ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

MACROMOLECULAR ENGINEERING BY END GROUP MODIFICATIONS

Ph. D. Thesis by
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Department : Polymer Science and Technology

Programme : Polymer Science and Technology

SEPTEMBER 2009

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

UÇ GRUP MODİFİKASYONLARI İLE MAKROMOLEKÜLER TASARIMLAR

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FOREWORD

First, I would like to thank my advisor, Professor Yusuf Yağcı, for his encouragement, guidance, and his insightful view of the polymer field. Not only did he open my eye to the fascinating world of polymer chemistry, more importantly, he also educated me on how to appreciate the beauty of polymer science and how to develop the focus on scientific research. He gave me the encourage in my diffucult times by reminding me "The harder one works the more luck one gets". Without his knowledge and expertise, I would have never been able to accomplish the work of my graduate research.

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Finally, I would like to dedicate this thesis my husband Hakan Durmaz for his patience, understanding moral support and importantly for our scientific discussion during all stages involved in the preparation of this thesis.

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ABBREVIATIONS

^{1}H NMR : Hydrogen Nuclear Magnetic Resonance Spectroscopy
FT-IR : Fourier Transform Infrared Spectrophotometer
UV : Ultra Violet
GPC : Gel Permeation Chromatography
DSC : Differential Scanning Calorimetry
GC-MS : Gas Chromatography Mass Spectrometry
TEMPO : 2,2,6,6-Tetramethylpiperidine-*N*-oxyl
PMDETA : *N, N, N',N'', N''*-Pentamethyldiethylenetriamine
RAFT : Reversible Addition Fragmentation Chain Transfer
NMP : Nitroxide Mediated Polymerization
AIBN : 2,2'-Azobis-(isobutyronitrile)
CH_2Cl_2 : Dichloromethane
$CDCl_3$: Deuterated chloroform
THF : Tetrahydrofuran
MMA : Methyl Methacrylate
HEMA : 2-Hydroxyethyl Methacrylate
St : Styrene
CMS : Chloromethylstyrene
PSt : Polystyrene
PS : Photosensitizer
PI : Photoinitiator
ISC : Inter System Crossing
COI : Coinitiator
TEA : Triethylamine
Bpy : 2,2-Dipyridyl
PP : 4-Phenylpyridinium *N*-oxide
IQ : Isiquinoline *N*-Oxide
MDC : Morpholine-4-Ditiocarbamate

LIST OF SYMBOLS

λ : Wavelength
$h\upsilon$: Radiation
$R^{\cdot}$: Radical
mW : Miliwatt
nm : Nanometer
E : Excitation energy
h : Planck’s constant
l : Light path length
C : Concentration
A : Absorbance
ε : Molar extinction coefficient
k : Rate constant
$\Phi_{R\cdot}$: Quantum yield of radical formation
Φ_P : Quantum yield of photoinitiation
f_P : Initiation efficiency of photogenerated radicals
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
E_T : Triplet energy
F : Faraday constant
$E_{½}^{ox}\ (D/D^{+\cdot})$: Oxidation potential of donor
$E_{½}^{red}\ (A/A^{-\cdot})$: Reduction potential of acceptor
E_{PS} : Singlet state energy of the photosensitizer
ΔE_c : Coulombic stabilization energy
ΔG : Gibbs Energy Change
Å : Angström
ppm : Parts per million
K : Kelvin
°C : Celsius
N : Normality
M : Molarity
T_g : Glass-transition temperature
M_n : The number average molecular weight
M_w : The weight average molecular weight
M_w/M_n : The molecular weight distribution
(c) : Conversion
T : Time
ΔH_t : Reaction heat evolved at time t
ΔH_0^{theory} : Theoretical heat for complete conversion

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MACROMOLECULAR ENGINEERING BY END GROUP MODIFICATIONS

SUMMARY

Nowadays there is a considerable interest not only in the synthesis of new types of polymeric materials, but also in the modification of existing polymers in order to alter their properties to meet the requirements for new applications. During the last decade the controlled/living radical polymerization (CLRP) became an established synthetic method to prepare new complex architectures of polymers such as block, graft, star and functional polymers with well-defined structures. Recent developments in controlled /living radical polymerization provide the possibility to synthesize polymers with controlled functionalities also with radical routes. The most widely used methods for CLRP include atom transfer radical polymerization (ATRP), nitroxide mediated radical polymerization (NMRP), and reversible addition-fragmentation chain transfer polymerization (RAFT). Among the three standard methods for controlled/living radical polymerization, atom transfer radical polymerization (ATRP) is the most frequently used one. Polymer functionalization by ATRP can be achieved through several ways. Quite a number of functional initiators were successfully used in ATRP to prepare functional styrene and acrylate type polymers. Obviously, this process leads to the formation of monofunctional telechelics since the other chain end always contains halogen due to the fast deactivation process in ATRP.

Photoinduced processes have been recognized as a useful synthetic methodology applied to macromolecular chemistry offering molecules ranging from cross-linked networks to the block and graft copolymer. As such, they are particularly important in preparative methods, in which low-temperature, low energy consumption and high conversions are desirable. Photoinduced block and graft copolymerizations can readily be achieved by the incorporation of photoactive groups at the chain ends and side-chains of preformed polymers, respectively.

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. A transformation reaction is an elegant way to synthesize block and graft copolymers of monomers that polymerize with different mechanisms. In this concept, a polymer, obtained by a particular polymerization mechanism, is functionalized either by initiation or termination steps. The polymer is isolated and purified, and finally the functional groups are converted to another kind of species capable of initiating polymerization of the second monomer. Living polymerization techniques are essential processes for obtaining well-defined

macromolecules with controlled molecular weight, polydispersity index, and architecture and terminal functionalities. A wide range of transformation reactions combining various living ionic polymerization methods were successfully used to synthesize block copolymers that can not obtained by a single method. Living ionic polymerizations have also been combined with conventional free radical polymerization.

In this thesis, we describe the synthesis of block and graft copolymers by end group transformation. Transformation reactions were achieved using *N*-alkoxy pyridinium salts, morpholine–4–dithiocarbamate sodium salt and hydroxyl functional benzodioxinone compound.

In the first strategy, photoactive *N*-alkoxy 4-phenylpyridinium and *N*-alkoxy isoquinolinium ion terminated polystyrenes with hexafluoroantimonate counter anion were prepared and characterized. For this purpose, mono- and dibrominated polystyrenes were prepared by ATRP. The reaction of these polymers with silver hexafluoroantimonate in the presence of 4-phenylpyridine *N*-oxide and isoquinoline *N*-oxide in CH_2Cl_2 produced desired polymeric salts with the corresponding functionalities. Irradiation of these photoactive polystyrenes produced alkoxy radicals at chain ends capable of initiating free radical polymerization of methyl methacrylate (MMA) and depending on the number of functionality, AB or ABA type block copolymers were formed. Moreover, a new strategy by combination of NMP and photoinitiated polymerization is reported for the synthesis of graft copolymers. For this purpose, first, the copolymer backbones of poly (styrene-*co*-chloromethylstyrene) P(St-*co*-CMS) with different chloromethyl contents were prepared by NMP. Then chloro functions of these precursor polymers were converted to photosensitive 4-phenylpyridinium-*N*-oxide ion functions via substitution in the presence of silver hexafluoroantimonate. Finally, photoactive polymers were irradiated in the presence of MMA in CH_2Cl_2 to obtain the graft copolymers (Figure 1). Graft copolymer as well as the precursors at various stages were characterized by spectral and gel permeation chromatography analysis. It was also demonstrated that the irradiation of photoactive polymers in the presence of a hydrogen donor such as THF facilitates conversion of pyridinium ions to hydroxyl groups.

