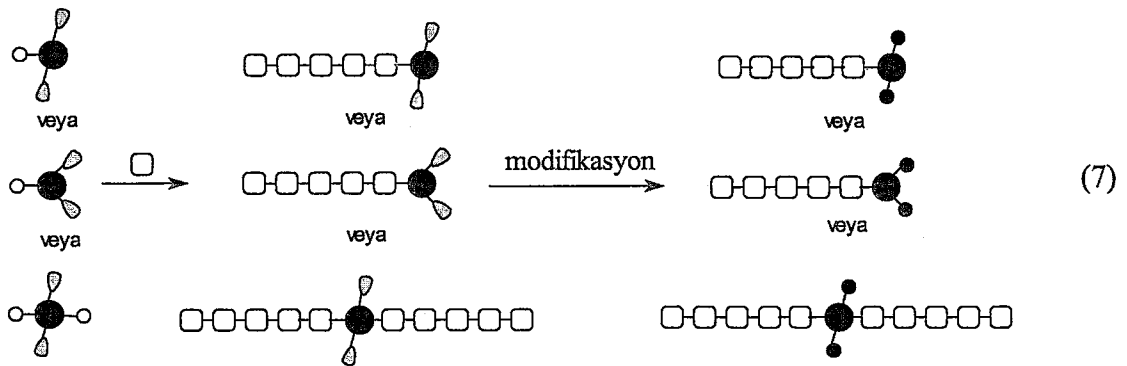
Blok-aşı kopolimer
(Fırça tipli kopolimer)

İlave olarak, 2-(dimetilamino)etil metakrilatın hiper-dallanmış polimer hazırlamada kullanılabileceği gösterildi. Monomer, çözelti içinde benzofenon varlığında fotokimyasal olarak polimerleştirildi. Polimerin yüzey morfolojisi Atomik Kuvvet Mikroskopisiyle (AFM) görüntülenerek incelendi.

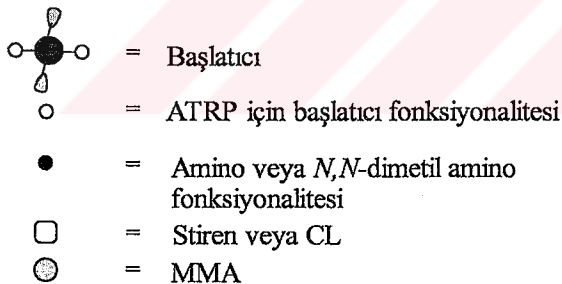


Rastgele aşılınmış MMA zincirleri taşıyan
kopolimer

- = AIBN
- = Stiren
- ◻ = *N,N*-dimetilamino fonksiyonlu monomer
- = MMA



A₂B ve A₂B₂ tipli farklı kollu yıldız kopolimerleri



Çalışmanın son kısmında, farklı kollu yıldız kopolimer sentezi yapıldı. Tasarlanan zincir uzunluklarında merkezde veya zincir sonunda 2,5-dibromo-1,4-fenilen, 2,5-dibromo-benzen ya da 3,5-dibromobenzen grupları taşıyan polistiren (PSt) veya poli(ϵ -kaprolakton) başlangıç polimerleri ATRP veya ROP yöntemleriyle sentezlendi. Bu polimerlerin aromatik brom atomlarından tek veya iki basamaklı tepkimede modifikasyonu sonucu çift fonksiyonlu ön polimerler elde edildi. İlk tepkime aromatik brom fonksiyonlu polimerler ile 3-aminofenilboronik asit arasındaki Suzuki kenetlenmesi tepkimesidir ve bunun sonucu di-amino içeren polimerler hazırlanmıştır. İkinci tepkime di-amino fonksiyonlu polimerler ile 4-(dimetilamino)-benzaldehid arasında gerçekleşen kondensasyon tepkimesidir. Böylece, dimetil amino fonksiyonlu polimerler de elde edilmiştir. Ön polimerlerin yapısında amino ya da *N,N*-dimetil amino fonksiyonel gruplarının bulunuşu, metil metakrilatin benzofenon veya Eritrosin B varlığında fotokimyasal olarak kopolimerizasyonuna imkan verir.

Sonu olarak, 4- veya 3- kollu yıldız kopolimerler (PSt-PMMA ya da PCL-PMMA) elde edildi. İlgili mekanizma Őematik olarak (7) ve (8) de g sterilmiŐtir. BaŐlangı, ara ve sonu polimerlerinin yapıları spektral y ntemler (^1H -NMR, IR) ve GPC  l mleriyle aydınlatıldı. BaŐlangı polimeri ve kopolimere ait DSC analizleri yapıldı ve sonular karŐılaŐtırıldı.



1. INTRODUCTION

The synthesis of novel polymeric materials has recently become a widespread issue in polymer science. Block and graft copolymers that provide specific combinations of physical properties are the most suitable materials for various purposes [1]. Polymer alloys consisting of block and graft copolymers might be useful in the fabrication of polymeric devices exhibiting desirable sophisticated physical phenomena [2].

Polymer brushes refer to an assembly of polymer chains that are attached to a surface at a high grafting density. When the brush regime is attained, the grafted chains begin to stretch away from the surface to avoid crowding. Because of the confinement and the uniform polymer constitution, the brush reacts collectively to environmental stimuli such as changes of the pH or ion strength, temperature, solvent quality, or mechanical forces [3]. These brush properties provide the basis for fabrication of functional devices on a nanometer scale [4].

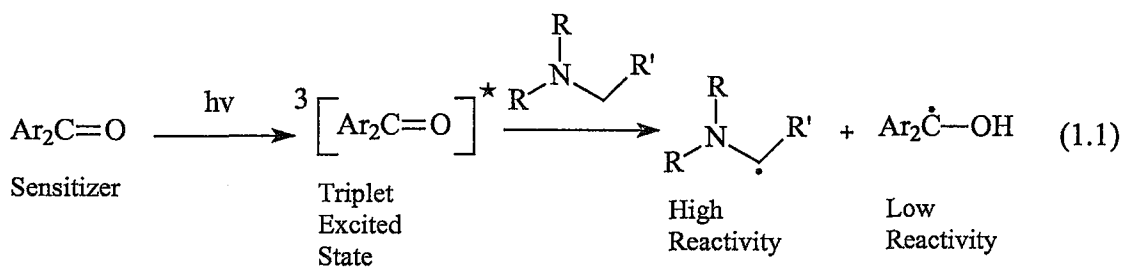
Star polymers are among the macromolecular architectures receiving growing interest, due to their distinct properties in bulk, melt and solutions. They often exhibit lower solution and melt viscosities compared to those of the linear counterparts [5]. These polymers have found applications in various areas where low viscosity polymer formulations are desirable, especially in the fabrication of polymers with relatively low thermal stabilities such as polylactone [6]. They may also be employed in oil industry owing to their potential to decrease the viscosity of lubricating oils in a wide temperature range and increase the viscosity index [7]. In addition, star polymers possess high degrees of functionalities that give rise to many specialized applications [8].

Compared with ionic polymerization techniques, radical polymerizations are applicable to a wide variety of vinylic monomers and require milder reaction conditions. Controlled/"living" radical polymerization processes have proven to be versatile in the preparation of well-defined polymers during the latest few years.

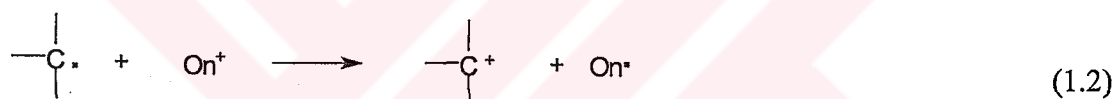
Polymers involving various macromolecular architectures, such as block, graft, star, and hyper-branched, were prepared via controlled/"living" radical polymerizations such as atom transfer radical polymerization (ATRP) [9-14], nitroxide-mediated polymerization (NMP) [15-19], and reversible addition fragmentation chain transfer (RAFT) [20-22] polymerization.

Poly lactones such as poly(ϵ -caprolactone) represent a class of potentially useful materials in biomedical applications due to their potential benefits of biocompatibility and non-toxicity. Tin octoate, $\text{Sn}(\text{O}(\text{O})\text{CCH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9)_2$, in short $\text{Sn}(\text{Oct})_2$, is the most widely used [23,24] initiator in ring opening polymerization (ROP) to synthesize designed polymers based on poly(ϵ -caprolactone). In particular when used in conjunction with hydroxyl functional compounds or prepolymers, telechelics, linear and star-shaped block copolymers or networks can be obtained [25-31] via corresponding alkyl octoate formation.

Photoinitiated polymerization is an important method used for the production of coatings, inks, adhesives, and photolithography. Using this method commercially important olefinic monomers, and epoxides and vinyl ethers can be polymerized via free radical and cationic modes, respectively. Although photoinitiated cationic polymerization has gained importance in recent years, the corresponding free radical polymerization is still the most widely employed route in such applications. Photoinitiated radical polymerization may be initiated by both cleavage (type I) and H-abstraction type (type II) initiators [32,33]. Because the initiation is based on a bimolecular reaction, polymerizations promoted by type II photoinitiators are generally slower than those utilizing type I photoinitiators, which are based on unimolecular formation of radicals. On the other hand, type II photoinitiators possess better optical absorption properties in the near-UV spectral region. Photolysis of aromatic ketones, such as benzophenone, thioxanthenes, benzil, and quinoxones, in the presence of hydrogen donors, such as alcohols, amines, or thiols leads to the formation of a radical produced from the carbonyl compound (ketyl-type radical) and another radical derived from the hydrogen radical [34,35]. The photopolymerization of vinyl monomers is usually initiated by the radical produced from the hydrogen donor. The ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of the unpaired electron. The overall mechanism of the photoinitiation is represented in reaction 1.1.



After the pioneering work on the use of onium salts such as sulphonium and iodonium salts with non-nucleophilic counter anions as cationic photoinitiators, cationic polymerization also received more interest [36,37]. Various modes of photoinitiation involving both direct and indirect photolysis of onium salts have been described. Among the several indirect systems developed to extend the applicability of onium salt photoinitiators towards longer wavelengths, the so-called radical promoted cationic polymerization appeared to be the most elegant and fairly flexible method. Many photochemically formed radicals can be oxidized by onium salts, resulting in cations which are able to initiate cationic polymerization (reaction 1.2).



The use of xanthene dyes in the generation of oxidizable radicals have been reported [38]. The effect of various xanthene dyes, namely rose bengal, eosin B, erythrosin B, rhodamine B, methylene blue on the efficiency of cationic polymerization of cyclohexene oxide was examined. It was found that Erythrosyn B, with the lowest oxidation potential but bearing two negative charges, was the most efficient among these. Different from aliphatic amines, which terminate the growth of cationic chains, aromatic amines were found to be efficient in initiation with negligible contribution in termination owing to their lower basicity.

This study describes the preparation of various macromolecular structures comprising block, graft, brush, star copolymers, and hyper-branched polymers by a combination of controlled polymerization methods with photoinduced polymerizations. First, well-defined prepolymers possessing suitable radical generating sites when used in conjunction with certain photosensitizers were obtained by ATRP and ROP. Subsequent photoinduced polymerization of these prepolymers afforded desired copolymers.

2. THEORETICAL PART

2.1 Controlled Polymerization

Living polymerization was first defined by Szwarc [39] as a chain growth process without chain breaking reactions (transfer and termination). While such a polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition, it does not necessarily provide polymers with molecular weight (MW) control and narrow molecular weight distribution (MWD). Additional prerequisites to achieve these goals include that the initiator should be consumed at early stages of polymerization and that the exchange between species of various reactivities should be at least as fast as propagation [40-42]. It has been suggested to use a term “controlled polymerization” if these additional criteria are met. 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, which often occur in real systems, 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.

Among the controlled polymerization methods such as radical, cationic, group transfer, the former will be discussed in the following part, as the present thesis involves the use of controlled radical polymerization method in the experimental section.

2.1.1 Controlled Radical Polymerization (CRP)

Radical polymerization (RP) is a very convenient commercial process for the preparation of high molecular weight polymers since it can be employed for the polymerization of numerous vinyl monomers under mild reaction conditions, requiring an oxygen free medium, but tolerant to water, and can be conducted over a large temperature range (-80 to 250°C) [43]. Furthermore, many monomers can easily

be copolymerized through a radical route, and this leads to an infinite number of copolymers with properties dependent on the proportion of the incorporated comonomers. One of the main disadvantages of RP is the poor control over the microstructure of the synthesized macromolecules. This includes the relatively high polydispersity index (PDI), 1.5 or 2.0, and also the practical impossibility to synthesize block copolymers, and other advanced structures.

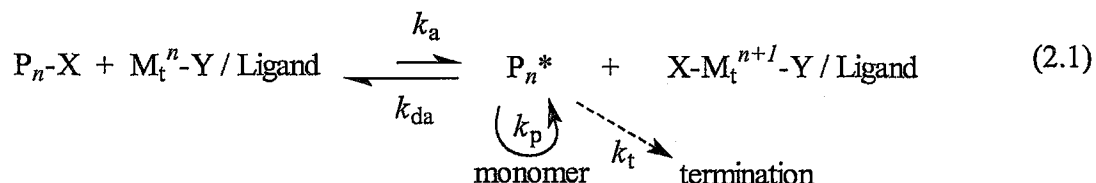
Advanced structures can be synthesized via living polymerization techniques. Notable example of these techniques is anionic polymerization [44], which is known to allow the synthesis of low PDI materials as well as block copolymers. The main disadvantages of anionic polymerization are the limited choice of monomers, and the extremely demanding reaction conditions.

In order to overcome the disadvantages of RP without sacrificing the above-mentioned advantages, it was recognized that a living character had to be realized in conjunction with the free-radical mechanism. Thus, we have witnessed a real explosion of academic and industrial research on controlled/"living" radical polymerizations with over 4000 papers and hundreds of patents devoted to this area since the late 1990s. At present three main mechanisms exist that ensure this living character by establishing an equilibrium between active (radical) and dormant chains. These are atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP) or stable free radical polymerization (SFRP) and reversible addition-fragmentation chain transfer polymerization (RAFT). In either of these controlled radical polymerization methods (CRP), all chains are started early in the reaction, and are allowed to grow throughout the reaction. In general, the result of a successful CRP will be a polymer with low PDI, and predetermined (number-average) molar mass.

2.1.1.1 Atom Transfer Radical Polymerization (ATRP)

The name atom transfer radical polymerization comes from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of the polymeric chains. ATRP was developed by designing a proper catalyst (transition metal compound and ligands), using an initiator with an appropriate structure, and adjusting the polymerization conditions, such that the molecular weights increased

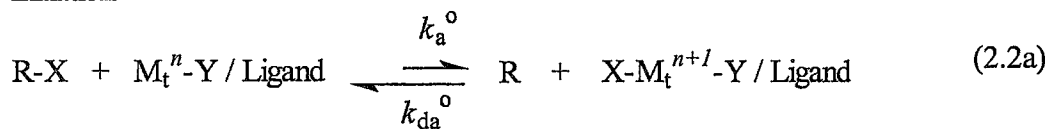
linearly with conversion and the polydispersities were typical of a living process [45]. This allowed for an unprecedented control over the chain topology (stars, combs, branched), the composition (block, gradient, alternating, statistical), and the end functionality for a large range of radically polymerizable monomers [46,47].



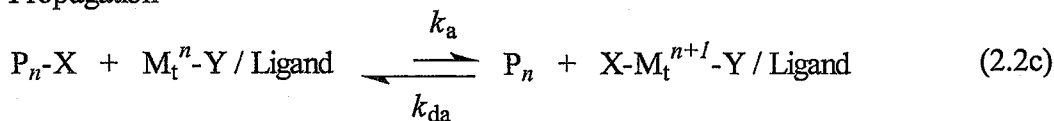
A general mechanism for ATRP is represented by (2.1). The radicals, i.e., the propagating species P_n^* , are generated through a reversible redox process catalyzed by a transition metal complex (activator, $\text{M}_t^n\text{-Y / ligand}$, where Y may be another ligand or a counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, $\text{P}_n\text{-X}$. Radicals react reversibly with the oxidized metal complexes, $\text{X-M}_t^{n+1}\text{-Y / ligand}$, the deactivator, to reform the dormant species and the activator. This process occurs with a rate constant of activation, k_{a} , and deactivation k_{da} , respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_{p} . Termination reactions (k_{t}) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Elementary reactions consisting of initiation, propagation, and termination are illustrated below [48]. (2.2a-e)

Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes, the deactivators, which behave as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination at later stages [49]. A successful ATRP will have not only small contribution of terminated chains but also uniform growth of all the chains; this is accomplished through fast initiation and rapid reversible deactivation.

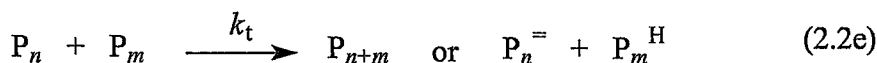
Initiation



Propagation



Termination



As a multicomponent system, ATRP includes the monomer, an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Both activating and deactivating components of the catalytic system must be simultaneously present. Sometimes an additive is used. Basic components of ATRP, namely, monomers, initiators, catalysts, ligands, and solvents are discussed as follows:

(a) Monomers

A variety of monomers have been successfully polymerized using ATRP: styrenes, (meth)acrylates, (meth)acrylamides, dienes, and acrylonitrile, which contain substituents that can stabilize the propagating radicals [46]. In fact, all vinyl monomers are susceptible to ATRP except for a few exceptions. Notable exceptions are unprotected acids (eg (meth)acrylic acid). Some other monomers may be difficult to polymerize since they exhibit side reactions, which may be affected by the choice of reaction conditions, nature of the catalyst, etc. An example of such a monomer is 4-vinyl pyridine (4-VP), which can undergo quaternization by the (alkyl halide) initiator [50]. Nevertheless, successful polymerization of 4-VP has been reported.

The most common monomers in the order of their decreasing ATRP reactivity are methacrylates, acrylonitrile, styrenes, acrylates, (meth)acrylamides.

(b) Initiators

The main role of the initiator is to determine the number of growing polymer chains. The initiation in ATRP may occur in one of two different ways. The common way to initiate is via the reaction of an activated (alkyl) halide with the transition-metal complex in its lower oxidation state. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, should rapidly and selectively migrate between the growing chain and the transition metal complex. Thus far, when X is either bromine or chlorine, the molecular weight control is best. Iodine works well for acrylate polymerizations in copper-mediated ATRP and has been found to lead to controlled polymerization of styrene in ruthenium and ruthenium-based ATRP [51,52]. Many different types of halogenated compounds have the potential to initiate ATRP. Typical examples would be the use of ethyl 2-bromoisobutyrate and a Cu(I) complex for the initiation of a methacrylate polymerization [53], or 1-phenylethyl chloride for the initiation of a styrene polymerization [54]. In addition, there are initiators like 2,2,2-trichloro-ethanol [55] that appear to be very efficient, and that result in hydroxy-functional polymer chains. Percec and co-workers reported the use of sulfonyl chlorides as universal initiators in ATRP [56]. Also the use of di-, tri-, or multifunctional initiators is possible, which will result in polymers growing in two, three, or more directions. Besides, some pseudohalogens, specifically thiocyanates and thiocarbamates, have been used successfully in the polymerization of acrylates [57].

The alternative way to initiate ATRP is via a conventional free-radical initiator, which is used in conjunction with a transition-metal complex in its higher oxidation state. Typically one would use AIBN in conjunction with a Cu(II) complex. Upon formation of the primary radicals and/or their adducts with a monomer unit, the Cu(II) complex very efficiently transfers a halogen to this newly formed chain. In doing so the copper complex is reduced, and the active chain is deactivated. This alternative way of initiation was termed “reverse ATRP” [58].

(c) Catalysts

Perhaps the most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of

exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst.

1. The metal center must have at least two readily accessible oxidation states separated by one electron.
2. The metal center should have reasonable affinity toward a halogen.
3. The coordination sphere around the metal should be expandable on oxidation to selectively accommodate a (pseudo)halogen.
4. The ligand should complex the metal relatively strongly.
5. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system. To differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species [59].

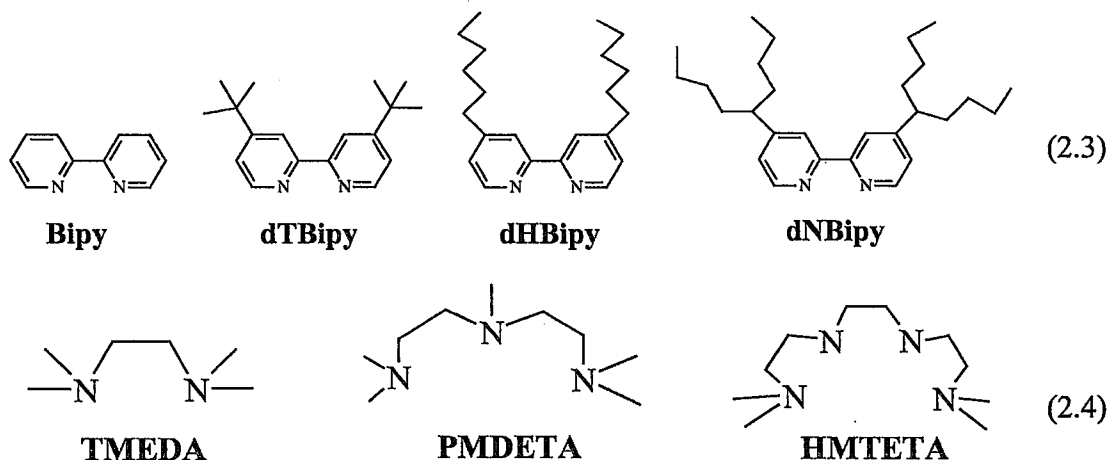
A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. The majority of work on ATRP has been conducted using copper as the transition metal. Apart from copper-based complexes, Fe [60], Ni [61], Ru [62], etc have been used to some extent. Recent work from Sawamoto and co-workers shows that the Ru-based complexes can compete with the Cu-based systems on many fronts. A specific Fe-based catalyst has also been reported to polymerize vinyl acetate via an ATRP mechanism [63].

(d) Ligands

The main roles of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal. It should also allow expansion of the coordination sphere and should allow selective atom transfer without promoting other reactions.

The most common ligands for ATRP systems are substituted bipyridines, alkyl pyridylmethanimines and multidentate aliphatic tertiary amines such as N,N,N',N'',N''

pentamethyldiethylenetriamine (PMDETA), and tris[2-(dimethylamino) ethyl]amine (Me₆-TREN). Examples of ligands used in copper-mediated ATRP are illustrated below [64,65].



In addition to those commercial products, it has been demonstrated that triethylene tetramine (TETA) possessing six hexyl groups provides better solubility of the copper complexes in organic media and entirely homogeneous reaction conditions [66]. Since copper complexes of this new ligand are almost insoluble in water, ATRP technique can be employed in preparing poly(acrylate esters) in aqueous suspensions [67].

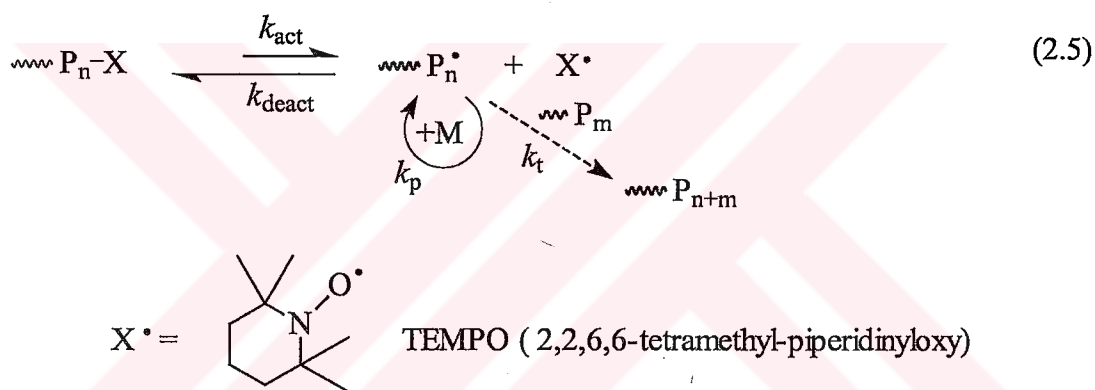
(e) Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used in the polymerization of different monomers. A solvent is sometimes necessary, especially when the polymer is insoluble in its monomer (e.g., polyacrylonitrile). ATRP has been also successfully carried under heterogeneous conditions in (mini)emulsion, suspension, or dispersion. Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, potential interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper-based ATRP) [68] and solvent-assisted side

reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent, [69] should be minimized.

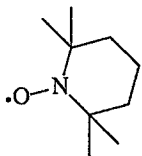
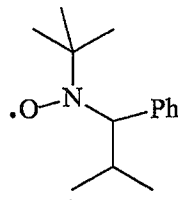
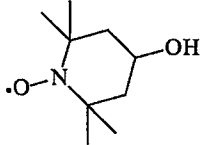
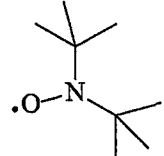
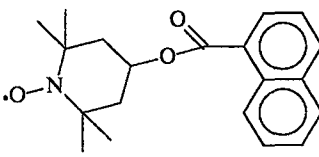
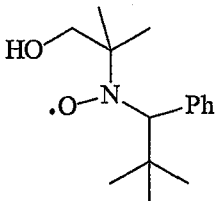
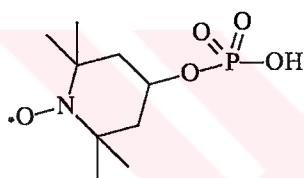
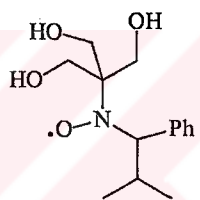
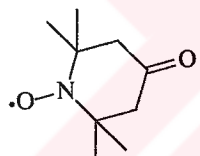
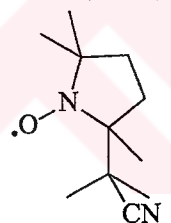
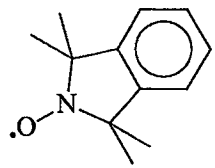
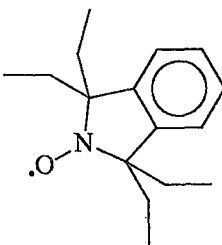
2.1.1.2 Stable Free Radical Polymerization (SFRP)

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 ($P_n^\bullet$) reacts with a stable radical ($X^\bullet$) as seen in reaction (2.5) [70]. The most commonly used stable radicals have been nitroxides, especially 2,2,6,6-tetramethylpiperidinyloxy (TEMPO). The resulting dormant species (P_n-X) can then reversibly cleave to regenerate the free radicals once again. Once $P_n^\bullet$ forms it can then react with a monomer, M, and propagate further.



Unfortunately, TEMPO can only be used for the polymerization of styrene-based monomers at relatively high temperatures ($>120^\circ\text{C}$). With most other monomers, the bond formed is too stable and TEMPO acts as an inhibitor in the polymerization, preventing chain growth. Numerous advances have been made in both the synthesis of unimolecular initiators (alkoxyamines) that can be used not only for the polymerization of St-based monomers, but other monomers as well [71-75]. Most recently, the use of more reactive alkoxyamines and less reactive nitroxides has expanded the range of polymerizable monomers to acrylates, dienes, and acrylamides [76-78]. Several nitroxides that have been employed as mediators in Stable free-radical polymerizations are given in Table 2.1.

Table 2.1: Structures of Several Nitroxides Employed in SFRP

<i>Structure</i>	<i>Reference</i>	<i>Structure</i>	<i>Reference</i>
	[79]		[85]
	[80]		[86]
	[81]		[87]
	[82]		[88]
	[83]		[89]
	[84]		[90]

2.1.1.3 The Reversible Addition–Fragmentation Chain Transfer Process

In terms of polymerizable monomers, RAFT is at present the most versatile technique for conducting CRP, that is, it can be applied to a larger range of monomers than SFRP and ATRP. In contrast to the previously described NMP and ATRP, this system relies on chain transfer for the exchange between active and dormant chains. The chain end of a dormant chain carries a thiocarbonylthio moiety, which is chain-

transfer-active. Upon chain transfer, the thiocarbonylthio moiety is transferred to the previously active chain, which now becomes dormant, and the previously dormant chain carries the radical activity and is able to propagate.

There are four classes of thiocarbonylthio RAFT agents, depending on the nature of the Z group: (1) dithioesters (Z = aryl or alkyl), (2) trithiocarbonates (Z = substituted sulfur), (3) dithiocarbonates (xanthates) (Z = substituted oxygen), and (4) dithiocarbamates (Z = substituted nitrogen). Representative examples of thiocarbonylthio RAFT agents are shown in Figure 2.1.

To some extent the choice of RAFT agent determines the degree of control obtained. The general structure of a RAFT agent is depicted in Figure 2.1, where the Z group is the activating group, and R is the homolytically leaving group. To a large extent, the Z group determines the rate of addition, and the R group determines the rate of fragmentation. The choice of Z and R groups is dependent on the nature of the monomer to be polymerized.

RAFT polymerization is performed by adding a chosen quantity of an appropriate RAFT agent (Figure 2.1) to a conventional free radical polymerization mixture and yields polymers of predetermined chain length and narrow polydispersity. Polydispersity indices of less than 1.1 can be usually achieved under optimal conditions. The RAFT process offers the same versatility and convenience as conventional free-radical polymerization being applicable to the same range of monomers (e.g., (meth)acrylates, styrenes, acrylamides, vinyls), solvents, functional groups (e.g., OH, CO₂H, NR₂, NCO) and reaction conditions (e.g., bulk, solution, suspension and emulsion). The RAFT process yields thiocarbonylthio-terminated polymers (or 1,1-disubstituted alkene-terminated oligomers if macromonomers are used as RAFT agents) that can be chain extended to yield a variety of copolymers (e.g., AB, ABA blocks, gradient).

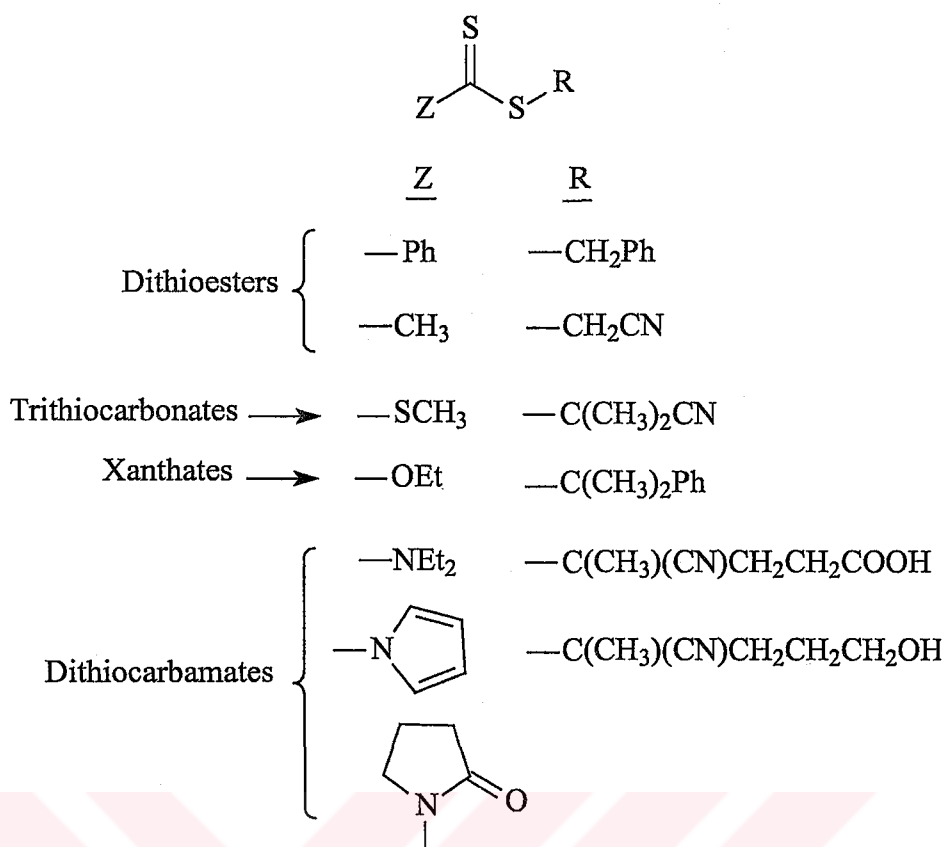


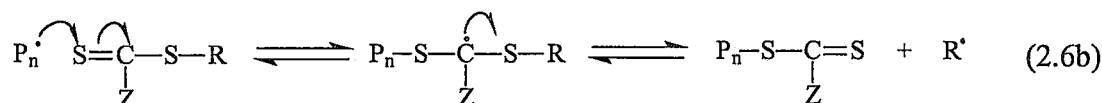
Figure 2.1 : Examples of the different classes of thiocarbonylthio RAFT agents

The mechanism of RAFT polymerization with the thiocarbonylthio-based RAFT agents involves a series of addition–fragmentation steps as depicted below (2.6a-e). As for conventional free-radical polymerization, initiation by decomposition of an initiator leads to formation of propagating chains. In the early stages, addition of a propagating radical ($P_n\cdot$) to the RAFT agent $[S=C(Z)SR]$ followed by fragmentation of the intermediate radical gives rise to a polymeric RAFT agent and a new radical ($R\cdot$). The radical $R\cdot$ reinitiates polymerization by reaction with monomer to form a new propagating radical ($P_m\cdot$). In the presence of monomer, the equilibrium between the active propagating species ($P_n\cdot$ and $P_m\cdot$) with the dormant polymeric RAFT compound provides an equal probability for all the chains to grow. This feature of the RAFT process leads to the production of narrow polydispersity polymers. When the polymerization is complete, the great majority of the chains contain the thiocarbonylthio moiety as the end group (2.6e) which has been identified by ^1H -NMR and UV–vis spectroscopy [91]. Additional evidence for the proposed mechanism was provided by the identification of the intermediate thioketal radical ((A) and/or (B), 2.6b,d) by ESR spectroscopy [92,93].

Initiation and propagation



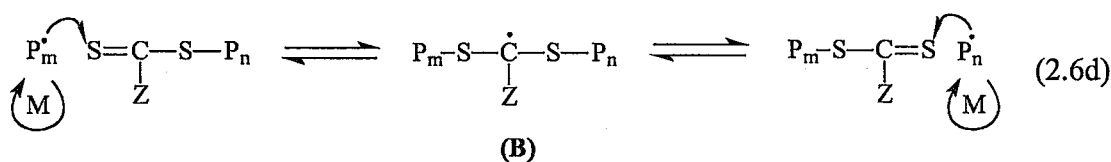
Addition to RAFT agent



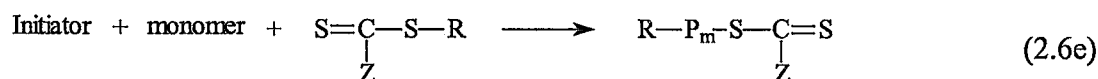
Reinitiation



Chain equilibration by reversible addition fragmentation



Overall



2.1.2 Controlled Ring-Opening Polymerization (ROP)

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

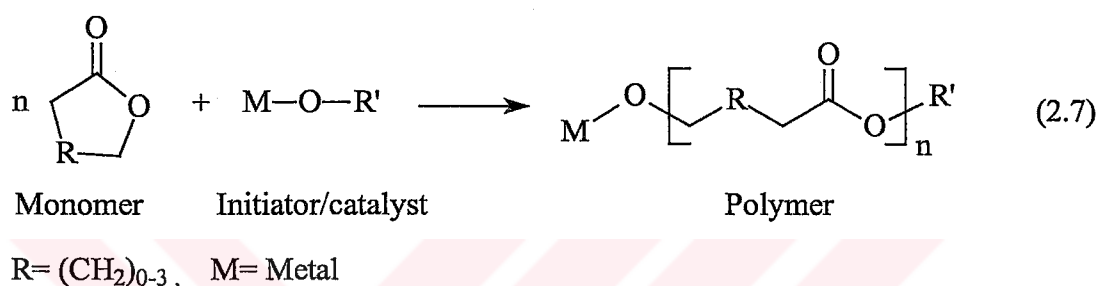
Degradable materials with new mechanical properties and modified degradation profiles have been produced and characterized. The increasing demands of a larger number of biomedical applications have resulted in an increasing interest in producing macromolecules through controlled polymerization.

Poly lactones and poly lactides 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.

2.1.2.1 Ring-Opening Polymerization of Cyclic Esters

Poly lactones 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 2.7 presents the reaction pathway for the ROP of a cyclic ester.



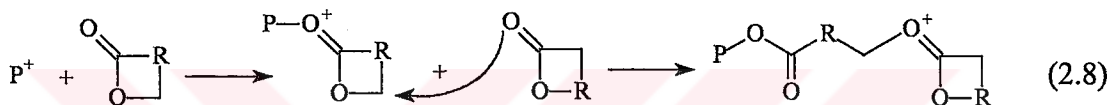
Each macromolecule formed generally contains one chain end-terminated with a functional group originating from the termination reaction and one terminus end capped with a functional group originating from the initiator. By altering the catalyst or initiator and the termination reaction, the nature of 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 [94]. 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 [95], *via* cationic, anionic, or “coordination-insertion” mechanisms [96-98]. In addition, radical, zwitterionic [99], or active hydrogen [95] initiation is possible, although such techniques are not used to any great extent.

2.1.2.2 Cationic Ring-Opening Polymerization

Among the cyclic esters, 4-, 6-, and 7- membered rings form polyesters when reacted with cationic catalysts [95]. The cationic ROP involves the formation of a positively charged species which is subsequently attacked by a monomer (reaction 2.8). The attack results in a ring-opening of the positively charged species through an S_N2 -type process.

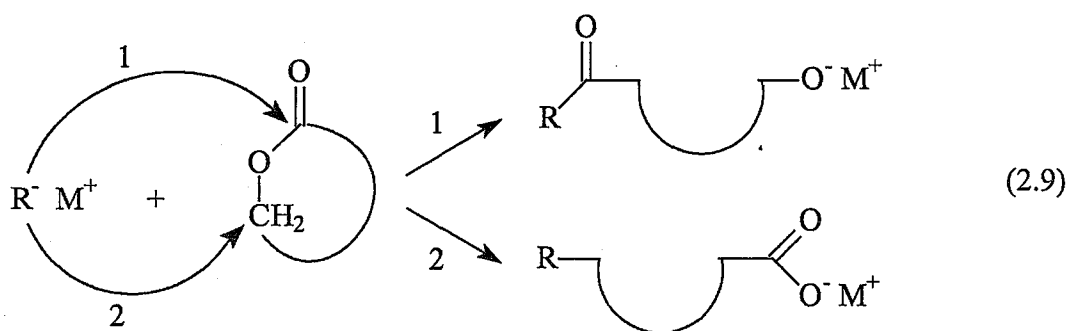


P= Polymer

The cationic polymerization is difficult to control and often only low-molecular weight polymers are formed. When the bulk and solution polymerization of 1,5-dioxepan-2-one (DXO) with cationic initiators were studied, the highest molecular weight achieved was about 10,000. More detailed reviews on cationic ROP have been published by Penczek and coworkers [100,101].

2.1.2.3 Anionic Ring-Opening Polymerization

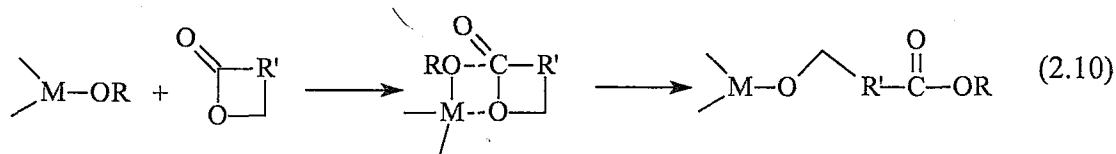
Anionic ROP of cyclic ester monomers takes place by the nucleophilic attack of a negatively charged initiator on the carbonyl carbon or on the carbon atom adjacent to the acyl oxygen, resulting in linear polyester. Reaction 2.9 shows the reaction pathway for the ROP of a cyclic ester by anionic initiation, ring-opening of monomer by 1) acyl-oxygen bond cleavage and 2) alkyl-oxygen bond cleavage [102]. The propagating species is negatively charged and is counter-balanced with a positive ion. Depending on the nature of the ionic propagating chain end and the solvent, the reacting complex varies from completely ionic to almost covalent.



One of the best controlled methods leading to high molecular weight polymers is anionic polymerization carried out in a polar solvent. The Jedlinski group developed living anionic ROP methods for 4- and 5-membered ring lactones and has reported well-defined polymers and copolymers of high molecular weight [103]. The anionic ring-opening of four-membered rings (β -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.

2.1.2.4 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 [96,97]. Reaction 2.10 shows a schematic presentation of the proposed reaction pathway for the ROP of a cyclic ester by the coordination-insertion mechanism. The growing chain remains attached to the metal through an alkoxide bond during the propagation. The reaction is terminated by hydrolysis forming a hydroxy end group. With functional alkoxy-substituted initiators, macromers with end groups active in post-polymerization reactions are produced.



The coordination-insertion type of polymerization has been thoroughly investigated since it may yield well-defined polyesters through living polymerization [97]. When two monomers of similar reactivity are used, block copolymers can be formed by sequential addition to the “living” system.

2.1.2.5 Initiators for the ROP of Lactones and Lactides

Various organometallic compounds, e.g., metal alkoxides and metal carboxylates, have been studied as initiators or catalysts in order to achieve effective polymer synthesis [104]. 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. Most frequently used initiators and catalysts in ROP of lactones are stannous octoate [Sn(Oct)₂], aluminum tri-isopropoxide, tin(IV) alkoxides, tin(II) alkoxides, and lanthanide alkoxides.

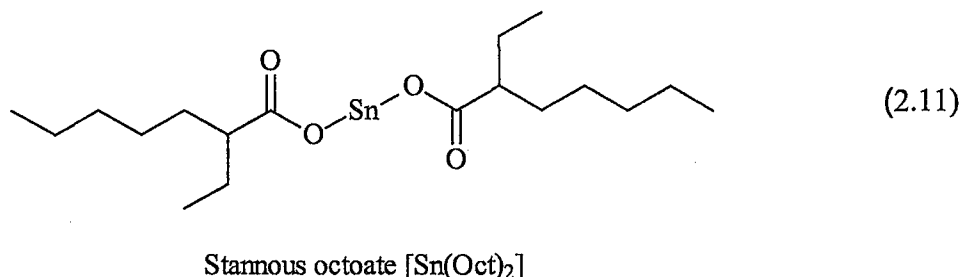
The broad range of initiators and catalysts offer different advantages and possibilities. Sn(Oct)₂ is rather easy to use, but it is also a strong transesterification catalyst and it cannot therefore be recommended for the synthesis of advanced molecular structures.

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 (tri-block, star, or comb polymers).

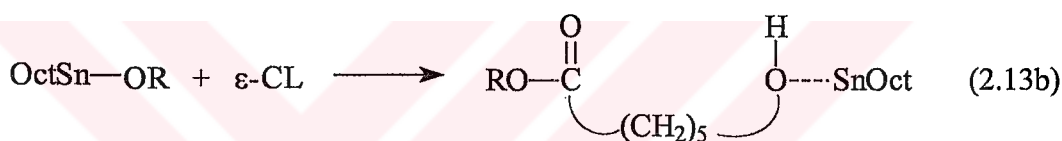
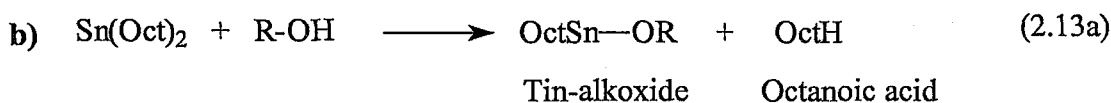
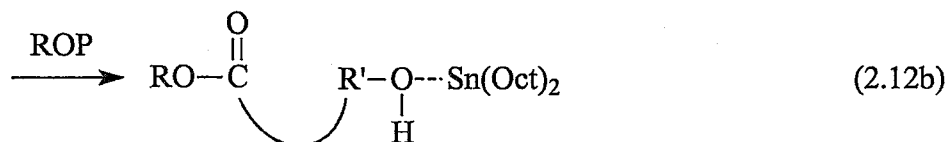
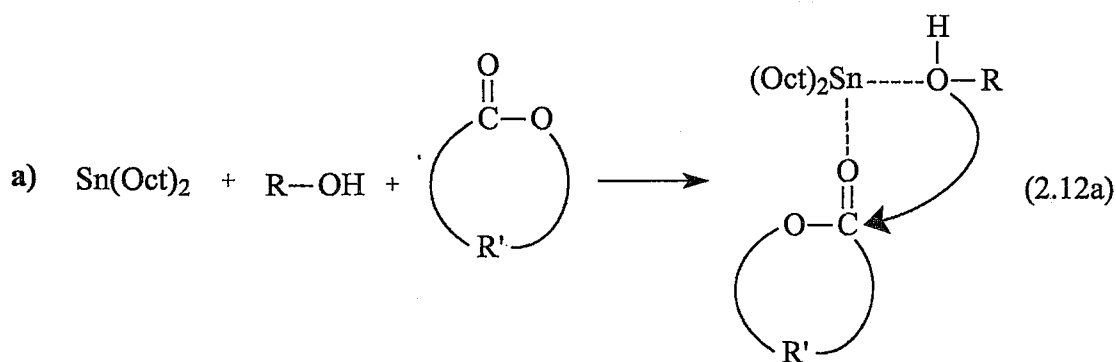
Lanthanide-based initiator systems offer a fourth possibility, permitting the block copolymerization of lactones with compounds such as ethylene, tetrahydrofuran, trimethylene carbonate, and methyl methacrylate. Detrimental side reactions such as macrocyclic formation, transesterification, and racemization are absent and the reactions are extremely fast.

The present work involves the use of stannous octoate (2.11) in the ring opening polymerization of ϵ -caprolactone. Therefore, it will be described in more detail throughout the following discussion.



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 [105]. 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 [106] over a long period of time, it is not until now that the ROP mechanism is about to be elucidated [107,108]. 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 [108] 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 [107] 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 and ϵ -CL polymerization. Reactions 2.12a,b and 2.13a,b show the two different proposals. The main ROP mechanism proposals with Sn(Oct)₂ as catalyst are a) complexation of a monomer and alcohol prior to ROP and b) formation of tin-alkoxide before ROP of CL.



The $\text{Sn}(\text{Oct})_2$ catalyst is a strong transesterification agent, and the resulting copolymers normally have a randomized microstructure [109]. An increase in reaction temperature or reaction time increases the amount of transesterification reactions.

The ROP of lactide with $\text{Sn}(\text{Oct})_2$ 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.

2.2 Photoinitiated Polymerization

Photopolymerizations, which use light energy (photons) to initiate chain reactions to form polymer materials, are the basis for a growing, billion-dollar industry. Applications in which photopolymerization is used include films and coatings, inks, adhesives, fiber optics [110]. There are some other interesting applications such as

production of laser video discs and curing of acrylate dental fillings. Each of these industries has benefited from the high productivity and lower costs afforded by photopolymerization systems.

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, either the 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.

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.

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 sunlight. These features make photopolymerization an ecologically friendly and economical technology that has high potential for further development.

2.2.1 Photoinitiated Free Radical Polymerization

Photoinitiated free radical polymerization consists of photoinitiation (reactions 2.14a-c), propagation, chain transfer, and termination. The role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating radicals. The reaction of these radicals with monomer, propagation, transfer and termination are purely thermal processes; they are not affected by light.



Photoinitiation

Photoinitiation involves 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. Repeated addition of monomer units to the chain radical produces the polymer backbone (Propagation).

Chain transfer also takes place, that is, growing chains are terminated by hydrogen abstraction from various species (e.g., from solvent) and new radicals capable of initiating other chain reactions are formed.

Finally, 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.

2.2.1.1 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 (Eq:2.1), where I_o 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 molar extinction coefficient ϵ .

$$I_a = I_o (1 - e^{-\epsilon l[S]}) \quad (\text{Eq:2.1})$$

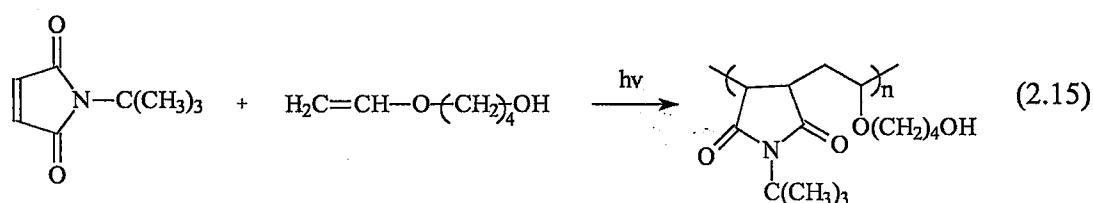
If the monomer possesses chromophoric groups and is sensitive towards light (i.e., it undergoes photoinduced chemical reactions with high quantum yields) one can carry out photopolymerizations by just irradiating the monomer. In many cases, however, monomers are not efficiently decomposed into radicals upon irradiation. Furthermore, monomers are often transparent to light at $\lambda > 320$ nm, where commercial lamps emit. In these cases, photoinitiators are used. These compounds absorb light and bring about the generation of initiating radicals [111].

2.2.1.2 Radical Generation

a) Radicals via Monomer Irradiation

In some cases, a monomer may function as a photoinitiator and become incorporated into a copolymer chain. This has been shown for styrene and other conjugated

monomers when exposed to deep-UV light; however, the initiation efficiency in these systems is substantially less than when a photoinitiator is present. A better polymerizable initiator scheme is illustrated by the acceptor-donor chemistry of maleimide-donor systems [112]. Maleimide acts as both photoinitiator and comonomer in the presence of hydrogen donors such as vinyl ethers or vinyl esters [113,114]; an example of this copolymerization is shown below (reaction 2.15). It shows the molecular structure of the acceptor *tert*-butylmaleimide (left), the donor 4-hydroxy-butyl vinyl ether (right), and their corresponding copolymer repeating unit [115].

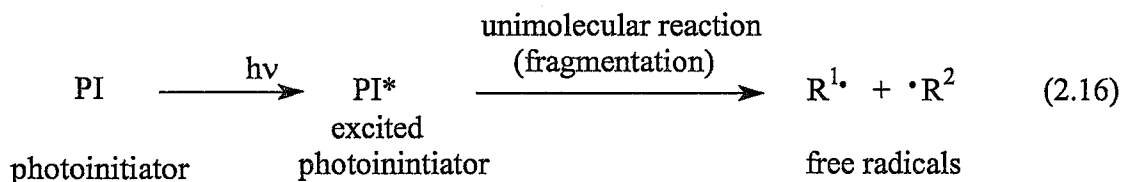


Readily available monomers which to some extent undergo polymerization and copolymerization upon UV irradiation are as follows: Allyl methacrylate, barium acrylate, cinnamyl methacrylate, diallyl phthalate, diallyl isophthalate, diallyl terephthalate, 2-ethylhexyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, styrene, methylenebisacrylamide, methyl methacrylate, pentaerythritol, tetramethacrylate, tetraethylene glycol, dimethacrylate, tetrafluoroethylene, *N*-vinylcarbazole, vinyl cinnamate, vinyl 2-fluorate, and vinyl 2-furylacrylate [111].

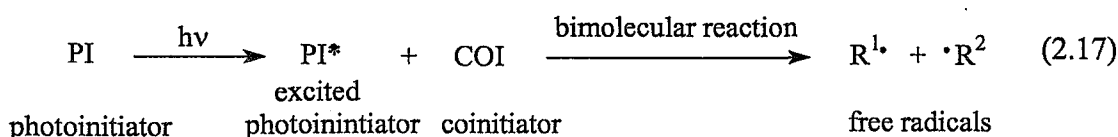
b) Radicals via Photoinitiators

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.

Compounds which undergo unimolecular bond cleavage upon irradiation as shown in reaction 2.16 are termed “type I photoinitiators”.



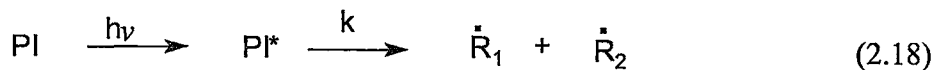
If the excited state photoinitiator interacts with a second molecule (a coinitiator) to generate radicals in a bimolecular reaction as shown in reaction 2.17, the initiating system is termed a “type II Photoinitiator”.



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

These substances undergo a homolytic bond cleavage upon absorption of light (reaction 2.18). The fragmentation that leads to the formation of radicals is, from the point of view of chemical kinetics, a unimolecular reaction (Eq:2.2).



$$\frac{d[\dot{\text{R}}_1]}{dt} = \frac{d[\dot{\text{R}}_2]}{dt} = k [\text{PI}^*] \quad (\text{Eq:2.2})$$

The number of initiating radicals formed upon absorption of one photon is termed as quantum yield of radical formation ($\Phi_{R\cdot}$) (Eq:2.3).

$$\Phi_{R\cdot} = \frac{\text{Number of initiating radicals formed}}{\text{Number of photons absorbed by the photoinitiator}} \quad (\text{Eq:2.3})$$

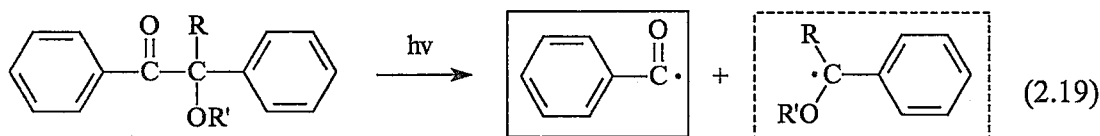
Theoretically, cleavage type photoinitiators should have a $\Phi_{R\cdot}$ value of two since two radicals are formed by the photochemical reaction. The values observed, however, are much lower because of various deactivation routes of the photoexcited initiator other than radical generation. These routes include physical deactivation such as fluorescence or non-radiative decay and energy transfer from the excited 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:

$$f_p = \frac{\text{number of chain radicals formed}}{\text{number of primary radicals formed}} \quad (\text{Eq:2.4})$$

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

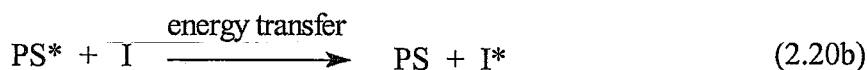
$$\Phi_p = \Phi_{R\cdot} \times f_p \quad (\text{Eq:2.5})$$

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 2.19. The benzoyl radical formed by the reaction depicted is very reactive towards the unsaturations of vinyl monomers [116].



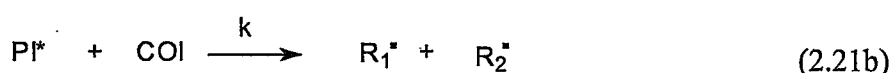
The α -cleavage often referred to as Norrish Type I reaction [117] of carbonyl compounds starts from the initiator's triplet state, which is populated via intersystem crossing. Notably, the excited triplet states are usually relatively short lived that prevents excited molecules to undergo side reactions 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 ($E_T = 259 \text{ kJ mol}^{-1}$ [118]).

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 photosensitizers (PS) with matching absorption spectra is recommendable. Photosensitizers 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 sensitizer's 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 photosensitizer molecules return to their ground state upon energy transfer; they are therefore not consumed in the process of initiation (reactions 2.20a-c).



Type II Photoinitiators

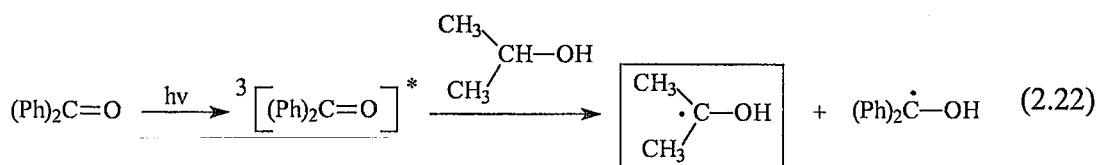
The excited states of certain compounds do not undergo Type I reactions because their excitation energy is not high enough for fragmentation, i.e., their excitation energy is lower than the bond dissociation energy. The excited molecule can, however, react with another constituent of the polymerization mixture, the so-called coinitiator (COI), to produce initiating radicals (reactions 2.21a,b). In this case, radical generation follows 2nd order kinetics (Eq.2.6).



$$\frac{d[\dot{\text{R}}_1]}{dt} = \frac{d[\dot{\text{R}}_2]}{dt} = k [\text{PI}^*] [\text{COI}] \quad (\text{Eq.2.6})$$

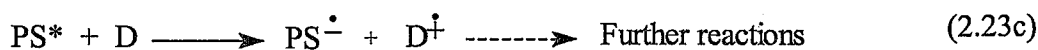
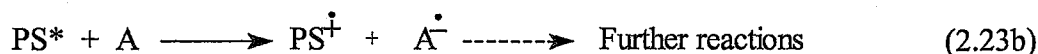
There are two distinct pathways of radical generation by Type II initiating systems:

(1) Hydrogen abstraction from a suitable hydrogen donor. As a typical example, the photoreduction of benzophenone by isopropanol is depicted (reaction 2.22). Bimolecular hydrogen abstraction is limited to diaryl ketones [117]. 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) Photoinduced electron transfer reactions and subsequent fragmentation. In electron transfer reactions, the photoexcited molecule, termed as photosensitizer for the convenience, can act either as electron donor (D) or electron acceptor (A) according to the nature of the photosensitizer 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 (reactions 2.23a-c).



The electron transfer is thermodynamically allowed, if Gibbs Energy Change (ΔG) calculated by the Rehm-Weller equation (Eq:2.7) [119] is negative.

$$\Delta G = F [E_{1/2}^{\text{ox}} (\text{D/D}^+) - E_{1/2}^{\text{red}} (\text{A/A}^{\cdot-})] - E_{\text{PS}} + \Delta E_{\text{c}} \quad (\text{Eq:2.7})$$

where,

F = Faraday constant,

$E_{1/2}^{\text{ox}} (\text{D/D}^+)$ = oxidation potential of donor,

$E_{1/2}^{\text{red}} (\text{A/A}^{\cdot-})$ = reduction potential of acceptor,

E_{PS} = Singlet state energy of the photosensitizer,

ΔE_{c} = Coulombic stabilization energy.

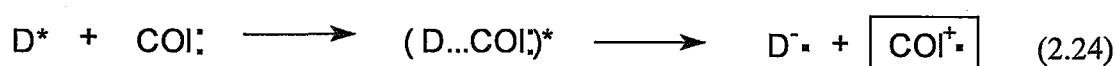
Electron transfer is often observed for aromatic ketone/amine pairs and always with dye/coinitiator systems.

2.2.1.3 Dye Sensitized Initiation

Most of the photoinitiators are sensitive to light at wavelengths below 400 nm. This enables an easy processability, since the sun and many artificial sources of light do overwhelmingly emit light of higher wavelengths and therefore photoinduced reactions before the intended initiation by UV light may be kept at low level. However, if the strong emission of mercury lamps or the sun in the visible region of the spectrum is to be used, photoinitiating systems that absorb visible light are required. Such systems often involve dyes as light absorbing chromophores. Initiating radicals are generated by photoinduced electron transfer. Energy transfer is not

thermodynamically favorable in these systems due to low excitation energies of dyes. Depending on the nature of the dye involved, two distinct mechanisms are to be considered:

1) Electron transfer from coinitiator to the excited, *photoreducible dye* molecule yields radical cations of the coinitiator and radical dye anions. The former can initiate the polymerization. In many cases, however, initiating radicals are formed in subsequent thermal reactions. Species deriving from the dye molecule (D) do not react with monomer molecules (2.24).



2) Electron transfer from the excited, *photooxidizable dye* to the coinitiator. In this case too, the initiating radicals stem mostly from coinitiator (2.25).

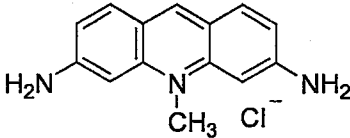
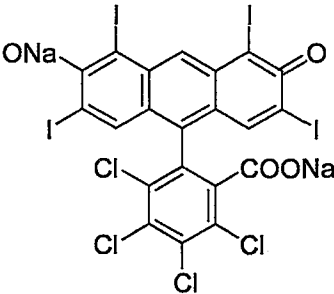
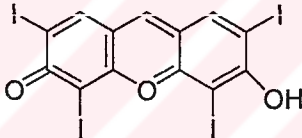
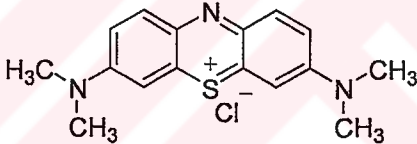
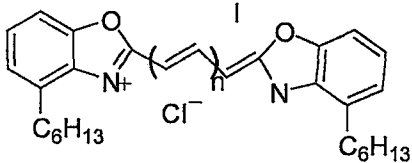


For initiating radical polymerizations, the first depicted scheme (2.24) is commonly followed.

a) Photoreducible Dye / Coinitiator Systems

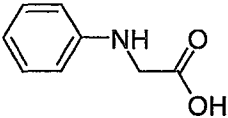
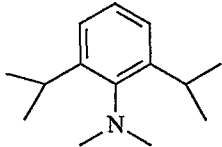
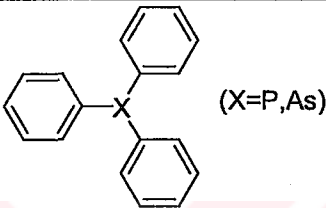
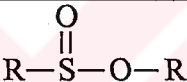
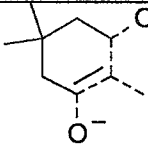
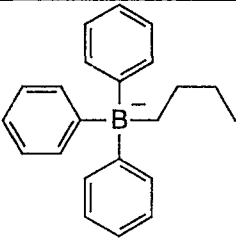
As can be seen in Table 2.2, differently colored photoreducible dyes are used for sensitizing cationic polymerizations.

Table 2.2: Absorption Characteristics of Typical Photoreducible Dyes

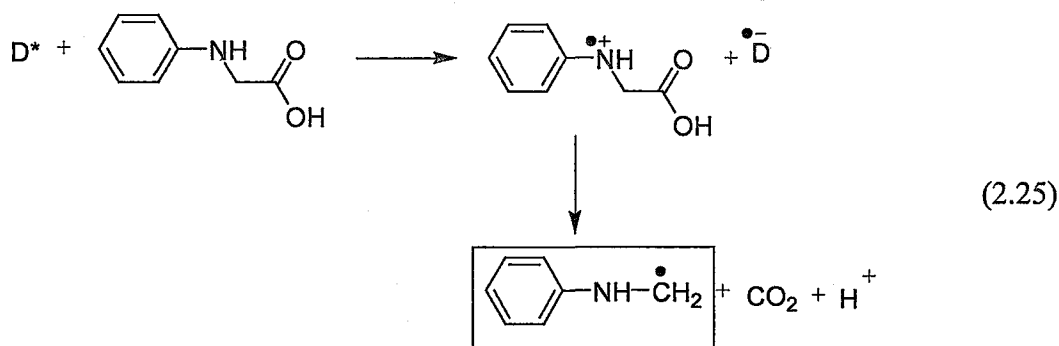
Type	Example	λ_{max} (nm)
Acridinium		460
Xanthene	Acriflavine 	565
Fluorone	Rose Bengale 	536
Thiazene		645
Polymethylene	Polymethylene Blue 	490...700, depending on n
	Cyanine Dye	

As coinitiators, the following substances have found application in conjunction with photoreducible dyes (Table 2.3).

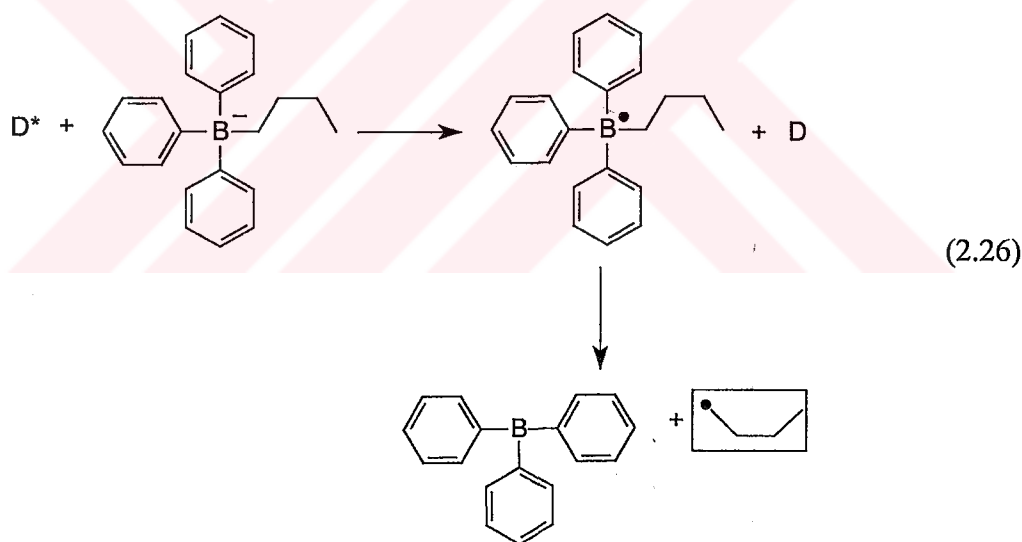
Table 2.3: Coinitiators for Dye Sensitized Free Radical Polymerization

Type	Formula	Name	Reference
Amines		<i>N</i> -Phenylglycidine	[120]
		<i>N,N</i> -dimethyl-2,6-diisopropyl aniline	[121]
	$\text{H}_2\text{N}-\text{NH}_2$	Hydrazine	[122]
Phosphines and Arsines	 (X=P,As)	Triphenyl-phosphine, Triphenylarsine	[123]
Sulphinates			[124]
Heterocycles		Imidazole	[125]
		Thiazole	[125]
Enolates		Dimedone Enolate	[126]
Borates		Triphenylbutyl borate	[127]

Among amine coinitiators, phenylglycidine has been reported to be particularly efficient. As depicted in (2.25), the formation of initiating radicals owes to a thermal fragmentation reaction.



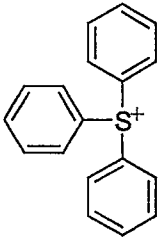
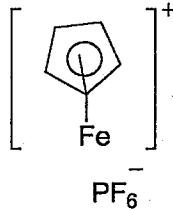
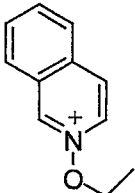
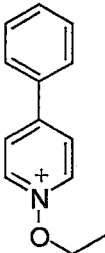
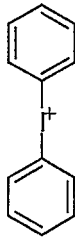
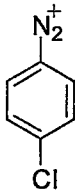
Borate salts are especially useful in combination with cyanine dyes. Depending on the cyanine used, there are different absorption maxima in the visible region with usually high molar extinction coefficients ($\epsilon = \text{ca. } 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$). Radical formation by borate is illustrated in (2.26). In contrast to many other initiating systems based on dye sensitization, cyanine/borate complexes are ionic before electron transfer and are transformed into neutral species. Other systems are neutral before electron transfer and get ions thereafter.



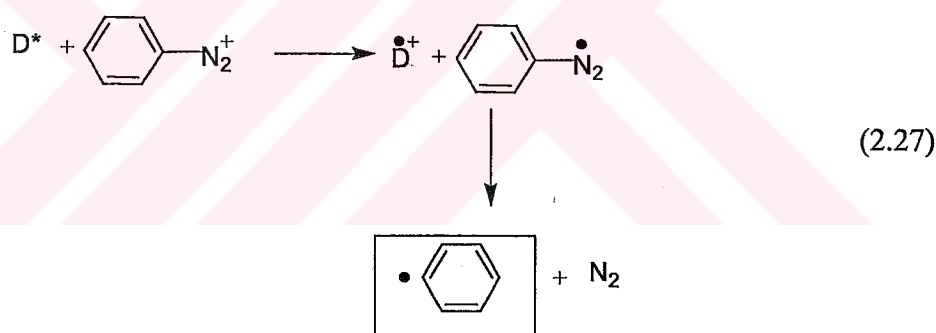
b) Photooxidizable Dye/Coinitiator Systems

As far as photooxidizable dyes are concerned, the oxidation of dyes such as acridine or xanthene by onium salts is to be mentioned. Onium salts, like aryldiazonium, diaryliodonium, phosphonium and sulphonium salts are able to oxidize certain dyes. In Table 2.4, reduction potentials of various onium salts are depicted. Notably, the higher (more positive) the value of $E_{1/2}^{\text{red}}(\text{On}^+)$ is, the more capable is the salt to oxidize a dye.

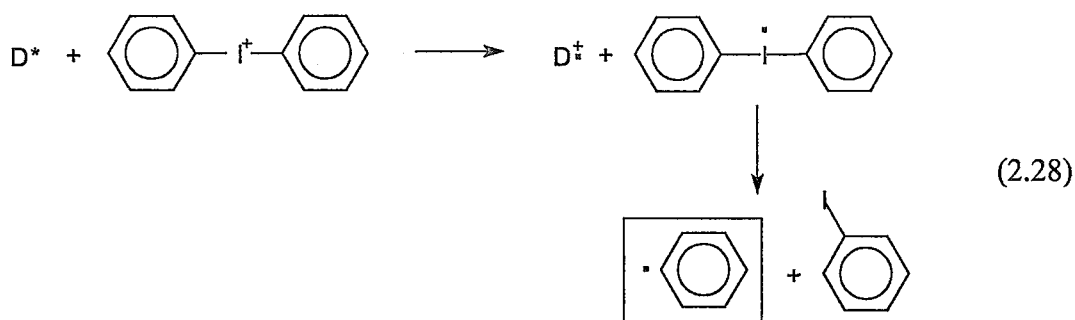
Table 2.4: Reduction Potentials of Onium Salt Cations, $E_{1/2}^{\text{red}}$ (On^+) in V

					
-1.1 [128]	-0.7 [129]	-0.5 [130]	-0.5 [130]	-0.2 [131]	0.35 [132]

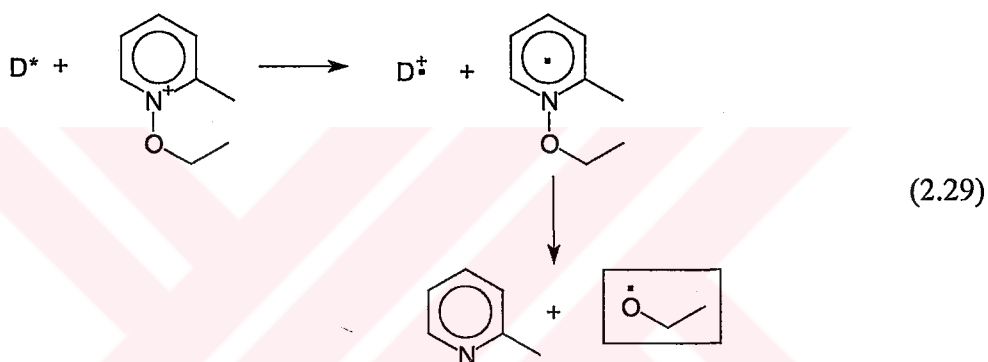
The decomposition of diazonium salts by excited xanthene dyes (eosin, erythrosin, rhodamin B) in ethanol solution has been attributed to the oxidation of the dye [133]. These systems were employed for a photopolymerization process in which vinyl monomers (vinylpyrrolidone, bis(acrylamide)) were crosslinked by visible light [134]. The initiation is depicted below:



The oxidation of various dyes by iodonium salts and the use of these systems for free radical polymerization has been reported by several authors [135]. While the radical initiating species derive from the onium salt, dye radical cations are able to initiate cationic polymerizations (reaction 2.28).



Pyridinium salt has been reduced by anthracene. This reaction was utilized for the light induced polymerization of methyl methacrylate. In this case, ethoxy radicals have been found to react with monomer molecules (reaction 2.29) [136].



2.2.2 Photoinitiated Cationic Polymerization

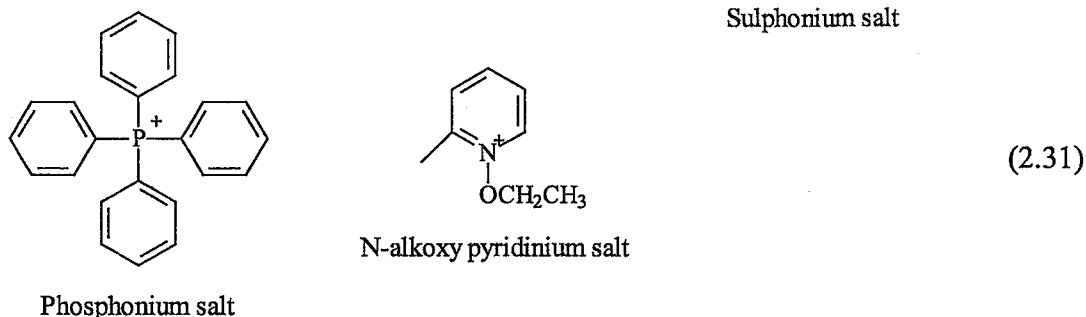
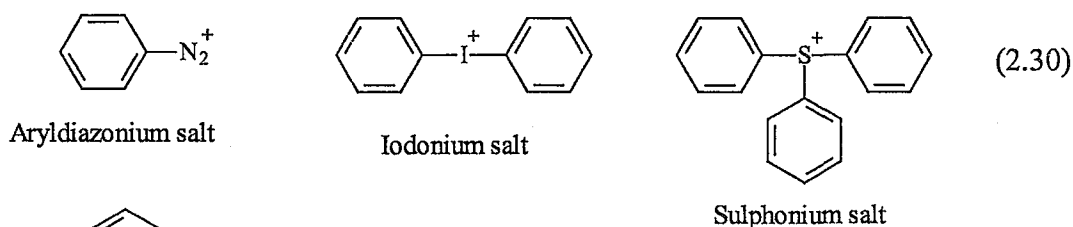
UV-initiated cationic photopolymerizations exhibit several advantages when compared with the free-radical photopolymerization. First of all the cationic photopolymerizations are not inhibited by oxygen. This feature provides a significant practical advantage for industrial processes since it is not necessary to blanket the system with nitrogen to achieve rapid cure rates. Secondly, in contrast to the free-radical photopolymerizations which experience a rapid decrease in polymerization rate when the light source is removed (due to radical–radical termination reactions), the cationic polymerizations proceed long after the irradiation has ceased, consuming nearly all of the monomer. Finally, cationic photopolymerization is a very versatile technique and may be used to polymerize important classes of monomers, including epoxides and vinyl ethers. Although these classes of monomers cannot be cured by free-radical photopolymerizations, they exhibit many desirable properties, including low volatility, good rheological properties, and low toxicity [137]. Furthermore, the

cured polymer films associated with these monomers exhibit excellent clarity, adhesion, abrasion resistance, and chemical resistance. In addition, the cationic ring-opening polymerizations of epoxides exhibit less shrinkage, as low as 1–2% [138,139], than do polymerizations of unsaturated monomers such as acrylates and methacrylates, which is typically 5–20%. However, the presence of water vapor may impede the cationic curing, notably if thin films are cured at a low light intensity.

In spite of the above mentioned advantages, cationic polymerization has not 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 [140].

Since the photoinitiator is one of the most important parts 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.

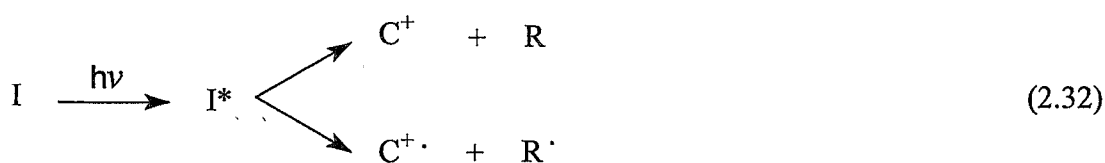
Onium salts depicted in (2.30) and (2.31) are the most widely employed cationic photoinitiators. They mainly absorb light with wavelengths between 225 and 350 nm [141-144]. These salts are compounds containing heteroatoms, with a cationic center on the heteroatom. As counterions, mostly inorganic metal complex anions are used.



Upon irradiation of the onium salt, a cation can be formed either directly or through interaction of the onium salt with a sensitizer. This latter process is termed indirect excitation of the photoinitiator (indirect photolysis).

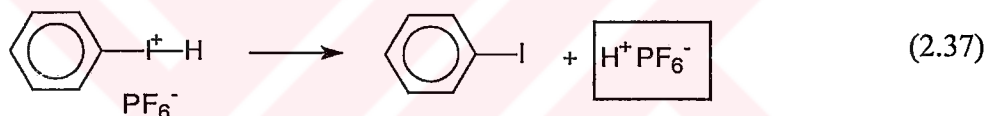
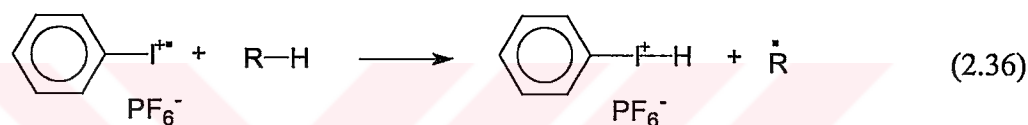
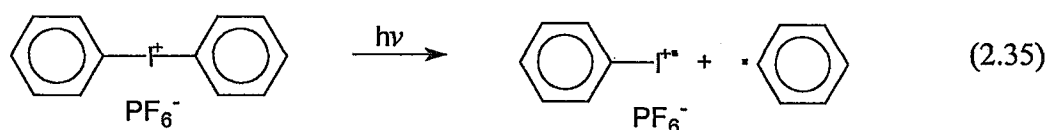
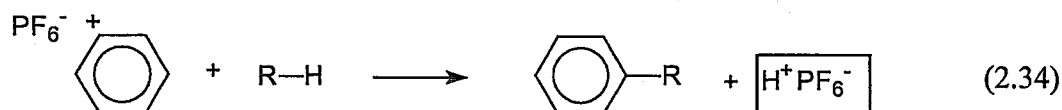
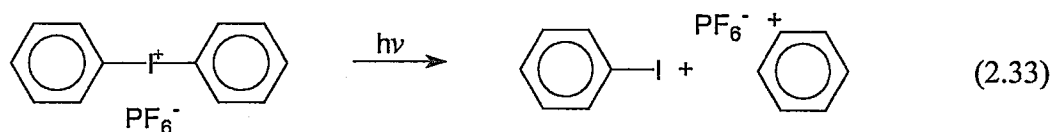
2.2.2.1 Direct Photolysis

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 (reaction 2.32).



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 (reactions 2.33-37).



2.2.2.2 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. One possible pathway is the chemical attachment of chromophoric groups to the onium salt making it absorb at higher wavelengths.

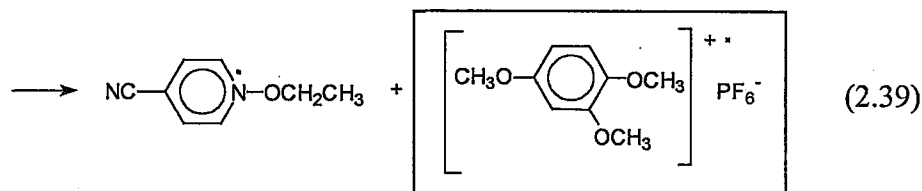
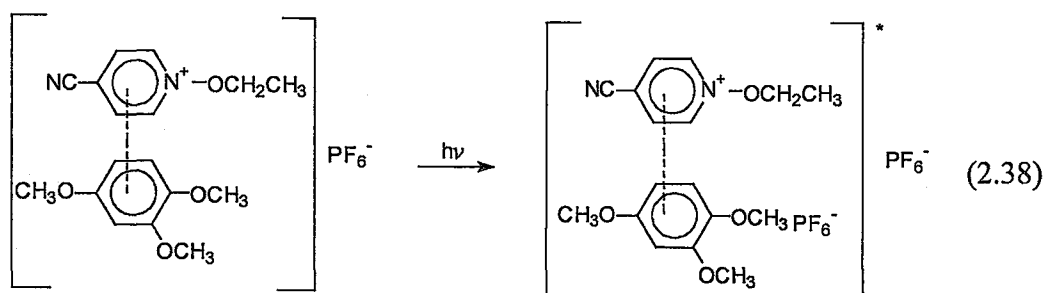
Besides that, appropriate chemicals may be added to the polymerization mixture. Some aromatic compounds, like 1,2,4-trimethoxybenzene or hexamethylbenzene are able to form “charge-transfer (CT) complexes” with pyridinium salts. Being formed in the electronic ground state, these complexes exhibit higher optical absorptions than

the pyridinium salt alone. In these circumstances, the incident light is absorbed by the CT complexes.

Furthermore, strongly light absorbing compounds may be added to the polymerization mixtures. At the wavelength chosen for the polymerization, the onium salt initiator is virtually transparent. Incident light is almost entirely absorbed by the additive. Provided the systems thus obtained do initiate cationic polymerizations, the initiation can be explained through one of the following mechanisms: "Classical energy transfer", "electron transfer via exciplexes", "oxidation of free radicals", and "addition fragmentation reactions".

a) Charge-transfer Complex Initiated Cationic Polymerization

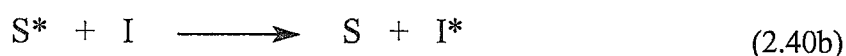
Pyridinium salts are capable of forming charge transfer (CT) complexes with electron rich donors such as methyl- and methoxy-substituted benzene [145]. Notably, these complexes absorb at relatively high wavelengths, where the components are virtually transparent. For example, the complex formed between *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 2.38 and 2.39 for the initiation of the cationic polymerization has been suggested [145].



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.

b) Classical Energy Transfer

This mechanism involves the electronic excitation of the sensitizer, a molecule possessing a suitable absorption spectrum, to its excited state (2.40a). Energy may be transferred from the sensitizer (S^*) to the onium salt (I) by either resonance excitation or exchange energy transfer. Depending upon the two components involved the energy transfer may proceed either in the excited singlet or in the triplet state.



In consequence of the transfer process, the sensitizer returns to its ground state and excited onium salt species (I^*) are formed (2.40b). Further reactions may also differ from those, taking place when the onium salt is excited by direct absorption of light. This conclusion has been drawn on the bases of product analyses [146]. An obvious

explanation for this difference is the spin multiplicity: in the below discussed sensitized excitations triplet states of the onium salts are populated. In contrast to this, through direct irradiation of the onium salt, electrons are excited primary to the singlet state.

A sufficient energy transfer requires the excitation energy of the sensitizer $E^*(S)$ to be at least as large as the excitation energy of the photoinitiator $E^*(I)$ (Eq:2.8).

$$E^*(S) \geq E^*(I) \quad (\text{Eq:2.8})$$

The photopolymerization with most onium salts can be sensitized by commonly used photosensitizers, such as acetophenone or naphthalene. However, in many cases this reaction does not proceed via energy transfer, since most onium salts are capable of oxidizing these sensitizers in an exciplex formed between sensitizer and onium salt.

In Tables 2.5 and 2.6, the triplet energies of two onium salts and selected photosensitizers are summarized.

Diphenyliodonium cations were excited to their first excited triplet state by energy transfer from *m*-trifluoromethyl acetophenone [147]. As seen from Tables 2.5 and 2.6, the energy transfer is energetically allowed. Electron transfer in the exciplex can be excluded, since the oxidation potential of *m*-trifluoromethyl acetophenone is relatively low. The oxidation potential of unsubstituted acetophenone is about 0.2 V higher than that of *m*-trifluoromethyl acetophenone. The former was found to sensitize the photoreactions of diphenyliodonium salts via electron transfer in the exciplex state.

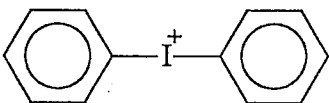
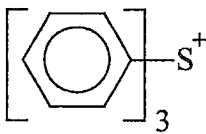
In the case of triphenylsulphonium salts, energy transfer may occur from sensitizers with triplet energies above or equal to 314 kJ/mol. It has been shown that in the presence of both acetophenone and 1-indanone diphenylsulphide is formed at wavelengths, at which the sulphonium salt is transparent but the sensitizers absorb light [146].

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

Photosensitizer	$E^{\text{ox}}_{1/2}$ (V)	E^* (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)

Although the triplet state of triphenylsulphonium salts is considered to be labile, it can be the precursor of chemical reactions [148]. However, the product distribution after sensitized decomposition was found to differ significantly from that obtained after direct irradiation. Products, predicted to be generated by homolytic bond rupture have not been detected after triplet sensitized decomposition. In direct irradiation, the singlet state is populated giving rise to predominantly heterolytic C-S-bond scissions.

Table 2.6: Reduction Potential and Triplet Excitation Energies of Selected Onium Ions

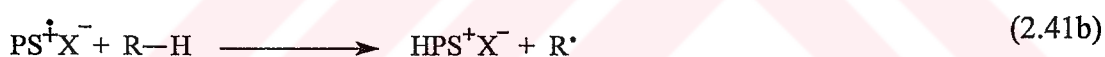
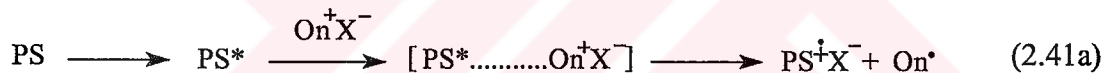
Onium Cation	$E^{\text{red}}_{1/2}$ (V) (vs SCE)	E^*_t (kJ mol ⁻¹)
	-0.2	268
	-1.1	314

Energy transfer sensitization did not turn out technically useful, although being a possible pathway in starting the decomposition of onium salts. The reason is that the

high triplet energies required allow only the use of sensitizers absorbing at wavelengths below 350 nm. Other multicomponent initiating systems show a more practical spectral response.

c) Electron Transfer via Exciplexes

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 of cationic initiation, the following general mechanism holds (2.41a-c):



The electron transfer is energetically allowed, if ΔG calculated by (Eq:2.9) (extended Rehm-Weller equation) is negative.

$$\Delta G = F [E^{\text{ox}}_{1/2}(\text{S}) - E^{\text{red}}_{1/2}(\text{On}^+)] - E(\text{S}^*) \quad (\text{Eq:2.9})$$

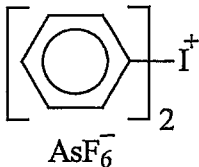
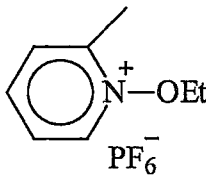
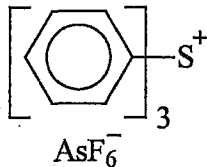
F ... Faraday constant

$E(\text{S}^*)$... Excitation energy of the sensitizer (singlet or triplet)

Since the oxidation potentials of sensitizers $E^{\text{ox}}_{1/2}$ 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}

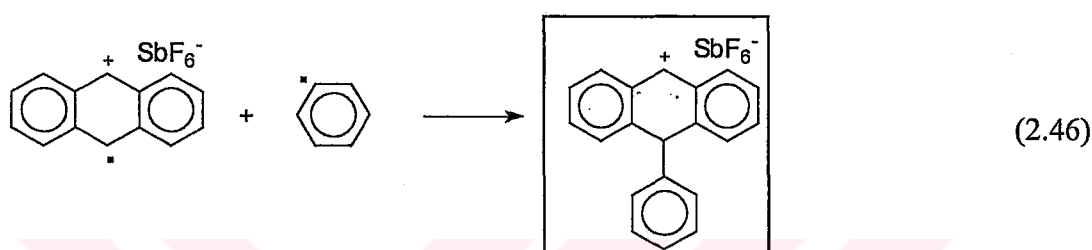
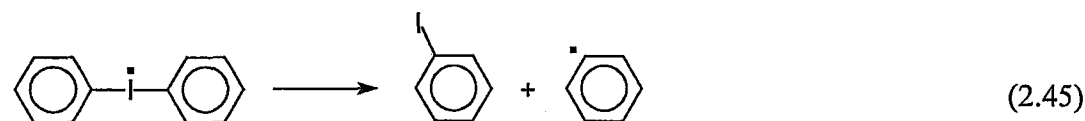
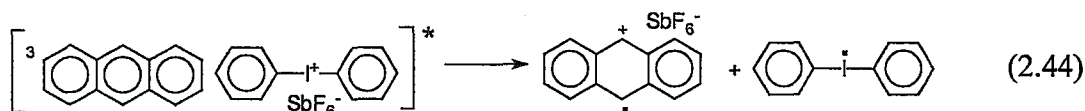
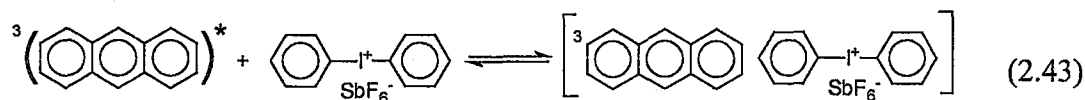
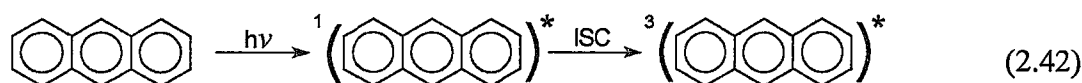
						
<i>Sensitizer</i>	ΔG	<i>sens.</i> ^a	ΔG	<i>sens.</i> ^b	ΔG	<i>sens.</i> ^a
Benzophenone	- 8	+	+ 39.8	-	+ 88	-
Acetophenone			+ 41.2	-		
Thioxanthone	- 92	+	- 44.2	+	+ 4	-
Anthracene	- 193	+	- 144.4	+	- 96	+
Perylene	- 171	+	- 121.8	+	- 71	+
Phenothiazine	- 159	+	- 112.9	+	- 63	+

^apolymerization of the diepoxide 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate [149]

^bpolymerization of cyclohexene oxide [150]

However not all sensitizers are suitable in conjunction with onium salts. According to Eq:2.9, the requirements are low oxidation potentials, $E^{\text{ox}}_{1/2}$, and relatively high excitation energies E^* of the sensitizer. It should also be noticed that only onium salts with high (low negative) reduction potentials $E^{\text{red}}_{1/2}(\text{On}^+)$, such as diphenyliodonium or alkoxy pyridinium salts, are easily reduced by sensitizers.