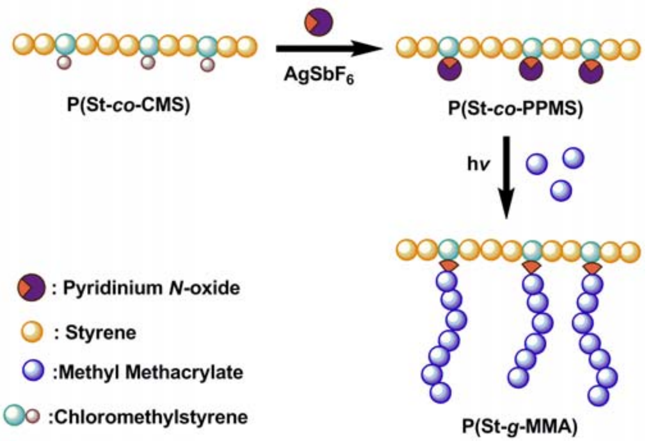


Figure 1 : Photoinduced grafting bu using *N*-alkoxy pyridinium ion functionalized polymers.

Secondly, the transformation approach was further extended to the preparation of block copolymers by combining ATRP and photoiniferter processes. Photoactive morpholine-4-dithiocarbamate terminated polystyrene was prepared by the reaction of dibrominated polystyrene, obtained by ATRP, with morpholine-4-dithiocarbamate sodium salt in DMF. The capability of photoactive morpholine-4-dithiocarbamate terminated polystyrene to act as a photoiniferter for the block copolymerization of methyl acrylate (MA) was examined (Figure 2) and polymerization shows a “living” character at up to 25 % conversions and produces well-defined polymers with molecular weights close to those predicted from theory and relatively narrow poyldispersities (M_w/M_n ~1.40).

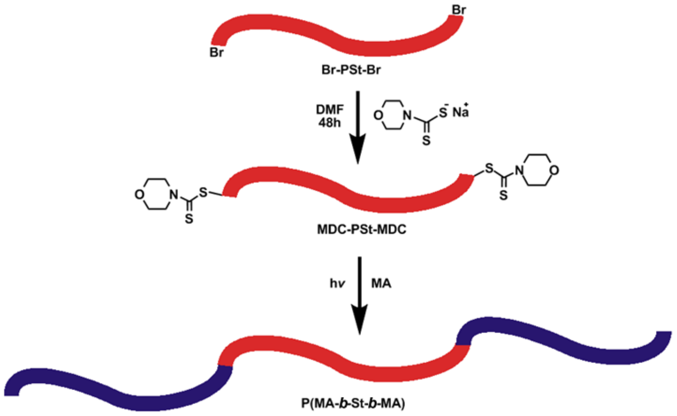


Figure 2 : Block copolymerization of MA by using morpholine-4-dithiocarbamate terminated polystyrene as an photoiniferter.

Finally, synthesis of graft copolymers by combination of ATRP and photoinduced reaction of benzodioxinone was described. Poly(hydroxyethyl methacrylate-*co*-methyl methacrylate)-*graft*-poly(styrene) copolymer with well-defined main and side chains was synthesized by the “grafting onto” method via combination of ATRP and photoinduced ester formation reaction of benzodioxinones (Figure 3). This approach toward the preparation of graft copolymers is unique in the way that the process can be performed at room temperature in the absence of any catalyst. The graft copolymers and the intermediates were characterized in detail by using ^{1}H NMR, GPC, UV, FT-IR, DSC, and AFM measurements.

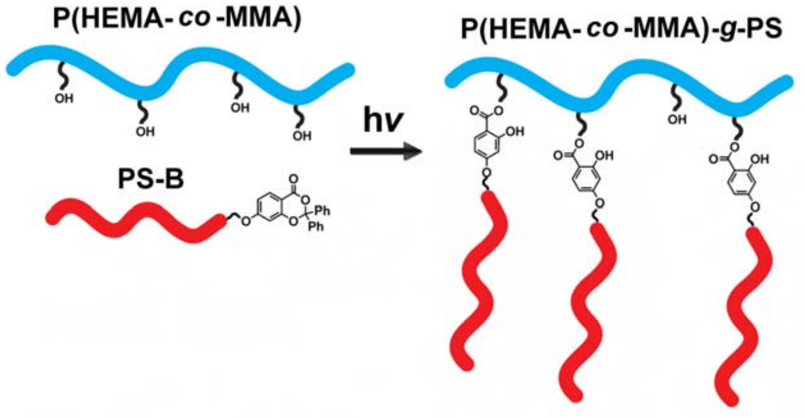


Figure 3 : Synthesis of graft copolymers by photochemical acylation reaction.

UÇ GRUP MODİFİKASYONLARI İLE MAKROMOLEKÜLER TASARIMLAR

ÖZET

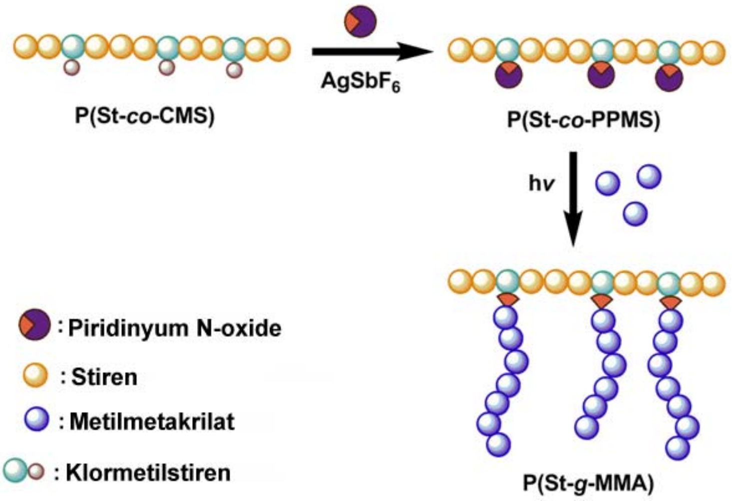
Günümüzde, sedece yeni tür polimerik malzemelerin sentezi değil, varolan polimerlerin yeni uygulamalarda kullanılmak üzere modifikasyonları da ciddi derecede önem kazanmıştır. Son yıllarda, Kontrollü/Yaşayan Radikal Polimerizasyonu (CLRP), iyi tanımlanmış blok, aşı ve fonksiyonel polimerlerin sentezinde önemli bir yol haline gelmiştir. CLRP daki en son gelişmeler radikalik olarak fonksiyonlandırmayı mümkün kılmıştır. Atom Transfer Radikal Polimerizasyonu (ATRP), Nitroksit Ortamlı Radikal Polimerizasyonu (NMP), ve Tersinir Eklenme-Ayrılma Zincir Transfer Polimerizasyonu (RAFT) en yaygın kullanım alanı olan CLRP yöntemleridir. Bu üç standart CLRP metodundan ATRP en sık kullanılanıdır. ATRP ile polimer fonksiyonlandırma farklı yollarla yapılabilir. Örneğin, ATRP de fonksiyonel bir başlatıcı kullanarak, foksiyonel polistiren ve metilmetakrilat elde edilmiştir. Bu yolla monofonksiyonlu telekelik elde edildiği açıktır. Çünkü, polimer zincirinin diğer ucu ATRP daki hızlı deaktivasyon prosesine uygun olan halojen uç grubu içermektedir.