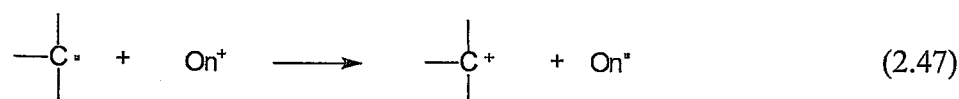
The sensitization of onium salts (Ar_2I^+ and Ar_3S^+) by anthracene has been investigated in detail in a number of papers [151,152]. Exciplex formation is followed by a partly loss of anthracene's aromatic system as concluded from the decrease in the sensitizer fluorescence. These reactions are illustrated in reactions 2.42-2.46 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 [153].



The sensitization of thioxanthone follows only partly the general mechanism described for the exciplex formation [153]. To some extent, this sensitization is based upon the oxidation of photolytically formed radicals.

d) Oxidation of Free Radicals

Radicals formed through photochemical treatment of various compounds, such as benzoin derivatives, acylphosphine oxides, amines, vinyl halides, polysilanes, can be oxidized by onium salts according to the following reaction (2.47):



The cations thus generated are used as initiating species for cationic polymerization. This process is usually termed as the free radical promoted cationic polymerization and is an elegant and fairly flexible type of sensitized cationic polymerization [154].

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 $E_{\text{red}}^{1/2}(\text{On}^+)$.

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. 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 2.10) whether a radical can be oxidized by a given onium salt or not.

$$\Delta G = F [E_{\text{ox}}^{1/2}(\text{R}^\cdot) - E_{\text{red}}^{1/2}(\text{On}^+)] \quad (\text{Eq:2.10})$$

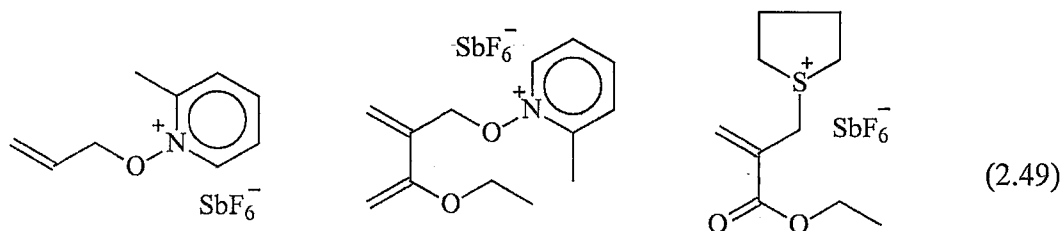
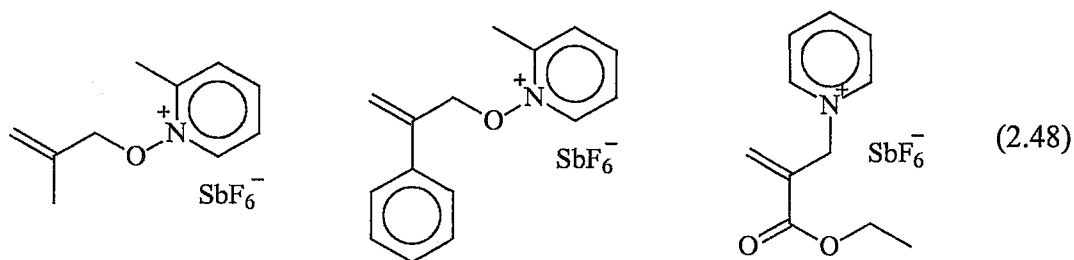
However, the calculation of ΔG is usually not feasible since the exact oxidation potentials $E_{\text{ox}}^{1/2}(\text{R}^\cdot)$ of most radicals involved in radical promoted polymerizations are unknown.

Bi and Neckers [38] demonstrated cationic photopolymerizations of epoxides initiated using a three-component initiator system containing a variety of xanthene dyes, amines with low basicity, and iodonium salts with a nonnucleophilic anion. Using this system, the polymerization was initiated by a tungsten lamp equipped with filters that eliminated light below 520 nm (where the iodonium salt does not directly absorb light). The authors further reported that presence of all the three components is required for photopolymerization above this wavelength. The authors attributed the reaction to a mechanism with three primary steps: absorption of light by the dye; production of radicals by reaction of the photoexcited dye with the amine; and production of initiating carbocations by oxidation of the radicals by the iodonium salt.

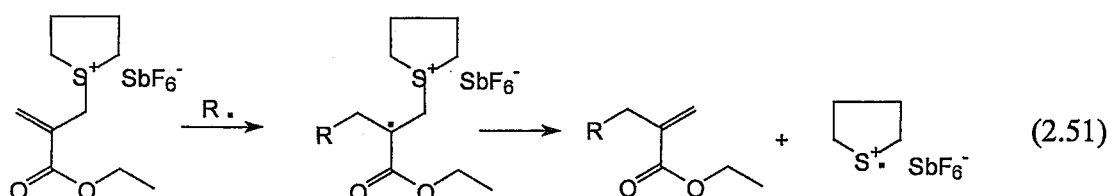
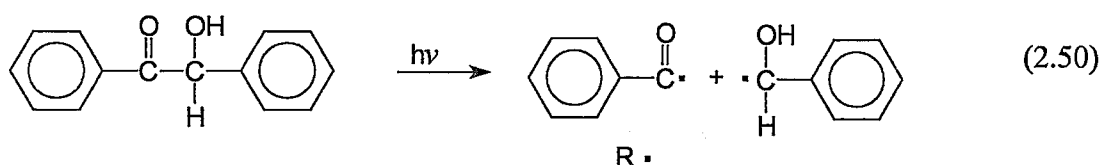
Three-component initiator systems are flexible and versatile photoinitiators that were initially developed for free-radical photopolymerizations, but may, with careful selection of the components, be used for cationic photopolymerizations. Such systems offer a number of advantages that have been demonstrated in free-radical photopolymerizations, and are also relevant for cationic photopolymerizations. For example, a wide variety of dyes may be used with the same electron donor and iodonium salt, thereby providing tremendous flexibility in selection of the initiating wavelength and therefore the light source. Indeed, effective visible-light-sensitive systems may allow the use of very inexpensive light sources such as halogen and tungsten incandescent lamps. In addition, three-component systems have consistently been found to be faster, more efficient, and more sensitive than other photoinitiator systems.

e) Addition-Fragmentation Reactions

Allylic salts can undergo addition fragmentation reactions, providing the advantage of using virtually all sorts of thermal and light-sensitive radical initiators for cationic polymerization. In contrast to radical promoted cationic polymerization based on the oxidation of radicals, this route is not limited to oxidizable radicals. Various addition-fragmentation agents (AFAs) used in cationic polymerization are illustrated as follows (2.48 and 2.49):



The mechanism of the addition fragmentation type initiation is depicted below on the example of ETM salt and benzoin photoinitiator (reactions 2.50 and 2.51).



The first step consists of 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 allyl onium 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 [155].

2.3 Telechelic Polymers

Telechelic polymers are macromolecules that possess two reactive end groups. The range of monomers and functional groups employed in the preparation of telechelic polymers has been expanded in recent years owing to developments in the controlled radical polymerization routes as well as metathesis polymerization. A lot of new catalysts, used in metathesis polymerization, have been developed and applied to the preparation of advanced materials [156,157].

A telechelic contains end groups that react selectively to give a bond with another molecule. Depending on the functionality, which must be distinguished from the functionality of the end group itself, telechelics can be classified as mono-, di-, tri-, and multi-functional telechelics (polytelechelics). The functionality (f) is defined as follows (Eq:2.11):

$$f = \frac{\text{number of functional groups}}{\text{number of polymer chains}} \quad (\text{Eq:2.11})$$

Telechelic polymers can be used as cross-linkers, chain extenders, and precursors for block and graft copolymers. Furthermore, star and hyper-branched or dendritic polymers are obtained by coupling reactions of monofunctional and multifunctional telechelics with appropriate reagents. A variety of macromolecular architectures obtained by the reactions of telechelics are represented in Figure 2.2.

The end group functionality, whether it is mono- or bi-functional, is also important. Telechelic polymers carrying bifunctional groups such as vinyl groups are called macromolecular monomers or macromonomers because they can participate in polymerization reactions, yielding graft copolymers or networks.

Industrial use of telechelics was encouraged by the development of thermoplastic elastomers (TPE). Liquid telechelic polymers are the basis for reaction injection moulding (RIM). Liquid telechelics that can be used for network formation offer advanced processibility and may result in materials with improved properties [158].

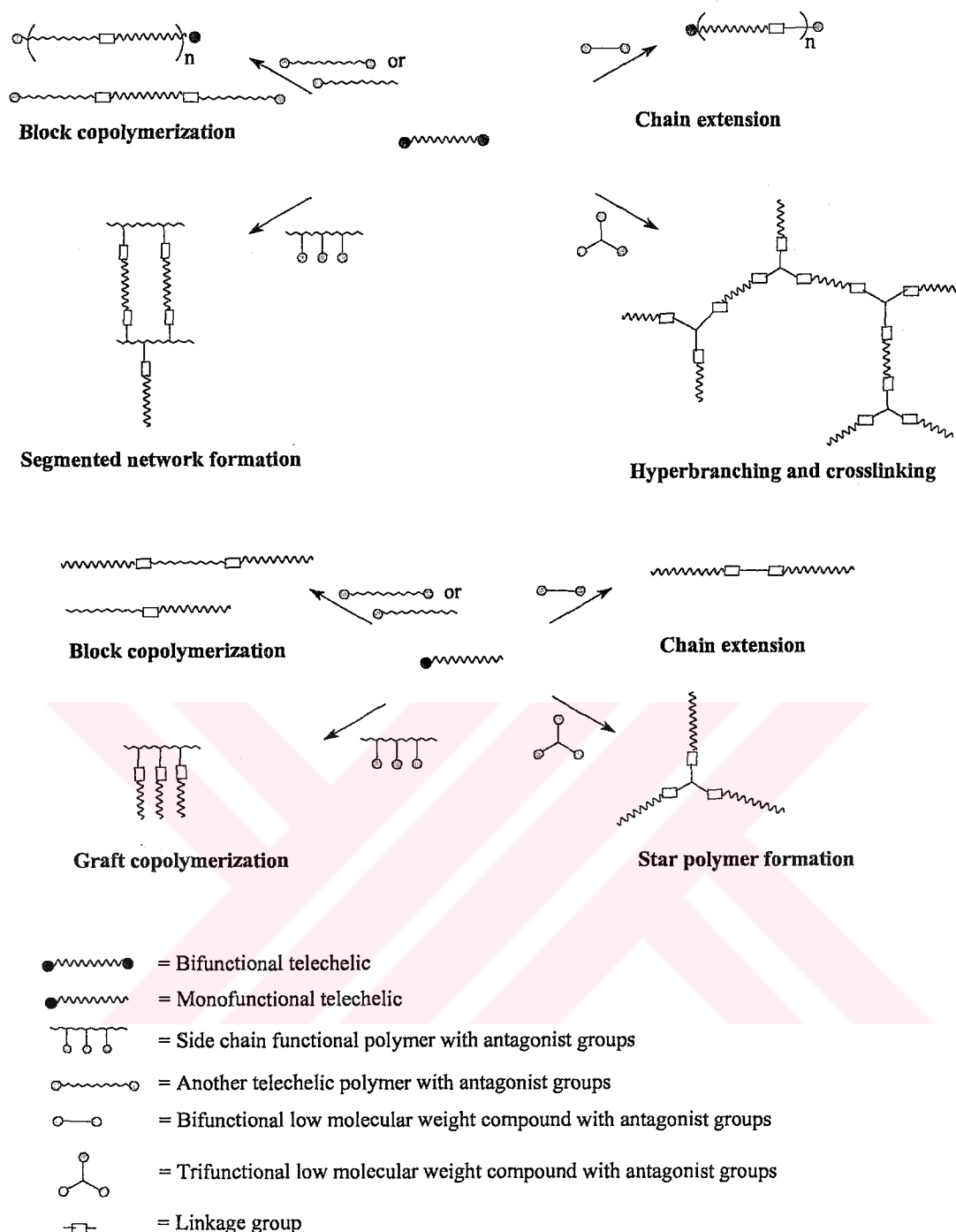


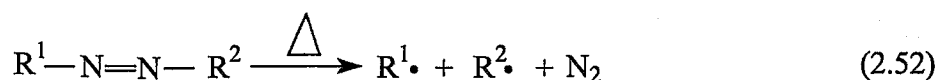
Figure 2.2 : Various architectures obtained by the reactions of telechelics

2.3.1 Preparation of Telechelics by using Radical Polymerization Method

Telechelics can be synthesized by radical polymerization in two ways. End groups can be controlled with a large number of initiators (dead-end polymerization), or

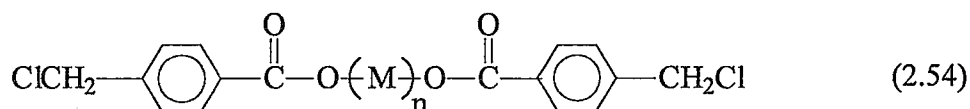
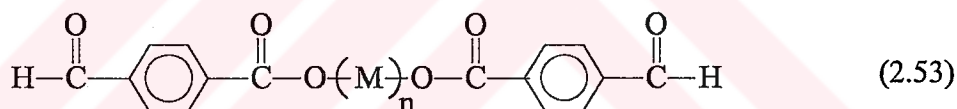
polymerization can be conducted in the presence of suitable transfer agents (telomerization) [159].

Telechelics can be prepared from thermally labile azo compounds. Upon heating the aliphatic azo compounds, nitrogen is evolved, and two carbon centered free radicals are formed (reaction 2.52).

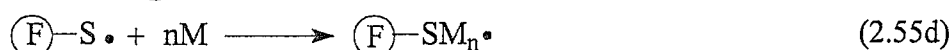
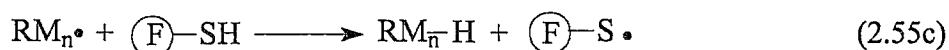


In order to obtain telechelics, the initiating azo compound has to be at least bifunctional - it must carry one or more functional sites other than the azo function itself. Due to the potential variability in the chemical nature of the azo initiators it is possible to prepare telechelics with a wide variety of functional groups [160-162].

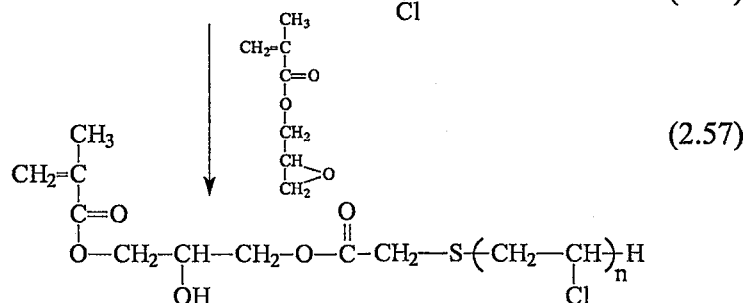
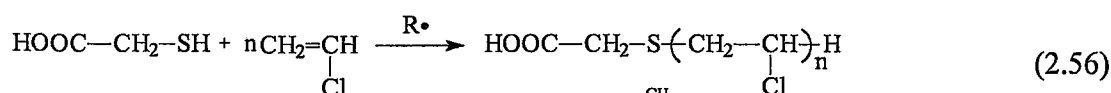
Aroyl peroxides give styryl telechelics [163]. When employing benzoyl peroxides *p*-substituted with formal groups (2.53) or chloromethyl (2.54), the telechelics require no further modification before being used as prepolymers.



In addition to the initiator controlled polymer functionalization, transfer reactions may result in functional polymers. In free radical polymerization, thiols are often employed as chain transfer agents. Chain transfer reactions involving thiols proceed via atom abstraction as illustrated below (2.55a-d):



Consequently, these molecules do not offer any scope for introducing functionalities at both ends. However, monofunctional telechelics have been successfully prepared by using thiols. For example, Boutevin and co-workers [164] introduced polymerizable vinyl groups to polyvinylchloride using 3-Mercaptopropionic acid as functional chain transfer agent. Carboxylic acid group has then been reacted with glycidyl methacrylate (reactions 2.56 and 2.57).

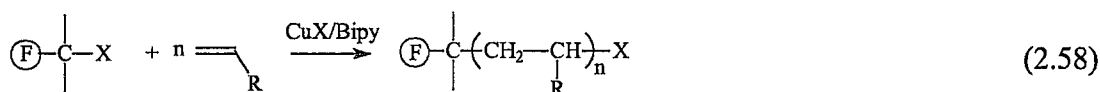


2.3.2 Preparation of Telechelics by using Controlled Radical Polymerization Methods

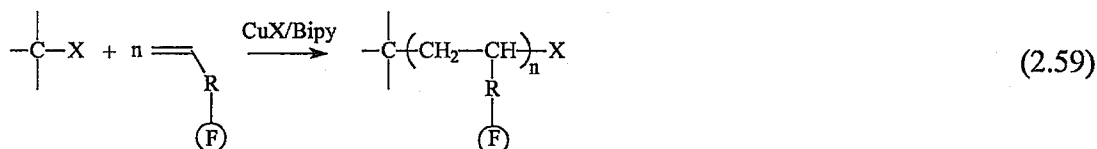
Polymer functionalization by ATRP can be achieved by using functional initiators and monomers and the chemical transformation of the halogen end groups. These routes are summarized in reactions 2.58-2.60.

Quite a number of functional initiators were successfully used in ATRP to prepare functional styrene and acrylate type polymers [165].

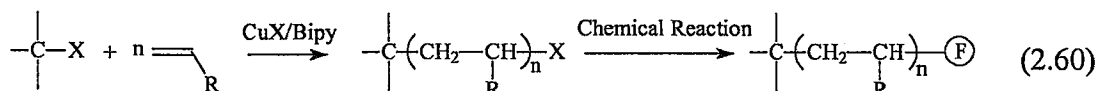
Through Initiator Functionality



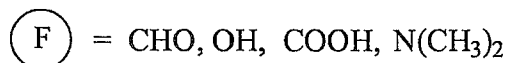
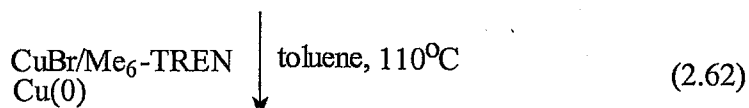
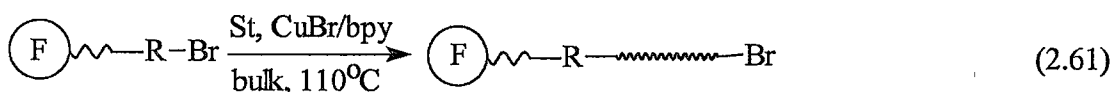
Through Monomer Functionality



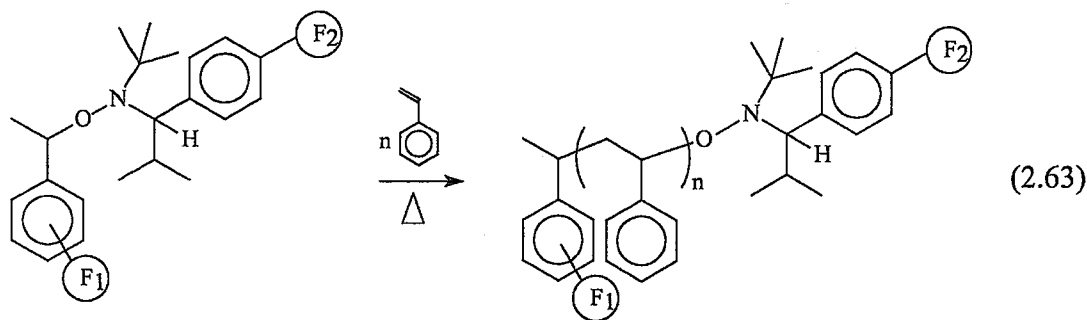
Through Chemical Reaction of Halide End Groups



Bifunctional telechelics can be synthesized via atom transfer coupling process. In a recent work [166], polymers monofunctionalized with aldehyde, aromatic hydroxyl, dimethyl amino groups were obtained by ATRP of styrene using functional initiators in the presence of the CuBr/bpy catalytic complex. Bifunctional telechelics with double molecular weights as compared to the starting materials, were prepared by coupling of monofunctional polymers in atom transfer radical generation conditions, in the absence of monomer, using CuBr as catalyst, tris[2-(dimethylamino)ethyl]amine (Me₆TREN) as ligand, Cu(0) as reducing agent and toluene as solvent. The overall process is depicted below (reactions 2.61 and 2.62).



It is also possible to prepare telechelic polymers by NMP procedure since it tolerates a wide variety of functional groups [167]. For the synthesis of telechelics by NMP there are two general methods, i.e., functional groups can be placed at the initiating chain end, F₁, or the nitroxide mediated chain end, F₂ (reaction 2.63).



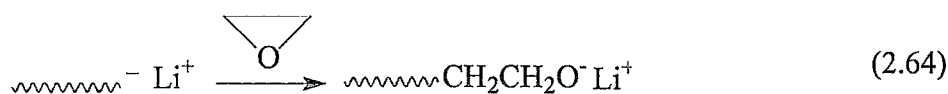
Telechelics with a variety of functional groups can essentially be prepared by using functional nitroxides [168-170].

2.3.3 Preparation of Telechelics by Using Anionic Polymerization Method

Anionic polymerization [171] and, in particular, living polymerization can be used for the synthesis of telechelics. Living polymerisation is characterized by the absence of termination and transfer, by narrow dispersity that can be described by a Poisson distribution, and by linear increase of molecular weight with conversion. The propagating species are carbanions or other negatively charged species. Bivalent growing chains allow the generation of two terminal end groups and the facile synthesis of telechelic polymeric materials, depending on the monomer, initiator, solvent, and termination agent.

Termination of bifunctional living polystyrene by solid CO_2 yields polymers with carboxyl end groups [172]. Because of its commercial potential, this reaction has been studied in depth. In addition to carboxyl groups (60 %), dimeric ketones (30 %) and trimeric carbinols (10 %) are formed with gaseous CO_2 .

Living polystyrene, terminated by the addition of ethylene oxide, generates hydroxylate end groups as illustrated in reaction 2.64.



The alcoholate ion can initiate the polymerization of ethylene oxide, but since the rate is low, polyether formation can be avoided by quenching immediately after termination.

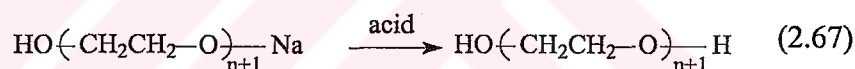
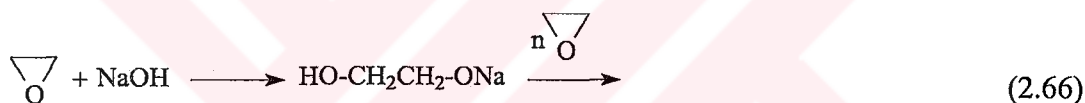
Telechelics with halide terminal groups can be prepared by the reaction of living polymers with a halogen or an excess of primary α,ω -dihalides as depicted in reaction 2.65 [173].



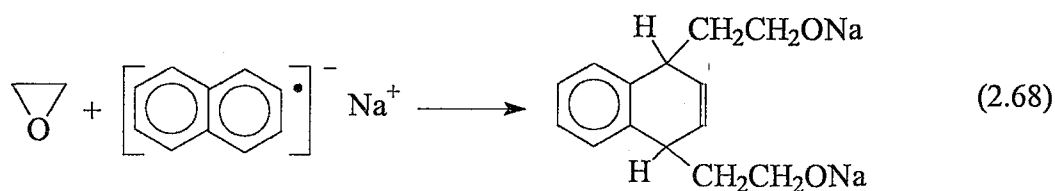
2.3.4 Preparation of Telechelics via Ring-opening Polymerization

The synthesis of telechelics by ring opening has attracted great interest because of the commercial potential of the resulting compounds, such as polyether polyols. The end groups are introduced by initiation, end capping, or transfer reactions.

Both anionic and cationic polymerization can be used to synthesize telechelics from oxiranes. Anionic polymerization of oxirane (ethylene oxide) yields α,ω -dihydroxy poly(ethylene oxide) as illustrated in reactions 2.66 and 2.67 [174].

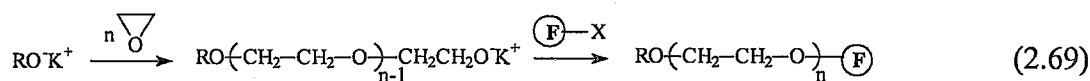


Polymerization with sodium naphthalene yields two simultaneously growing chains (reaction 2.68).



Hydroxyl end-groups can be converted to various other functional groups [175]. Oxirane telechelics can be synthesized either by one of the following methods; (a) end-capping of the living polymerization (termination method) (reaction 2.69), (b) initiation of living polymerization (reaction 2.70), and (c) transformation of hydroxyl end-groups [176].

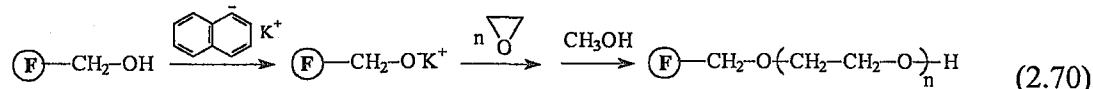
Termination



X = Cl, C(O)Cl

F = Functional group

Initiation



This way many poly(ethylene oxide)s with various functional groups were prepared [177]. Moreover, suitable combinations of termination and initiation methods yield heterofunctional telechelics.

2.3.5 Macromonomers

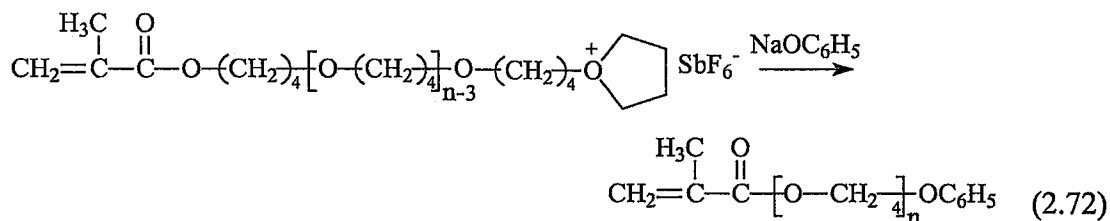
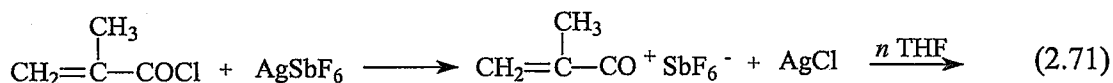
Macromolecular monomers, called macromonomers or macromers, can be defined as oligomers or polymers with polymerizable end groups. Such groups may be vinyl, acrylic, or heterocyclic (ring-opening polymerization) or dicarboxylic or dihydroxylic (step-growth polymerization). The increasing interest in these materials stems from the growing need for well-defined graft copolymers for which macromonomers often are an ideal starting material [178-180]. The length and number of branches of the graft copolymers can be controlled by the molar mass and feed ratio of macromonomers to comonomers.

There are basically three methods for preparing such reactive polymers:

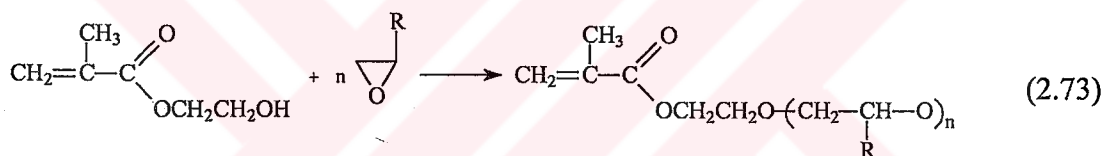
1. On choosing an initiator containing a polymerizable group, macromonomers can be derived provided this reactive group is totally inert toward the active species generated by its carrier.
2. Macromonomers can also be obtained by functionalization of growing chains. Again, it is essential that the end-capping reaction does not involve the polymerizable group.
3. The last route consists in modifying o-functional polymers into macromonomers using post-functionalization methodologies. When chains are

grown by free-radical polymerization, it is the easiest way to prepare macromonomers.

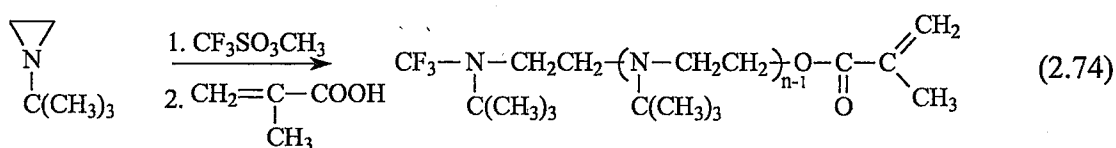
For example, telechelics were prepared through the first route from polytetrahydrofuran (PTHF) as illustrated in reactions 2.71 and 2.72.



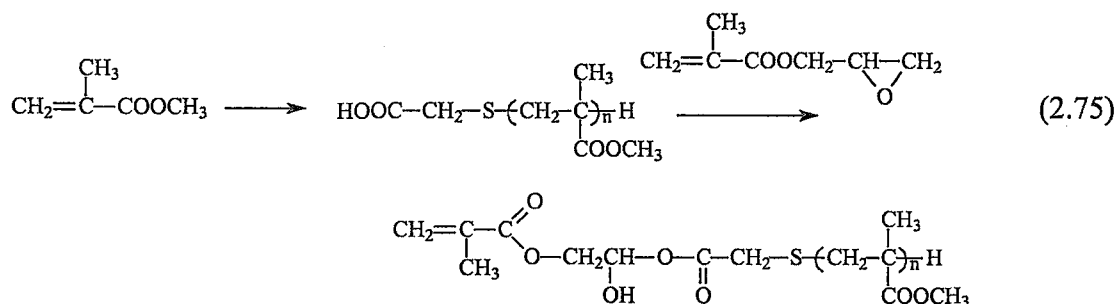
Oxiranes also polymerize under similar conditions (reaction 2.73).



Termination of the cationic ring-opening polymerization of *N*-*t*-butylaziridine with methacrylic acid yields macromonomers [181], which is the case of functionalization of growing chains through end-capping reactions (2.74).



Another example to this type employs radical polymerization in the preparation of macromonomers as shown in reaction 2.75 [182].



As for macromonomers derived by post-functionalization, an example was described by Haddleton and colleagues [183]. Starting from separately prepared o-bromo PMMA, they obtained o-unsaturated macromonomers on addition of methyl(2-bromomethyl)acrylate (MBrMA), a monomer known to undergo addition-fragmentation.

2.4 Copolymers

2.4.1 Statistical, Gradient and Alternating Copolymers

When two or more comonomers are simultaneously copolymerized, either of statistical, gradient, or alternating copolymers can be obtained (Figure 2.3). This is a simple and common way to prepare polymers with modified or improved mechanical and physical properties. The type of copolymer to be prepared is highly dependent on the reactivity ratios of the comonomers since relative rate of incorporation of each monomer is determined by its reactivity ratio. One can get statistical copolymers upon choosing comonomers with reactivity ratios close to 1. In this case, the radical chain ends tend to react with either type of monomers. Conventional free radical polymerization can simply be used in obtaining statistical copolymers. The samples formed contain polymer chains with different comonomer composition, because comonomers are often consumed at different rates—unless being copolymerized under azeotropic conditions—and also because the lifetime of growing radicals is very short. “Random copolymers” refers to a specific type of copolymers, which results when Bernoullian statistics is followed during copolymerization. However, polymerization may follow other types of statistics, such as Markovian, resulting in a variety of statistical copolymers.

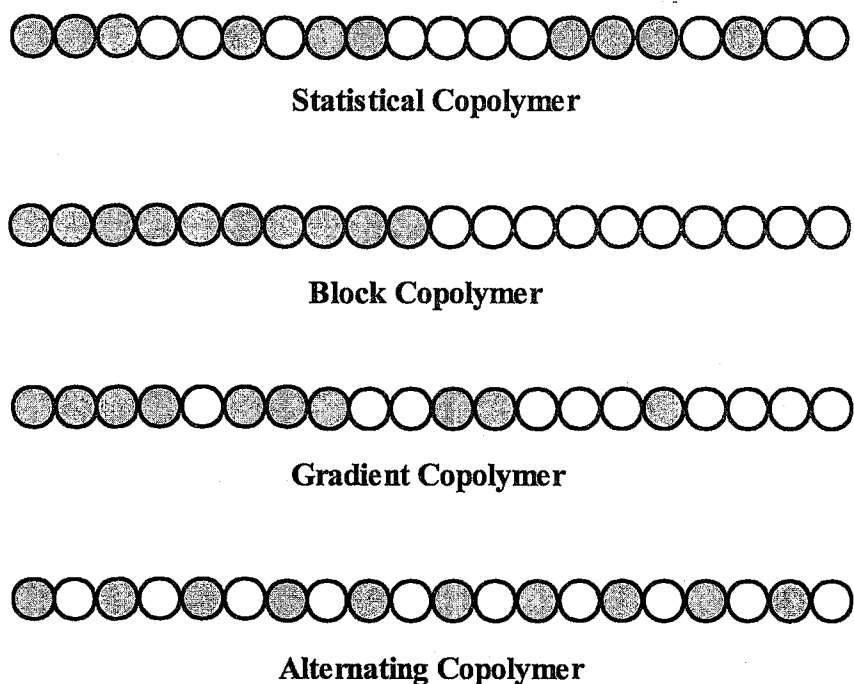


Figure 2.3 : Schematic representation of miscellaneous copolymers of various compositions

Choosing both reactivity ratios significantly higher than 1 results in a more blocky structure, because the radical would prefer to homopropagate rather than cross-propagate.

In controlled and/or, “living” copolymerizations, all chains grow simultaneously nearly at the same rate and therefore have the same chemical composition. The drift in the comonomer ratio that occurs is recorded in all individual chains; the composition in the copolymers formed continuously changes from one end to the other. Such copolymers are termed gradient or tapered copolymers. They are intermediates between statistical and block copolymers, as illustrated in Figure 2.3. Gradient copolymers are expected to exhibit distinct physical properties as compared to those of random or block copolymers of same composition. These copolymers result from copolymerizations, in which one active species would prefer to homopropagate and the other to cross-propagate, but neither tendency is extreme.

Alternating copolymers are obtained when both reactivity ratios are much lower than 1, indicating that both radicals would prefer to cross-propagate. Maleic anhydride and styrene are examples of monomers that spontaneously undergo alternating copolymerization by RP, especially if the reaction temperature is kept below 80°C. Li

and colleagues observed that the atom transfer radical copolymerization of maleimide derivatives—namely, *N*-(2-acetoxy-ethyl) and *N*-phenylmaleimide—with styrene produced well-defined copolymers with predominantly alternating structures, whatever the comonomer feed ratio employed [184,185].

2.4.2 Block Copolymers

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 [186,187]. 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 compatibilizers, 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 [188,189].

A number of techniques for the preparation of block copolymers have been developed [39,190]. These will be described in detail in the following parts.

2.4.2.1 Block Copolymers by Anionic Polymerization

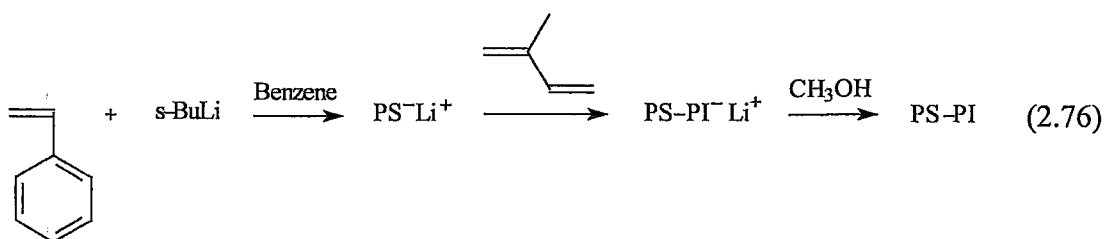
Anionic living polymerization is a powerful synthetic tool for the preparation of well-defined polymers, i.e., narrow molecular weight distribution polymers with controlled molecular characteristics including molecular weight, composition, microstructure, and architecture. Its ability to form well-defined macromolecules is mainly due to the absence of termination and chain transfer reactions, under appropriate conditions.

Under appropriate experimental conditions, due to the absence of termination and chain transfer reactions, carbanions (or, in general, anionic sites) remain active after

complete consumption of monomer, giving the possibility of block copolymer formation, in the simplest case, by introduction of a second monomer into the polymerization mixture. However, a variety of different synthetic strategies have been reported for the preparation of linear block copolymers by anionic polymerization.

Linear AB block copolymers are the simplest block copolymer structures where two blocks of different chemical structures are linked together through a common junction point. The most general method for the preparation of AB block copolymers is sequential monomer addition. In this method one of the monomers is polymerized first. After its complete consumption, the second monomer is added, and the polymerization is again allowed to proceed to completion. At this point an appropriate terminating agent is added, and the diblock copolymer can then be isolated (usually by precipitation in a nonsolvent).

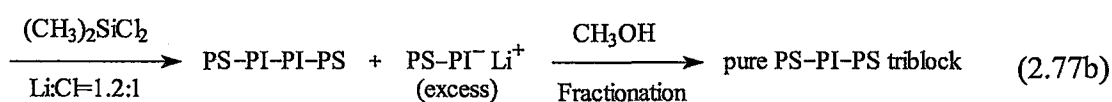
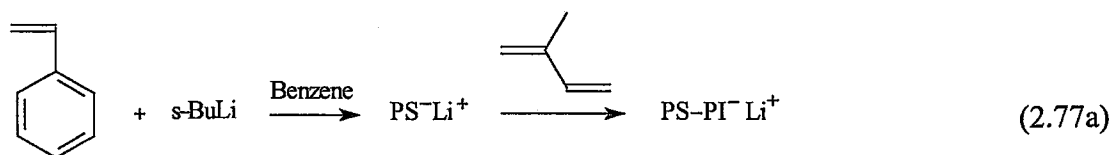
A wide variety of diblock copolymers of styrene and isoprene or butadiene, having predictable molecular weight and composition as well as narrow molecular weight and compositional distribution, have been synthesized by sequential addition of monomers [191]. Synthesis of these diblocks starts with styrene, and then the diene is added to the reaction mixture because it is well established that PSLi active centers can initiate efficiently the polymerization of dienes in hydrocarbon solvents (reaction 2.76).



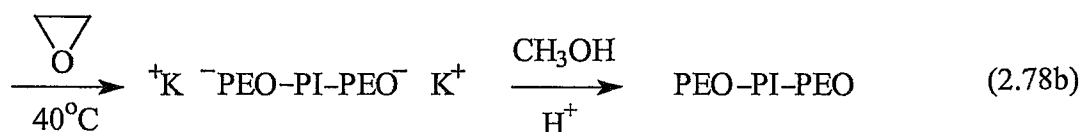
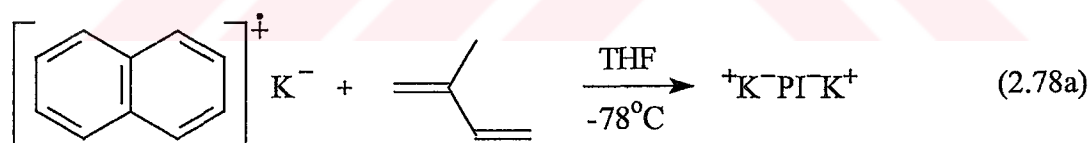
A variety of triblock copolymer architectures, i.e., block copolymers containing three sequences of monomers, are possible because they can be comprised of two (ABA copolymers) or three (ABC terpolymers) different monomers. Each type of triblock can be synthesized according to an appropriate synthetic pathway depending on the monomers used and their sequence in the triblock chain.

In the coupling methodology, a living diblock AB copolymer, having the same composition but half the molecular weight of the final triblock copolymer, is

synthesized by sequential addition of monomers. Then an appropriate coupling agent, i.e., a compound having two functional groups able to react with the active anions forming covalent bonds, is used to connect two AB chains producing the desired symmetric triblock copolymer. PS-PI (or PBd)-PS triblock copolymers have been synthesized by the coupling method by Morton and coworkers [191] using $(\text{CH}_3)_2\text{SiCl}_2$ as the coupling reagent (reactions 2.77a,b).



In another strategy, difunctional initiators can be used. PEO-PI-PEO symmetric triblock copolymers were synthesized using sodium or potassium naphthalene as the difunctional initiator [192]. Isoprene was polymerized first followed by addition of ethyleneoxide (reactions 2.78a,b). The copolymers had a variety of block compositions. Their molecular weight distributions were narrow and monomodal.



The usual method of choice for the synthesis of linear triblock copolymers consisting of three different monomers (ABC Triblocks) by anionic polymerization is the sequential three-step addition of monomers [193,194]. As in the case of simple AB diblocks, the most important part of the design of the synthetic methodology to be followed is the order of monomer addition.

2.4.2.2 Block Copolymers by Cationic Polymerization

Advances in cationic polymerization methodology, starting in the middle 80s with the discovery of the true living cationic polymerization of vinyl ethers by Higashimura et al. [195], have shown their real potential for the synthesis of tailor-made macromolecules. In recent years, many investigations have demonstrated that almost all classes of cationically polymerizable vinyl and alkene-type monomers can be polymerized in a controllable way [196]. The formation of polymers having predictable molecular weight and narrow molecular weight distributions gives unambiguous experimental evidence for elimination or suppression of termination and chain transfer reactions in these systems. These studies opened the way for block copolymer synthesis using cationically polymerizable monomers, extending the range of block copolymers available for basic research and for possible technological applications. Many important monomers like isobutylene and alkyl vinyl ether can be polymerized only by cationic polymerization.

Cationic polymerization can be described as an additional polymerization reaction where chain propagation is achieved through a carbocation, which can be generated by a cationic initiator and a vinyl monomer [197].

Carbocations, in general, are very reactive and unstable; consequently, they can participate in a number of side reactions like termination, chain transfer, and carbocation rearrangement. The major side reaction is chain transfer to monomer. Since the positive charge is present on the α -carbon of the double bond, the hydrogen atom on the β -carbon is acidic. The monomers used in cationic polymerization are nucleophilic; therefore, this kind of side reaction is intrinsic to most systems and difficult to eliminate. However, several methods have been proposed in order to overcome this difficulty. The most successful strategy is the stabilization of the carbocationic intermediate using [198]:

- i) An appropriate counterion.
- ii) A carefully selected Lewis base.

Both methods aim to decrease the positive charge on α -C and, as a result, decrease β -H acidity, suppressing the chain transfer reaction. A typical example of case (i) is the combination HI/I_2 and of case (ii) are systems containing cationogenic compounds,

like tertiary esters, ethers and alcohols, with organometallic substances, like EtAlCl_2 , BCl_3 , TiCl_4 , which produce weak nucleophilic counter-anions. A variety of initiating systems have been reported in the literature. The two methods have to be considered as complementary. Because there are no systems that can be used with all available monomers, each initiating system must be chosen according to the monomer used, i.e., its reactivity and stability of the carbocation formed.

The most common cationically polymerizable monomers are isobutylene, vinyl ethers, styrene and its derivatives with electron donating groups, *N*-vinylcarbazole, furan, and some other heterocyclic monomers. A few examples of diblock and triblock copolymers prepared by cationic polymerization and sequential addition of monomers are given in Table 2.8.