Fotouyarılmış prosesler çaprazbağlı ağyapılı polimerlerden blok ve aşı polimerlere kadar birçok makromolekülü sentezleme olanağı sağlayan, makromoleküler kimyada kullanışlı, sentetik metodlar olarak tanımlanırlar. Öyleki, düşük sıcaklık ve enerji tüketimi ve yüksek verim ile önemli bir preperatif yöntemdir. Fotouyarılmış blok ve aşı kopolimerizasyon, zincir ucundaki fotoaktif grup ile blok, yan zincirdeki fotoaktif grup ile de aşı kopolimer sentezi kolaylıkla başarılabilir.

Yapısal olarak farklı örneğin kondensazyon ve vinil polimerlerin blok kopolimerlerini tek bir polimerizasyon yöntemi ile hazırlamak ilgili polimerizasyonların doğası gereği oldukça zordur. Dahası, tek bir metod kullanımı farklı bir mekanizmayla polimerleşen monomerleri kapsamaz. Blok kopolimer sentezlenebilecek monomerleri genişletmek için, polimerizasyon mekanizmasını bir mekanizmadan başka bir monomeri polimerleştirebilecek diğerine değiştirebilen transformasyon yaklaşımı kabul görmüştür. Transformasyon yaklaşımı blok ve aşı kopolimer sentezi için etkin bir yoldur. Bu bağlamda, belirli bir polimerizasyon yöntemi ile sentezlenmiş bir polimer başlama ya da sonlanma aşamasında fonksiyonlandırılabilir. Polimer saflaştırıldıktan sonra fonksiyonel grup ikinci monomeri polimerleştirebilecek yeni bir tür gruba dönüştürülür. Yaşayan polimerizasyon teknikleri, molekül ağırlığı, molekül ağırlığı dağılımı, yapısı ve fonksiyonalitesi iyi tanımlanmış polimerler elde etmek için etkin bir yoldur. Çeşitli yaşayan iyonik polimerizasyon yöntemlerini başarıyla birleştiren çok sayıda transformasyon reaksiyonu tek bir yöntemle elde edilemeyecek blok kopolimerler sentezlenmesini saplamıştır. Hatta, yaşayan iyonik polimerizasyon yöntemleri serbest radikal polimerizasyon yöntemi ile birleştirilebilmiştir.

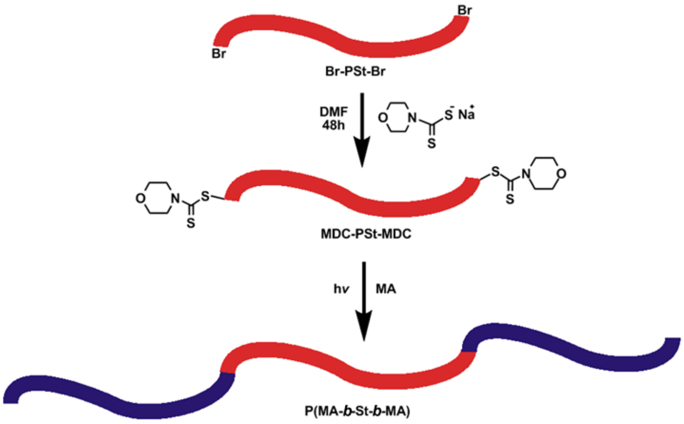
Bu tezde, uç grup transformasyonu ile blok ve aşı kopolimer sentezi tanımlanmıştır. Transformasyon reaksiyonları, *N*-alkoksi piridinyum tuzu, morfolin-4-ditiyokarbamat sodyum tuzu ve hidroksil fonksiyonlu benzodioksinon bileşikleri kullanılarak yapılmıştır.

İlk aşamada, fotoaktif *N*-alkoksi 4-fenilpiridin ve *N*-alkoksi isokinolin iyon sonlu ve hekzafloroantimonat karşı iyonlu polistiren hazırlanmış ve karakterize edilmiştir. Bu amaçla tek ve iki brom fonksiyonlu polistiren ATRP ile sentezlenmiştir. Bu polimerin gümüşhekzafloroantimonat ile 4-fenilpiridin *N*-oksit ya da isokinolin *N*-oksit varlığında diklorometan içerisindeki reaksiyonu istenilen fotoaktif polimeri vermektedir. Bu fotoaktif polimerin aydınlatılması sonucu zincir ucunda oluşan alkoksi radikali MMA'ın serbest radikal polimerizasyonunu başlatabilmektedir. Bu yolla, polistirenin fonksiyonalitesine bağlı olarak, AB ve ABA tipi blok kopolimer elde edilmiştir. Buna ek olarak, NMP ve fotopolimerizasyonun birleşmesinden oluşan yeni bir strateji ile aşı kopolimer sentezlenmiştir. Bu amaç için ilk olarak, farklı klor birleşimine sahip poli(stiren-*co*-klormetilstiren) kopolimeri NMP ile ana zincir olarak sentezlenmiştir. Sonra, bu öncü kopolimerin klor fonksiyonalitesi, gümüşhekzafloroantimonat varlığında fotoaktif 4-fenilpiridinyum *N*-oksit iyon fonksiyonalitesine dönüştürülmüştür. Son olarak, fotoaktif polimer CH_2Cl_2 içinde MMA varlığında aydınlatıldığında aşı kopolimer elde edilmiştir (Şekil 1). Aşı kopolimer öncü polimer gibi çeşitli aşamalarında spektral ve jel geçirgenlik kromotografi analizi ile karakterize edilmiştir. Ayrıca, bu fotoaktif polimerin THF gibi hidrojen donör varlığında aydınlatılması ile piridinyum iyonu hidroksi grubuna dönüştürülmüştür.



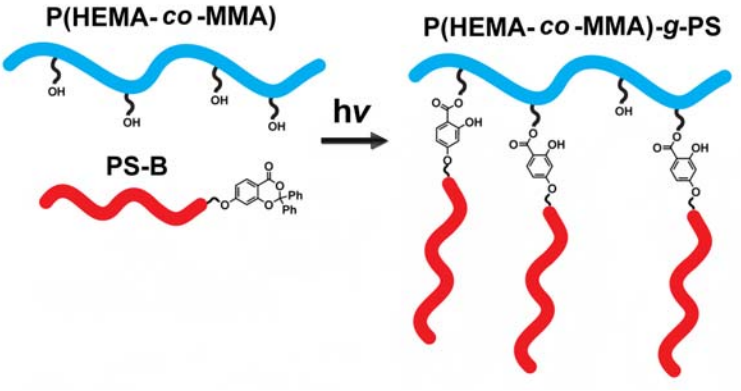
Şekil 1 : *N*-Alkoksi piridinyum iyon fonksiyonlu polimerler kullanılarak fotouyarılmış aşılama.

İkinci olarak, blok kopolimer sentezi için transformasyon yaklaşımı ATRP ve fotoiniferter yönteminin birleştirilmeri ile genişletilmiştir. Fotoaktif morfolin-4-ditiyokarbamet sonlu polistiren, ATRP ile hazırlanan iki brom fonksiyonlu polistiren ve morfoline-4-ditiyokarbamat sodyum tuzu ile dimetilformamid içerisindeki reaksiyonu sonucu elde edilmiştir. Bu fotoaktif morfolin-4-ditiyokarbamat sonlu polistirenin fotoiniferter olarak davranabilme etkinliği metil akrilatın (MA) blok kopolimerizasyonu ile test edilmiş (Şekil 2) ve polimerizasyon % 25 dönüşüme kadar yaşayan karakter, molekül ağırlığı teorik molekül ağırlığına yakın ve dar molekül ağırlığı dağılımlı (M_w/M_n ~1.40) polimerler elde edilmiştir.



Şekil 2 : Fotoiniferter olarak morfolin-4-ditiyokarbamat sonlu polistiren kullanarak MA'ın blok kopolimerizasyonu.

Son olarak, ATRP ve benzodioksinonun fotouyarılma reaksiyonunun birleşimi ile aşı kopolimer sentezi tanımlanmıştır. İyi tanımlanmış ana ve yan zincirleri ile poli(hidroksietilmetakrilat-*co*-metilmetakrilat)-*graft*-poli(stiren) kopolimeri "grafting onto" yöntemi kullanılarak, ATRP ve benzodioksinon fotouyarılmış ester oluşumu yöntemlerini birleştirerek sentezlenmiştir (Şekil 3). Bu aşı kopolimer hazırlama yöntemi, oda sıcaklığında ve hiçbir katalist gerektirmeden yapılabilen ender bir yöndemdir. Aşı kopolimer ve ara bileşenler ^{1}H NMR, GPC, UV, FT-IR, DSC, ve AFM kullanılarak karakterize edilmiştir.



Şekil 3 : Fotokimyasal açilasyon reaksiyonu ile aşı kopolimerlerin sentezi

1. INTRODUCTION

In recent years, the main scientific and applied interest in polymeric materials is focused on the development of novel synthetic methods that allow control over the composition, functionality, molecular structure, and molecular weight. During the last decade, the controlled/living radical polymerization became an established synthetic method to prepare new complex architectures of polymers such as block, graft, star and functional polymers with well-defined structures [1-4].

Recent developments in controlled/living radical polymerization provide the possibility to synthesize polymers with controlled functionalities also with radical routes. The most widely used methods for CLRP include atom transfer radical polymerization (ATRP) [2, 3, 5, 6], nitroxide mediated radical polymerization (NMP) [7, 8], and reversible addition-fragmentation chain transfer polymerization (RAFT) [9, 10]. Among the three standard methods for controlled/living radical polymerization, atom transfer radical polymerization (ATRP) is the most frequently used one. Polymer functionalization by ATRP can be achieved through several ways. Quite a number of functional initiators were successfully used in ATRP to prepare functional styrene and acrylate type polymers. Obviously, this process leads to the formation of monofunctional telechelics since the other chain end always contains halogen due to the fast deactivation process in ATRP.

Photoinduced processes have been recognized as a useful synthetic methodology applied to macromolecular chemistry offering molecules ranging from cross-linked networks to the block and graft copolymer. As such, they are particularly important in preparative methods, in which low-temperature, low energy consumption and high conversions are desirable. Photoinduced block and graft copolymerizations can readily be achieved by the incorporation of photoactive groups at the chain ends and side-chains of preformed polymers, respectively.

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 the 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

A transformation reaction is an elegant way to synthesize block and graft copolymers of monomers that polymerize with different mechanisms. In this concept, a polymer, obtained by a particular polymerization mechanism, is functionalized either by initiation or termination steps. The polymer is isolated and purified, and finally the functional groups are converted to another kind of species capable of initiating polymerization of the second monomer. Living polymerization techniques are essential processes for obtaining well-defined macromolecules with controlled molecular weight, polydispersity index, and architecture and terminal functionalities. A wide range of transformation reactions combining various living ionic polymerization methods were successfully used to synthesize block copolymers that can not obtained by a single method. Living ionic polymerizations have also been combined with conventional free radical polymerization.

Mechanistic transformations can be achieved not only between different polymerization methods, but also by the same mechanism using different initiating systems. For example, ATRP can be combined with NMP, both being controlled radical polymerization methods. This way, limitation of particular initiating system to certain monomers is overcome and block copolymers from all kinds of free radical polymerizable monomers with controlled structures can be obtained.

In this thesis, we describe the synthesis of block and graft copolymers by end group transformation. Transformation reactions were achieved using *N*-alkoxypyridinium salts, morpholine–4–dithiocarbamate sodium salt and hydroxyl functional benzodioxinone compound.

N-Alkoxy pyridinium salts, together with iodonium and sulphonium salts are most widely used photoitiators for cationic polymerization. The objective of this part is to overview the photoactivity of *N*-alkoxy pyridinium salts in terms of direct and indirect photoinitiation for cationic polymerization. The usage of *N*-alkoxy pyridinium salts is not restrained to cationic polymerization. Pyridinium radical cations and ethoxy radicals are formed concomitantly upon direct photolysis. Ethoxy radicals are able to initiate free radical polymerization. In order to obtaine block copolymer, *N*-alkoxy 4-phenylpyridinium and *N*-alkoxy isoquinolinium ion terminated polystyrenes were used as photoinitiators for the polymerization of monomers such as MMA that readily polymerize by a free radical mechanism [11]. It is posssible that obtained graft copolymer via same strategy [12]. It was also demonstrated that the irradiation of photoactive polymers in the presence of a hydrogen donor such as THF facilitates conversion of pyridinium ions to hydroxyl groups.

Dithiocarbamates are kind of important control agents that have been widely used in controlled free radical polymerization, such as photoiniferters and RAFT agents in thermal conditions. We demonstrated that mechanistic transformation from ATRP to photoiniferter process can be achieved by taking advantage of end-group modification of polymers obtained by ATRP. Well-defined block copolymers of St and MA were synthesized using polystyrene with morpholino-4-dithiocarbamate end-groups as a photoiniferter under UV irradiation at ambient temperature [13].

Benzodioxinones are relatively new photosensitive compounds, which form salicylate esters when irradiated in the presence of alcohols and phenols. The acylation occurs under neutral conditions and is tolerant to a wide range of sterically hindered alcohols. Poly(hydroxyethyl methacrylate-*co*-methyl methacrylate)-graft-poly(styrene) copolymer with well-defined main and side chains was synthesized by the “grafting onto” method via combination of ATRP and photoinduced ester formation reaction of benzodioxinones. Our approach toward the preparation of graft copolymers is unique in the way that the process can be performed at room temperature in the absence of any catalyst [14].

2. THEORETICAL PART

2.1 Controlled/Living Polymerization

The term of "living polymerization" was first defined by Szwarc in 1956. A living polymerization is as a chain growth process without irreversible chain breaking reactions such as transfer and termination [15]. 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 [16-18]. 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, radical polymerization 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)

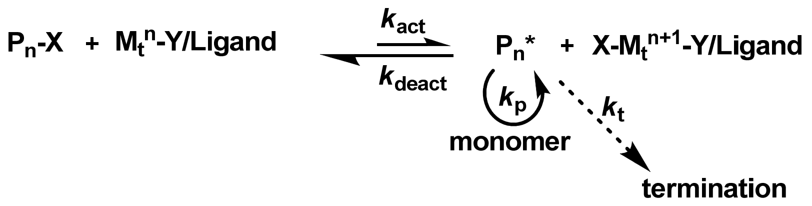
Today, radical polymerization (RP) is a very convenient commercial process for the preparation of high molecular weight polymers since it can be employed for the polymerization of numerous vinyl monomers under mild reaction conditions, requiring an oxygen free medium, but tolerant to water, and can be conducted over a large temperature range (-80 to 250°C) [19]. Furthermore, a wide range of 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. Moreover, the polymerization does not require rigorous process conditions. On the other hand, some important elements of the polymerization process that would lead to the well-defined polymers with controlled molecular weight, polydispersity, composition, structural architecture, and functionality are poorly controlled.