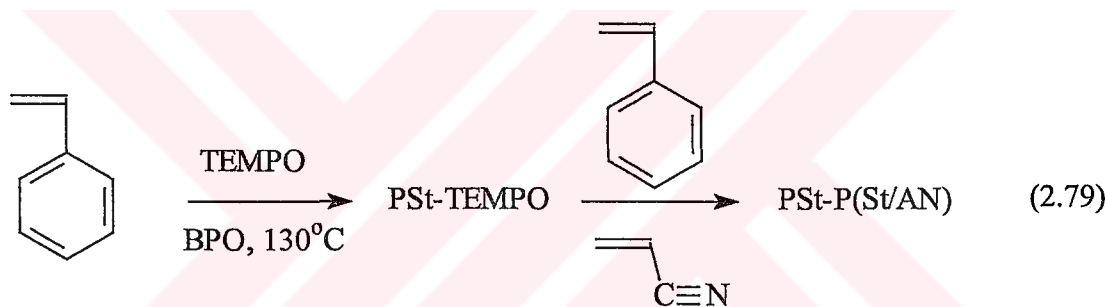
Table 2.8: Examples of Diblock and Triblock Copolymers Prepared by Cationic Polymerization

<i>Monomer A</i>	<i>Monomer B</i>	<i>Reference</i>
Isobutylene	Styrene	[199]
Alkyl vinyl ethers	p-Methoxy styrene	[195]
Isobutyl vinyl ether	Ethyl propenyl ether	[200]
p-Methoxy styrene	p-Hydroxy styrene	[201]
Ethyl vinyl ether	N-Vinyl carbazole	[202]
Tert-butyl styrene	Isobutylene	[203]
Indene	Isobutylene	[203]
2-methyl-2-oxazoline	Tetrahydrofuran	[204]

2.4.2.3 Block Copolymers by Controlled Radical Polymerization

Diblock copolymers can be synthesized by controlled radical polymerization with the technique of sequential monomer addition. Because the mechanism involves propagation through radicals, considerations involving monomer purity and reactivity in conjunction with relative rates of crossover and propagation reactions for the second monomer still exist, but they are more relaxed than in the case of ionic mechanisms. This is a consequence of the fact that, in both nitroxide-mediated and

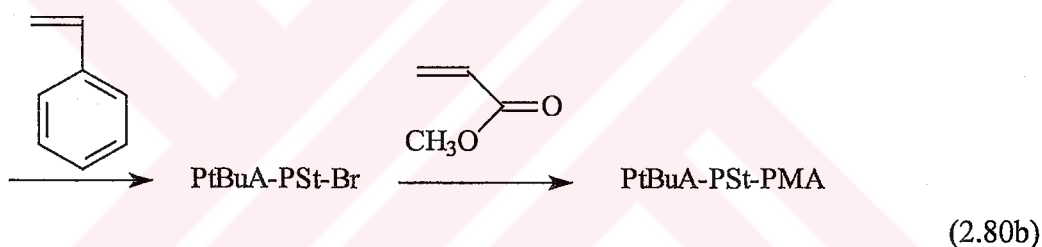
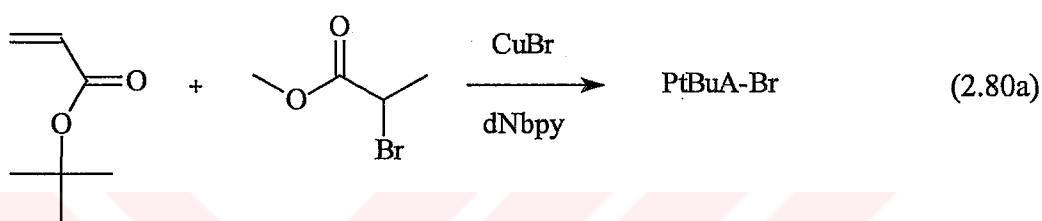
atom-transfer variations of the method, the intermediate products can actually be isolated and further purified (purification mainly involves elimination of traces of the first monomer). The polymerization of the second monomer can be initiated by the macromolecular initiator already formed, in more or less the same way as it would be done in a normal homopolymerization. Nitroxide-mediated stable free radical polymerization (SFRP) has been used for the preparation of block copolymers containing PSt as the first block and a random copolymer of styrene (St) and acrylonitrile (AN) as the second block [205]. Styrene was polymerized first using BPO/TEMPO at low conversion to give TEMPO-terminated PSt of high functionality. This macromolecule was isolated and purified. It was used for the polymerization of an azeotropic mixture of St and AN (St:AN=63:100). The final copolymer had rather low polydispersity and composition close to the expected one, with no detectable homo-PSt impurity (reaction 2.79).



A larger variety of diblock copolymers have been synthesized by ATRP due to the greater flexibility of the method, in terms of polymerizable monomers. However, as in the SFRP case, two fundamental criteria must be fulfilled for the production of well-defined block copolymers. The first is chain-end functionality, i.e., the chain end of the first block must be fully functionalized with the appropriate halogen atom, so each chain must be able to initiate polymerization of the second monomer. Complete functionalization can be achieved if termination and transfer reactions are eliminated completely. Usually, functionalization efficiency can be increased by varying reaction conditions, i.e., initiating system, reaction temperature, and reaction time [206]. The second criterion is efficiency of the cross-propagation reaction, in relation to the propagation reaction of the second monomer, a common feature in all living polymerizations. In order to obtain block copolymers with controllable molecular weight characteristics, initiation of the second monomer must be faster than its

propagation. Experimental evidence suggests that the initiation rate depends strongly on the alkyl halide structure and actually increases in the order: primary <secondary <tertiary [207].

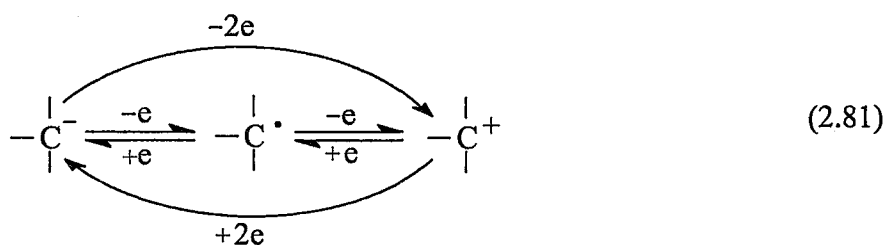
The synthesis of triblock copolymers containing three different monomers is accomplished by a three-step sequential monomer addition. Matyjaszewski and coworkers [206] reported the synthesis of a PtBuA-*b*-PSt-*b*-PMA triblock using this method. *tert*-BuA was polymerized first using methyl 2-bromopropionate as the initiator, and the CuBr system followed by the addition of styrene and methyl acrylate (MA) (reactions 2.80a,b).



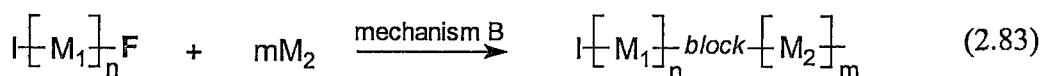
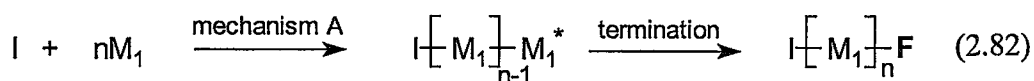
2.4.2.4 Synthesis of Block Copolymers by Combination of Different Polymerization Routes

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 of the respective polymerization mechanisms. Furthermore, utilization of a single method often excludes monomers that polymerize by other 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 [208,209]. 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 as depicted below.



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 of 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. The mechanism is illustrated by reactions 2.82 and 2.83 below.



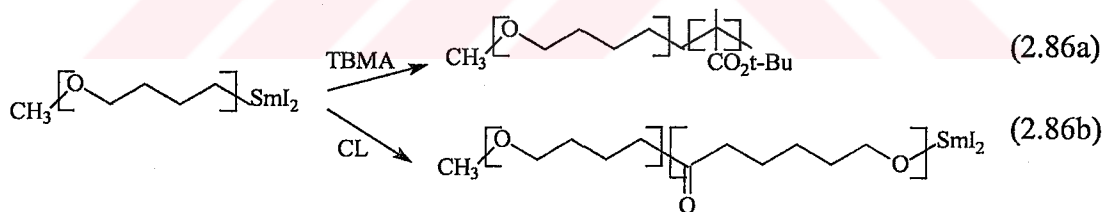
a) Direct Transformations

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 as follows (2.84) for the transformation involving anionic and cationic systems.

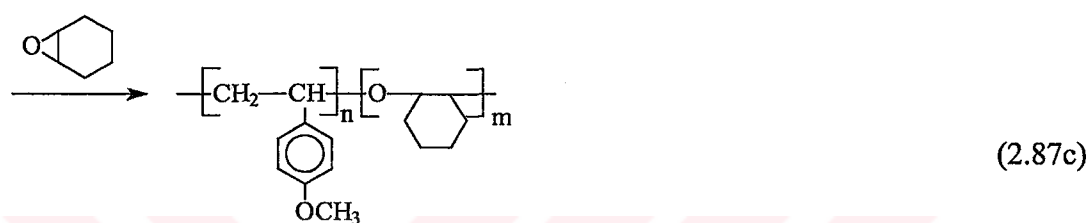
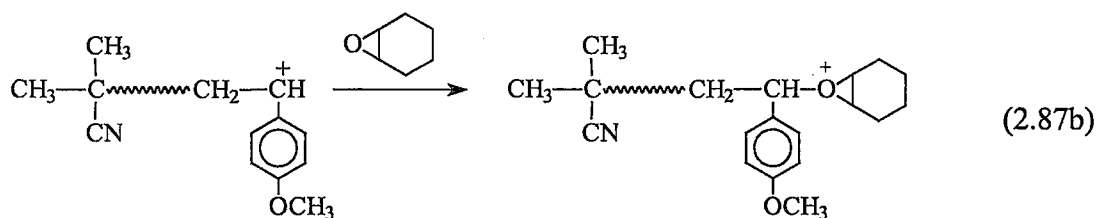
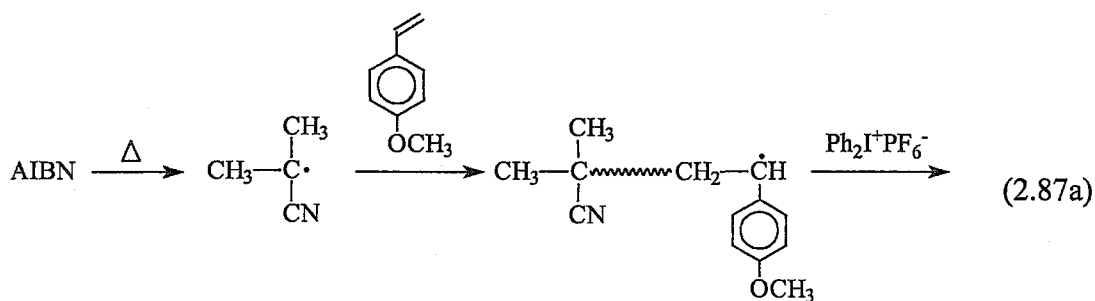


There has been a lack of interest in the direct transformation, mainly because of the short life time of propagating sites, particularly radicals. The active center must have a lifetime sufficient to permit transformation. Furthermore, a thermodynamic limitation for a successful redox process may result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

The first reported development for the direct transformation was by Endo and co-workers [210]. 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) [211] ϵ -caprolactone (CL) [212] and σ -valerolactone (VL) [213] to yield a block copolymers of THF with respective monomers, as shown in reactions 2.85 and 2.86a,b.



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 [214]. 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 2.87a-c).



b) 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 2.9: Transformation Reactions Used for Block Copolymer Synthesis

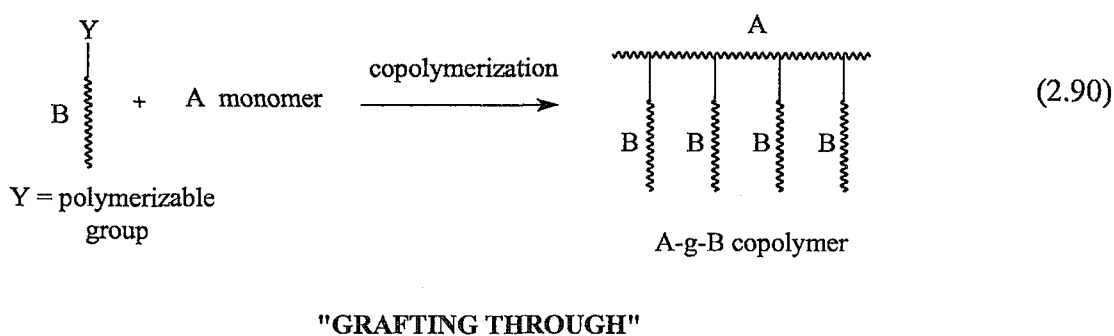
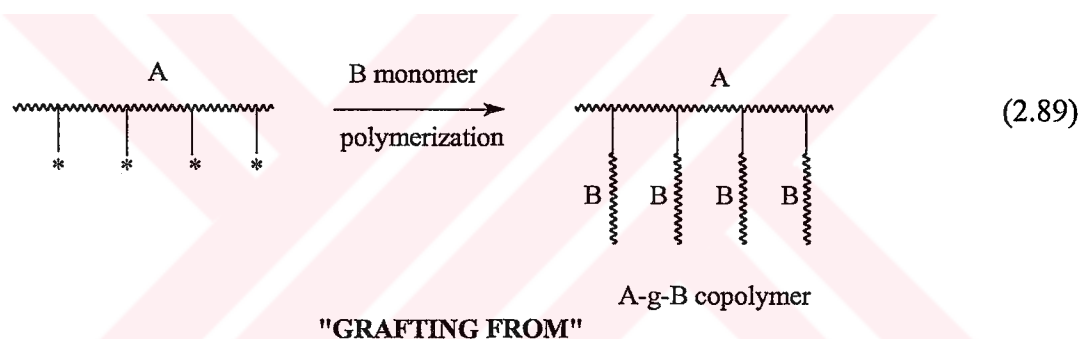
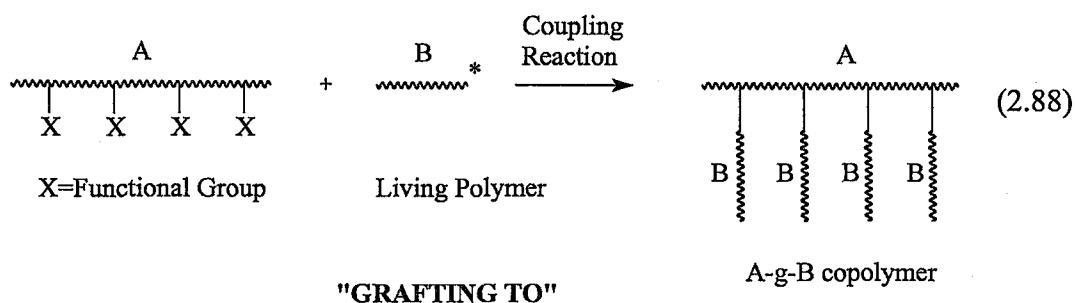
<i>Types of Transformation Reactions</i>	<i>Reference</i>
1- Transformations Involving Condensation Polymerization	[215]
- Transformation of Condensation Polymerization to Radical polymerization	[216]
- Transformation of Condensation Polymerization to Living Radical Polymerization	[217]
- Transformation of Macrocyclic Polymerization to Condensation Polymerization	[218]
2- Transformation of Anionic Polymerization to Radical Polymerization	[219]
- Anionic to Photoinduced Radical Transformation	[220]
- Anionic to “Living” Radical Transformation	[221]
3-Transformation of Cationic Polymerization to Radical Polymerization	[222]
- Cationic to “Living” Radical Transformation	[223]
4- Transformation of Radical Polymerization to Anionic Polymerization	[224]
5- Transformation of Radical Polymerization to Cationic Polymerization	[225]
6- Transformations Involving Anionic and Cationic Polymerizations	[226]
7- Transformations Involving Activated Monomer Polymerization	[227]
8- Transformations Involving Metathesis Polymerization	[228]
9- Transformations Involving Ziegler-Natta Polymerization	[229]
10- Transformations Involving Group Transfer Polymerization	[230]

2.4.3 Graft Copolymers

The current interest in branched polymers that are molecularly well defined is fueled by the growing demand for structures exhibiting shape persistence; the role played by the branching points are to lower the conformational entropy of such objects [231,232]. Graft copolymers contain branching points that may be distributed along

the polymer backbone either randomly or under a controlled manner. These materials may be useful in applications requiring surface modification and control of the surface properties.

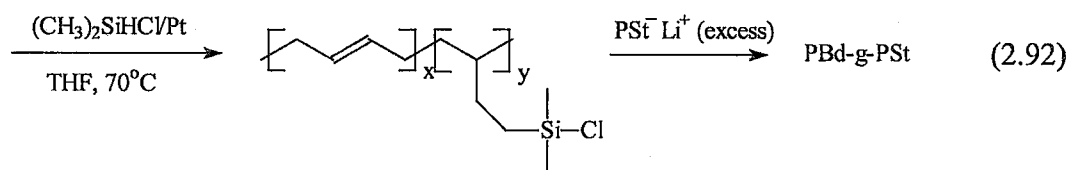
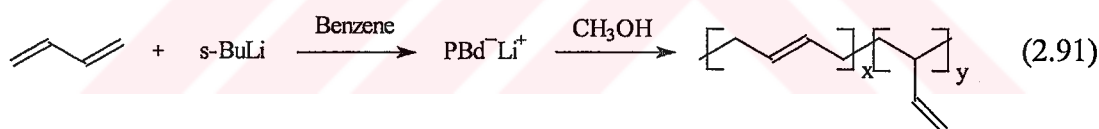
Randomly branched graft copolymers can be prepared by three general synthetic methods: 1) the “grafting to”, 2) the “grafting from”, and 3) the “grafting through” or macromonomer method [233,234] (reactions 2.88-2.90).



2.4.3.1 “Grafting To” Method

In this method, the backbone and the arms are prepared separately by a living polymerization mechanism. The backbone bears reactive groups distributed along the chain that can react with the living branches. Mixing the backbone and the living

branches in the desired proportion and under the appropriate experimental conditions, a coupling reaction takes place resulting in the final graft copolymer. By the use of a living mechanism, the molecular weight, molecular weight polydispersity, and the chemical composition of the backbone and branches can be controlled. Additionally, both backbone and branches can be isolated, before coupling reaction, and characterized separately. The average number of branches can be controlled primarily by the number of the functional groups (branching sites) present in the backbone and sometimes by the ratio of the functional groups to the active chain-end concentration of the branches. Branches of graft copolymers are commonly prepared by anionic polymerization, and backbones with electrophilic functionalities, such as anhydrides, esters, pyridine, chlorosilane, or benzylic halide groups, are employed. The actual average number of branches in the final copolymer can be determined from the overall molecular weight of the copolymer and the molecular weights of the backbone and the branches. A representative example is the preparation of poly(butadiene-*g*-styrene) and poly(butadiene-*g*-styrene₂) copolymers [235], where the PBd backbone is synthesized by anionic polymerization, followed by introduction of chlorosilane groups, via postpolymerization hydrosilylation, and, finally, linking with living polystyrene anions (reactions 2.91 and 2.92).

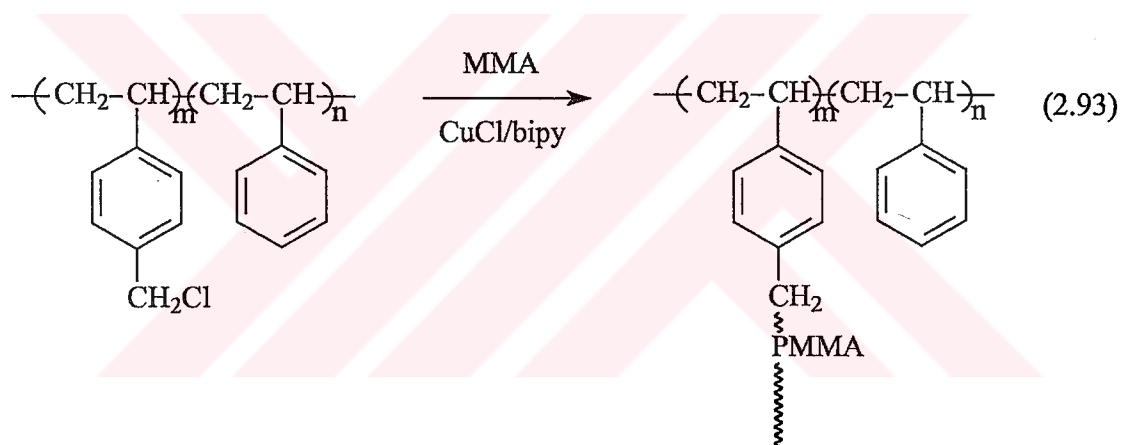


2.4.3.2 “Grafting From” Method

In this method after the preparation of the backbone, active sites are produced along the main chain, which are able to polymerize the monomer(s) that will comprise the branches. Polymerization of the second monomer results in the formation of branches and the graft copolymer. The number of branches can be controlled by the concentration of active sites generated along the backbone, assuming that each one of

them participates in the formation of one branch. Obviously, the isolation and characterization of each part of the graft copolymer in this case is almost impossible.

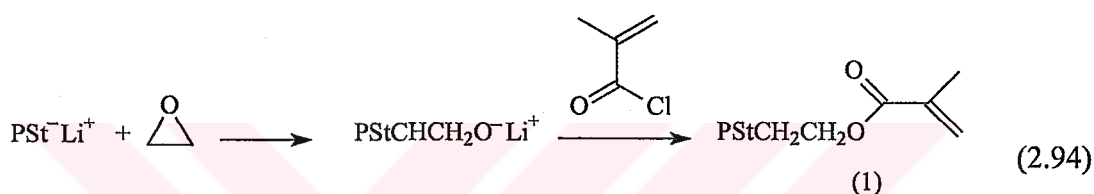
Following “grafting from” methodology several graft copolymers can be synthesized by the use of a number of different polymerization techniques because radicals, anions, and cations can be generated along a polymer chain. Generation of radicals on a preformed backbone has proven to be a very versatile and commercially attractive way of producing graft copolymers due mainly to its simplicity in performing the various reaction steps. The new advances in the living (controlled) radical polymerization techniques led to the preparation of well-defined graft copolymers. A typical example is the use of chloromethylated polystyrene, produced by controlled radical copolymerization of styrene and chloromethylstyrene, as a multifunctional ATRP initiator for the formation of graft copolymers with polystyrene backbones and branches comprised of different (meth)acrylate monomers (reaction 2.93) [236].



2.4.3.3 “Grafting Through” Method

According to this strategy, preformed macromonomers are copolymerized with another monomer in order to produce the graft copolymer. As described in the previous parts, macromonomers are oligomeric or polymeric chains that have a polymerizable end group. In this case the macromonomer comprises the branch of the copolymer, and the backbone is formed in situ. The number of branches per backbone can be generally controlled by the ratio of the molar concentrations of the macromonomer and the comonomer. Several other factors have to be considered. Among them the most important one is the copolymerization behavior of the macromonomer and the comonomer forming the backbone. Depending on the

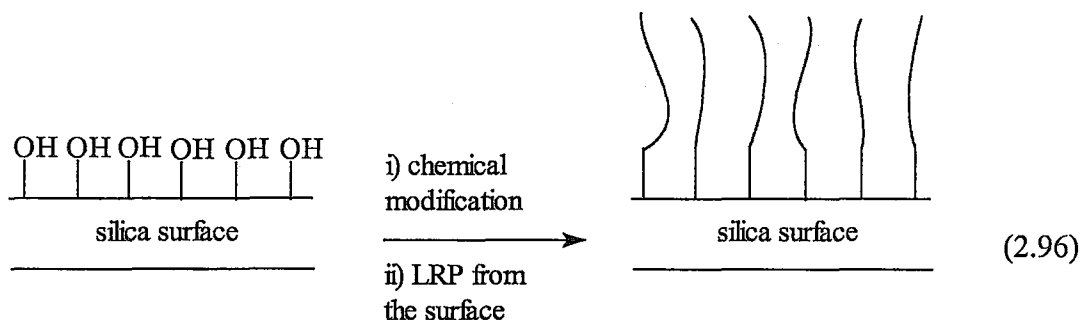
reactivity ratios, r_1 and r_2 , of the reacting species, different degrees of randomness can be achieved, with respect to the placement of the branches. Because macromonomer and comonomer incorporation in the graft copolymer can vary in the course of the copolymerization reaction due to changes in the concentration of the two compounds in the mixture, different kinds of graft copolymers are formed as a function of time. Phase separation can also occur in these systems due to the formation of the copolymers, leading to increased compositional and molecular weight heterogeneity of the final product. PSt macromonomer formation by anionic polymerization and its subsequent use for preparation of graft copolymer with polymethyl methacrylate backbone are given as a representative example of the use of macromonomers in the synthesis of graft copolymers [237] (reactions 2.94 and 2.95).



2.5 Polymer Topology

2.5.1 Polymer Brushes

Polymer brushes result from chains that are tethered to a solid surface and forced to adopt a stretched conformation because of an unusually high density [232]. On covalently anchoring appropriate initiating sites onto inorganic surfaces through their reactive functions, one can grow densely packed grafts, which will therefore adopt the conformation of brushes (reaction 2.96).



The above mentioned techniques for the preparation of grafted layers including attachment of end-functionalized polymers ("grafting onto" method) [238], and polymerization initiated from solid surfaces ("grafting from" method) [239], as well as physical adsorption of block copolymers [240], are employed in the synthesis of brush polymers. Block copolymer adsorption is a simple and reproducible technique. However, it results in a low grafting density and the immobilized polymers do not remain permanently on the surface. The "grafting onto" methods are self-limiting because the grafted chains hinder the approach of additional polymer chains to the surface. The polymer brushes obtained by "grafting from" technique, in which self-assembled monolayers of initiators are used to grow chains outward from the surface, possess extremely high density of the attached chains [241].

The first study on such polymer brush synthesis was reported by the group of Fukuda, who utilized the Langmuir–Blodgett technique to tether a well-organized set of arylsulfonyl chloride groups onto a silicon surface, the monolayer formed on water surface then being transferred for the subsequent growth of PMMA chains via ATRP [242]. These authors then investigated the forces of interaction in their PMMA brushes by AFM and also examined the effect of chain length and that of grafting density [243]. AFM analysis confirmed that these structures were “exceptionally” dense (0.4 chains/nm^2). The same team applied a similar methodology associating the Langmuir–Blodgett technique and surface initiation to grow by ATRP their sugar containing poly(methacrylate) grafts from modified silica gel [244]. On deprotection of the hydroxyl groups carried by the sugar substituent, a solid surface covered with polymer brushes of low polydispersity and carrying pendant saccharide residues could be obtained.

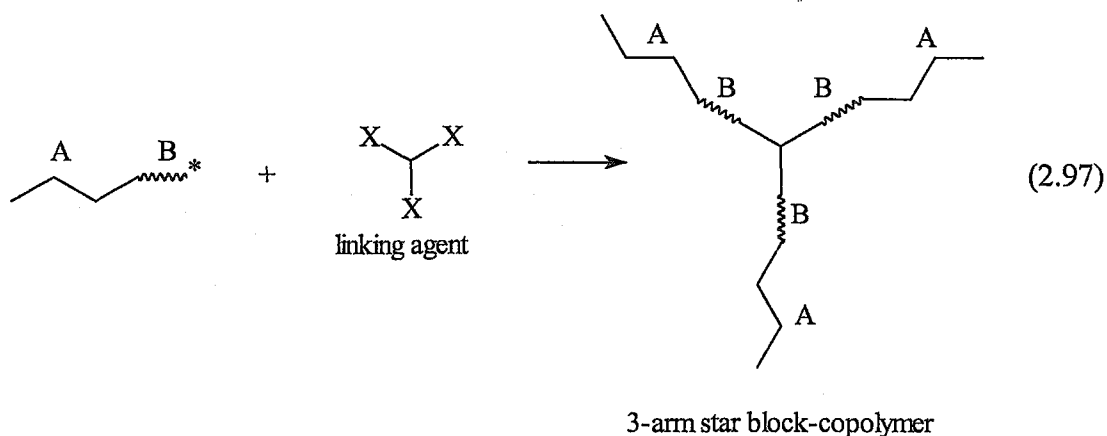
2.5.2 Star Polymers

In a star polymer, the number of branches can vary from a few to several tens. The topological difference of this kind of macromolecules, with respect to linear block copolymers, is focused on the existence of a central branching point, which, by itself, brings a certain symmetry in the macromolecule and sometimes defines a certain amount of intramolecular ordering.

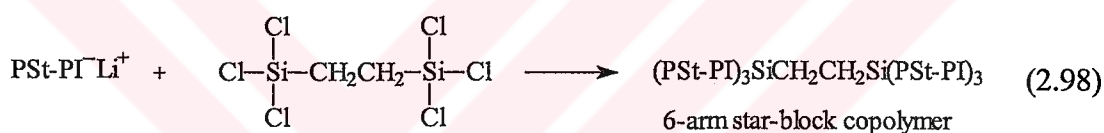
In general, there are two routes to get access to star polymers: the “arms-first” and “core-first” approaches. The two approaches are complementary with their respective merits and drawbacks.

2.5.2.1 Stars by the “Arms-First” Strategy

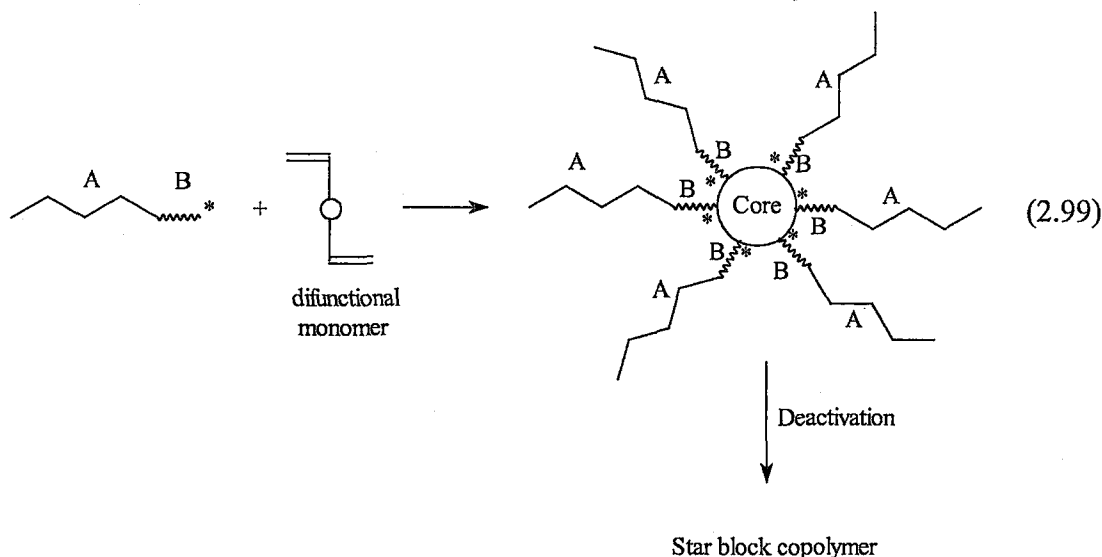
They can be classified into two major categories: the method of linking agents and the method of difunctional polymerizable monomers. In the method of the linking agents, the block copolymer arms are synthesized first by a living polymerization mechanism. Then they are deactivated by a multifunctional compound having an appropriate number of functional groups equal to the number of arms of the desired final star block copolymer (reaction 2.97). The functional groups must be able to react with the living centers in a quantitative, fast, and controlled way, giving no undesirable byproducts. The living active centers are usually employed in excess of the available functional groups in order to ensure complete substitution of the reactive groups of the linking agent by the block copolymer chains. The excess arms can be eliminated, after neutralization, from the crude reaction product by fractionation. The major advantage of this synthetic methodology is that the number of arms present on each star macromolecule is well-defined and predetermined.



Following this methodology, star block copolymers of styrene and isoprene having 3 to 18 diblock arms were synthesized by anionic polymerization using chlorosilanes as linking agents [245,234]. The final materials had well-defined molecular weights and functionality as well as narrow molecular weight distributions (reaction 2.98).



According to the second method of synthesis of star block copolymers, a difunctional polymerizable monomer is used for the formation of the stars core [246]. In this approach, the living block copolymer arms react with a predetermined amount of the difunctional monomer (reaction 2.99). Due to the existence of two reactive sites, the polymerization results in the formation of a network of small dimensions, which serves as a connecting point for the arms. By this procedure star molecules with a relatively broad distribution in the number of arms, due to the statistical nature of the last step are prepared. Therefore, the number of arms in the final star block copolymer is not well-defined although some control can be exercised, mainly through the ratio of the concentration of the difunctional monomer to the concentration of the active centers [247]. A small amount of unlinked arm is always present in the final crude reaction product, and sometimes presence of gel has been detected.



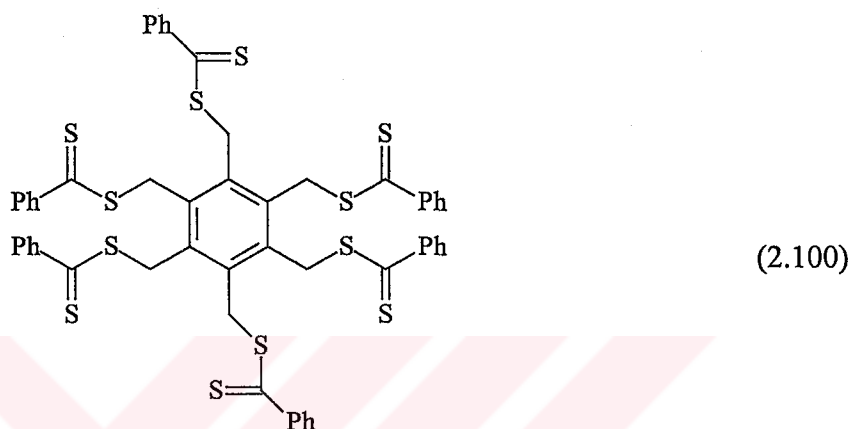
2.5.2.2 Stars by the “Core-First” Strategy

In this approach, the polymer chains are grown “out of” a multifunctional initiator [248]. Accordingly, the number of arms can be controlled by the number of functionalities. However, this route is limited in anionic polymerization due to the poor solubility of the multiply charged initiator molecules, and it dominates the preparation of star polymers by free radical processes.

A trifunctional cationic polymerization initiator, derived from tricumylchloride, has been used for the preparation of three-arm star block copolymers of polyisobutylene (PIB) and polystyrene [249]. Another trifunctional initiator system composed of tris(trifluoroacetate) and ethyaluminum chloride has been used for the preparation of poly-(isobutyl vinyl ether)-*b*-poly(2-hydroxyethyl vinyl ether) star block copolymers having narrow molecular weight distributions [250]. Using the same initiator as Storey et al., Kennedy and coworkers prepared three-arm star polyisobutylenes by cationic polymerization. The terminal Cl groups were converted to isobutyryl bromide groups, and they were used for initiation of the free radical polymerization of methylmethacrylate, resulting in three-arm star block copolymers with PIB inner blocks and PMMA outer blocks [251].

Compared with ionic polymerization techniques, radical polymerizations are applicable to a wide variety of vinylic monomers and require milder reaction conditions. Controlled/“living” radical polymerization processes have proven to be versatile in the preparation of well-defined star polymers. The core-first approach is

the most commonly used method via controlled/"living" radical polymerizations. Star block copolymers of MMA and nBuMA were prepared by ATRP methodology, using a calyx[8]arene based multifunctional initiator in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{Al}(\text{OiPr})_3$ [252]. Rizzardo's group [253] has described the synthesis of relatively well-defined tetra- and hexaarmed PSt stars that were obtained by RAFT methodology, using transfer agents containing a precise number of dithiocarbonyl thio groups (2.100).

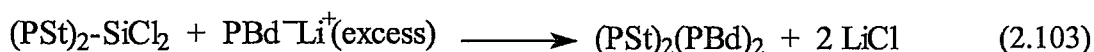
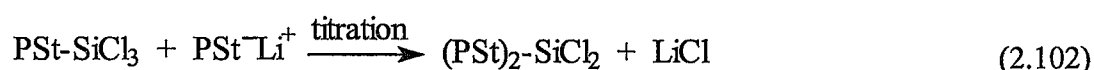


2.5.2.3 Miktoarm Star Copolymers

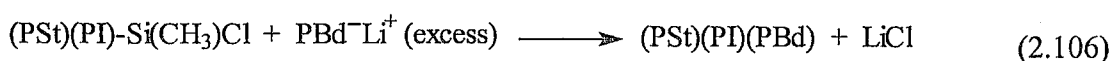
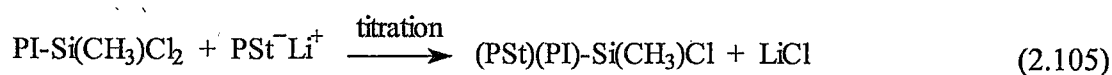
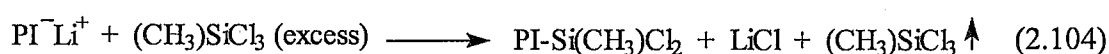
Miktoarm (mikto from the Greek word meaning mixed) star copolymers are a special class of nonlinear block copolymers where arms of different chemical nature and/or composition are linked to the same branch point. These block copolymers have been synthesized mainly by anionic polymerization methods, although some examples of synthesis by other methodologies have appeared in the literature. The number of different kinds of arms can be varied as well as the total number of arms, giving rise to a variety of miktoarm stars like A_2B , A_3B , A_5B (or generally A_nB), A_nB_n , ABC, or even ABCD. Several approaches have been reported for the preparation of miktoarm stars, with each one of them having specific advantages and disadvantages. In the so-called chlorosilane method, chlorosilane compounds of various functionalities are used as linking agents where living chains are linked in a controllable way in order to produce different types of miktoarm stars. Using this method A_2B miktoarms can be synthesized by reaction of living B chains with excess of trichlorosilane, producing a macromolecule having two reactive Si-Cl bonds at its end [254]. After elimination of excess unreacted silane under high vacuum conditions, the macromolecular linking

agent can be reacted with excess living A arms to give the A₂B miktoarm star (A and B can be PSt, PI, or PBd).

A₂B₂ miktoarm stars with A=PSt and B=PBd were obtained by adding the first PSt arm to SiCl₄, followed by slow addition of the second PSt arm until complete substitution of the second chlorine atom (as evidenced by SEC analysis) [255]. The final miktoarm can be formed after complete reaction of A₂SiCl₂ with excess of the second living arms (reactions 2.101-2.103).



ABC miktoarm stars containing PSt, PI, and PBd have been synthesized following the procedure outlined in reactions 2.104-2.106 [256]. The first step involved addition of PI arm to excess of SiMeCl₃, followed by titration of PI-Si(CH₃)Cl₂ with continuous SEC monitoring of the linking reaction. Finally, living PBd arm was added in excess, and the (PSt)(PI)(PBd) ABC miktoarm star terpolymer was produced.



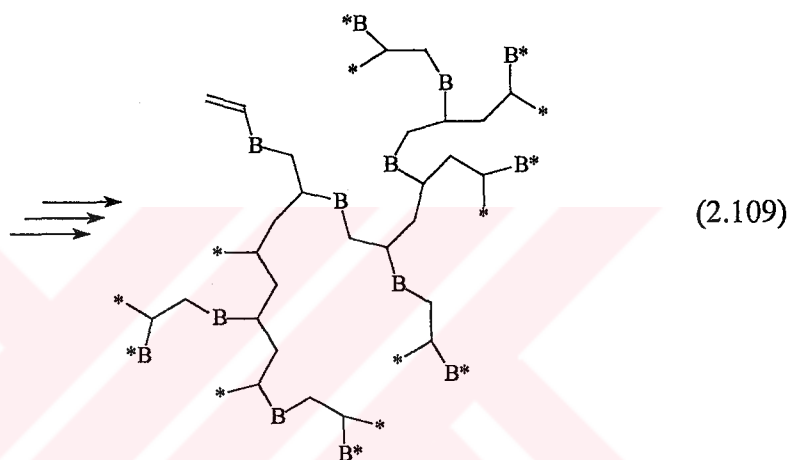
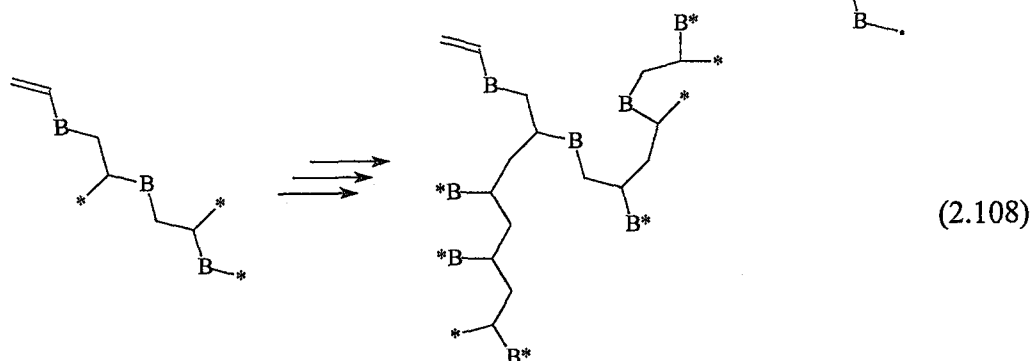
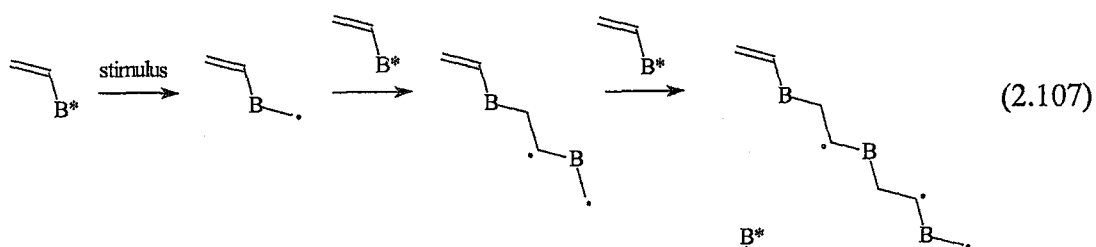
2.5.3 Hyperbranched and Dendritic Polymers

The search for simple methods to obtain highly branched macromolecules whose behavior would resemble that exhibited by dendrimers resulted in the development of the so-called hyperbranched polymers. Hyperbranched macromolecules appear at first glance as an attractive alternative to regular dendrimers since they can be obtained at low cost by a convenient “one-pot” polycondensation of AB₂-type monomers.

However, they generally exhibit a broad molar mass distribution and irregular structures with, in particular, numerous unreacted B sites that correspond to linear units coexisting with dendritic and terminal units. Therefore, their properties (high solubility, low viscosity, absence of chain entanglement, thermal stability) are known to depend not only on their degree of branching but also on the type of their terminal functions.

2.5.3.1 Self-Condensing Vinyl Polymerization (SCVP)

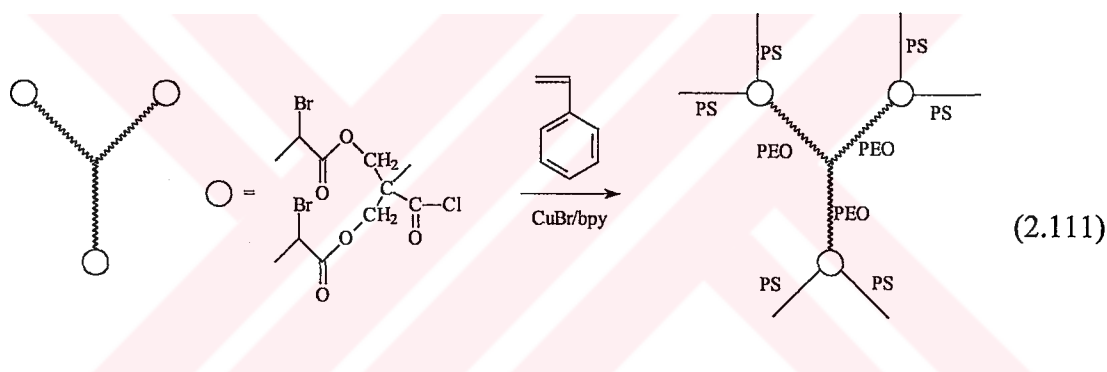
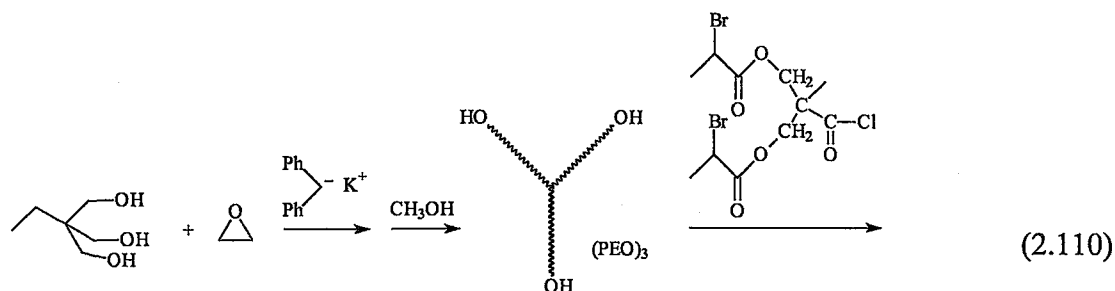
Besides the “conventional approach” that involves polycondensing AB_x -type monomers, progress has been made toward better controlling both the branching pattern and the molar mass distribution in hyperbranched polymers. Among these new developments, the self-condensing vinyl polymerization (SCVP) of latent AB_2 -type monomers was first described by Frechet and colleagues for cationically polymerizing 3-(1-chloroethyl)styrene [257]. SCVP was later applied to the NMP of an alkoxyamine-containing styrenic, and then to ATRP of styrenics and (meth)acrylics. SCVP combines chain addition polymerization with self-condensation of chains (reactions 2.107-2.109). It involves an AB^* vinylic compound, where A represents a double bond and B^* , a latent initiating site that can be activated by an external stimulus. Generally, indirect methods, such as viscometry and light scattering measurements are necessary to glean information about the shape taken by such hyperbranched objects in solution [258].