Obviously, living polymerization is an essential technique for synthesizing polymers with controlled structures. Moreover, living polymerization techniques allow preparation of macromonomers, macro initiators, functional polymers, block, graft copolymers, and star polymers. In this way, the need for specialty polymer having a desired combination of properties can be fulfilled. Notable example of these techniques is anionic polymerization [20], 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)

Metal-catalyzed controlled/living radical polymerization (C/LRP), mediated by Cu, Ru, Ni, and Fe metal complexes, is one of the most efficient methods to produce polymers in the field of C/LRP [21] Among aforementioned systems, copper-catalyzed LRP in conjunction with organic halide initiator and amine ligand, often called atom transfer radical polymerization (ATRP), received more interest. 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, which is the most versatile method of the controlled radical polymerization system, uses a wide variety of monomers, catalysts, solvents, and reaction temperature. 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 [5]. 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 [22, 23].



(2.1)

The 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, M_t^n –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, P_n–X. Radicals react reversibly with the oxidized metal complexes, X–M_t^{n+1} / ligand, the deactivator, to reform the dormant species and the activator. These processes are rapid, and the dynamic equilibrium that is established favors the dormant species. By this way, all chains can begin growth at the same time, and the concentration of the free radicals is quite low, resulting in reduced amount of irreversible radical-radical termination. Also chain growth occurs with a rate constant of activation, k_{act}, and deactivation k_{deact}, 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 (reactions 2.2a-e) [24].

Initiation

$$\mathrm{R\text{-}X} + \mathrm{M_t^{n}\text{-}Y/Ligand} \underset{k_{\mathrm{deact}}}{\overset{k_{\mathrm{act}}}{\rightleftharpoons}} \mathrm{R^{\bullet}} + \mathrm{X\text{-}M_t^{n+1}\text{-}Y/Ligand} \qquad \textbf{(2.2a)}$$

$$\mathrm{R^{\bullet}} + \mathrm{M} \xrightarrow{k_{\mathrm{i}}} \mathrm{P_1} \qquad \textbf{(2.2b)}$$

Propagation

$$\mathrm{P_n\text{-}X} + \mathrm{M_t^{n}\text{-}Y/Ligand} \underset{k_{\mathrm{deact}}}{\overset{k_{\mathrm{act}}}{\rightleftharpoons}} \mathrm{P_n^{\bullet}} + \mathrm{X\text{-}M_t^{n+1}\text{-}Y/Ligand} \qquad \textbf{(2.2c)}$$

$$\mathrm{P_n^{\bullet}} + \mathrm{M} \xrightarrow{k_{\mathrm{p}}} \mathrm{P_{n+1}} \qquad \textbf{(2.2d)}$$

Termination

$$\mathrm{P_n} + \mathrm{P_m} \xrightarrow{k_{\mathrm{t}}} \mathrm{P_{n+m}} \quad \text{or} \quad \mathrm{P_n^{=}} + \mathrm{P_m^{H}} \qquad \textbf{(2.2e)}$$

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 [25]. 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.

The rates of polymerization and polydispersity in ATRP, assuming steady-state kinetics, are given in Equation 2.1 and 2.2, respectively [2, 26, 27].

$$R_p = k_{\mathrm{p}}.K_{\mathrm{eq}}\frac{[\mathrm{R\text{-}X}][\mathrm{Mt^{n}}]}{[\mathrm{Mt^{n+1}}]}[\mathrm{M}] \quad \text{or} \quad \ln\left(\frac{[\mathrm{M_0}]}{[\mathrm{M}]}\right) = \frac{k_{\mathrm{p}}.k_{\mathrm{act}}[\mathrm{R\text{-}X}][\mathrm{Mt^{n}}]}{k_{\mathrm{deact}}[\mathrm{Mt^{n+1}}]}t = k_{\mathrm{app}}t \qquad \textbf{(Eq.2.1)}$$

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_p[\mathrm{R\text{-}X}]}{k_{\mathrm{deact}}[\mathrm{Mt^{n+1}}]}\right)\left(\frac{2}{\mathrm{p}} - 1\right) = 1 + \frac{2}{k_{\mathrm{act}}[\mathrm{Mt^{n}}]\,t} \qquad \textbf{(Eq.2.2)}$$

From Eq. (2.1), the rate of polymerization, R_p, is directly proportional to the equilibrium constant, K_{eq}, and the propagation rate constant. The proper selection of the reaction components of an ATRP process led to establishment of an appropriate equilibrium between activation and deactivation processes. The equilibrium constant ($K_{eq} = k_{act}/k_{deact}$) plays an important role in the fate of ATRP because it determines the concentration of radicals and, therefore, the rates of polymerization and termination. K_{eq} must be low to maintain a low stationary concentration of radicals; thus the termination reaction is suppressed. For the ATRP system, the rate of polymerization, R_p, is first order with respect to the monomer [M] and the activator [Mt^n] concentrations and increases with the concentrations of activator, monomer, and initiator [R-X] and decreases with the increasing deactivator [Mt^{n+1}] concentration. Equation 2.2 shows that lower polydispersities are obtained at higher conversion, higher k_{deact} relative to k_p, higher concentration of deactivator, and higher monomer to initiator ratio, $[M]_0/[I]_0$.

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:

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 [23]. Each monomer has its own equilibrium constant, K_{eq}, which determined the polymerization rate in ATRP according to Equation 2.1. In fact, all vinyl monomers are susceptible to ATRP except for a few exceptions. Notable exceptions are unprotected acids (e.g. (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 [28]. 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 [29].

Initiators

Organic halides having a labile carbon-halogen bond are the most successfully employed initiators in ATRP. In general, these organic halides possess electron withdrawing groups and/or atoms such as carbonyl, aryl, cyano, or halogens at α-carbon to stabilize the generated free radicals. 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 [30-32]. The carbon–fluorine bond strength is too strong for the fast activation–deactivation cycle with atom transfer. To obtain similar reactivity of the carbon-halogen bond in the initiator and the dormant polymer end, the structure of the alkyl group, R, of the initiator should be similar to the structure of the dormant polymer end. Typical examples would be the use of ethyl 2-bromoisobutyrate and a Cu(I) complex for the initiation of a methacrylate polymerization [33], or 1-phenylethyl chloride for the initiation of a styrene polymerization [5]. In addition, there are initiators like 2,2,2-trichloro-ethanol [34]. 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 [35]. 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 [36].

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" [37].

Catalysts

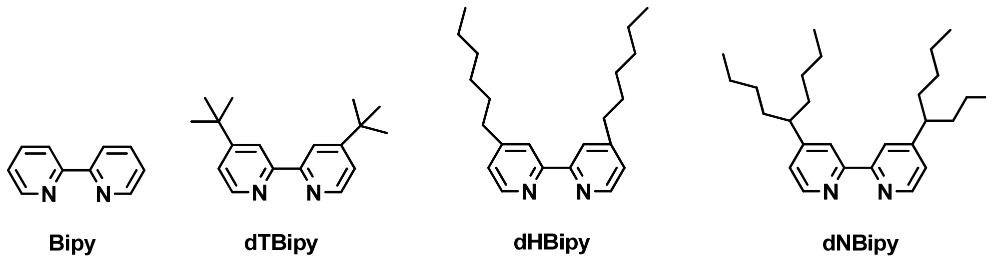
Perhaps the most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. First, the catalyst should react with initiator fast and quantitatively to ensure that all the polymer chains start to add monomer at the same time. Second, the catalyst must have moderate redox potential to ensure an appropriate equilibrium between dormant and active species. In general, a low redox potential of the catalyst leads to formation of the high Cu(II) concentration (equilibrium is shifted toward transient radicals). Consequently, a fast and uncontrolled polymerization is observed. In contrast, high redox potential strongly suppresses Cu(II) formation (equilibrium is shifted toward dormant species) via a halogen atom abstraction process leading to very slow polymerization. Third, the catalyst should be less sterically hindered, because excessive steric hindrance around the metal center of catalyst results in a reduction of the catalyst activity. Fourth, a good catalyst should not afford side reactions such as Hoffman elimination, β-H abstraction, and oxidation/reduction of radicals [38].

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, iron [39], nickel [39], rhenium [32], ruthenium [6], rhodium [40, 41], and palladium [42] 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 [43].

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 (Me$_6$-TREN). Examples of ligands used in copper-mediated ATRP are illustrated below [5, 44].



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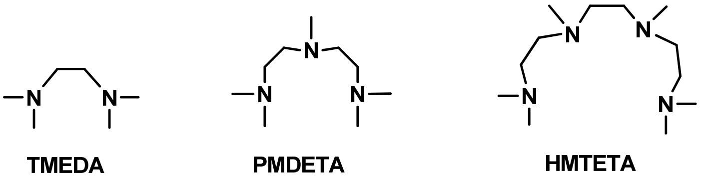


(2.4)

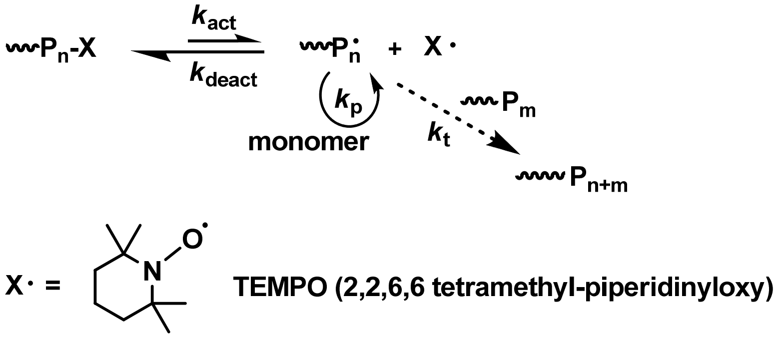
In addition to those commercial products, it has been demonstrated that hexamethyltriethylene tetramine (HMTETA) provides better solubility of the copper complexes in organic media and entirely homogeneous reaction conditions [45]. Since copper complexes of this new ligand are almost insoluble in water, ATRP technique can be employed in preparing poly(acrylate esters) in aqueous suspensions [46].

Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Common solvents, including nonpolar (toluene, xylene, benzene), polar aprotic (diphenyl ether, dimetoxy benzene, anisole, *N,N*-dimethylformamide, ethylene carbonate, acetonitrile), and polar protic (alcohols, water), are employed not only for solubilizing the monomers, the produced polymers, and the catalyst, but also to achieve the controlled polymerization condition. A solvent is sometimes necessary, especially when the polymer is insoluble in its monomer (e.g., polyacrylonitrile). ATRP has also been successfully carried out 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) [47] and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent [48], 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 ($P_n\cdot$) reacts with a stable radical ($X\cdot$) as seen in reaction 2.5 [49]. The most commonly used stable radicals have been nitroxides, especially 2,2,6,6- tetramethylpiperidine-*N*-oxyl (TEMPO). The resulting dormant species (P_n-X) can then reversibly cleave to regenerate the free radicals once again. Once $P_n\cdot$ forms it can then react with a monomer, M, and propagate further.



(2.5)

Two initiation systems have been generally employed in the NMP. First is a bimolecular system consisting of conventional radical initiator such as BPO or azoisobutyronitrile (AIBN), and a nitroxide (i.e., TEMPO). The conventional radical initiator is decomposed at an appropriate temperature to initiate free-radical polymerization. The initiator-monomer adduct is trapped by the nitroxide leading to formation of the alkoxyamine *in situ*. Second is the unimolecular system using the alkoxyamine that is decomposed into a nitroxide and an initiating radical. This radical subsequently initiates the free-radical polymerization (2.5). By using the unimolecular initiator, the molecular weight can be properly controlled, because the number of initiating sites per polymeric chain is defined. In addition, functionalized unimolecular initiators can afford the fully functional groups at the ends of the polymer chain.

Unfortunately, TEMPO can only be used for the polymerization of styrene-based monomers at relatively high temperatures (>120ºC). 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 [50-54]. Most recently, the use of more reactive alkoxyamines and less reactive nitroxides has expanded the range of polymerizable monomers to acrylates, dienes, and acrylamides [55-57]. Several nitroxides that have been employed as mediators in stable free-radical polymerizations [29].

2.1.1.3 The reversible addition–fragmentation chain transfer process

Reversible addition-fragmentation chain transfer (RAFT) polymerization is one of the most efficient methods in controlled/living radical polymerization. An important advantage of this method over ATRP and NMP is its tolerance to a wide range of functionalities, namely -OH, -COOH, $CONR_2$, NR_2, SO_3Na, etc., in monomer and solvent. This provides the possibility of performing the polymerization under a wide range of reaction conditions and polymerizing or copolymerizing a wide range of monomers in a controlled manner. 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, 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.

The RAFT system basically consists of a small amount of RAFT agent and monomer and a free-radical initiator. Radicals stemming from the initiator are used at the very beginning of the polymerization to trigger the degenerative chain transfer reactions that dominate the polymerization. Free radicals affect both the molecular weight distribution of the polymer as the dead polymer chains of uncontrolled molecular weight are formed and the rate of polymerization. Therefore, the concentration of free radicals introduced in the system needs to be carefully balanced. For example, radical concentration was constant between 10^{-6}–10^{-7} (mol L^{-1}) depending on the conditions in the RAFT polymerization of styrene with RAFT agents such as benzyl (diethoxyphosphoryl) dithioformate or benzyl dithiobenzoate [58]. In RAFT polymerization radicals may be generated in three different ways: (1) by decomposition of organic initiators, (2) by the use of an external source (UV–vis or γ-ray), and (3) by thermal initiation. Polymerization temperature is usually in the range of 60–80 ^{o}C, which corresponds to the optimum decomposition temperature interval of the well-known initiator AIBN. However, even room temperature and high-temperature conditionscan also be applied [59, 60]. Generally, a RAFT agent/free-radical ratio of 1:1 to 10:1 yields polymers with narrow molecular weight distributions.

Photo- and γ-ray-induced reactions, which use light energy to generate radicals in RAFT polymerization, offer a number of advantages compared with thermally initiated ones.

The major advantage is to allow the polymerization to be conducted at room temperature with relatively shorter reaction times. In photoinduced reactions, however, the RAFT agent should carefully be selected, as in some cases control over the molecular weight cannot be attained, particularly at high conversions because it may also decompose under UV light [61]. γ-Ray-induced RAFT polymerization appeared to be more penetrating compared with the corresponding UV-induced processes [62, 63].