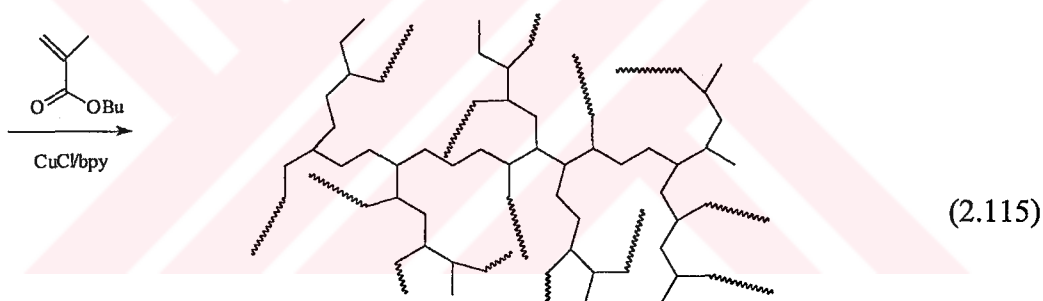
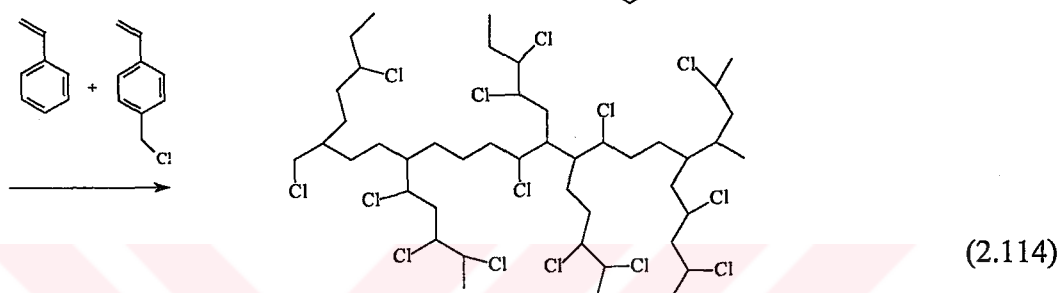
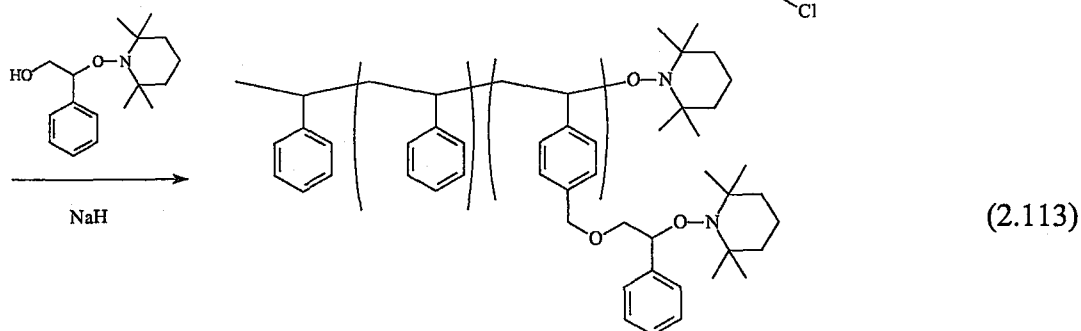
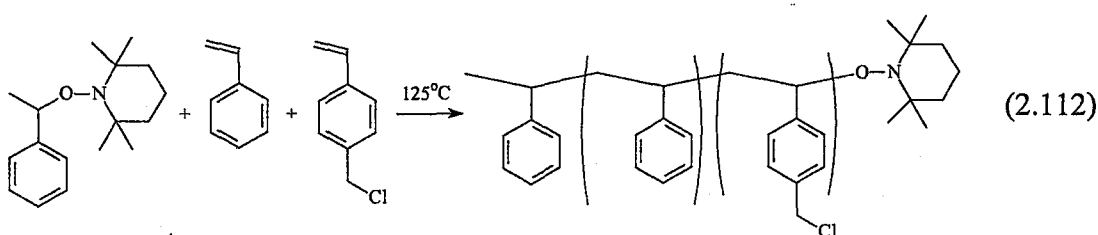
2.5.3.2 Dendrimerlike (Co)polymers

Highly branched copolymers are “dendrigrraft” or “dendrimerlike” copolymers. The former species resemble randomly branched macromolecules containing polymeric segments between the branching points [259]. They are obtained from the successive graftings of “living” linear polymers used as building blocks. The term “dendrimerlike” coined by the group of Hedrick [260] designates architectures that exhibit features similar to those of regular dendrimers (i.e., precise number of branching points and outer functions in all molecules, presence of a central core) but, unlike the latter, their successive generations consist of polymeric chains. They are obtained by combination of chain addition polymerization and functionalization of the chain ends.

Dendrimer-like macromolecules containing styrene and ethylene oxide were prepared by Gnanou and coworkers [261]. The synthetic strategies involve the use of multifunctional initiators, carrying hydroxyl groups, for the synthesis of star-like PEOs. The end groups of the resulting polymers could be transformed to suitable derivatives for the controlled radical polymerization of styrene. Using the appropriate functionalization chemistry, each end group can produce two PS arms, resulting in dendritic macromolecules with amphiphilic properties (reactions 2.110 and 2.111).



Combining NMP of styrenics and ATRP of MMA (reactions 2.112-2.115), Frechet and colleagues covalently arrange PSt and PMMA chains to form a “dendrigrift” structure, which is simply an irregular dendrimer whose branching points are randomly distributed along the chains [259]. However, it should be noted that the benzyl chlorides are slow initiators for the ATRP of MMA, which should likely result in the formation of grafts with a broad distribution in size.



2.6 Cross-Coupling Reactions

The cross-coupling reaction now accessible via a variety of organometallic reagents may provide a fundamentally common synthetic methodology (reaction 2.116).



Kumada and Tamao [262] and Corriu [263] reported independently, in 1972, that the reaction of organomagnesium reagents with alkenyl or aryl halides could be markedly catalyzed by Ni(II) complex. Kochi [264] found the efficiency of Fe(III) catalyst for

the cross-coupling of Grignard reagents with 1-halo-1-alkenes and $\text{Li}_2\text{-CuCl}_2$ catalyst for haloalkanes. The palladium-catalyzed reaction of Grignard reagents was first reported by Murahashi [265], the synthetic utility of which was then amply demonstrated by Negishi [266] on the reactions of organoaluminum, zinc, and zirconium reagents. Afterwards, many other organometallic reagents such as organolithiums, organostannans, 1-alkenylcopper(I), have proven to be highly useful as nucleophiles for the cross-coupling reaction [267].

In the experimental part of the present thesis, palladium-catalyzed cross-coupling reactions of 3-aminophenylboronic acid hemisulfate with the bromine functionalized prepolymers were employed, and, consequently, amino-functional precursor polymers were obtained. Therefore, in the following section, only the palladium-catalyzed cross-coupling reactions of organoboron compounds will be described in detail to illuminate the coupling mechanism.

2.6.1 Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds (Suzuki Coupling)

The palladium-catalyzed cross-coupling reaction between organoboron compounds and organic halides or triflates provides a powerful and general methodology for the formation of carbon-carbon bonds. Recently, this reaction has been called the Suzuki coupling, Suzuki reaction, or Suzuki-Miyaura coupling. The availability of the reagents and the mild reaction conditions all contribute to the versatility of this reaction. The coupling reaction offers several additional advantages, such as being largely unaffected by the presence of water, tolerating a broad range of functional groups, and proceeding generally regio- and stereoselectively. Moreover, the inorganic by-product of the reaction is non-toxic and easily removed from the reaction mixture thereby making the Suzuki coupling suitable not only for laboratories but also for industrial processes [268].

Organoboron compounds are highly electrophilic, but the organic groups on boron are weakly nucleophilic, thus limiting the use of organoboron reagents for the ionic reactions. The coordination of a negatively charged base to the boron atom has been recognized to be an efficient method of increasing its nucleophilicity to transfer the organic group on boron to the adjacent positive center (1,2-migration reaction).

However, intermolecular transfer reaction such as the Grignard-like reaction are relatively rare. Fortunately, organoboron compounds, even organoboronic acids and esters, have sufficiently enough reactivity for the transmetalation to other metals. In 1978, Negishi reported that iodobenzene selectively couples with the 1-alkynyl group on lithium 1-hexynyl(tributyl)borate through a palladium-catalyzed addition-elimination sequence (Heck-type process) [266]; however, the cross-coupling reaction of organoboron compounds, which involves the transmetalation to palladium(II) halides as a key step, was found to proceed smoothly when these were activated with suitable bases and have proven to be a quite general technique for a wide range of selective carbon-carbon bond formation [269]. Many organometallic reagents undergo similar cross-coupling reactions, but much attention has recently been focused on the use of organoboronic acids in laboratories and industries since they are convenient reagents, which are generally thermally stable and inert to water and oxygen, thus allow their handling without special precautions.

2.6.1.1 Mechanism of Suzuki Coupling Reactions

A general catalytic cycle for the cross-coupling reaction of organometallics, which involves oxidative addition-transmetalation-reductive elimination sequences, is depicted in Figure 2.4. Although each step involves further knotty processes including ligand exchanges, there is no doubt about the presence of those intermediates (1 and 2 in Figure 2.4) which have been characterized by isolation or spectroscopic analyses. It is significant that the great majority of cross-coupling reactions catalyzed by Ni(0), Pd(0), and Fe(I) are rationalized in terms of this common catalytic cycle.

Oxidative addition of 1-alkenyl, 1-alkynyl, allyl, benzyl, and aryl halides to a palladium(0) complex affords a stable trans- σ -palladium(II) complex (1). The reaction proceeds with complete retention of configuration for alkenyl halides and with inversion for allylic and benzylic halides. Alkyl halides having β -hydrogen are rarely useful because the oxidative addition step is very slow and may compete with β -hydride elimination from the σ -organopalladium-(II) species. However, it has been recently shown that iodoalkanes undergo the cross-coupling reaction with organoboron compounds [270].

Oxidative addition is often the rate-determining step in a catalytic cycle. The relative reactivity decreases in the order of $I > OTf > Br \gg Cl$. Aryl and 1-alkenyl halides activated by the proximity of electron-withdrawing groups are more reactive to the oxidative addition than those with donating groups, thus allowing the use of chlorides such as 3-chloroenone for the cross-coupling reaction. A very wide range of palladium(0) catalysts or precursors can be used for cross-coupling reaction. $Pd(PPh_3)_4$ is the most commonly used, but $PdCl_2(PPh_3)_2$ and $Pd(OAc)_2$ plus PPh_3 or other phosphine ligands are also efficient since they are stable to air and readily reduced to the active $Pd(0)$ complexes with organometallics or phosphines used for the cross-coupling.

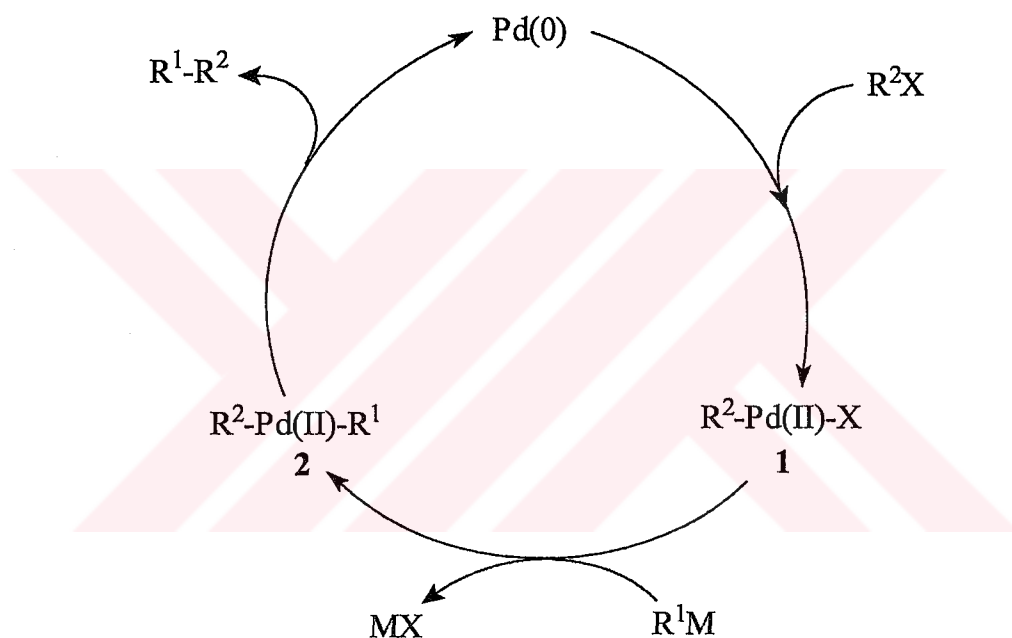
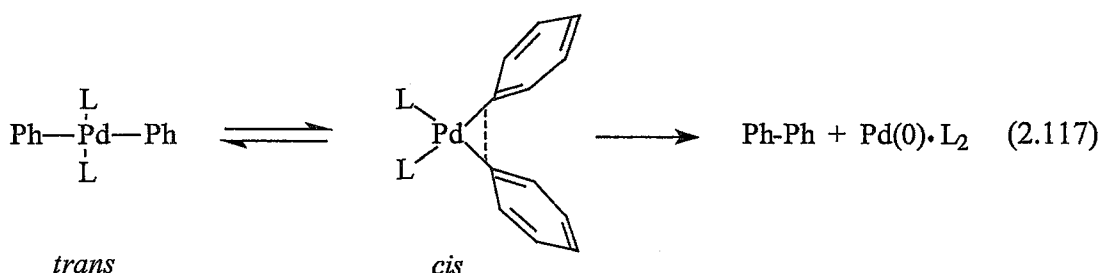
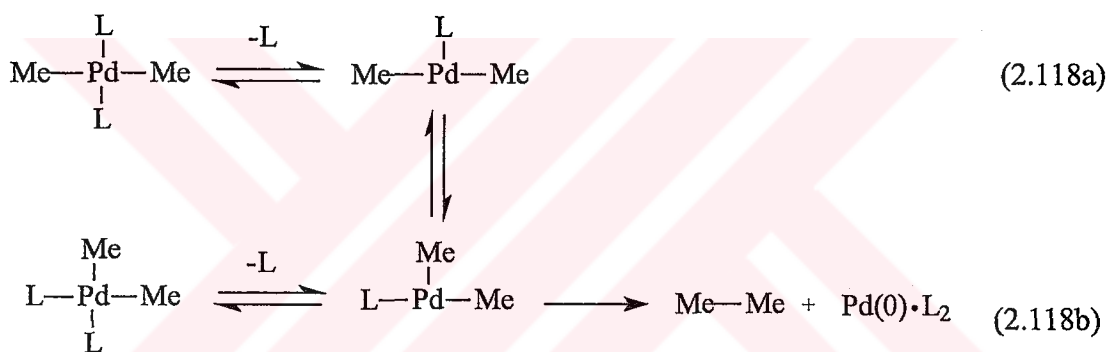


Figure 2.4 : A general catalytic cycle for cross-coupling

Reductive elimination of organic partners from **2** reproduces the palladium(0) complex. The reaction takes place directly from *cis*-**2**, and the *trans*-**2** reacts after its isomerization to the corresponding *cis*-complex (reactions 2.117 and 2.118a,b). The order of reactivity is diaryl- > (alkyl)aryl- > dipropyl- > diethyl- > dimethylpalladium(II), suggesting participation by the π -orbital of aryl group during the bond formation (reaction 2.117).



The thermolysis of *cis*-(dialkyl)palladium(II)·L₂, which is an intermediate on the alkyl-alkyl coupling, is inhibited by excess phosphine (L), hence it is considered to be initiated by the rate-determining dissociation of phosphine ligand (L) producing a three-coordinated *cis*-(dialkyl)palladium(II)·L complex (dissociative mechanism, reactions 2.118a,b). Thus, the effect of phosphine ligands is comparable to the order of ease of their dissociation: dppe << PEt₃ < PEt₂Ph < PMePh₂ < PEtPh₂ < PPh₃.

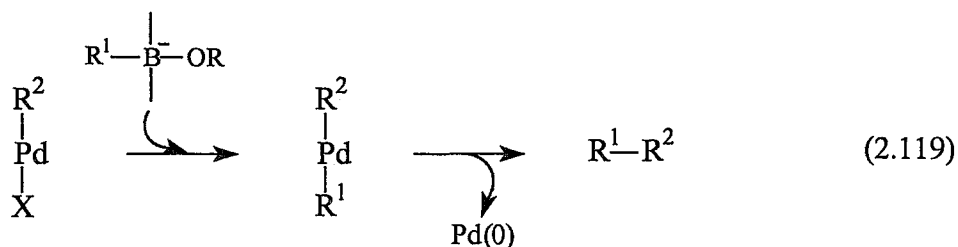


On the other hand, *cis*-alkenyl- and *cis*-arylpalladium(II) complexes, which are intermediates in most of cross-coupling reactions discussed here, directly eliminate organic partners from the four-coordinated complex (nondissociative-nonassociative mechanism, reaction 2.117).

Although the mechanism of oxidative addition and reductive elimination sequences are reasonably well understood and are presumably fundamentally common processes for all cross-coupling reactions of organometallics, less is known about the transmetalation step because the mechanism is highly dependent on organometallics or reaction conditions used for the couplings.

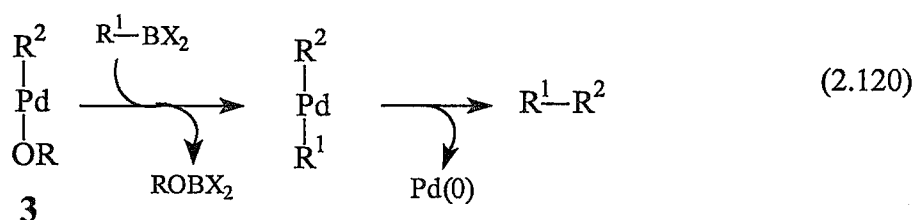
The cross-coupling reaction of organoboron compounds with organic halides or triflates selectively reacts in the presence of a negatively charged base, such as sodium or potassium carbonate, phosphate, hydroxide, and alkoxides. The bases can

be used as aqueous solution, or as suspension in dioxane or DMF. In contrast, the cross-coupling reaction with certain electrophiles, such as allylic acetates, 1,3-butadiene monoxide, and propargyl carbonates, occurs under neutral conditions without any assistance of base. The transmetalation of organoboron compounds with palladium halides under basic or neutral conditions can be considered to involve the following three processes illustrated by the reactions 2.119-2.121.

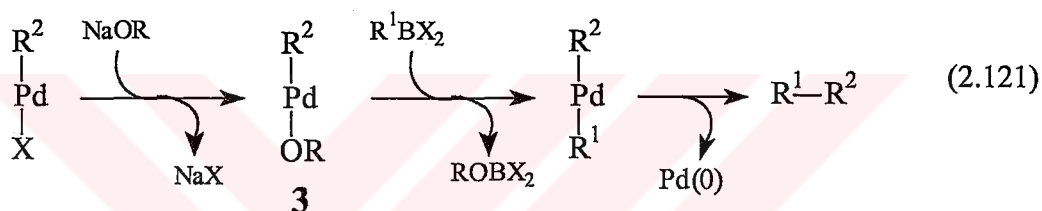


It is apparent that the transmetalation between organopalladium(II) halides and organoboron compounds does not occur readily due to the low nucleophilicity of organic group on boron atom. However, the nucleophilicity of organic group on boron atom can be enhanced by quaternization of the boron with negatively charged bases giving the corresponding "ate" complexes. The quaternization of trialkylboranes accelerates the transmetalation to the palladium(II) halides. Although there is no direct evidence that the boronate anions, such as RB(OH)_3^- , are capable of effecting the transmetalation, it is quite reasonable to assume the similar effect of base for the transmetalation of organoboronic acids. The cross-coupling reaction of arylboronic acids with aryl halides at $\text{pH} = 7-8.5$ is retarded relative to the reaction at $\text{pH} = 9.5-11$. The $\text{p}K_{\text{A}}$ of phenylboronic acid is 8.8, thus suggesting the formation of the hydroxyboronate anion $[\text{RB(OH)}_3]^-$ at $\text{pH} > \text{p}K_{\text{A}}$ and its transmetalation to the palladium(II) halides.

An alternative transmetalation process is that organoboron compounds readily transfer their organic groups to (alkoxo)-palladium(II) complexes under neutral conditions (reaction 2.120).



Finally, it is of interest to note the possibility of involvement of the (alkoxo)palladium intermediate **3** in the palladium/base-induced cross-coupling reaction (2.121). It is known that the halogen ligand on organopalladium(II) halide is readily displaced by alkoxy, hydroxy, or acetoxy anion to provide the reactive Pd-OR complexes (**3**), which have been postulated as reaction intermediates or isolated from the reaction of organopalladium(II) halides with sodium hydroxide or methoxide.



It is not yet obvious in many reactions which process shown in reaction 2.119 or 2.121 is predominant; however, the formation of alkoxo-, hydroxo-, or acetopalladium(II) intermediate should be considered to be one of the crucial transmetalation processes in the base/palladium-induced cross-coupling reactions.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Styrene (St) (Aldrich)

It was first washed with 5% aq. NaOH solution in order to remove inhibitors, and then washed with water. It was dried with calcium chloride (CaCl_2) several hours and distilled over calcium hydride (CaH_2) at reduced pressure.

Cyclohexene oxide (CHO) (Aldrich)

It was distilled at reduced pressure over calcium hydride (CaH_2) before use.

Methyl Methacrylate (MMA) (Aldrich)

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

***N,N*-Dimethyl-4-vinylphenethylamine (PTA)**

It was purified according to the conventional method for anionic living polymerization [271].

ϵ -Caprolactone (CL) (Aldrich)

It was vacuum distilled over CaH_2 just before use.

3.1.2 Solvents

Diethyl ether (J.T. Baker)

It was dried with CaCl_2 and distilled over sodium wire.

Dichloromethane (J.T. Baker)

It was first washed with conc. H_2SO_4 until the acid layer remained colorless, and then with water, followed by another washing with 5% NaOH (aq.) and finally with water again. It was dried with CaCl_2 and distilled over CaH_2 . It was stored over molecular sieves for use as a solvent in the photopolymerization experiments.

Tetrahydrofuran (THF) (J.T. Baker (a), Katayama Chemical Co. (b))

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

(b) It was purified according to the conventional method for anionic living polymerization [272].

n-Hexane (Aldrich)

It was used as a solvent for polycyclohexene oxide in the separation of polycyclohexene oxide homopolymer from the block copolymer and used without further purification.

Cyclohexane (Aldrich)

It was used as a solvent for polystyrene at a temperature of 60°C in the separation of homopolymer from the copolymer and used without further purification.

Acetonitrile (Aldrich)

It was used as a solvent for polymethyl methacrylate at room temperature in the separation of homopolymer from the copolymer and used as received.

Toluene (Aldrich)

It was purified by usual drying and distillation methods.

Methanol (Technical)

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

3.1.3 Other Chemicals

Diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) (Fluka)

It was used as received.

2-Bromopropionyl bromide (Aldrich)

It was used as received.

α -Bromo-p-toluic acid (Acros)

It was used without further purification.

4-(Dimethylamino)-benzaldehyde (Aldrich)

It was used as received.

Sodium Borohydride (NaBH_4) (Merck)

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.

Benzophenone (Fluka)

It was used as a sensitizer as received.

Erythrosin B (Aldrich)

It was used as a sensitizer without further purification.

Thionyl chloride (Fluka)

It was distilled over calcium hydride prior to use.

Triethylamine (TEA) (J.T. Baker)

It was distilled over calcium hydride before use.

***N,N*-Dimethylaniline (Aldrich)**

It was distilled over calcium hydride prior to use.

Cumyl potassium (Aldrich)

It was purified according to the conventional method for anionic living polymerization [269].

4-Hydroxy-2,2,6,6-tetramethyl-1-piperidiny-1-oxy (HTEMPO) (Aldrich)

It was used without further purification.

2,5-Dibromo-*p*-xylene (Aldrich)

It was used as received.

2,5-Dibromotoluene (Aldrich)

It was used without further purification.

3,5-Dibromotoluene (Aldrich)

It was used as received.

***N*-Bromosuccinimide, 99% (NBS) (Acros)**

It was used directly.

3-Aminophenylboronic acid hemisulfate (Acros)

It was used as received.

Pd(PPh₃)₄ (Aldrich)

It was used as a catalyst in Suzuki coupling reactions without further purification.

***p*-Toluene sulfonic acid monohydrate, 99% (Acros)**

It was used as received.

Tin octoate Sn(Oct)₂ (Sigma)

It was used as an initiator in Ring Opening Polymerization of ϵ -caprolactone and used as received.

3.2 Equipment**3.2.1. Photoreactor**

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

3.2.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

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

3.2.3 Elemental Analysis

Elemental analyses were carried out using a CHNS-932 (LECO) instrument.

3.2.4 Infrared Spectrophotometer (IR)

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

3.2.5 UV-visible Spectrophotometer

UV-Visible spectra were recorded on a Shimadzu UV-1601 UV-visible spectrophotometer.

3.2.6 Gel Permeation Chromatography (G.P.C)

Gel permeation chromatography (GPC) analyses were performed with a set up consisting of a Waters 410 Differential Refractometer, a Waters 515 HPLC Pump and an apparatus equipped with three Waters ultrastyrigel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min. Molecular weights were calculated on the basis of a calibration curve recorded with monodisperse polystyrene standards.

3.2.7 Differential Scanning Calorimeter (D.S.C)

A Du Pont modular thermal analyzer system in conjunction with a 910 differential scanning calorimeter was used to perform thermal analysis. A constant heating rate of 10 °C/min was used during DSC experiments.

3.2.8 Atomic Force Microscopy (AFM)

NT-MDT Solver P47 AFM was used in the tapping mode to measure the film thicknesses and to characterize the resulting morphology. Film thicknesses were determined by scraping the polymer film in an area of 2 μm x 2 μm by the AFM tip in contact mode and then taking the height image of the scraped area in tapping mode. Ultrasharp Si cantilevers having force constants of 3 N/m or 48 N/m were used.

3.2.9 Monochromator

An Amko Light Technology Instruments, Lamphousing A1000 series, monochromator was used.

3.3 Preparation Methods

3.3.1 Synthesis of Atom Transfer Radical Polymerization (ATRP) Initiators

3.3.1.1 Preparation of 4-(Dimethylamino)benzyl 4-(bromomethyl) benzoate [273]

3.3.1.1a Synthesis of 4-(Bromomethyl)-benzoyl chloride

α -Bromo-*p*-toluic acid (16.128 g, 0.075 mol) and 80 mL of thionyl chloride were refluxed for 12 h. Thionyl chloride was removed by distillation under reduced pressure and the remaining reddish liquid was extracted several times with dry hexane. The solution was concentrated and upon cooling 4-(bromomethyl)-benzoyl chloride was deposited as pale yellow crystals. A second crystallization from hexane furnished the pure product as white crystals (63% yield). m.p (DSC): 33-34°C.

$^1\text{H-NMR}$ (CDCl_3) (δ , ppm): 8.12-8.11 (d, 2H, Ar *ortho* to CO), 8.09-8.06 (d, 2H, Ar *ortho* to CH_2), 4.63 (s, 2H, CH_2Br).

$^{13}\text{C-NMR}$ (CDCl_3) (δ , ppm): 167.32 (C=O), 147.93 ($\text{C}_{\text{Ar}}-\text{CH}_2$), 133.87 ($\text{C}_{\text{Ar}}-\text{CO}$), 132.89 (C_{Ar} *ortho* to CO), 132.16 (C_{Ar} *ortho* to CH_2), 33.65 (CH_2).

IR (cm^{-1}): 1772 and 1740 (C=O). The band at 1685 in the spectrum of the initial acid disappeared in the spectrum of 4-(bromomethyl)-benzoyl chloride.

Anal. $\text{C}_8\text{H}_6\text{BrClO}$ Calc. C 41.15; H 2.59;

Found C 41.73; H 1.94;

3.3.1.1b Synthesis of [4-(dimethylamino)phenyl]methanol

4-(Dimethylamino)benzaldehyde (7.4595 g, 0.05 mol) and 25 mL of methanol were introduced into a 100-mL, round-bottomed flask equipped with magnetic stirrer, condenser and dropping funnel. NaBH_4 (1.89g, 0.05 mol) dissolved in 10 mL methanol was added slowly. The mixture was heated at solvent reflux for 2 h, and then stirred at room temperature overnight. The contents of the flask were poured into water and the solution was extracted several times with CH_2Cl_2 . After drying the resulting solution over MgSO_4 and removing the solvent, the product was obtained as a pale yellow liquid. Chromatography using a silicagel column and diethyl ether as eluent afforded [4-(dimethylamino)phenyl]methanol as a colorless liquid (yield 96%).

¹H-NMR (acetone-*d*₆) (δ, ppm): 7.25-7.21 (d, 2H, *Ar ortho* to CH₂), 6.76-6.71 (d, 2H, *Ar ortho* to N), 4.54 (s, 2H, CH₂), 4.3 (s, 1H, OH), 2.89 (s, 6H, CH₃)

¹³C-NMR (CDCl₃) (δ, ppm): 150.41 (C_{Ar}-N), 129.76 (C_{Ar}-CH₂), 128.73 (C_{Ar ortho} to CH₂), 113.11 (C_{Ar ortho} to N), 65.13 (CH₂), 41.18 (CH₃).

IR (cm⁻¹): 3380, 1008 (OH)

The peak at 1660 cm⁻¹ corresponding to aldehyde group in the spectrum of starting material was not present in the spectrum of [4-(dimethylamino)phenyl]methanol.

Anal. C₉H₁₃NO Calc. C 71.49; H 8.67; N 9.26

Found C 70.85; H 9.13; N 9.58

3.3.1.1c Synthesis of 4-(Dimethylamino)benzyl 4-(bromomethyl) benzoate

[4-(Dimethylamino)phenyl]methanol (3.02g, 0.02 mol), 25 mL of dry diethyl ether and TEA (3.066g, 0.03 mol) were added into a 100-mL, three-necked, round-bottomed flask fitted with a condenser, a magnetic stirrer, nitrogen inlet-outlet, and an addition funnel containing 4-(bromomethyl)-benzoyl chloride (3.5025 g, 0.015 mol) in 30 mL of diethyl ether. The flask was placed in an ice-water bath. The mixture was stirred under nitrogen as the solution of 4-(bromomethyl)-benzoyl chloride was added dropwise over a period of 1 h. Then the mixture was stirred at 0°C for 4h and additional one hour at room temperature. The white precipitate, which formed, was removed by filtration. The solution was washed three times with water. After drying over MgSO₄, the solution was passed through a silica gel column. The solvent was removed and the crude product was recrystallized twice from hexane. White crystals were obtained (yield 57%), m.p. (DSC) 90-91 °C

¹H-NMR (CDCl₃) (δ, ppm): 8.05-8.02 (d, 2H, *Ar ortho* to CO), 7.56-7.53 (d, 2H, *Ar ortho* to CH₂Br), 7.43-7.40 (d, 2H, *Ar ortho* to CH₂O), 6.75-6.69 (d, 2H, *Ar ortho* to N), 5.26 (s, 2H, *Ar-CH*₂-O), 4.58 (s, 2H, CH₂Br), 2.96 (s, 6H, CH₃).

¹³C-NMR (CDCl₃) (δ, ppm): 166.28 (C=O), 150.80 (C_{Ar}-N), 142.26 (C_{Ar}-CH₂Br), 131.15 (C_{Ar}-CH₂O), 130.68 (C_{Ar ortho} to CH₂O), 129.19 (C_{Ar ortho} to C=O), 128.67 (C_{Ar}-C=O), 128.55 (C_{Ar ortho} to CH₂Br), 112.57 (C_{Ar ortho} to N), 67.56 (CH₂-O), 40.88 (CH₃), 31.30 (CH₂- Br).

IR (cm⁻¹): 1700 (C=O ester)

Anal. C₁₇H₁₈BrNO₂ Calc. C 58.63; H 5.21; N 4.02

Found C 59.15; H 4.87; N 4.34

3.3.1.2 Synthesis of 1,4-Dibromo-2,5-bis(bromomethyl)benzene

It was prepared by the bromination of methyl groups of 2,5-dibromo-*p*-xylene with *N*-bromosuccinimide (NBS) [274,275].

$^1\text{H-NMR}$ (CDCl_3): $\delta = 4.5$ (s, 4H, CH_2), 7.65 (s, 2H, aromatic); white crystals, m.p. (DSC): 159-160°C

Anal. ($\text{C}_8\text{H}_6\text{Br}_4$): Calc. C 22.78; H 1.43

Found C 22.52; H 1.35

3.3.1.3 Synthesis of 1,4-Dibromo-2-(bromomethyl)benzene

It was prepared by the bromination of methyl groups of 1,4-dibromotoluene with *N*-bromosuccinimide (NBS) [274,275].

$^1\text{H-NMR}$ (CDCl_3): $\delta = 7.58$ (s, 1H, ArH -3-position), 7.43-7.40 (d, 1H, ArH -5 position), 7.28-7.26 (d, 1H, ArH -6 position), 4.51 (s, 2H, CH_2Br); white crystals, m.p. (DSC): 94-95°C.

Anal. ($\text{C}_7\text{H}_5\text{Br}_3$) Calc. C 25.57; H 1.53

Found C 25.63; H 1.73

3.3.1.4 Synthesis of 1,3-Dibromo-5-(bromomethyl)benzene

It was prepared by the bromination of methyl groups of 3,5-dibromotoluene with *N*-bromosuccinimide (NBS) [274,275].

$^1\text{H-NMR}$ (CDCl_3): $\delta = 7.58$ (s, 1H, ArH -5-position), 7.45 (s, 2H, ArH- 4 and 6 positions), 4.34 (s, 2H, CH_2Br), white crystals, m.p (DSC): 97-98°C

Anal. ($\text{C}_7\text{H}_5\text{Br}_3$) Calc. C 25.57; H 1.53

Found C 25.32; H 1.66

3.3.2 Synthesis of Ring Opening Polymerization (ROP) Initiator

It was synthesized as described previously [276].

$^1\text{H-NMR}$ (acetone- d_6) (δ , ppm): 7.74 (s, 2H, Ar), 4.65 (s, 4H, CH_2), 3.29 (s, 2H, OH), white crystals, m.p. (DSC) : 217-218 °C

Anal. ($\text{C}_8\text{H}_8\text{Br}_2\text{O}_2$) Calc. C 32.47; H 2.72

Found C 32.61; H 2.93

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

A round bottom-flask equipped with magnetic stirrer and a lateral neck with tap was used. The system was vacuumed and back-filled with dry nitrogen several times. Catalyst (CuBr), ligand bipyridine (bpy), initiator and styrene were introduced under inert atmosphere. The flask was placed in an oil bath warmed at 110°C and kept under stirring at that temperature for a given time, after which the reaction was stopped and the mixture was diluted with THF and finally poured into ten-fold methanol. The solid was collected after filtration and dried in an oven at 40°C and at reduced pressure overnight. The polymers were purified by passing through a silicagel column using THF as eluent and reprecipitated in methanol.

3.3.4 General Procedure for Ring Opening Polymerization (ROP)

Certain amounts of monomer (CL), $\text{Sn}(\text{Oct})_2$ and bifunctional initiator were added under nitrogen in previously flamed and nitrogen-purged Schlenk tubes equipped with magnetic stirrers. The CL polymerizations were carried out in bulk at 110°C. After 24h, the mixtures were diluted with CH_2Cl_2 and poured into ten-fold excess of cold methanol. The polymers were collected after filtration and dried at room temperature at reduced pressure for 3 days.

3.3.5 General Procedure for the Suzuki Coupling Reaction Between the Bromine-functionalized Polymers and 3-Aminophenylboronic acid

A 100 mL three-necked round bottom flask equipped with a condenser, a rubber septum, a nitrogen inlet-outlet and a magnetic stirrer was charged with 10 mL, 1M NaHCO_3 aqueous solution and 15 mL THF. Solvents were previously bubbled with nitrogen over a period of 30 minutes and the mixture was refluxed under nitrogen for 4 h.

A 20 mL three-necked round bottom flask equipped in the same way as the previous one was charged under inert atmosphere with 0.208 mmol of bromine-functional polymer, 0.174g (1.04 mmol) 3-aminophenylboronic acid hemisulfate and 0.01 g (0.008 mmole) of $\text{Pd}(\text{PPh}_3)_4$. The solvent mixture (4 mL) was introduced with a syringe through the septum. The mixture was refluxed under nitrogen for 4 days,

maintaining vigorous stirring and with the exclusion of oxygen and light. The amino-functionalized polymers were separated by precipitation in methanol, filtrated, washed several times with water for the removal of inorganic salts and dried. Further purification was performed by passing the polymers through a silicagel column using THF as eluent and reprecipitated in methanol.

3.3.6 General Procedure for the Condensation of Amino-functionalized Polymers with 4-Dimethylamino benzaldehyde

In a 25 mL three-necked round bottom flask equipped with a Dean-Stark trap connected to a condenser, a nitrogen inlet-outlet, and a magnetic stirrer were introduced 0.6 mmol of amino-functionalized polymer and 3 mmol of 4-dimethylamino benzaldehyde in 7 mL toluene. Catalytic amounts of p-toluene sulfonic acid were added. The reaction mixture was refluxed for 24 h. Afterwards, the polymer was precipitated in methanol. Further purification of the product was achieved by dissolving the polymer in THF and reprecipitating it in methanol.

3.3.7 Synthesis of Macrophotoinitiators by ATRP of Styrene

3.3.7.1 Preparation of *N,N*-Dimethylaniline End-functional Precursor Polymer by ATRP

Well-defined polystyrene possessing *N,N*-dimethylaniline end-chain units was synthesized according to the procedure described for ATRP.

3.3.7.2 Preparation of Central Amino or *N,N*-Dimethyl Amino Bi-functional Polystyrene

3.3.7.2a Preparation of Precursor Polymer Containing Central 2,5-Dibromo-1,4-phenylene Moiety by ATRP

Well-defined polystyrene possessing central 2,5-dibromo-1,4-phenylene moiety was synthesized according to the procedure described for ATRP.

3.3.7.2b Preparation of Mid-chain Amino Bi-functional Polystyrene by Suzuki Coupling Reaction

Polystyrene possessing central 2,5-dibromo-1,4-phenylene moiety was modified to contain 2 central amino functions by a Suzuki coupling reaction as described above.

3.3.7.2c Condensation of the Mid-chain Amino Bi-functional Polymer with 4-Dimethylamino Benzaldehyde

Polystyrene possessing central *N,N*-dimethyl amino functions was prepared by a condensation reaction of amino groups with 4-dimethyl benzaldehyde as described above.

3.3.7.3 Preparation of End-chain Amino or *N,N*-Dimethyl amino Bi-functional Polystyrenes

3.3.7.3a Preparation of Precursor Polymers Containing End-chain 2,5-Dibromobenzene or 3,5-Dibromobenzene Moieties by ATRP

Well-defined polystyrenes possessing end-chain 2,5-dibromo-benzene or 3,5-dibromobenzene moieties were synthesized according to the procedure described for ATRP.

3.3.7.3b Preparation of End-chain Amino Bi-functional Polystyrenes by Suzuki Coupling Reaction

Polystyrenes possessing end-chain 2,5-dibromo-benzene or 3,5-dibromobenzene moieties were modified to contain 2 end-chain amino functions by Suzuki coupling reactions as described above.

3.3.7.3c Condensation of the End-chain Amino Bi-functional Polymers with 4-Dimethylamino benzaldehyde

Polystyrenes possessing end-chain *N,N*-dimethyl amino functions were prepared by a condensation reaction of amino groups with 4-dimethyl benzaldehyde as described above.

3.3.8 Synthesis of a Macrophotoinitiator by ROP of ϵ -Caprolactone

3.3.8.1 Preparation of Central Amino or *N,N*-Dimethyl amino Bi-functional Poly(ϵ -Caprolactone)

3.3.8.1a Preparation of Precursor Polymer Containing Central 2,5-Dibromo-1,4-phenylene Moiety by ROP

Well-defined poly(ϵ -caprolactone) possessing central 2,5-dibromo-1,4-phenylene moiety was synthesized according to the procedure described for ROP.

3.3.8.1b Preparation of Mid-chain Amino Bi-functional Poly(ϵ -Caprolactone) by Suzuki Coupling Reaction

Poly(ϵ -caprolactone) possessing central 2,5-dibromo-1,4-phenylene moiety was modified to contain 2 central amino functions by a Suzuki coupling reaction as described above.

3.3.8.1c Condensation of the Mid-chain Amino Bi-functional Polymer with 4-Dimethylamino benzaldehyde

Poly(ϵ -caprolactone) possessing central *N,N*-dimethyl amino functions was prepared by a condensation reaction of amino groups with 4-dimethyl benzaldehyde as described above.

3.3.9 Synthesis of a Diblock Copolymer Possessing Side-chain *N,N*-Dimethyl amino-functional Initiating Sites for Photoinduced Radical Polymerization

3.3.9.1 Preparation of Poly(*N,N*-dimethyl-4-vinylphenethylamine)-block-polystyrene

Poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene was kindly supplied by Prof. Kazunori SE (Department of Materials Science and Engineering, Faculty of Engineering, Fukui University, Bunkyo 3-9-1, Fukui 910-8507, Japan). *N,N*-Dimethyl-4-vinylphenethylamine (PTA), and cumyl potassium were prepared according to a previously described method. Preparation of the diblock copolymer was performed by sequential addition of the PTA and St to the polymerization solution. Polymerization was performed in a sealed glass apparatus at -78°C in THF under a pressure of 10^{-6} torr, following essentially the same procedures as described in previous studies [271,277,278].

3.3.9.2 Photosensitized Side Chain HTEMPO Capping of Poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene

Into a pyrex tube containing 40 mL of dichloromethane were added 0.30g (1.9×10^{-4} mol/L) of poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene, 0.22 g (3×10^{-2} mol/L) of benzophenone and 0.30 g (4.3×10^{-2} mol/L) of HTEMPO. The solution was degassed and the tube was sealed under nitrogen prior to irradiation in the photoreactor. Cupric sulfate aqueous solution was used as the photofilter in order to avoid the absorption of HTEMPO. After 24 hours of irradiation at 25°C, the polymer was precipitated in methanol, filtered and dried overnight at reduced pressure.

3.3.10 Synthesis of Random Copolymers Possessing H-donating Sites for Photoinduced Grafting

Styrene, and 2-(dimethylamino)ethyl methacrylate, in solution with dichloromethane, and AIBN were all put in a schlenk tube and degassed with nitrogen. It was placed in a thermostated oil bath, previously set at 80°C, and kept there for a given period. At the end of polymerization, the content of the tube was dissolved in dichloromethane

followed by precipitation in 10-fold excess n-hexane. Finally, the solid polymer was collected by filtration and dried overnight at reduced pressure.

3.3.11 Synthesis of Hyper-branched Polymers

The solution of monomer (2.96 mol.L^{-1}) containing $5 \times 10^{-2} \text{ mol.L}^{-1}$ benzophenone in methylene chloride was placed in a Pyrex tube; degassed with nitrogen; and irradiated for 60 minutes at a wavelength of 350 nm. The polymer solution was poured into n-hexane for precipitation. Finally, the solid polymer was collected by filtration at reduced pressure and dried overnight at reduced pressure.

3.3.12 General Procedure for Photoinduced Radical Polymerization of MMA Using Amino or *N,N*-Dimethylamino-functional Polymeric Co-initiators

Monomer (MMA) either in bulk form or in solution with dichloromethane, sensitizer (benzophenone or Erythrosin B), and polymeric co-initiator were put into a Pyrex tube; degassed with nitrogen; and irradiated at room temperature. In the case of sensitization with benzophenone, a merry-go-round type photoreactor equipped with 15 Philips lamps and emitting light nominally at 350 nm was used. However, polymerizations in which Erythrosin B was utilized as the sensitizer were essentially carried out with a monochromatic light source emitting radiation with a wavelength of 525 nm. At the end of irradiation, the content of the tube was dissolved in dichloromethane followed by precipitation in 10-fold excess methanol (cold methanol for the precipitation of PCL polymers). Finally, the solid polymer was collected by filtration and dried overnight at reduced pressure. Further extraction with cyclohexane was performed in the case of PSt polymers, in order to remove eventually unreacted portion. For the removal of homo-PCL polymer, a second precipitation in hot methanol was employed.

3.3.13 General Procedure for Photoinduced Radical Promoted Cationic Polymerization of CHO Using *N,N*-Dimethylaniline End-functional Polymeric Co-initiators

Monomer (CHO) either in bulk or in solution with dichloromethane, sensitizer (dye), polymeric co-initiator (*N,N*-dimethylaniline end-functional polymer), onium salt

(diphenyl iodonium hexafluorophosphate) were put into pyrex tubes and degassed with nitrogen prior to irradiation. The tubes were irradiated at room temperature using a monochromatic light source emitting radiation with a wavelength of 525 nm. The viscous solution, either alone or dissolved in dichloromethane, was poured into methanol for precipitation. Finally, the solid polymers were collected by filtration at reduced pressure and dried overnight at reduced pressure.

3.3.14 Thin Film Preparation for AFM Measurements

Polymers were dissolved in chloroform at a concentration of 16-20 mg/mL. The films were prepared by spin-coating from solutions onto glass or oxidized silicon substrates at 2000 rpm for 1 min. Silicon substrates were made hydrophilic prior to spin-coating by keeping them in UV-ozone cleaner for 20 min. A water drop completely wetted such hydrophilic surfaces. Spin-coated films were initially kept at 70°C for 1 h for solvent evaporation. The temperature was then increased to 130°C and the films were annealed for 2 h for equilibration of the microphase separated surface morphology. After annealing, the films were quenched to room temperature of 25°C.

4. RESULTS and DISCUSSION

4.1 The Use of *N,N*-Dimethylaniline End-functional Polymers in Photoinduced Block Copolymerization

Block copolymers are of particular interest since they combine the physical and mechanical properties of the corresponding homopolymers. Upon blending two or more homopolymers, they often do not form a homogeneous phase. However, linear arrangement of the blocks by chemical bonds results in a stable structure with the separation of corresponding phases. Each segment exerts its own character to the bulk of the copolymer. Hence, various properties are improved or combined to give possibility of using block copolymers as compatibilizers, impact modifiers, surfactants, coating materials, antistatic agents, viscosity improvers of lubricating oils and adhesives.

4.1.1 Preparation of *N,N*-Dimethylaniline End-functional Polymers by ATRP

A dimethylamino terminated ATRP initiator **3** was prepared, in order to explore the possibility of using photoinduced radical and cationic polymerization strategy to synthesize block copolymers from well-defined prepolymers [279]. Compound **3** was synthesized by the esterification of **1** and **2** in diethyl ether using TEA as acid scavenger (reaction 4.3). Quaternization of tertiary amino group in compound **3** with its own bromomethyl group might have occurred, however, there was no indication of such reaction taking place. Preparation of the acid chloride (**1**) and the alcohol (**2**) in one step from acid and aldehyde, respectively, are illustrated in reactions 4.1 and 4.2. Formation of compounds **1-3** was evidenced by ¹H-NMR spectra as shown in Figures 4.1-4.3.

The ATRP of St in bulk was performed by using **3** as the initiator, CuBr as a catalyst and bipy as a complexing ligand (reaction 4.4). The reaction conditions and results are presented in Table 4.1.

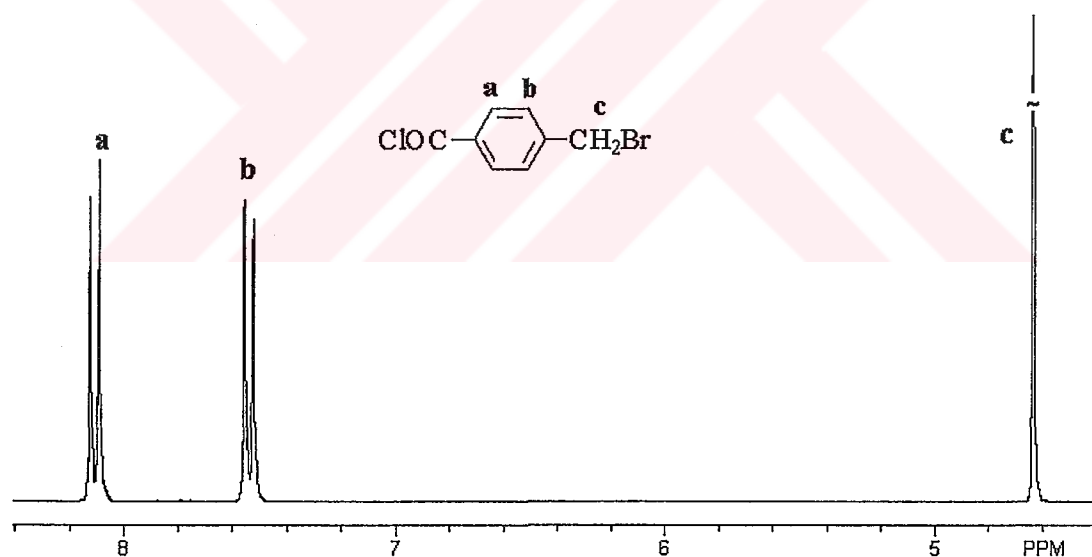
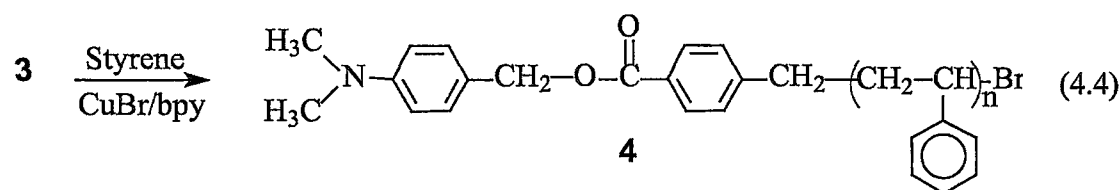
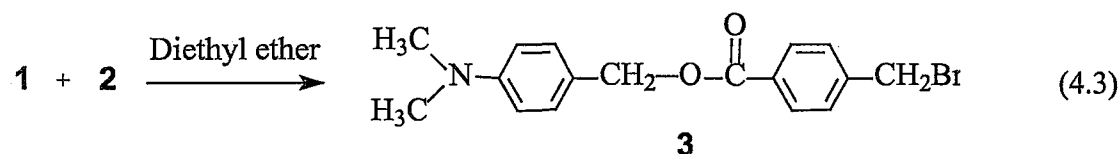
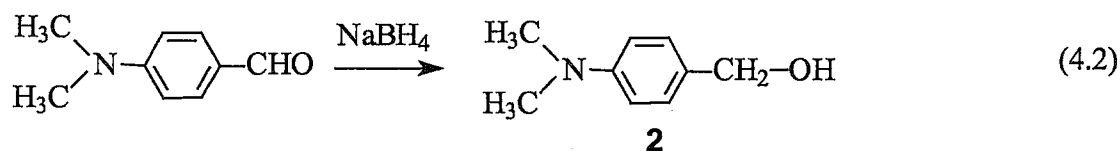
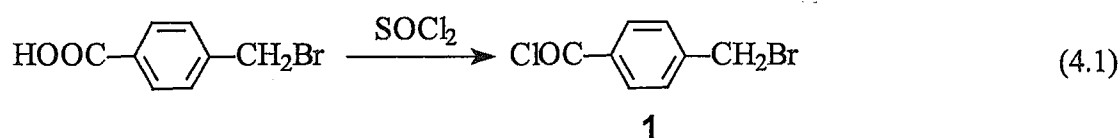


Figure 4.1 : ^1H -NMR spectrum of 4-(bromomethyl)-benzoyl chloride (1)

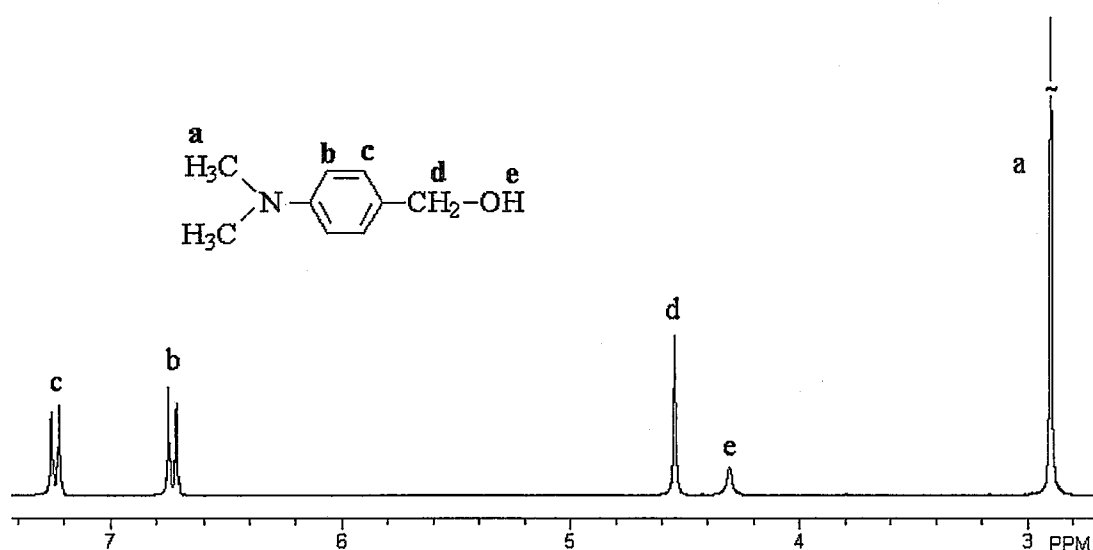


Figure 4.2 : ^1H -NMR spectrum of [4-(dimethylamino)phenyl]methanol (2)

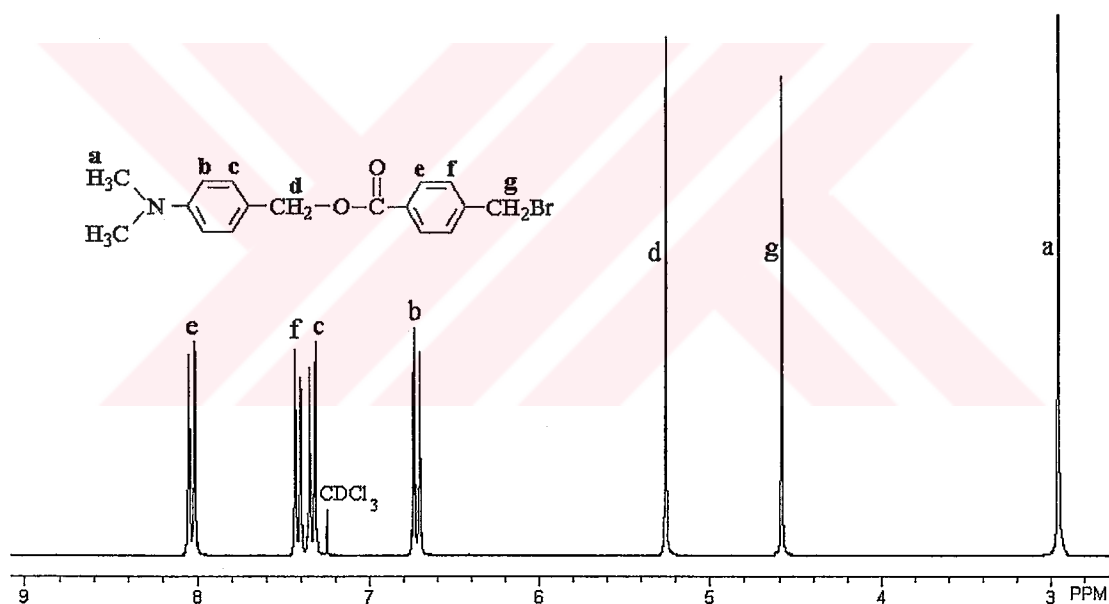


Figure 4.3 : ^1H -NMR spectrum of 4-(dimethylamino)benzyl 4-(bromomethyl) benzoate (3)

In all cases the conversions were determined gravimetrically. As expected, polymers with increasing chain lengths were obtained upon decreasing the initial concentration of the initiator and increasing the polymerization time. The molecular weights determined by ^1H -NMR were calculated from the ratio of integrals corresponding to aromatic protons and dimethylamino ones at about 6.58-7.05 ppm and 2.87 ppm, respectively (Figure 4.4). The molecular weights determined by GPC and ^1H -NMR

agreed well with the theoretical values calculated according to the equation given below:

$$\overline{M}_{n,th} = \frac{[M_0]}{[I_0]} \times 104 \times (\text{conversion}) + \overline{M}_{n,initiator} \quad (\text{Eq:4.1})$$

where M_0 and I_0 are the initial molar concentrations of the monomer and initiator, respectively.

The molecular weight distributions were narrow, which is the characteristic of a mediated polymerization. However, a slight increase in the polydispersities was observed for longer polymerization times indicating the presence of some side reactions, such that the second methyl groups of dimethyl amino functions might be involved in the radical generation and, hence, further polymerization, leading to chain extension.

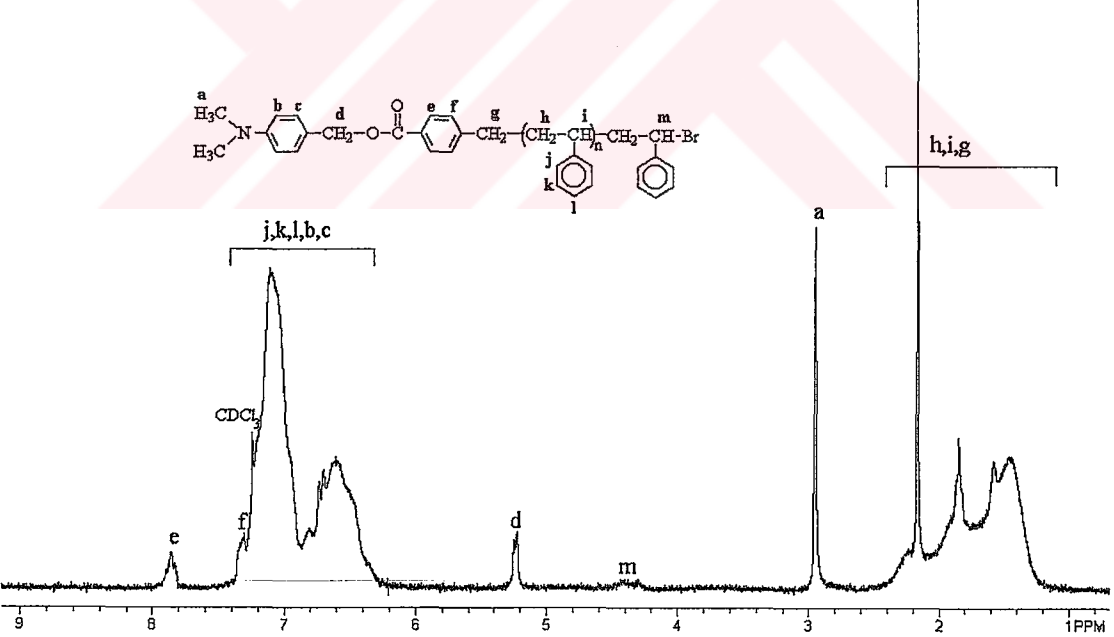


Figure 4.4 : ^1H -NMR spectrum of N,N -dimethyl amino end-functional polystyrene (4)

Table 4.1: ATRP of St in Bulk Using Bromine Terminal Initiator

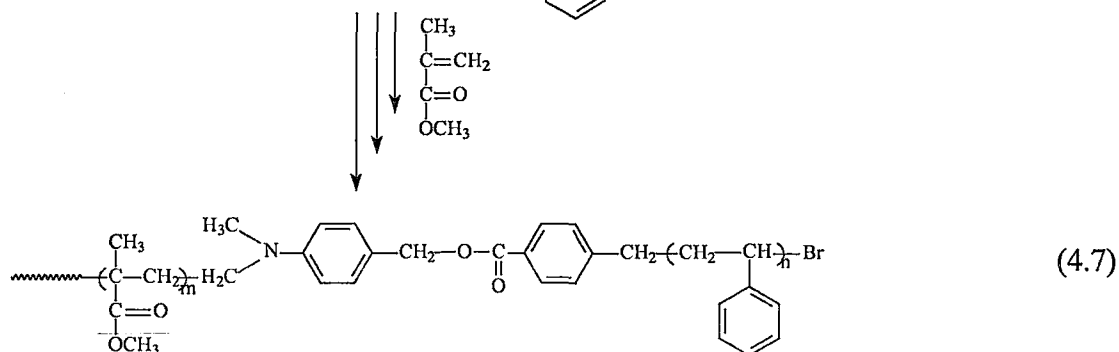
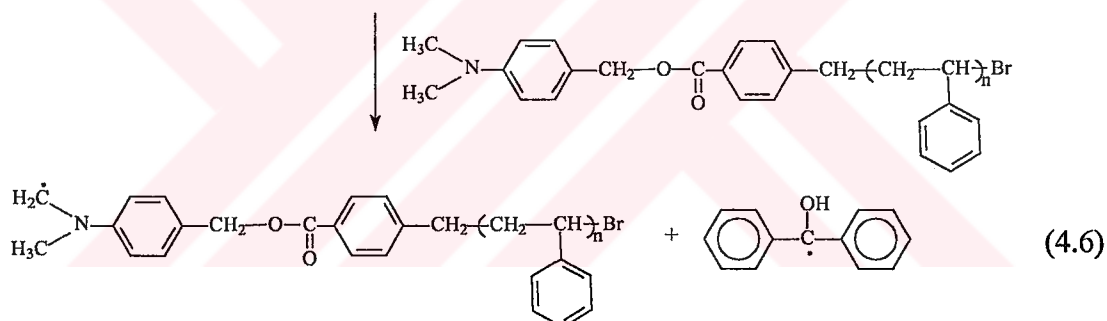
Run	Initial conc. (mol·L ⁻¹)	Polym. Time (min)	Polymer	Conv. (%)	Mn, th	Mn ^{H-NMR}	Mn ^{GPC}	M _w /M _n
1	0.15	47	4a	26.4	1950	2000	1850	1.24
2	0.08	120	4b	18	2400	2500	2600	1.34
3	0.08	380	4c	45	5500	4800	4950	1.37
4	0.02	1620	4d	43	20000	20200	19500	1.5

Bulk, Initiator = **3**, [I]₀/[CuBr]/[bpy] = 1/1/3 molar, temperature 110°C

Mn^{H-NMR} was calculated from the ratio of integrals corresponding to aromatic protons and dimethylamino ones.

4.1.2 Photoinduced Block Copolymerization of *N,N*-Dimethylaniline End-functional Prepolymers

Subsequent to the preparation of the macroinitiators by ATRP, several experiments were carried out to explore the photopolymerization of MMA and CHO via radical and radical promoted cationic polymerization routes, respectively. The former involves hydrogen abstraction by the photoexcited benzophenone from the dimethylamino bearing chain end. This leads to the formation of a carbon centered radical, which initiates the free radical polymerization of MMA as depicted in reaction 4.6. Polymerizations were performed in a merry-go-round type photoreactor in which light was emitted nominally at 350 nm. The results are summarized in Table 4.2.



Polymerization in neat MMA gave a polymer which gave rise to a bimodal GPC trace which is typical for these conditions as MMA is known to autopolymerize and part of the initial PSt was not involved in the formation of block polymer (Table 4.2, Run 6).

Table 4.2: Photoinduced Radical Polymerization of MMA in Bulk and Solution Using Various Macroinitiators with Differing Chain-lengths

Run	[M] (mol.L ⁻¹)	Macro- initiator	Irrad. time (min)	Conv. (%)	Blocking Yield (%)	M _n	M _w /M _n	St./MMA,r.u. (GPC)	St./MMA,r.u. (¹ H-NMR)
5 ^b	9.43	3	60	22.4	-	25500	1.48	-	-
6 ^b	9.43	4a	60	7.3	48	20370	1.93	1/9.6	1/10.2
7 ^s	4.72	4b	15	2.8	100	4140	1.66	1/0.7	1/0.3
8 ^s	4.72	4b	30	10.2	100	4630	1.86	1/0.9	1/0.6
9 ^s	4.72	4b	60	21.2	100	6000	1.86	1/1.5	1/1.1
10 ^s	4.72	4b	120	41.2	100	8580	2.02	1/2.5	1/2.3

[I] = 5 × 10⁻² mol.L⁻¹, ^bbulk, ^ssolution

However, after extraction with various solvents pure block copolymers with ca. 50 % blocking yield were obtained. As a control experiment this procedure was repeated with low-molar mass initiator **3**. Much higher conversion was observed (Table 4.2, Run 5). Thus, terminal amino groups participate effectively in radical generation process. Furthermore, repetition of the polymerization in solution generated materials with almost ideal blocking. The effect of the reaction time on the polymerization was also examined. Notably, the conversion increased from 2.8 to 41.2 by increasing irradiation time. The molecular weights were also increased as reflected by the shift of the initial GPC peak to higher elution volumes (Figure 4.5). The composition of copolymers was estimated from $^1\text{H-NMR}$ data by comparing the ratio of the peak intensities at 3.6 ppm ($-\text{OCH}_3$ of the PMMA segment) to that appearing at 6.5-7 ppm (aromatic protons of the PSt segment) (Figure 4.6).

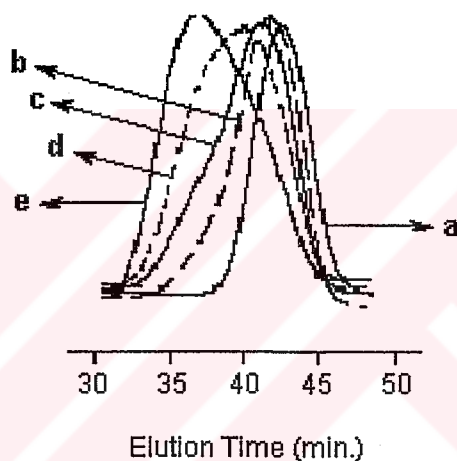


Figure 4.5 : GPC traces of PSt (Table 4.1, run 2) (a) and block copolymers (PSt-b-PMMA) at different conversions; 2.8 (b), 10.2 (c), 21.2 (d), and 41.2 (e)

A relatively good correlation between the composition of copolymers estimated from GPC and $^1\text{H-NMR}$ data was observed. The results are presented in Table 4.2. Some observed differences may be due to the differences in the hydrodynamic volumes of the corresponding segments of PSt and PMMA.

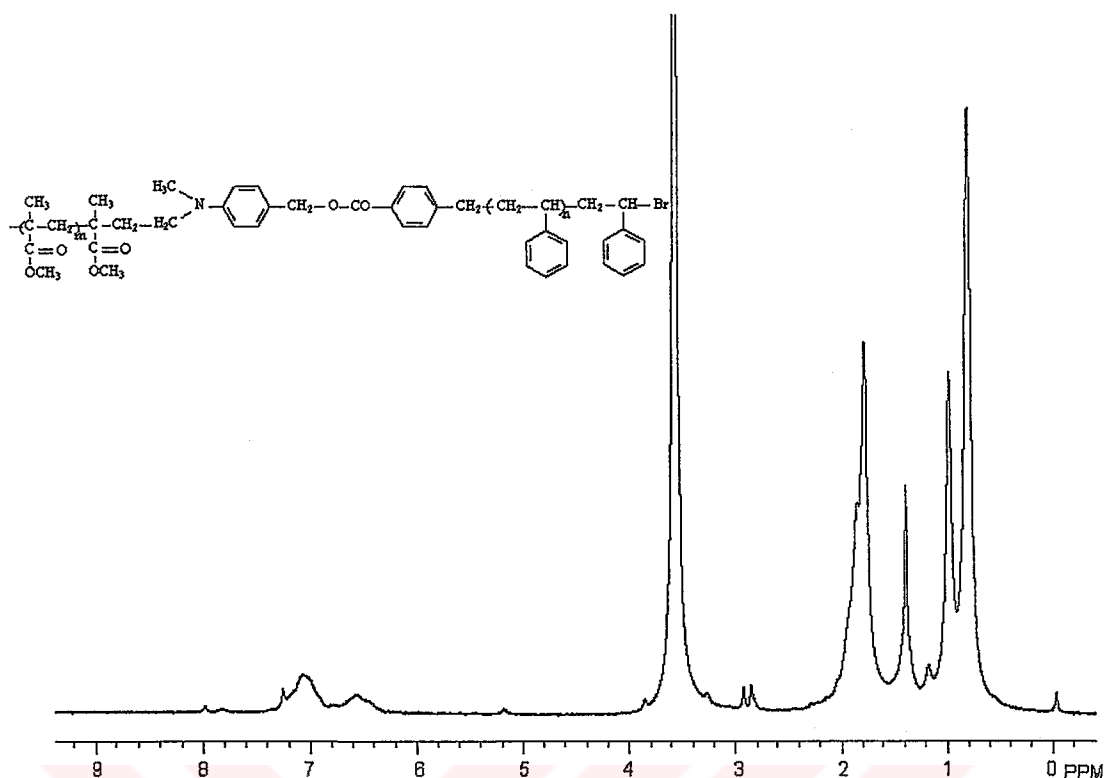


Figure 4.6 : H-NMR spectrum of poly(St-b-MMA) (Table 4.2, run 8)

Similar to the free radical process, the amino terminated polymers were used successfully as polymeric initiators for free radical promoted cationic polymerization of CHO to afford block copolymers. In this case, polymeric radicals, generated upon monochromatic irradiation of CHO in bulk containing a dye sensitizer and the macroinitiator, were oxidized by a diphenyl iodonium salt. The polymeric carbocations thus formed initiated cationic polymerization to yield block copolymers. The overall process of the block copolymerization is depicted in reactions 4.8-4.12.

It should be pointed out that at the irradiation wavelength, 525 nm, the iodonium salt is transparent and all the emitted light is absorbed by Erythrosin B. Therefore, direct decomposition of the iodonium salt can be disregarded. Notably, the three components of the initiating system are indispensable for the polymerization to occur. Either no polymer or negligible amount of polymer is formed in the absence of one or more compounds.

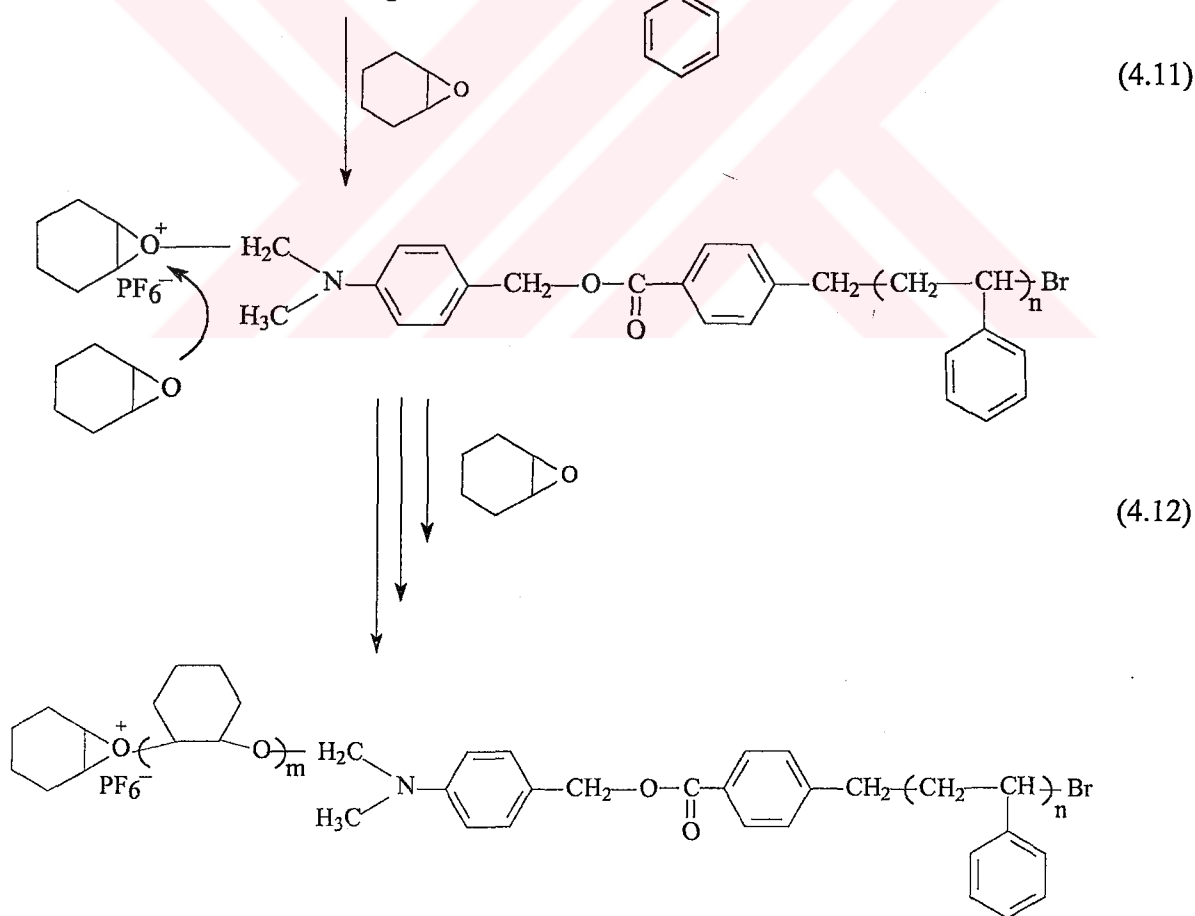
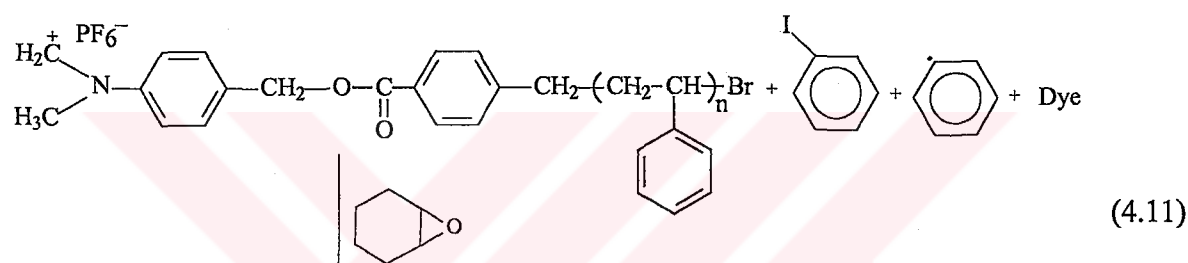
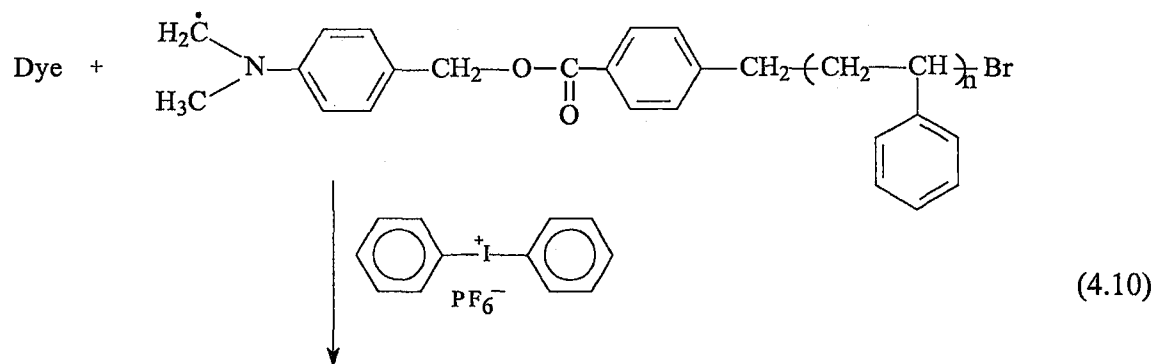
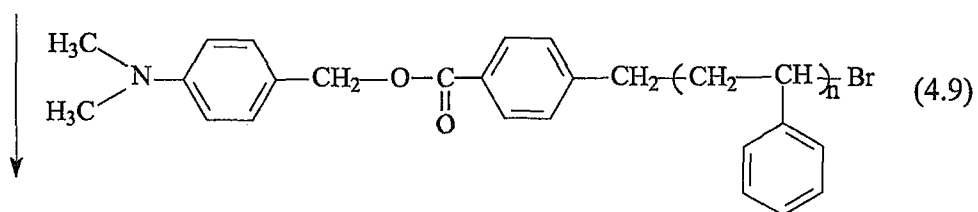


Table 4.3: Photoinduced Radical Promoted Cationic Polymerization of CHO in Bulk Using Various Macroinitiators with Differing Chain-lengths

Run	Macro-initiator	[I] x 10 ² (mol·L ⁻¹)	Conversion, (%)	Blocking Yield, (%)	M _n	PD
11	3	2	39	----	5100	1.69
12	4a	2	25	70	4430	1.73
13	4c	2	5.6	24	6000	1.22

Bulk, [M] = 9.90 mol·L⁻¹, λ_{inc.} = 525 nm. irradiation time = 120 min.

As can be seen from the data presented in Table 4.3, the chain length of the macroinitiator effects the conversion, and blocking yield. Block copolymer formation was evidenced by both ¹H-NMR and GPC analysis (Figures 4.7 & 4.8). Besides block copolymers, homopolymers of CHO are also formed and consequently block yields are relatively low. Homopolymer formation is due to the participation of phenyl radicals formed from the decomposition of the iodonium salt according to reaction 4.10. This represents a further cation generation process.

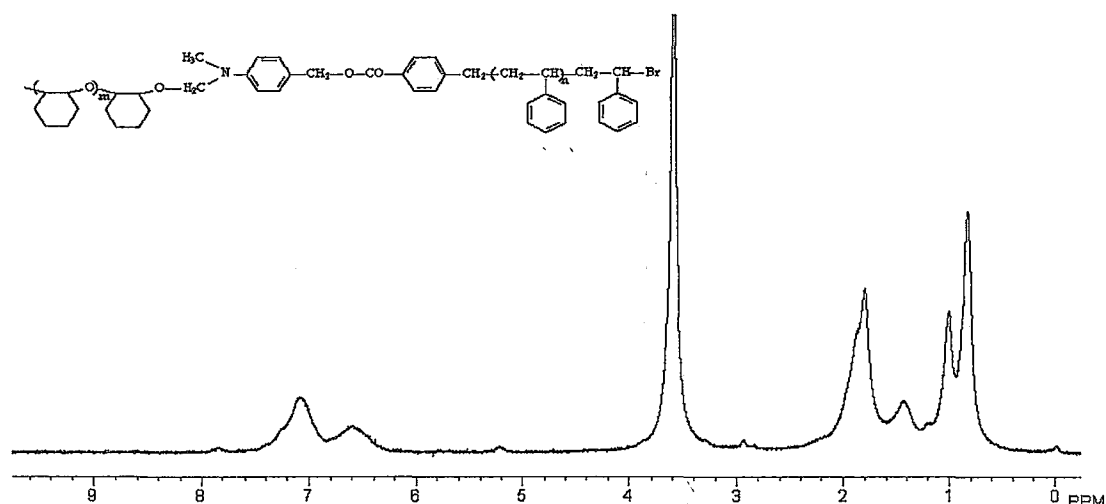


Figure 4.7 : ¹H-NMR spectrum poly(St-b-CHO) (Table 3, run 12)

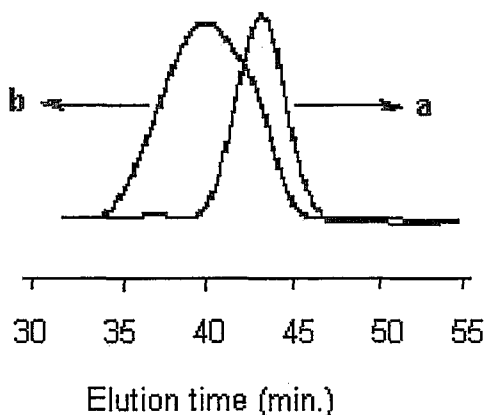


Figure 4.8 : GPC traces of (a) PSt (Table 4.1, run 1) (b) Poly-(St-co-CHO) (Table 4.3, run 12)

Thus, it has been demonstrated that well-defined amino terminated polymers can successfully be utilized in photoinduced polymerizations to prepare block copolymers of structurally different monomers. In this approach the ATRP is combined with photoinduced radical or cationic polymerization.

4.2. Photoinitiated Crosslinking and Grafting of Methylmethacrylate by Using *N,N*-Dimethyl amino Functional Polystyrene Block Copolymers

Polymeric photoinitiators are precursors for block or graft copolymers depending on the position of the photoinitiator moiety incorporated into the polymer chain. In this part, preparation of block-graft copolymers is discussed using a side-chain *N,N*-dimethylamino functional precursor polymer. Since the functional sites for grafting are placed in each repeating unit of a segment, the resulting polymer is a brush type block-graft copolymer.

4.2.1. Preparation of Precursor Poly(*N,N*-dimethyl-4-vinylphenethylamine-*block*-styrene)

Poly(*N,N*-dimethyl-4-vinylphenethylamine-*block*-styrene), [P(PTA-*b*-St)] block copolymer was synthesized by sequential addition of *N,N*-dimethyl-4-vinylphenethylamine (PTA) and styrene (St) by anionic living polymerization as described previously [271,277,278,280]. The experimental conditions and results are presented in Table 4.4.

Table 4.4: Experimental Conditions and Results for the Preparation^a of Poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene, PDPTA-*b*-PSt Diblock Copolymer

Run	DPTA (g)	Time (h)	St (g)	Time (h)	Solvent ^b (mL)	Initiator ^c (mmol)	Conv. (%)	PSt cont. (%)	$\overline{M}_n$ ($\times 10^{-4}$)	$\overline{M}_w/\overline{M}_n^d$
14	3.4	10	3.9	3.5	160	0.15	100	53	2.2	1.01

^a Polymerization was carried out at -78°C under a pressure of 10^{-6} torr,

^b THF, ^c cumyl K,

^d Determined from GPC measurement.

4.2.2. Photoinduced Radical Polymerization of MMA in the Preparation of Grafted Chains

The diblock copolymer containing *N,N*-dimethyl amino groups in one segment was used as a backbone in the photografting experiments for the preparation of polymer brushes by the ‘grafting from’ strategy. As depicted below (reactions 4.13-4.15), the mechanism involves hydrogen abstraction by the photoexcited benzophenone from *N,N*-dimethyl amino groups. The carbon centered radicals thus generated are able to initiate the free radical polymerization of methylmethacrylate (MMA).

Formation of block-graft copolymer was evidenced by GPC and ^1H -NMR analyses. Shifting of the initial unimodal GPC peak of precursor diblock copolymer to higher elution volumes indicates that grafting was successfully established (Figure 4.9). Furthermore, as seen in the ^1H -NMR spectrum of the polymer recorded after photopolymerization, the peak appearing at about 3.6 ppm corresponding to O-CH₃ protons shows the presence of grafted MMA units in the final polymer (Figure 4.10). The results are summarized in Table 4.5. It is interesting to note the effect of both initiator concentration and irradiation time in the conversion and molecular weights.

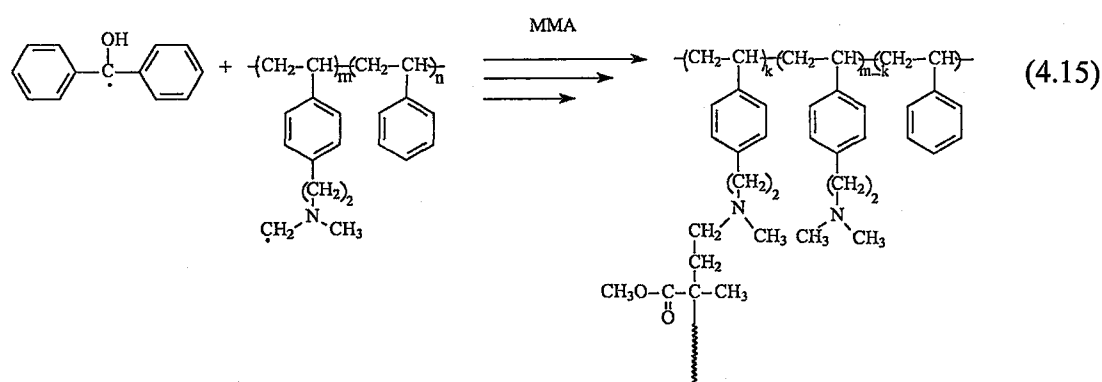
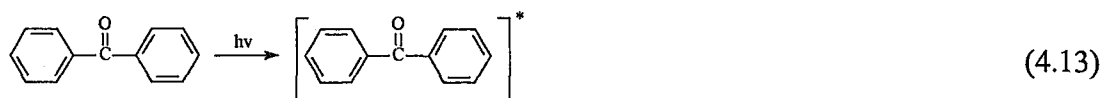


Table 4.5: Preparation of [poly(*N,N*-dimethyl-4-vinylphenethylamine)-*graft*-polymethyl-methacrylate]-*block*-polystyrene, (PDPTA-*g*-PMMA)-*b*-PSt Block-graft Copolymer via Photoinduced Radical Polymerization^a of MMA

Run	[M] (mol.L ⁻¹)	[I] ^d (g.L ⁻¹)	Irrad.time (min)	Conversion (%)	$\overline{M}_n^{e,f}$	$\overline{M}_w/\overline{M}_n^{e,f}$
15 ^b	9.43	10	30	9.0	75300	2.67
16 ^c	4.72	10	30	6.8	30600	1.29
17 ^c	4.72	5	30	18	51700	2.70
18 ^c	4.72	10	10	4.9	41850	2.77

^a $\lambda_{inc.}$ = 350 nm., ^bbulk, ^csolution, ^dpoly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene, ^esoluble polymer, ^fdetermined from GPC measurement.

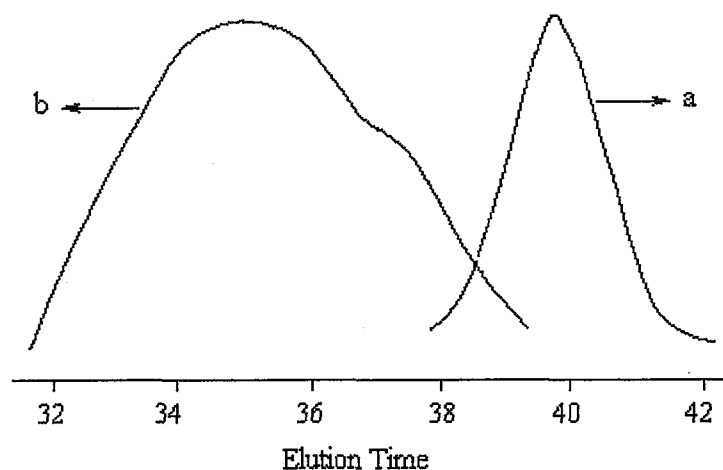


Figure 4.9 : GPC traces of precursor [P(PTA-*b*-St)] block copolymer (a), and final block graft copolymer (b)

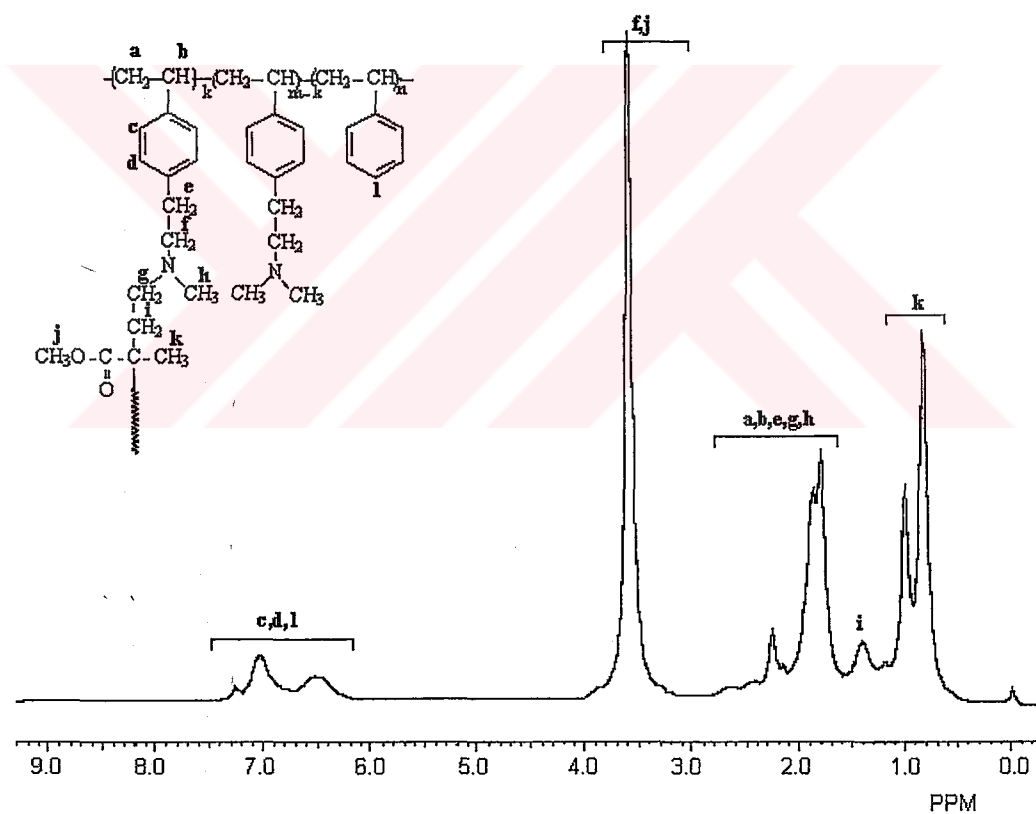


Figure 4.10 : ^1H -NMR spectrum of [poly((*N,N*-dimethyl-4-vinylphenethylamine)-*graft*-polymethylmethacrylate)]-*block*-polystyrene

In the experiments, formation of crosslinked polymer was observed to a greater extent. In all cases, crosslinking yield was as high as 80 % or more. The crosslinking mechanism may be explained with the participation of unsaturated chain ends, formed by the disproportionation reaction, in further radical attack. The presence of absorption bands belonging to methylmethacrylate appearing at about 1735 cm^{-1} (C=O stretching) and 1150 cm^{-1} (C-O stretching) in the IR spectrum of crosslinked polymer (Figure 4.11) supports that monomer was involved in crosslinking. Moreover, the possibility of macroradical attack by other growing species in the chain termination may be another reason for the crosslinking reactions as methylmethacrylate polymerization is known to be terminated partly by chain combination besides disproportionation. This possibility was further investigated by experiments carried out in the absence of monomer. A control experiment produced an insoluble polymer network after 30 minutes of irradiation under identical conditions except for the fact that no monomer was available in the reaction medium. This suggests that combination of backbone copolymers through the carbon centered radicals stemming from the *N,N*-dimethyl amino side groups may also contribute to crosslinking.