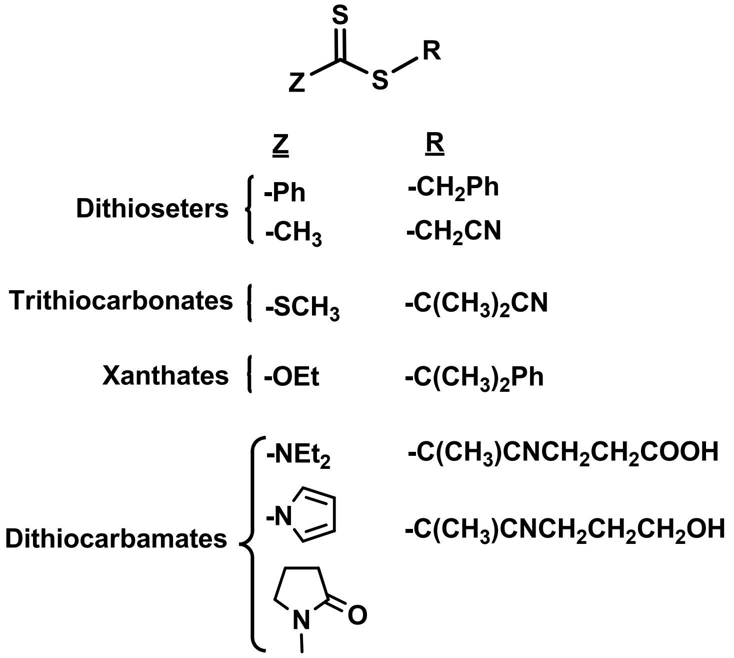
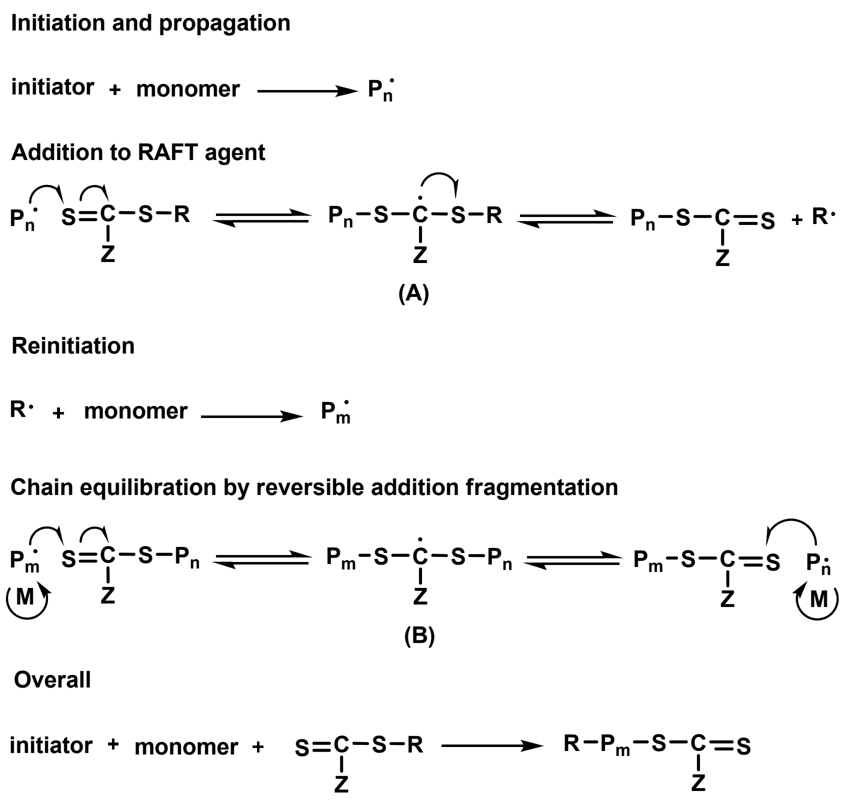


Figure 2.1 : Examples of the different classes of thiocarbonylthio RAFT agents.

The mechanism of RAFT polymerization with the thiocarbonylthio-based RAFT agents involves a series of addition–fragmentation steps as depicted below (reaction 2.6 a-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·). The radical R· 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 (reaction 2.6e) which has been identified by ^{1}H-NMR and UV–vis spectroscopy [64]. Additional evidence for the proposed mechanism was provided by the identification of the intermediate thioketal radical ((A) and/or (B), reaction 2.6b,d) by ESR spectroscopy [65, 66].



Initiation and propagation

$$\text{initiator} + \text{monomer} \longrightarrow P_n^{\bullet} \tag{2.6a}$$

Addition to RAFT agent

$$P_n^{\bullet} \quad S{=}\underset{Z}{C}{-}S{-}R \rightleftharpoons P_n{-}S{-}\underset{Z}{\dot{C}}{-}S{-}R \rightleftharpoons P_n{-}S{-}\underset{Z}{C}{=}S + R^{\bullet} \tag{2.6b}$$

(A)

Reinitiation

$$R^{\bullet} + \text{monomer} \longrightarrow P_m^{\bullet} \tag{2.6c}$$

Chain equilibration by reversible addition fragmentation

$$\underset{(M)}{P_m^{\bullet}} \quad S{=}\underset{Z}{C}{-}S{-}P_n \rightleftharpoons P_m{-}S{-}\underset{Z}{\dot{C}}{-}S{-}P_n \rightleftharpoons P_m{-}S{-}\underset{Z}{C}{=}S \quad \underset{(M)}{P_n^{\bullet}} \tag{2.6d}$$

(B)

Overall

$$\text{initiator} + \text{monomer} + S{=}\underset{Z}{C}{-}S{-}R \longrightarrow R{-}P_m{-}S{-}\underset{Z}{C}{=}S \tag{2.6e}$$

2.2 Photopolymerization

Photopolymerization is one of the most rapidly expanding processes for materials production and is employed over a wide range of applications. Since the technologies are extremely efficient and economical process as well as environmentally favorable process compared to traditional thermal polymerizations, photopolymerization process has continued to expand the growth of plastic market share. The use of light, rather than heat, to drive the reactions leads to a variety of advantages, including solvent-free formulations, very high reaction rates at room temperature, spatial control of the polymerization, low energy input, and chemical versatility since a wide variety of polymers can be polymerized photochemically. These advantages have been exploited in a variety of applications including: traditional films, fabrication of printed circuit boards, coatings for optical fibers, and replication of optical disks. In addition, photopolymerizations demand lower energy requirements because the polymerizations use a fraction of the energy of traditional thermal systems but the process provides high speed and high production rate at low curing temperature. Finally, the process may be used to rapidly form polymers without the use of diluting solvents and leads to lower volatile organic compounds than traditional thermal polymerization.

Photopolymerizations are simply polymerization reactions initiated by light, typically in the ultraviolet or visible region of the light spectrum. Photopolymerizations are initiated by certain types of compounds which are capable of absorbing light of a particular wavelength. The wavelength or range of wavelengths of the initiating source is determined by the reactive system including the monomer(s), the initiator(s), and any photosensitizers, pigments or dyes which may be present. An active center is produced when the initiator absorbs light and undergoes some type of decomposition, hydrogen abstraction, or electron transfer reaction. If necessary, the effective initiating wavelength may be shifted by adding small amounts of a second compound, termed a photosensitizer, to the reaction mixture. The photosensitizer absorbs light and populates an excited state which may then react with the photoinitiator to produce an active cation or radical capable of initiating the polymerization. Upon generation of active centers, photopolymerizations propagate and terminate in the same manner as traditional (i.e. thermal) polymerizations. Photopolymerization can be divided into two categories: photoinitiated free radical (e.g. of acrylates) and cationic (e.g. ring opening reaction of epoxides) polymerizations.

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 because of its applicability to a wide range of formulations based on acrylates, unsaturated polyesters, and polyurethanes and the availability of photoinitiators having spectral sensitivity in the near-UV or visible range.

2.2.1 Photoinitiated free radical polymerization

Photoinitiated free radical polymerization consists of photoinitiation (reactions 2.7a-c), propagation, chain transfer, and termination (reactions 2.7d-f). 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.