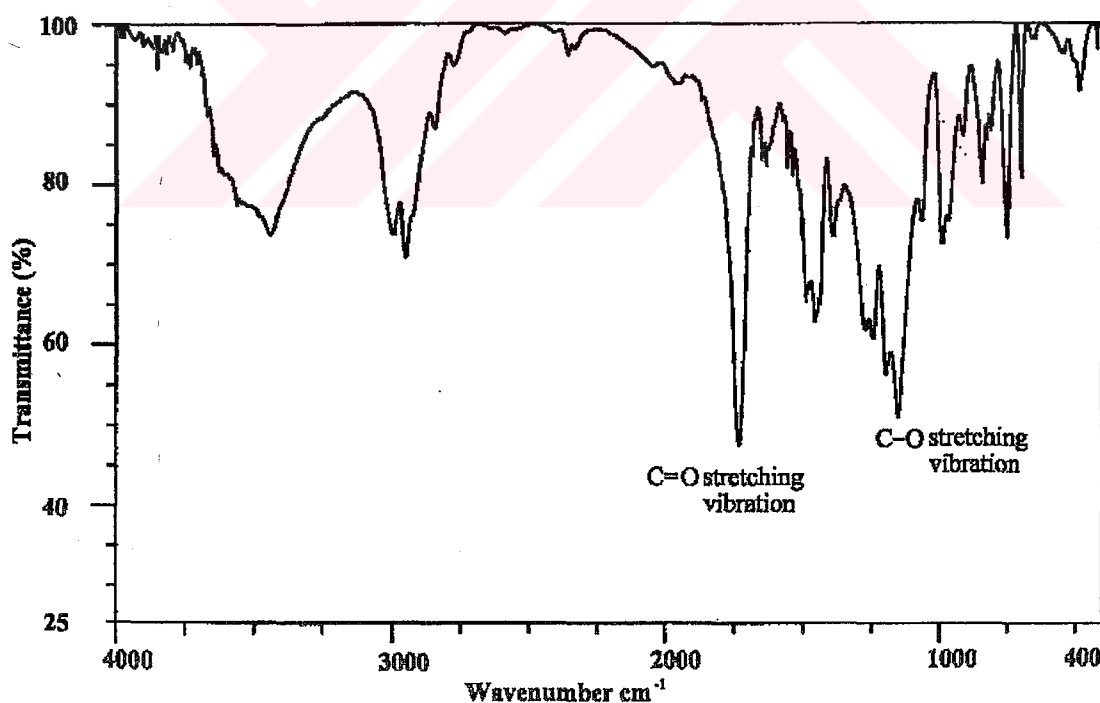
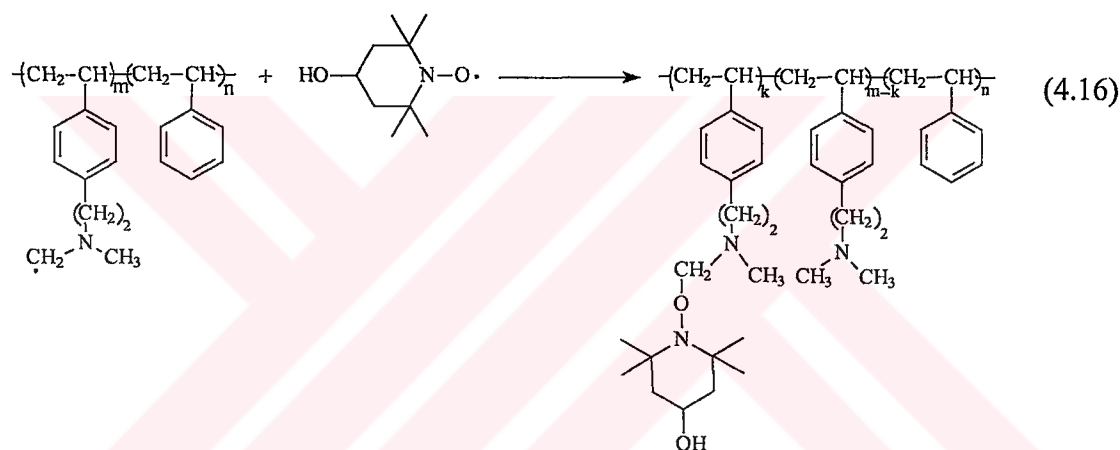


Figure 4.11 : IR spectrum of the crosslinked polymer on KBr disk

4.2.3. Photosensitized Side Chain HTEMPO Capping of Poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene

In order to give more insight to the grafting mechanism, photochemically generated radicals, formed according to reaction 4.14, were reacted with the stable radical, 4-hydroxy-2,2,6,6-tetramethyl-1-piperidiny-1-oxy (HTEMPO), in the absence of the monomer as illustrated in reaction 4.16. Figure 4.12 gives the $^1\text{H-NMR}$ spectra of poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene (A) before and (B) after capping with HTEMPO. The new proton signals appearing at 1.09 and 1.17- ($-\text{CH}_3$), 3.73 ($-\text{CH}-$), and 5.29 ($-\text{CH}_2-$) proved that HTEMPO moieties were incorporated into the polymer. This implies that upon irradiation, grafting takes place through the radicals formed on the side chains.



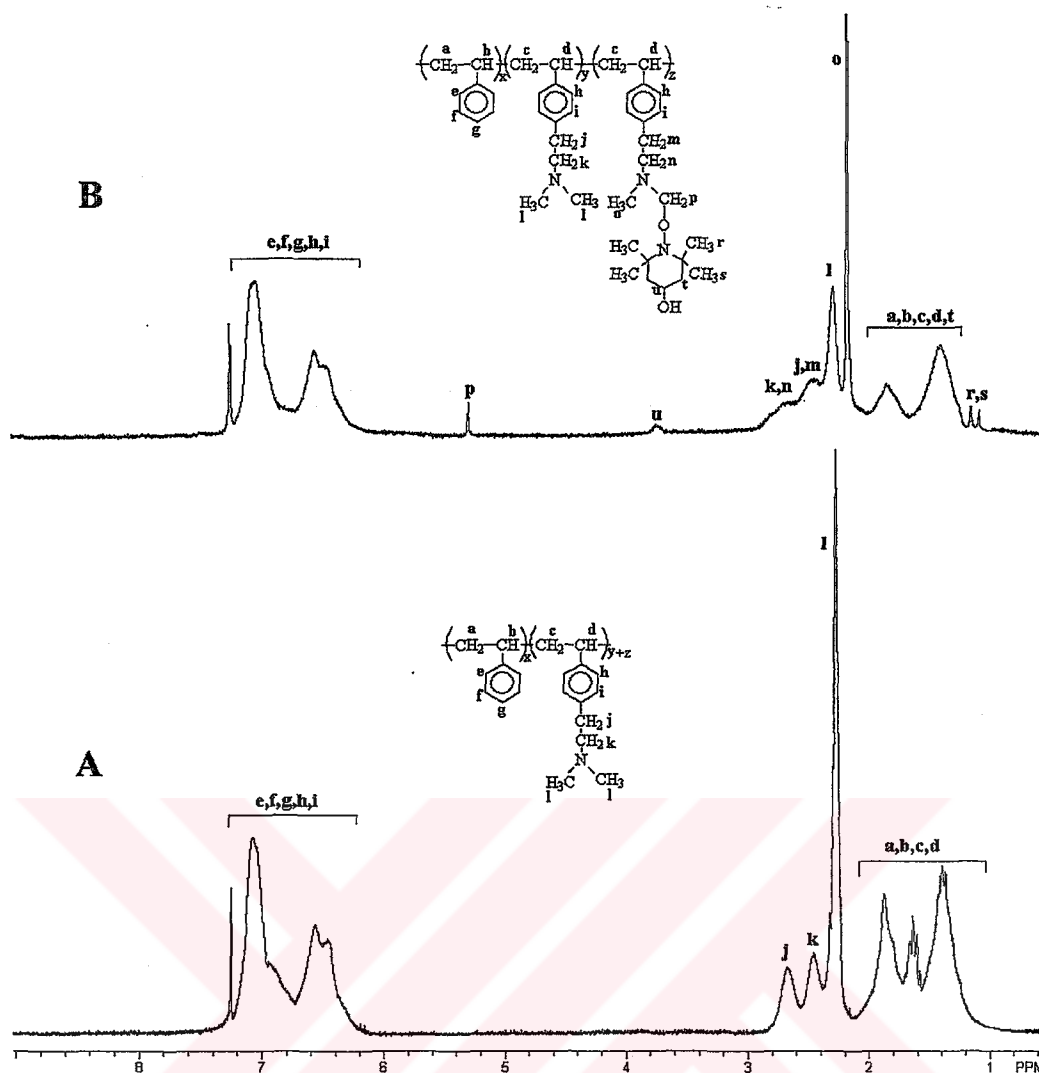


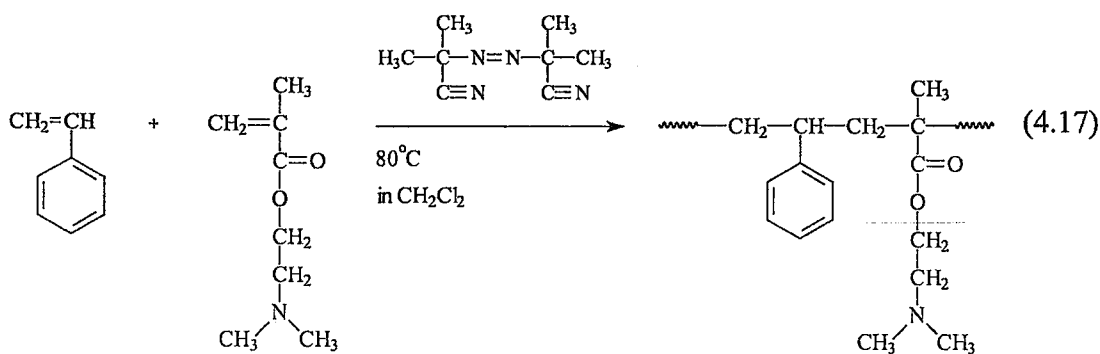
Figure 4.12 : ^1H -NMR spectra of poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block* polystyrene before (A) and after capping with HTEMPO (B)

4.3. Synthesis of Random Copolymers Possessing H-donating Sites for Photoinduced Grafting

Copolymerization is a powerful tool to combine the advantages of corresponding homopolymers. The simplest type of copolymers is one where two or more comonomers are simultaneously copolymerized. This technique is commonly used to modify and/or improve the mechanical and physical properties of many polymers. If the copolymerization obeys Bernoullian statistics, a random copolymer is formed. However, polymerization may follow other types of statistics (e.g., Markovian), resulting in a variety of statistical copolymers.

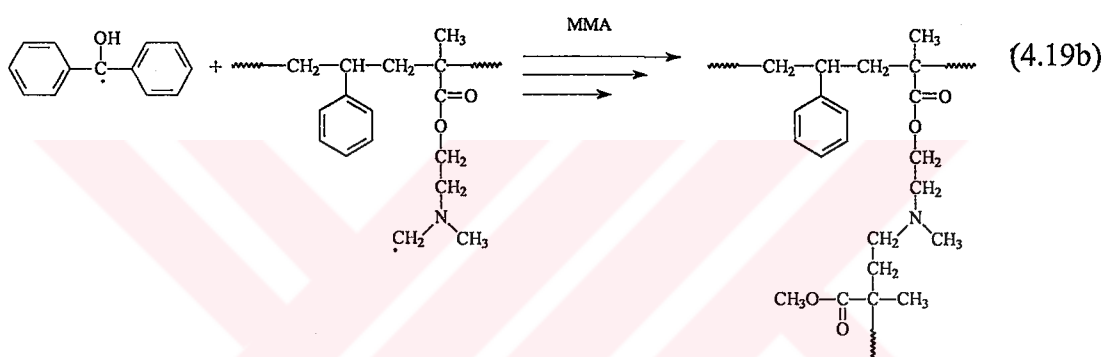
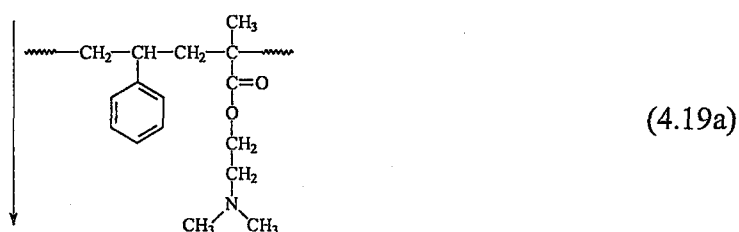
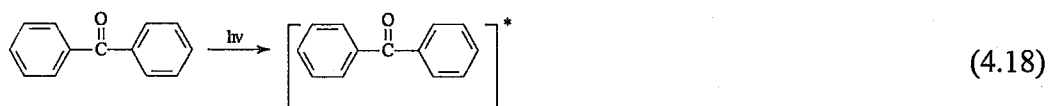
The current interest in branched polymers that are molecularly well defined is fueled by the growing demand for structures exhibiting shape persistence; the role played by the branching points are to lower the conformational entropy of such objects. Graft copolymers contain branching points that may be distributed along the polymer backbone either randomly or under a controlled manner. These materials may be useful in applications requiring surface modification and control of the surface properties.

Random copolymers of styrene and 2-(dimethylamino)ethyl methacrylate with varying compositions were prepared via classical radical polymerization initiated by AIBN, conducted at 80°C (reaction 4.17). The experimental conditions and results are presented in Table 4.6.



The random copolymer containing randomly distributed *N,N*-dimethyl amino groups in the side chain was used as a backbone to explore the possibility of using photoinduced radical polymerization technique in the preparation of a graft

copolymer by 'grafting from' method. Again, the free radical polymerization of MMA is initiated by the carbon centered radicals, generated due to hydrogen abstraction by the excited benzophenone (reactions 4.18-4.19a,b).



Successful grafting was evidenced by shifting of the initial unimodal GPC peak of precursor copolymer to higher elution volumes as shown in Figure 4.13. Further proof was supplied by the $^1\text{H-NMR}$ analysis. The peak appearing at about 3.6 ppm corresponding to O-CH₃ protons in the $^1\text{H-NMR}$ spectrum of the polymer recorded after photopolymerization shows the presence of grafted MMA units in the final polymer (Figure 4.14).

Table 4.6: Conditions^a and Results in the Preparation of Random Copolymers via Radical Polymerization

Run	Initial St Content (%)	[I] ^b ×10 ² (g.L ⁻¹)	Time (min)	Conversion (%)	St Cont. in Copolymer ^c (%)	M _n ^d	M _w /M _n ^d
19	0	2.03	30	39.3	0	15100	1.37
20	10	2.85	45	Nd ^e	17.4	14300	1.58
21	20	2.85	80	51.2	29.6	24500	1.32
22	50	2.85	75	32.1	59.1	18400	1.50
23	90	2.85	125	24.7	78.9	20600	1.23
24	100	3.33	60	33.5	100	13200	1.53

^aTemperature=80°C, solvent: CH₂Cl₂,

^bInitiator: AIBN,

^cDetermined from GPC measurement,

^dDetermined from ¹H-NMR calculations,

^end: not determined.

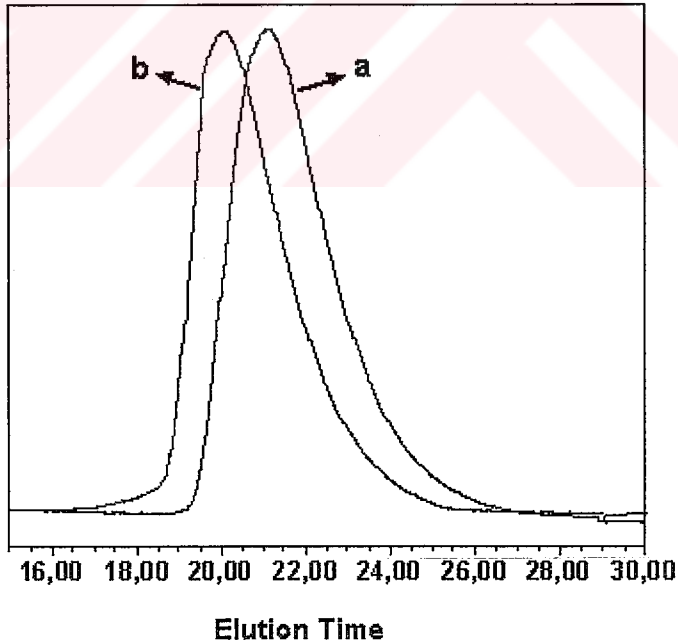


Figure 4.13 : GPC traces of the precursor random co-polymer (a), and the graft co-polymer after photopolymerization (b)

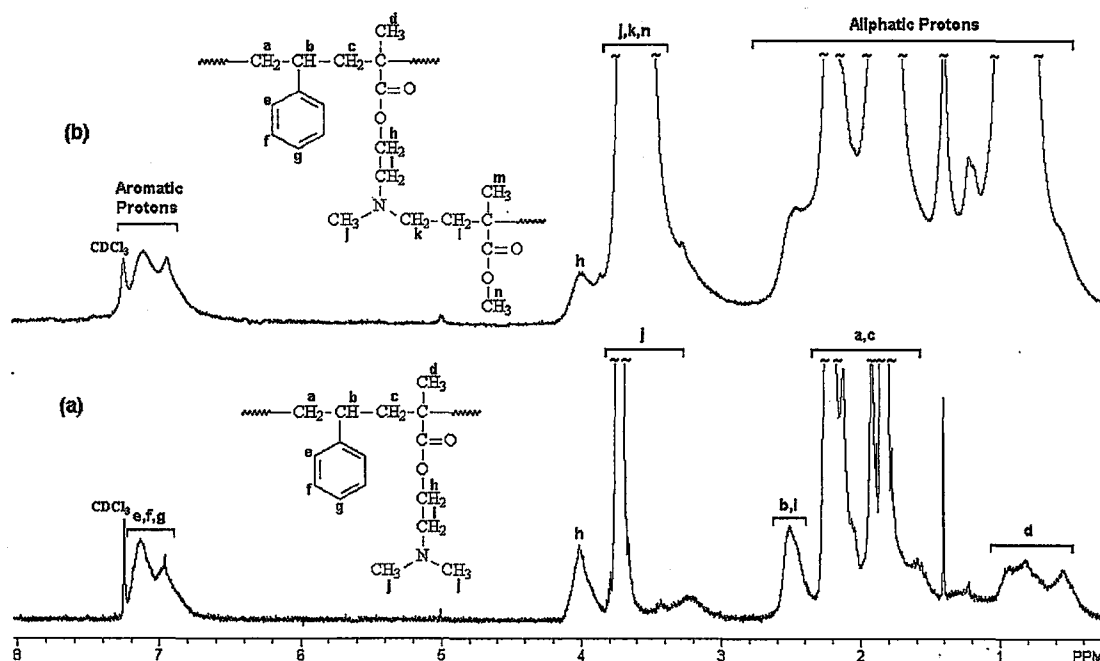
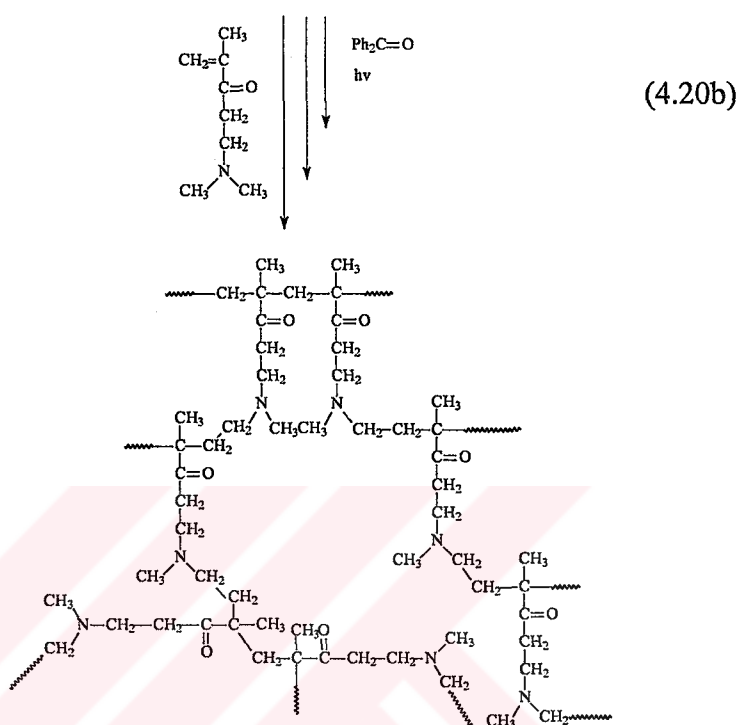
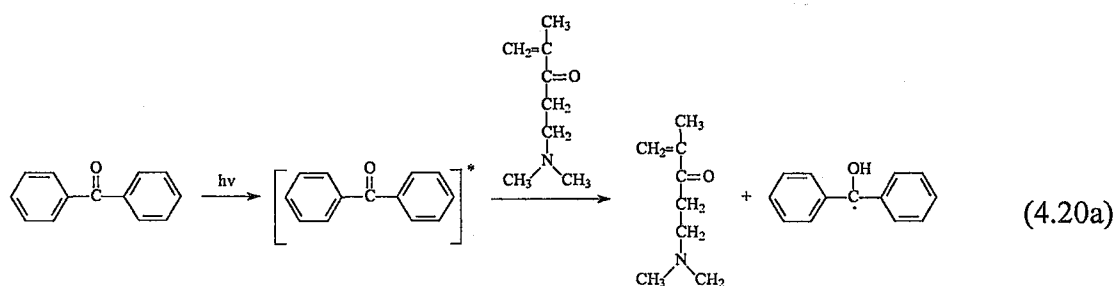


Figure 4.14 : ¹H-NMR spectra of the precursor random co-polymer (a), and the graft copolymer after photopolymerization (b)

4.4 Synthesis of Hyper-branched Polymers

Because of the nature of the photoinitiation and the structure of the monomer 2-(dimethylamino)ethyl methacrylate, it seemed appropriate to prepare hyper-branched polymers by photopolymerizing the monomer itself in the presence of benzophenone. The monomer possesses both hydrogen donating sites as well as the polymerizable methacrylate functionality. As stated in the theoretical part, monomers having both initiating sites and polymerizable group can lead to the formation of hyper-branched polymers via, so-called, self-condensing vinyl polymerization. In this process, chain addition polymerization is combined with self-condensation of chains (see reactions 2.107-2.109). It involves an AB* vinylic compound, where A represents a double bond and B*, a latent initiating site that can be activated by an external stimulus.

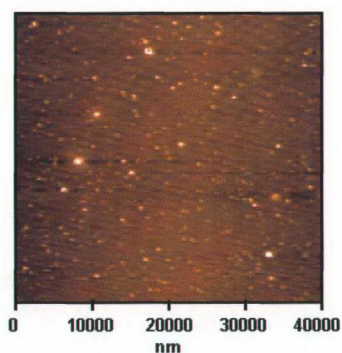
In our case, side-chain *N,N*-dimethyl amino groups form radicals after hydrogen abstraction by photoexcited benzophenone whereas methacrylate groups take part in propagation. The overall process is presented in reactions 4.20a,b.



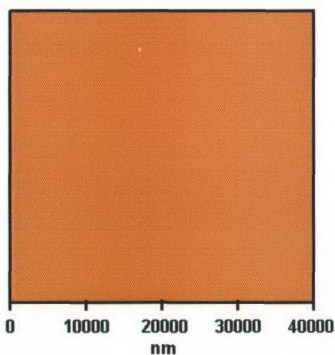
Experimentally, the solution of monomer (2.96 mol.L^{-1}) containing $5 \times 10^{-2} \text{ mol.L}^{-1}$ benzophenone in methylene chloride was irradiated for 60 minutes at a wavelength of 350 nm in a manner as described for photoinduced grafting reaction. At the end of irradiation, a polymer with 21 % conversion and $M_n = 1060$, $PD = 1.57$ was readily formed. Atomic force microscopy (AFM) was used to study the differences in morphologies of branched and linear polymers. For comparing the surface morphologies, a previously synthesized linear polymer of 2-(dimethylamino)ethyl methacrylate was examined by AFM (see Table 4.6, run 19). Thin films of polymer were prepared by spin-coating from polymer solutions in chloroform onto hydroxylated silicon substrates at 2000 rpm for 1 minute. The samples were kept at 70°C for 1 hour for complete removal of solvent. The spin-coated films are in a non-equilibrium state because of the rapid evaporation of solvent. Therefore, after performing the initial AFM measurements, the films were annealed at a temperature of 130°C , above glass transition temperature of poly(2-(dimethylamino)ethyl

methacrylate) for 2 hours, and changes in surface topography upon annealing were presented. The annealing process is crucial for equilibration of the microphase separated surface morphology. The measurements were conducted in the tapping mode. In this method, the lateral forces between the AFM tip and the surface are minimized and soft materials can be scanned with much less tip induced deformation.

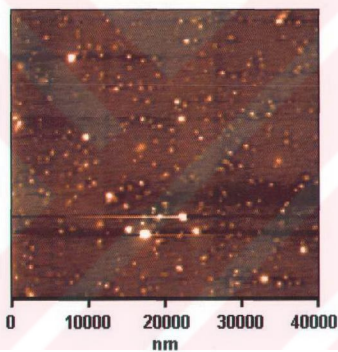
AFM height and phase images of linear poly(2-(dimethylamino)ethyl methacrylate) are shown in Figure 4.15 before and after annealing at 130°C for 2 hours. Both height images show irregular protrusions. However, in the phase image before annealing, the featureless surface is smooth while some dots rarely distributed in the matrix appear after annealing. The AFM images of branched poly(2-(dimethylamino)ethyl methacrylate) illustrated in Figure 4.16 exhibit a distinct domain structure when compared with that of the linear polymer. In the height image after annealing, very regular dotted structures appear. In the phase mode, comparable patterns are visible, which indicates the presence of two phases with different viscoelasticities. As more detailed images of the same scan are provided (Figure 4.17), these dotted structures have turned out to be surface undulations with depths ranging from 3 to 5 nm and with diameters varying between 230-330 nm (Figure 4.17c). In the phase image, corresponding phase separation is very obvious. Figure 4.18 shows height and phase images of thinner spin-coated films of branched poly(2-(dimethylamino)ethyl methacrylate) without annealing. (Thickness of the film is about 1/6 of that of the film presented in Figure 4.16.) In a thinner film, reorganization of different phase regions are seen even before annealing, but the size of circular regions is smaller and their number is large, which is the case illustrated by the images in Figure 4.18b,d. Annealing the film brings these regions together, which increases their size but decreases their number. The holes and other spheroid structures are clearly discernable in the height mode as well (Figure 4.18c).



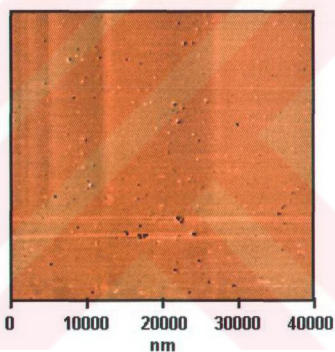
(a)



(b)



(c)



(d)

Figure 4.15 : AFM height images of linear poly(2-(dimethylamino)ethyl methacrylate) before (a) and after (c) annealing at 130°C for 2 hours. Corresponding AFM phase images (b) and (d)

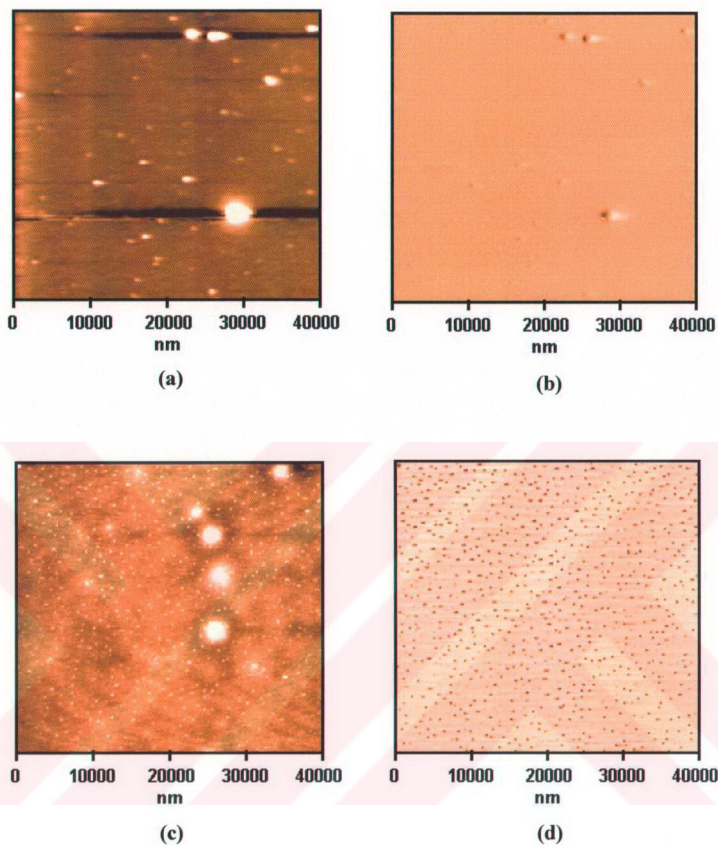
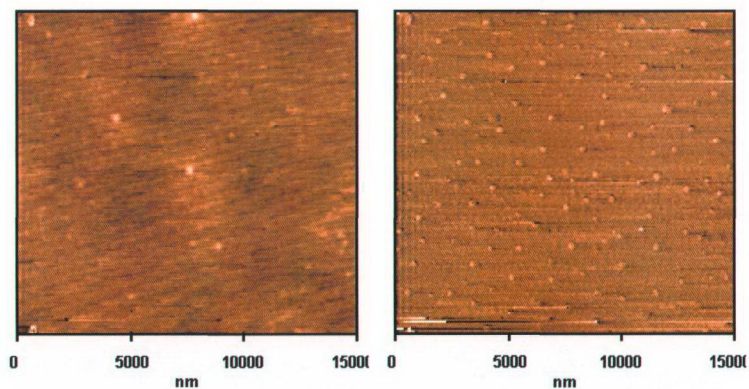
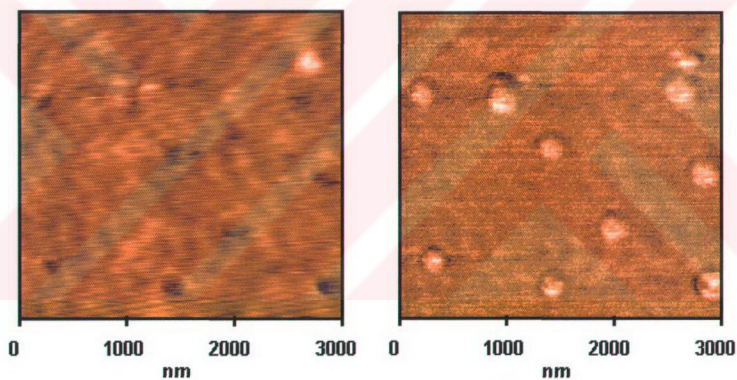


Figure 4.16 : AFM height images of branched poly(2-(dimethylamino)ethyl methacrylate) before (a) and after (c) annealing at 130°C for 2 hours. Corresponding AFM phase images (b) and (d)



(a)

(b)



(c)

(d)

Figure 4.17 : Zoomed AFM height (a,c) and phase (b,d) images of branched poly(2-(dimethylamino)ethyl methacrylate) in Figure 4.12 (c) and (d)

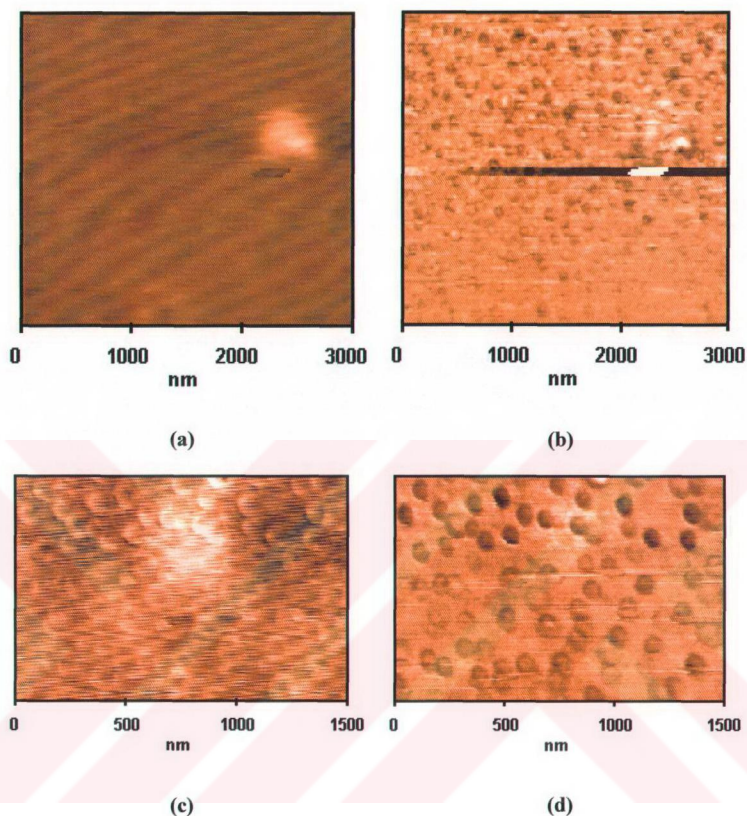


Figure 4.18 : AFM height images of thinner ($\sim 1/6$ of the film thickness of Fig. 14.16) branched poly(2-(dimethylamino)ethyl methacrylate) after spin coating without annealing: (a) and (c). Corresponding AFM phase images (b) and (d).

It is evident that physical characteristics of linear and branched polymers differ significantly as a result of differences in the chain mobilities, probably leading to the formation of two distinct phases. Such morphology as evidenced by the AFM images suggest phase separation between branched-polymer rich phase (spheres) and linear polymer rich phase. In other words, branched polymer rich discrete phases are regularly distributed in the continuous linear polymer rich phase. As the AFM results imply, the formation of linear or slightly branched polymers dominates that of

propagation steps in the self condensation mechanism as compared to the formation of initiating radicals through hydrogen abstraction by the photoexcited benzophenone. Obviously, propagation through the methacrylic double bond favors the formation of linear segments while photoinduced radical generation on the amino functions enhance branching.

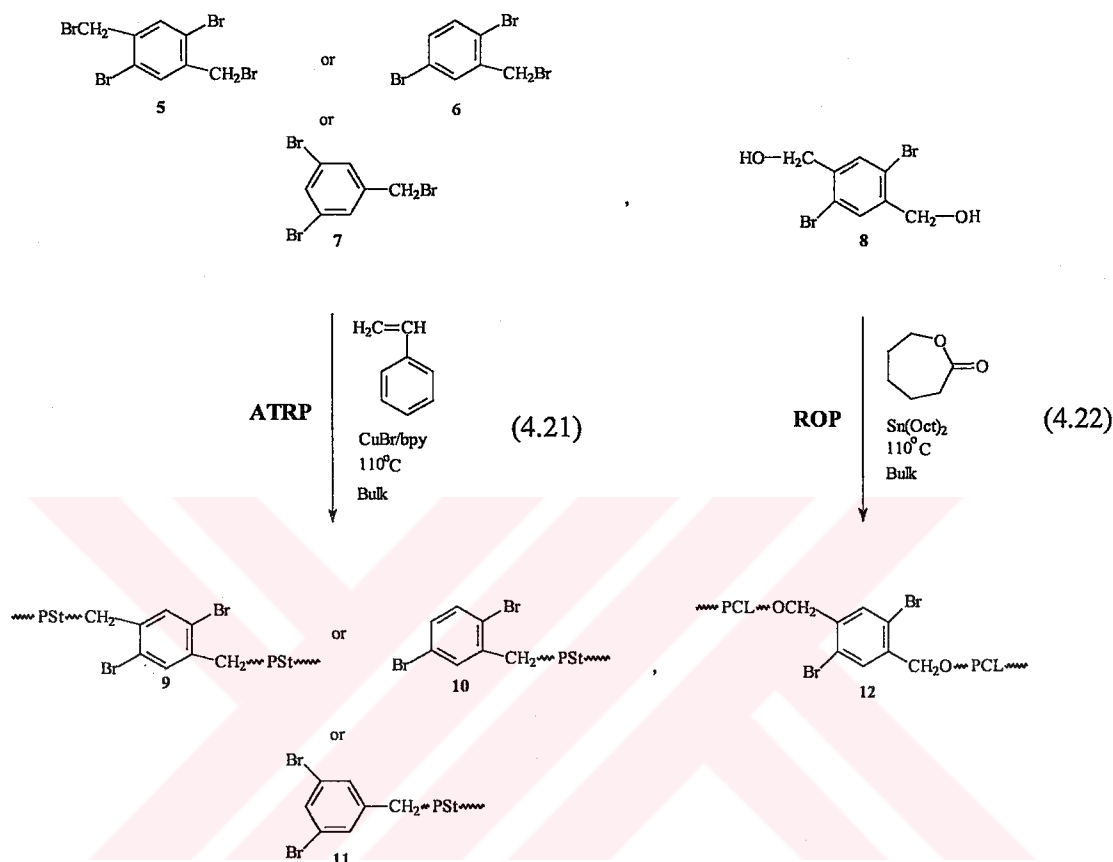
Although these results are preliminary in nature, they clearly indicate the possibility of preparing branched or hyper-branched polymers simply by using H-abstraction types of photoinitiation. The linear/hyper-branched ratio in the polymer may be adjusted by changing various experimental parameters, such as, monomer concentration and intensity of light.

4.5 Synthesis of A₂B and A₂B₂ type miktoarm star copolymers by combination of ATRP or ROP with photoinduced radical polymerization

Star-shaped polymers have been attracting interest as new polymer materials due to their various functions and properties stemming from their unique three dimensional structures. A great advantage of star polymers is that they offer lower melt and solution viscosities than their linear analogues with identical molecular weights [5]. These polymers have found applications in various areas where low viscosity polymer formulations are desirable, especially in the fabrication of polymers with relatively low thermal stabilities such as poly(lactone). Furthermore, star polymers possess high degrees of functionalities that give rise to many specialized applications.

In this work, synthesis of miktoarm star copolymers was carried out by combining controlled polymerization methods with photopolymerization. For this purpose, well-defined polymers, which contain central or lateral aromatic dibrominated moieties that give the possibility for further modification, were obtained by ATRP or ROP [281]. In the next step, these precursor polymers, modified to possess amino or *N,N*-dimethyl amino groups, were employed as coinitiators in Photoinduced Radical Polymerization in order to prepare the final miktoarm star copolymer. The ATRP of styrene in the presence of 1,4- dibromo-2,5-di(bromomethyl)benzene (5), 1,4-dibromo-2-(bromomethyl)benzene (6) or 1,3-dibromo-5-(bromomethyl)benzene (7) as bi- or monofunctional initiators, in conjunction with CuBr/2,2'-bipyridine as

catalyst afforded the desired starting polystyrenes (9-11) as depicted in reaction 4.21. In addition, a PCL type polymer (12) was obtained via ROP of ϵ -caprolactone, in which bifunctional initiator 2,5-dibromo-1,4-(dihydroxymethyl) benzene (8) was used in conjunction with $\text{Sn}(\text{Oct})_2$ catalyst (reaction 4.22).



The conditions and results of these experiments are given in Table 4.7. As these polymers were intended to be employed in further reactions, the efforts were directed toward obtaining polymers with low molecular weights and low polydispersities in acceptable yields.

Table 4.7: Conditions and Results for the Preparation of Precursor Polymers through ATRP or ROP

Run	Initiator	Method	Initiator conc. (mol.L ⁻¹)	Reaction time (min)	Polymer	Yield (%)	M _{n,th}	M _{n,H-NMR}	M _{n,GPC}	PD
25	5	ATRP ^a	0.1	50	9a	52	5150	5200	5300	1.18
26	5	ATRP ^a	0.1	45	9b	41	4153	4180	4230	1.23
27	6	ATRP ^b	0.15	60	10	27	1970	1860	2180	1.32
28	7	ATRP ^b	0.15	60	11	30	2150	2000	2500	1.31
29	8	ROP ^c	9.02	24h	12	-	4800	5700	5900	1.42

^abulk, 120°C, [I]/CuBr/bpy = 1/2/6

^bbulk, 120°C, [I]/CuBr/bpy = 1/1/3

^cbulk, 120°C [CL]/[I] = 40/1, [OH]/[Sn(oct)₂] = 200/1

In the case of PSt polymers with two arms (runs 25 and 26), a product with lower polydispersity (also higher molecular weight) was obtained as the polymerization time was increased. The theoretical molecular weights ($M_{n,th}$) were calculated by using the following equation:

$$\overline{M}_{n,th} = \frac{[M_0]}{[I_0]}(M_w)(\text{conversion}) + M_I \quad (\text{Eq:4.2})$$

where M_0 and I_0 are the initial molar concentrations of monomer and initiator, and M_w and M_I are the molecular weights of the monomer and initiator, respectively. In all cases, the calculated values are close to those found by GPC measurements.

As the molecular weights were low, the results could be verified by $^1\text{H-NMR}$ analysis (Figures 4.19 and 4.20). In the case of PSt prepolymers, the peak from the final CH-Br protons appears very clearly at about 4.5 ppm.

Molecular weights of the polymers were also calculated by comparing the intensity of this peak with those from aromatic region. In the case of **12**, the protons belonging to the rest of the initiator (**a** and **b** in Figure 4.20) are clearly evidenced and their integrals were compared with those of O-CH_2 protons (**g**) from the PCL chain.

The next step in our strategy was to introduce the hydrogen donating sites, capable of reacting with certain photoexcited molecules to produce initiating radicals, in the prepolymers. It is known that photolysis of aromatic ketones, such as benzophenone, thioxanthenes, benzil, and quinones, in the presence of hydrogen donors, such as alcohols, amines, or thiols leads to the formation of a radical produced from the carbonyl compound (ketyl-type radical) and another radical derived from the hydrogen radical. The photopolymerization of vinyl monomers is usually initiated by the radical produced from the hydrogen donor. The ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of the unpaired electron. The overall mechanism of the photoinitiation on the example of benzophenone is represented in reactions 4.23 and 4.24.

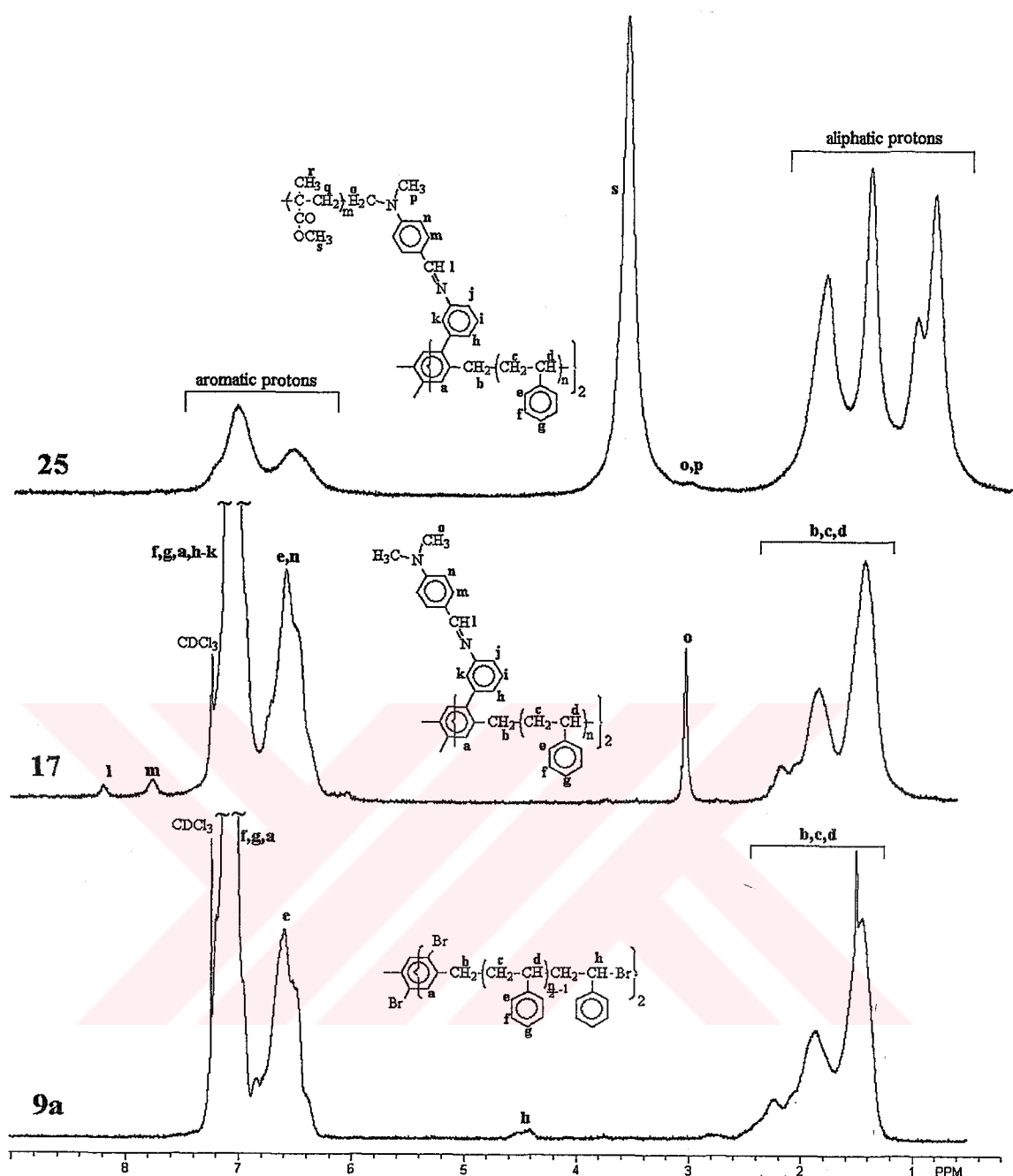


Figure 4.19 : ^1H -NMR spectra of PSt prepolymer **9a** (Table 4.7, run 25), *N,N*-dimethyl amino-functional PSt prepolymer **17** (Table 4.8, run 37) after condensation of amino groups with 4-dimethylamino benzaldehyde, and 4-armed star copolymer **25** (Table 4.8, run 37) after photoinduced radical polymerization of MMA

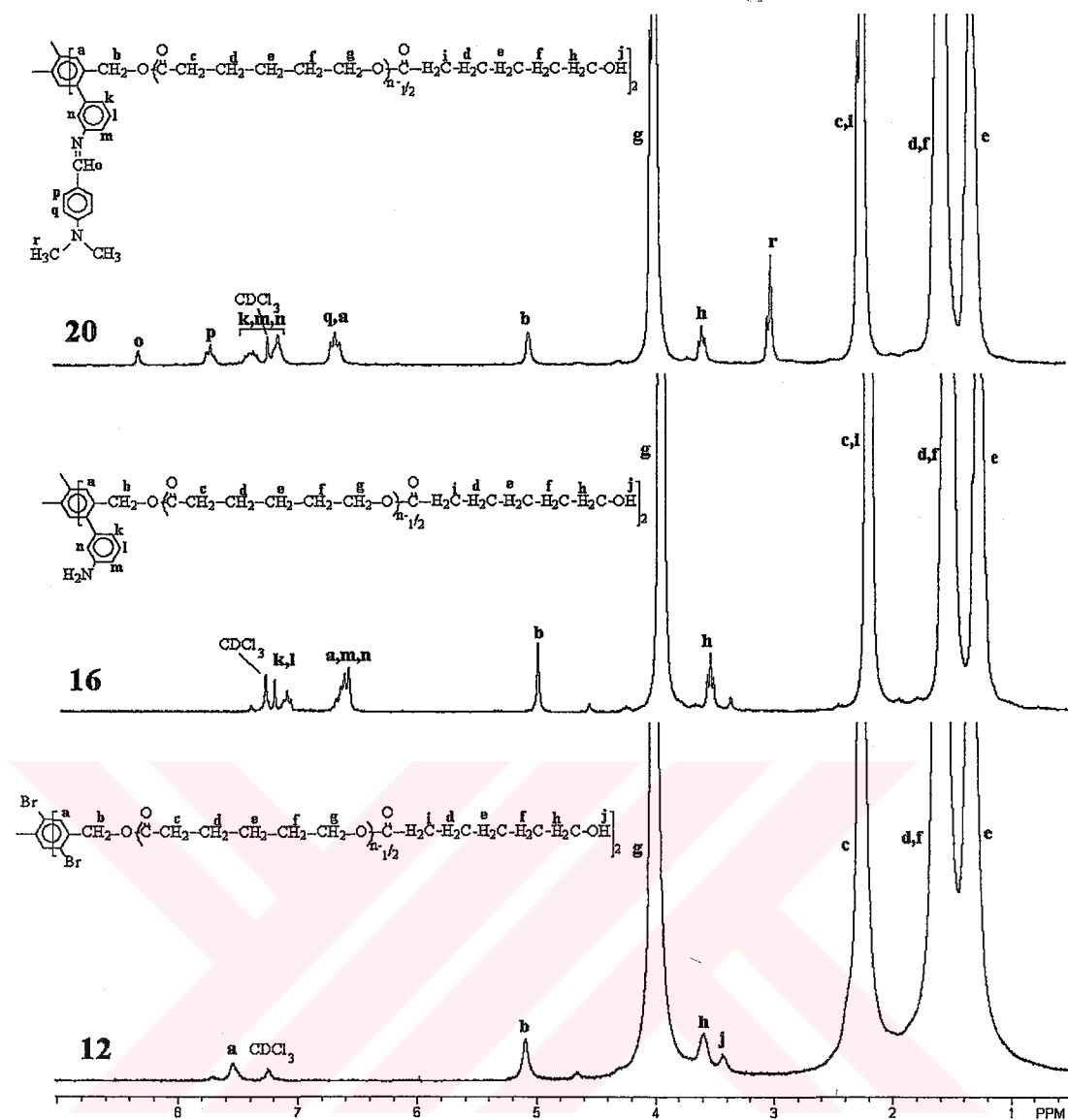
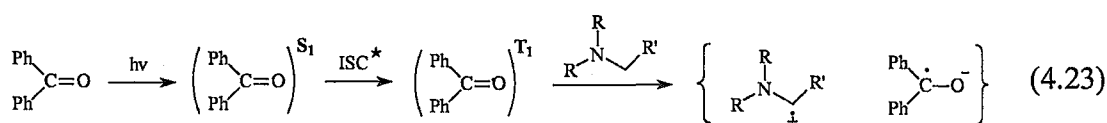
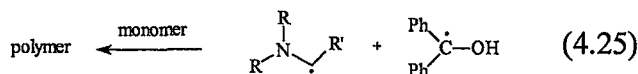


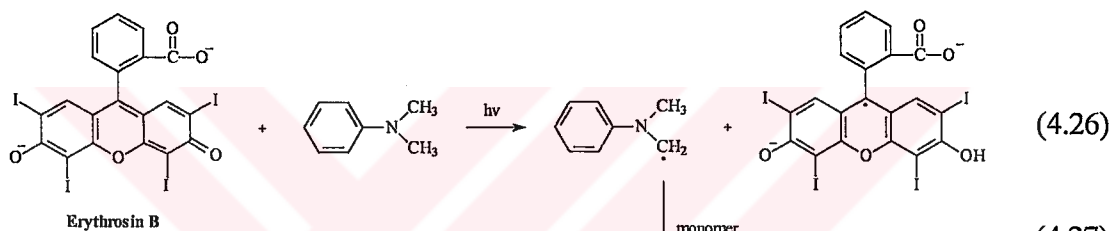
Figure 4.20 : ¹H-NMR spectra of PCL prepolymer 12 (Table 4.7, Run 29), amino-functional prepolymer 16 (Table 4.8, Run 36) after Suzuki coupling, and *N,N*-dimethyl amino-functional prepolymer 20 (Table 4.8, Run 40) after condensation of amino groups with 4-dimethylamino benzaldehyde



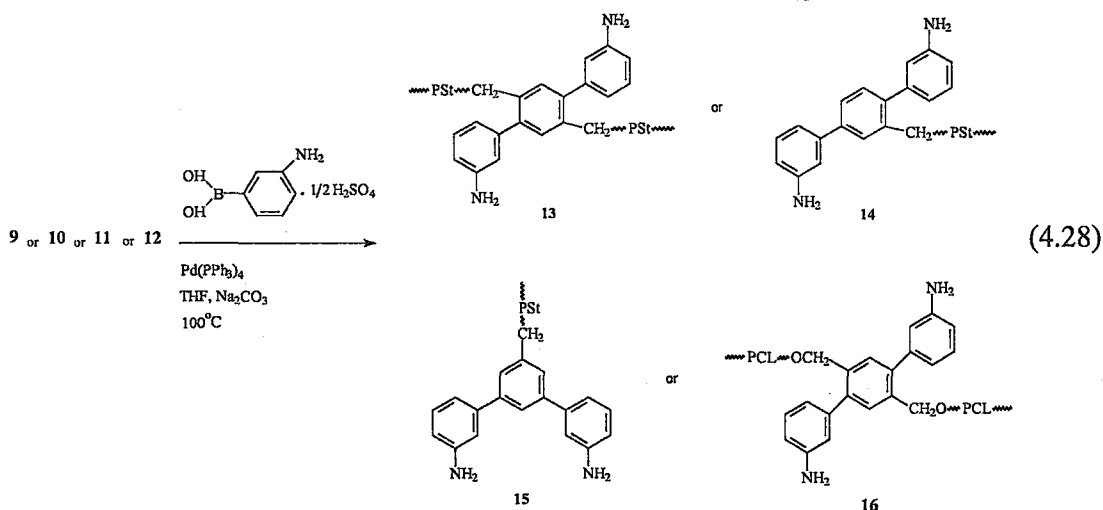
* : intersystem crossing



It is also possible [38] to generate initiating radicals from the photolysis of xanthene dyes such as eosin, erythrosin and rose bengal in combination with electron donating co-initiators such as aromatic amines, as depicted in reaction 4.26, for Erythrosin B.



Therefore, for the incorporation of amino functions into polymers, commercially available 3-aminophenylboronic acid hemisulphate was used as reaction partner in Suzuki type couplings as shown in reaction 4.28.



In order to assure the completion of the reaction, a high excess of the boronic acid was used and a long reaction time was maintained. In the $^1\text{H-NMR}$ spectra of the PSt polymers **13-15**, the rests from the boronic acid could not be identified, as the aromatic protons of styrene units give peaks in the same region. In the case of **16**, the PCL based polymer, the aromatic region is free of signals originating from the polymer. Thus, near the protons belonging to the starting initiator used for ROP of CL, the aromatic protons of the newly introduced groups are very clearly seen (polymer **16**, protons **k-n**, in Figure 4.20).

The amino groups could be identified in the IR spectra of the PSt polymers. The IR spectra of polystyrene prepolymer **9** and the corresponding amino-functionalized one, **13** are shown in Figure 4.21. The absorptions at 3450 cm^{-1} , and 1615 cm^{-1} or 790 cm^{-1} in the spectrum of **13**, which are not present in the spectrum of **9** indicates the presence of amino groups in the structure of the polymer. These new signals appear in all the other IR spectra of the amino functionalized polymers (**14-16**), as well.

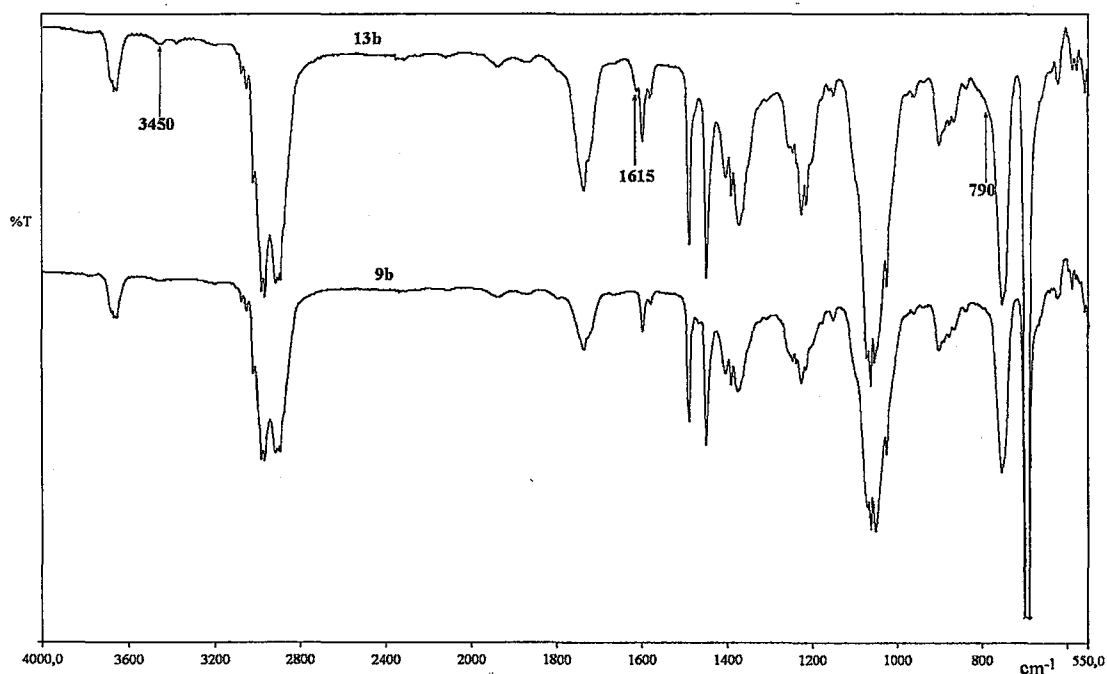
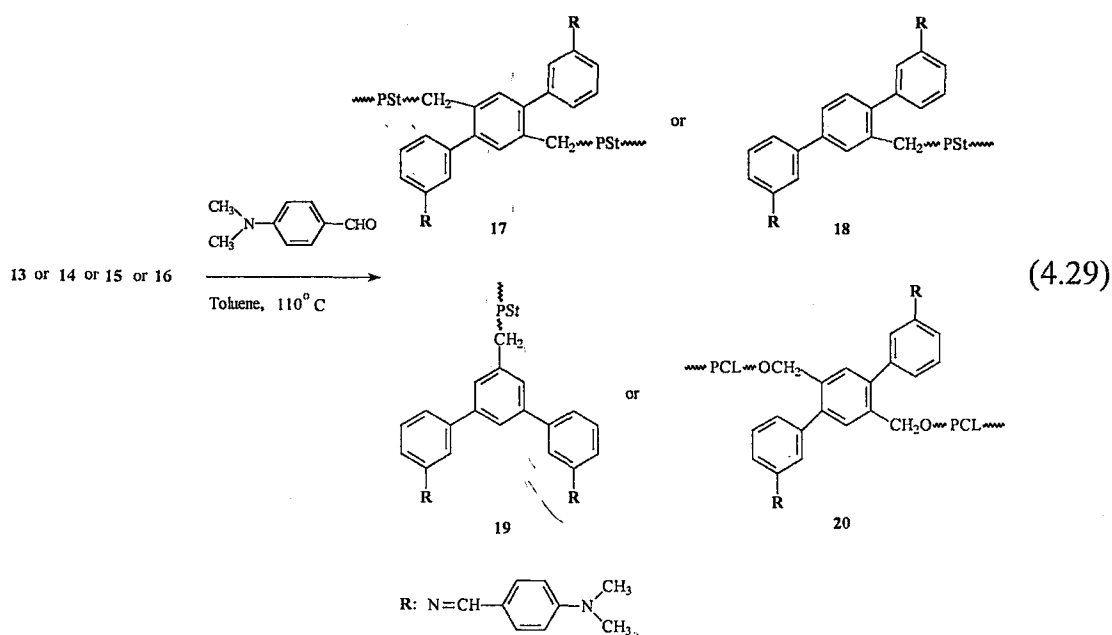


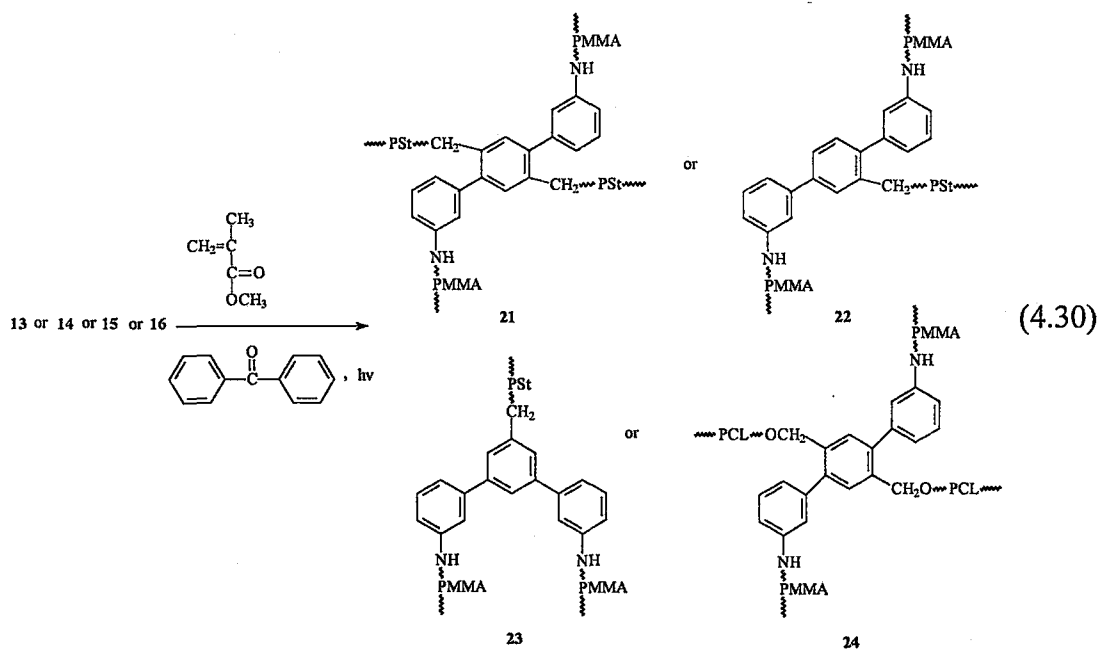
Figure 4.21 : IR spectra of prepolymer **9b** (Table 4.8, run 32) and amino-functional prepolymer **13b** (Table 4.8, Run 32) after Suzuki coupling

Further evidence for the successful functionalization of the polymers **13-16** was obtained in the next reaction step. Amino- containing polymers were employed in a condensation reaction with 4-dimethylamino benzaldehyde as depicted in reaction 4.29.



The newly formed azomethine groups are clearly evidenced by the ^1H -NMR spectra of all the polymers **17-20**, as the protons of imino group give clear signals at 8.2-8.4 ppm (for example, Figure 4.19, proton **l** in polymer **17** or Figure 4.20, proton **o** in polymer **20**). The peaks belonging to the aromatic protons of the phenylene ring originating from 4-dimethylamino benzaldehyde, in the proximity of the azomethine linkage, appear sufficiently far away from those of aromatic protons of polystyrene, appearing as a distinct signal around 7.8 ppm in the ^1H -NMR spectra of the polymers **17-19** (proton **m** from polymer **17** in Figure 4.19). In the case of PCL polymer **19** (Figure 4.20), proton **p** is also seen separately around 7.75 ppm. Moreover, the strong peak due to the protons of *N,N*-dimethylamino groups at 3.02 ppm is another evidence for the successful functionalization. The molecular weights can also be calculated by comparing the intensities of the integrals of these peaks, with those of aromatic ones from 6.3-7.4 ppm (in the case of PSt polymers **17-19**) or with those at about 4 ppm (corresponding to the $\text{CH}_2\text{-O}$ in the case of PCL polymer **20**). Notably, in both cases the values were found to be very close to those of the starting prepolymers **9-12** indicating that polymer chains were not destructed during functionalization and quantitative functionalization was achieved. Similar results are obtained when the molecular weight calculations are repeated based on the other end-group protons (**l** or **m** for polymer **17** in Figure 4.19 and **o** or **p** for polymer **20** in Figure 4.20).

Polymers **13-16**, containing amino groups or **17-20** with dimethylamino moieties were further used in copolymerization with methyl methacrylate by photoinduced radical polymerization method (reactions 4.30 and 4.31). The results are presented in Table 4.8. It should be pointed out that dye-sensitized systems were deliberately selected for dimethylamino functional polymers since the azomethine group present in the structure has a strong absorption at the wavelength where benzophenone absorbs the light. As can be noticed from Table 4.8, the conversion of MMA is generally low, and exceeds 10% only in few cases. At lower irradiation times, polymers with lower content of MMA repeating units are formed (runs 31 and 32).



As can also be noticed, in the case of initiation with dimethyl amino groups, much higher irradiation times are needed to obtain copolymers with compositions comparable to those produced by using primary amino functional prepolymers. This is due to the fact that the monochromator provides a much weaker light intensity as compared to that of the merry-go-round. Interestingly, increase in the initiator concentration did not have a significant influence on the copolymer composition (see runs 26 and 27).

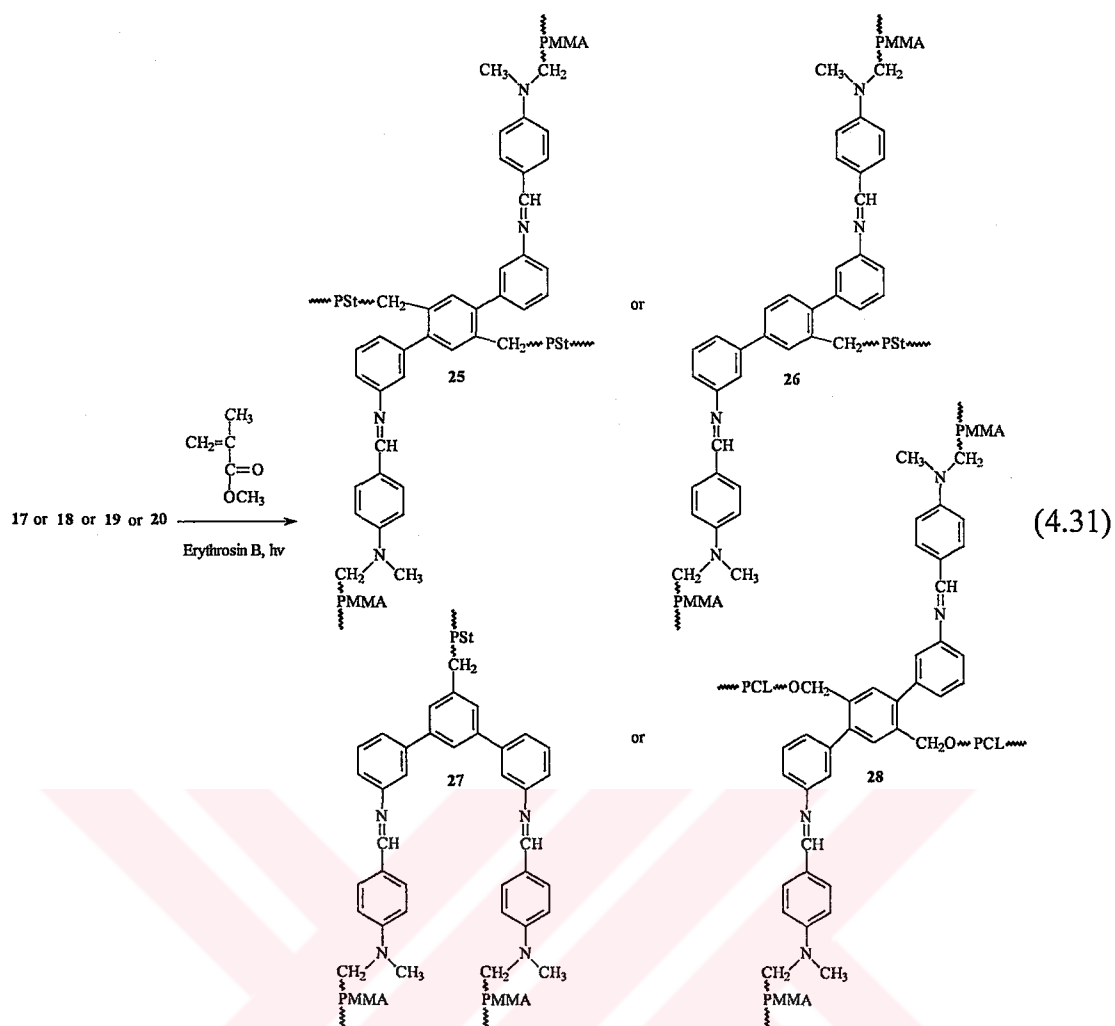


Table 4.8: Conditions^a and Results for the Preparation of Star Copolymers via Photoinduced Radical Polymerization of MMA from Amino or *N,N*-dimethyl amino-functional Prepolymers

Run	Prepolymer	Macroinit.	[Macroinit.] × 10 ² (mol L ⁻¹)	Irradiation Time (min)	Star Polymer	Conv. (%)	Blocking Yield (%)	M _n ^c × 10 ⁻³	M _w /M _n	MMA _{r.f.u.} ^f (%)
30 ^b	9a	13a	0.5	180	21a	9.40	77.0	40.0	4.80	84.3
31 ^b	9a	13a	3.0	60	21b	8.10	56.8	40.4	3.27	68.3
32 ^b	9b	13b	1.9	60	21c	8.50	51.7	39.3	2.96	71.3
33 ^{b,c}	10	14	3.0	135	22a	21.2	71.1	31.0	2.85	84.3
34 ^b	10	14	3.0	60	22b	11.5	65.4	29.4	3.10	78.3
35 ^b	11	15	3.0	60	23	7.30	46.9	33.5	2.53	78.2
36 ^b	12	16	3.0	60	24	5.90	42.2	45.9	2.54	80.9
37 ^d	9a	17	0.5	360	25	3.90	69.0	54.0	7.14	76.0
38 ^d	10	18	0.7	900	26	1.80	36.1	91.8	2.02	82.1
39 ^d	11	19	1.0	1620	27	2.60	41.0	196	1.65	93.6
40 ^d	12	20	0.7	1320	28a	12.2	38.2	165	1.86	90.4
41 ^d	12	20	0.7	430	28b	2.00	26.3	114	2.02	81.9

^abulk, ^bλ_{inc.} = 350 nm., ^cin dichloromethane, [M] = 6.60 mol.L⁻¹, ^dλ_{inc.} = 525 nm., ^edetermined by GPC, ^fdetermined by ¹H-NMR.

The ^1H -NMR spectra of the copolymers exhibit the presence of both components (MMA and St or CL repeating units). Generally, the protons of the end groups can not be identified because of the increase of molecular weight and polydispersity, and consequently the broadening of the peaks. For example, in Figure 4.19 (polymer **25**), in addition to the specific protons of PSt and PMMA blocks, only the protons of dimethyl amino groups can be noticed. However, the signal is too broad to perform other calculations as was made in the case of starting polymers **13-20**. On the other hand, the composition of the PSt containing copolymers presented in Table 4.8 can still be determined by using the intensities of integrals corresponding to aromatic peaks of PSt as compared with those of OCH_3 groups of PMMA at about 3.4 ppm. Similar observations are valid in the spectral investigations of PCL containing copolymers. In this case, the compositions of the copolymers were determined by comparing the intensities of O-CH_2 protons of PCL blocks at about 4 ppm with those of OCH_3 groups of MMA at about 3.4 ppm (Figure 4.22). In the spectrum of polymer **28**, two small peaks noted at around 3 ppm correspond to the protons of unreacted methyl amino group and to the reacted N-CH_2 - one, respectively. The presence of these two distinct signals is an additional proof of the mechanism implied in reaction 4.31, in which, the polymerization is shown to proceed from one of the methyl groups of dimethyl amino functions as a result of hydrogen abstraction.

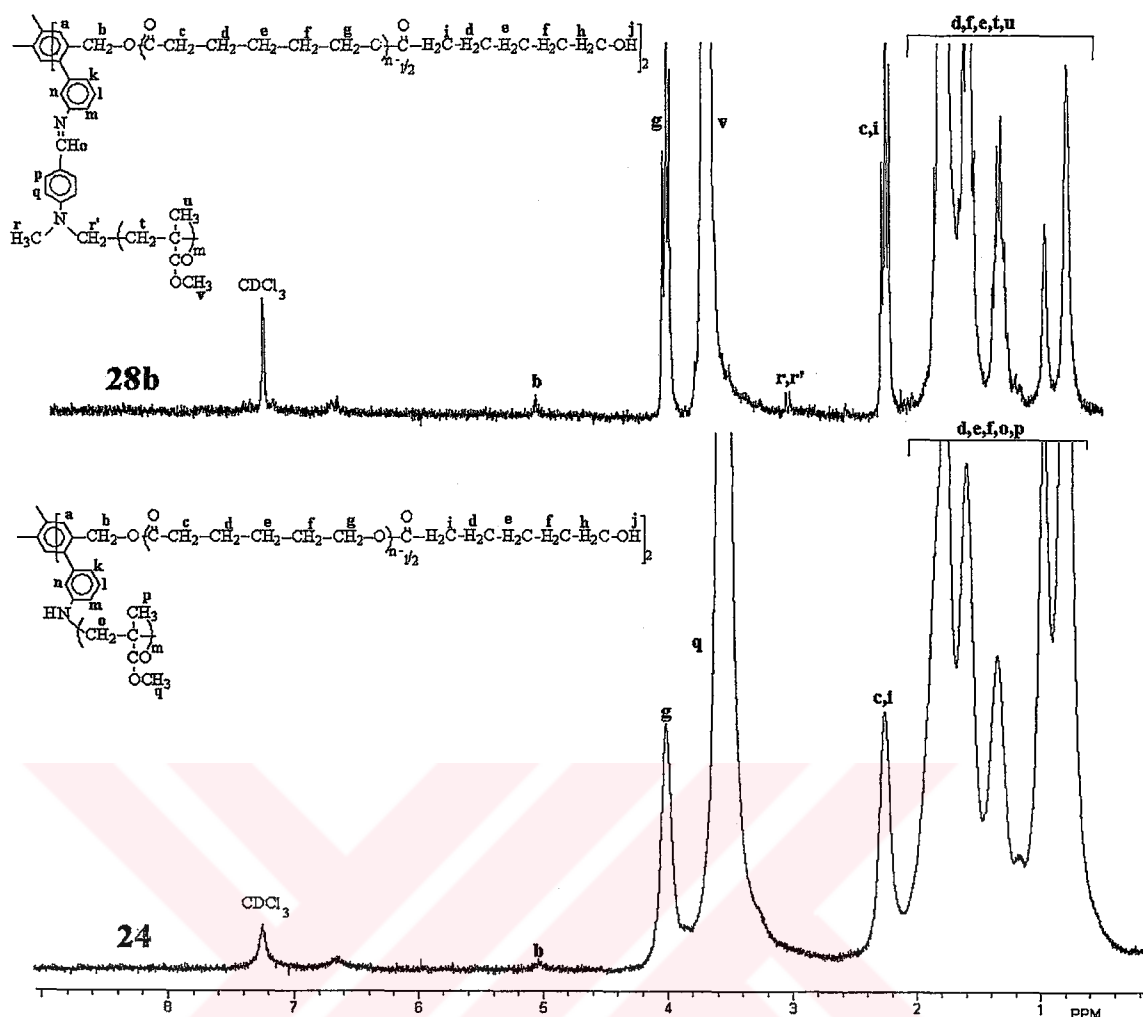


Figure 4.22 : 4-armed PCL-PMMA star copolymers **24** (Table 4.8, run 36) and **28b** (Table 4.8, run 41) after photoinduced radical polymerization of MMA

Due to the expected star structure and composition of the copolymers, the values of M_n , reported in Table 4.7, obtained from GPC calibrated with PSt standards, are not trustworthy. For this reason, comparison of the results of ¹H-NMR and GPC measurements was omitted. The data obtained from ¹H-NMR can be considered more reliable. However, the GPC traces of the copolymers are shifted to higher-molecular-weights and no significant amounts of unreacted starting polymers remained in the analyzed materials (Figures 4.23-4.25).

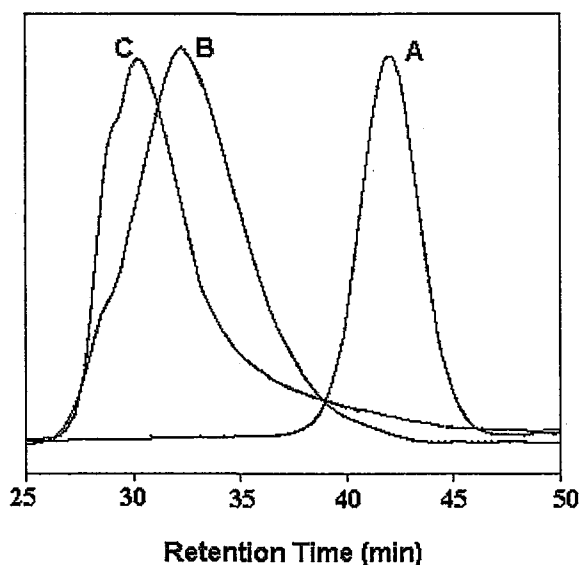


Figure 4.23 : GPC traces of PSt-prepolymer **9b** (Table 4.7, run 26) (**A**), 4-armed PSt-PMMA star copolymer **21c** (Table 4.8, run 32) (**B**), 4-armed PSt-PMMA star **25** (Table 4.8, run 37) (**C**)

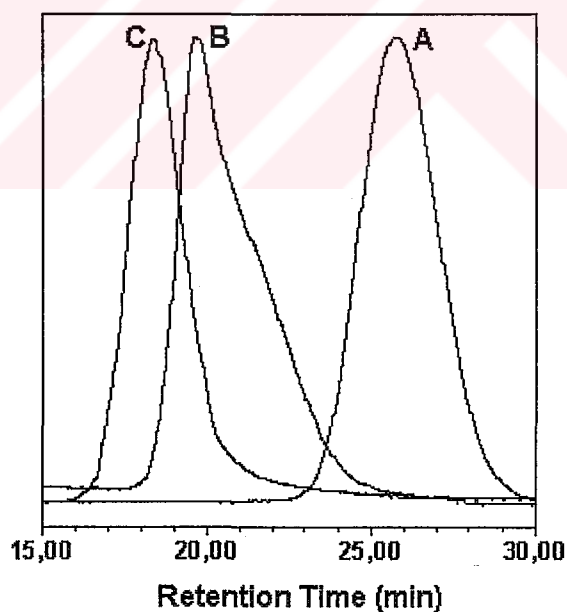


Figure 4.24 : GPC traces of PSt prepolymer **11** (Table 4.7, run 28) (**A**), 3-armed PSt-PMMA star copolymer **23** (Table 4.8, run 35) (**B**), 3-armed PSt-PMMA star **27** (Table 4.8, run 39) (**C**)

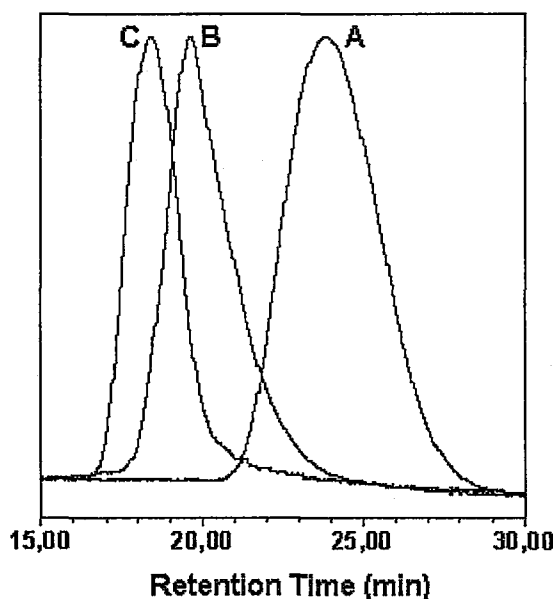


Figure 4.25 : GPC traces of PCL prepolymer **12** (Table 4.7, run 29) (**A**), 4-armed PCL-PMMA star copolymer **24** (Table 4.8, run 36) (**B**), 4-armed PCL-PMMA star **28a** (Table 4.8, run 40) (**C**)

The thermal behavior of synthesized copolymers was investigated using differential scanning calorimetry (DSC). Both glass transition temperature (T_g) of PSt component (100-110°C) and T_g of PMMA component (130-135°C) are observed in the DSC traces of polymers **21-23** and **25-27**. For example in Figure 4.26 is presented the DSC trace of **21c**, as compared with that of the initial polymer **9b** where T_g values of PSt and PMMA segments were observed at 101 °C and 133 °C, respectively. A slight decrease of transition temperature of PSt block as compared to that of the starting **9b** (106°C) is probably due to a decrease in the mobility of polystyrene chains in the copolymer.

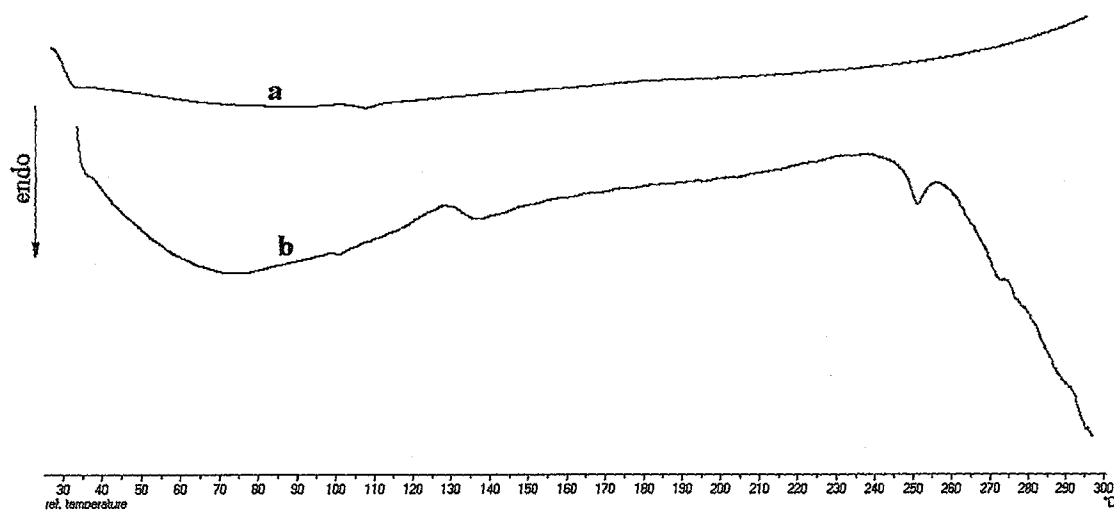


Figure 4.26 : DSC traces of PSt prepolymer 13 (Table 4.8, run 31) (a), and PSt-PMMA star copolymer 21 (Table 4.8, run 31) (b)

Similar behavior can be observed for the PCL containing copolymers. Figure 4.27 presents the DSC trace of PCL 12 as compared to that of PCL-PMMA copolymer.

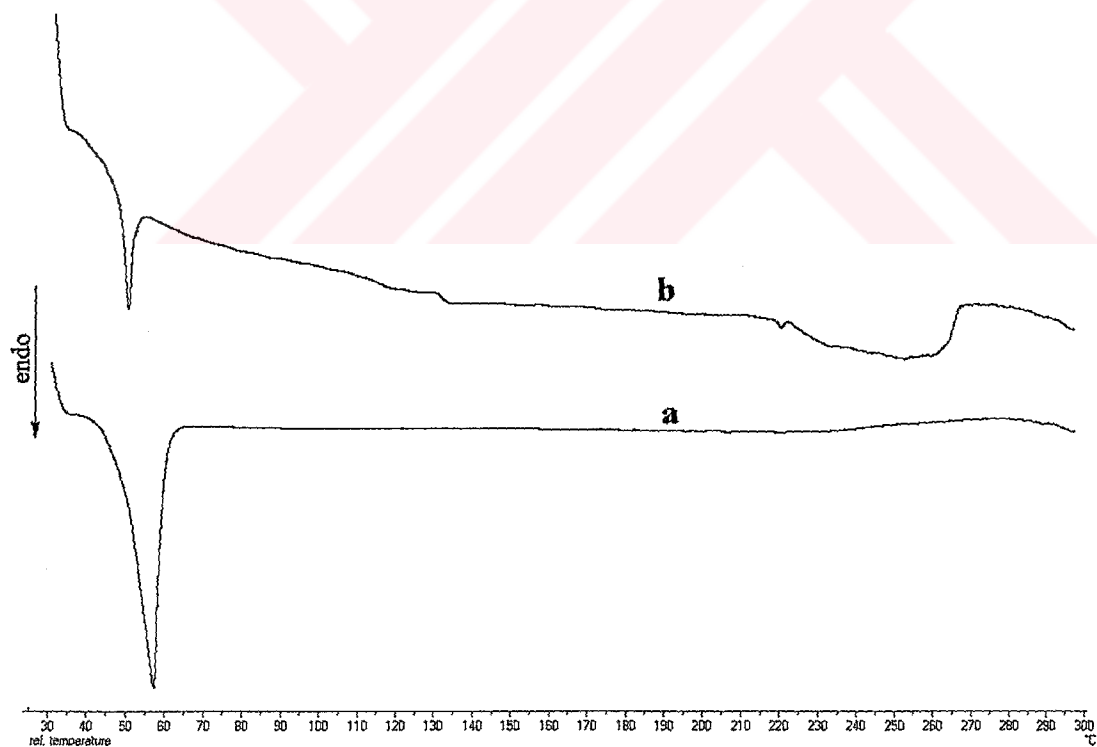


Figure 4.27 : DSC traces of PCL prepolymer 12 (Table 4.8, run 41) (a), and PCL-PMMA star copolymer 28b (Table 4.8, run 41) (b)

The endotherm peak that corresponds to the melting of PCL **12** appears at 57°C, while in the case of copolymer, this temperature is slightly lower (50°C). This behaviour can be due to the decrease of ordering length of PCL blocks in the copolymer. The DSC trace of **28** also shows an endotherm corresponding to the T_g of PMMA blocks at about 132°C.

Thus, all the evidence supplied by $^1\text{H-NMR}$, GPC and DSC analyses clearly show that synthesis of 3- and 4- armed star copolymers by combining controlled polymerization methods with photoinduced radical polymerization was successfully achieved.



5. CONCLUSIONS

In this thesis, macromolecular architectures involving block, graft, block-graft, brush, and miktoarm star copolymers as well as hyper-branched polymers were prepared successfully by combining ATRP or ROP with photoinduced radical or radical promoted cationic polymerizations. End-chain, mid-chain or side-chain mono- or bi-amino- or *N,N*-dimethylamino-functional precursor polymers synthesized by ATRP or ROP were, in the next step, employed in photoinduced radical or promoted cationic polymerizations affording the designed architecture.

ATRP was used in conjunction with photoinduced free radical or free radical promoted cationic polymerization method in block copolymerization. First, well-defined polystyrenes possessing aromatic amine end groups were prepared by ATRP using suitably functionalized initiators. Subsequently, macroinitiators thus obtained were photolysed in the presence of a sensitizer, benzophenone or Erythrosin B, at appropriate wavelengths to generate polymeric radicals via hydrogen abstraction. These radicals either initiated free radical polymerization or were oxidized to the carbocations capable of initiating cationic polymerization with the use of diphenyl iodonium hexafluorophosphate. While only block copolymers were obtained in the free radical route, both block copolymer and homopolymer formations were observed in the free radical promoted cationic polymerization. Hence, it has been shown that well-defined amino terminated polymers can successfully be utilized in photoinduced polymerizations to prepare block copolymers of structurally different monomers.

In the preparation of methylmethacrylate brushes on a diblock copolymer backbone, a photoinduced 'grafting from' strategy was employed. The AB-type precursor block copolymer was synthesized through living anionic polymerization; in which the 'A' segment contained no functional groups whereas 'B' segment held *N,N*-dimethyl amino groups in each repeating unit. In the following step, block-graft brushes were prepared by photoinitiated radical polymerization of methylmethacrylate from

corresponding *N,N*-dimethyl amino groups. Concomitant formation of crosslinked polymers was also observed.

In addition, synthesis of random copolymers possessing H-donating sites for photoinduced grafting were conducted, in which styrene and 2-(dimethylamino)ethyl methacrylate with varying compositions were copolymerized by classical radical polymerization using AIBN as the initiator. Grafting MMA chains from *N,N'*-dimethyl amino functional groups via photoinduced radical polymerization was successfully achieved by photosensitization of benzophenone. Resulting random graft-copolymer was characterized by GPC and ^1H -NMR analyses.

A hyper-branched polymer was also prepared by the photoinduced radical polymerization of 2-(dimethylamino)ethyl methacrylate. The hyper-branched structure was confirmed by atomic force microscopy (AFM).

Finally, synthesis of A_2B and A_2B_2 type miktoarm star copolymers was achieved successfully by combination of ATRP or ROP with photoinduced radical polymerization. Well-defined PSt or PCL mid-chain or end-chain functional prepolymers, synthesized by ATRP or ROP, were further modified at the aromatic bromine atoms to possess amino or *N,N*-dimethyl amino groups by a Suzuki coupling reaction followed by a condensation reaction. Copolymerizing the precursor polymers with MMA via photoinduced radical polymerization, 4- or 3-armed PSt-PMMA or PCL-PMMA stars were obtained. The characterizations were performed by ^1H -NMR, IR, GPC, and DSC analyses.

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