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{PI}^* \qquad \textbf{(Absorption)} \qquad \textbf{(2.7a)}$$

$$\mathrm{PI}^* \longrightarrow \mathrm{R}_1^{\bullet} + \mathrm{R}_2^{\bullet} \qquad \textbf{(Radical Generation)} \qquad \textbf{(2.7b)}$$

$$\mathrm{R}_1^{\bullet} + \mathrm{M} \longrightarrow \mathrm{R}_1\text{-}\mathrm{M}^{\bullet} \qquad \textbf{(Photoinitiation)} \qquad \textbf{(2.7c)}$$

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.

$$\left.\begin{array}{rcl} \mathrm{R}_1\text{-}\mathrm{M}^{\bullet} + \mathrm{M} & \longrightarrow & \mathrm{R}_1\text{-}\mathrm{MM}^{\bullet} \\ \mathrm{R}_1\text{-}\mathrm{MM}^{\bullet} + (n\text{-}2)\mathrm{M} & \longrightarrow & \mathrm{R}_1\text{-}\mathrm{M}_n^{\bullet} \end{array}\right\} \textbf{(Propagation)} \qquad \textbf{(2.7d)}$$

$$\left.\begin{array}{rcl} \mathrm{R}_1\text{-}\mathrm{M}_n^{\bullet} + \mathrm{R\text{-}H} & \longrightarrow & \mathrm{R}_1\text{-}\mathrm{M}_n\text{-}\mathrm{H} + \mathrm{R}^{\bullet} \\ \mathrm{R}^{\bullet} + \mathrm{M} & \longrightarrow & \mathrm{R\text{-}M}^{\bullet} \end{array}\right\} \textbf{(Transfer)} \qquad \textbf{(2.7e)}$$

$$\left.\begin{array}{rcl} \mathrm{R}_1\text{-}\mathrm{M}_n^{\bullet} + \mathrm{R}_1\text{-}\mathrm{M}_m^{\bullet} & \longrightarrow & \mathrm{R}_1\text{-}\mathrm{M}_{n+m}\text{-}\mathrm{R}_1 \\ \mathrm{R}_1\text{-}\mathrm{M}_n^{\bullet} + \mathrm{R}_2^{\bullet} & \longrightarrow & \mathrm{R}_1\text{-}\mathrm{M}_n\text{-}\mathrm{R}_2 \\ \mathrm{R}_1\text{-}\mathrm{M}_n^{\bullet} + \mathrm{R}_1\text{-}\mathrm{M}_m^{\bullet} & \longrightarrow & \mathrm{R}_1\text{-}\mathrm{M}_n + \mathrm{R}_1\text{-}\mathrm{M}_m \\ \mathrm{R}_1\text{-}\mathrm{M}_n^{\bullet} + \mathrm{R}_2^{\bullet} & \longrightarrow & \mathrm{R}_1\text{-}\mathrm{M}_n + \mathrm{R}_2 \end{array}\right\} \textbf{(Termination)} \qquad \textbf{(2.7f)}$$

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.

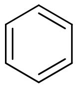
2.2.1.1 Absorption of light

Photochemistry is concerned with chemical reactions induced by optical radiation [67-69]. The radiation is most often ultraviolet (200–400 nm) or visible (400–800 nm) light but is sometimes infrared (800–2500 nm) light.

Absorption of a photon of light by any compound causes electronic excitation. The energy causing excitation, E, is described by $E=hc/\lambda$ where h is Planck's constant, c is the speed of light, and , λ is the wavelength of the exciting light. Light absorption is described by $A= \varepsilon C l$, where ε is the molar absorptivity (extinction coefficient), C is the concentration of the species, and l is the light path length.

The extinction coefficient, a constant for a compound at a specific wavelength, is an experimental measure of the probability of absorption at that wavelength. The magnitude of the extinction coefficient depends upon the compound's chromophore, the chemical moiety responsible for the absorption of light. Typical chromophores contain unsaturated functional groups such as C=C, C=O, NO_2, or N=N [67-70]. Table 2.1 lists some chromophores, their wavelength of maximum absorption, and the extinction coefficient at this wavelength. These values are qualitative because chromophore absorption is highly dependent upon neighboring substituent. For example, the absorption maximum and extinction coefficient of conjugated dienes are known to be influenced by the number of conjugated double bonds, alkyl substituent, and ring structure [67-70].

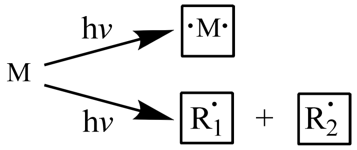
Table 2.1 : Local wavelength of maximum absorption and associated extinction coefficient for typical chromophores

Chromophore	λ_{max} (nm)	ε_{max}
$>C=C<$	195	10,000
$-C\equiv C-$	195	2,000
$-N=N-$	345	10
NO_2	270	18.6
$S=O$	210	1500
$R-\overset{O}{\overset{\|}{C}}-OH$	205	60
$R-\overset{O}{\overset{\|}{C}}-R$	190 280	900 15
$>C=\underset{\mid}{C}-\underset{\mid}{C}=C<$	215	20,000
	185 200 255	60,000 8,000 200

2.2.1.2 Photoinitiation

Radical generation by monomer irradiation

Some monomers can generate radical species via absorption of light. Two possibilities are suggested for photoinitiation of polymerization by photosensitive monomers. As shown in reaction 2.8, the biradical formed by a photoinduced cyclization or a simple α-cleavage of monomer may be responsible for initiating polymerization.



(2.8)

These species can react with intact monomer molecules and thus leading to growing chains. Readily commercially available monomers which undergo polymerization and copolymerization through UV irradiation to some extent are listed in Table 2.2 [71, 72].

Table 2.2 : Photosensitive monomers

Allyl methacrylate
Barium acrylate
Cinnamyl methacrylate
Diallyl phthatlate
Diallyl isophtalate
Diallyl terephthalate
2-Ethylhexyl acrylate
2-Hydroxyethyl methacrylate
2-Hydroxypropyl acrylate
N,N'Methylenebisacrylamide
Methyl methacrylate
1,6-hexanediol diacrylate
Pentaerythritol tetramethacrylate
Styrene
Tetraethylene glycol dimethacrylate
Tetrafluoroethylene
N-Vinylcarbazole
Vinyl cinnamate
Vinyl 2-furoate
Vinyl 2-furylacrylate

On the other hand, radical generation via irradiation of vinyl monomer does not play a role due to regarding technical applications such as very low efficiency of radical formation and usually unsatisfactory absorption characteristics. For example, styrene irradiated at 313 nm produces small amounts of polystyrene in addition to larger amounts of styrene oligomers [67].

Radicals via photoinitiators

A photoinitiator is a compound that, under absorption of light, undergoes a photoreaction, producing free radicals. These species are capable of initiating the polymerization of suitable monomers. 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 2.9 are termed "*Type I* photoinitiators".

$$\mathbf{PI} \xrightarrow{h\nu} \mathbf{(PI)^*} \xrightarrow[\text{fragmentation}]{\text{unimolecular reaction}} \underset{\text{free radicals}}{\boxed{R_1^\bullet} + \boxed{R_2^\bullet}} \qquad \mathbf{(2.9)}$$

If the excited state photoinitiator interacts with a second molecule (a coinitiator) to generate radicals in a bimolecular reaction as shown in reaction 2.10, the initiating system is termed a "*Type II* Photoinitiator".

$$\mathbf{PI} \xrightarrow{h\nu} \mathbf{(PI)^*} + \mathbf{COI} \xrightarrow[\text{hydrogen abstraction}]{\text{bimolecular reaction}} \underset{\text{free radicals}}{R_1^\bullet + \boxed{R_2^\bullet}} \qquad \mathbf{(2.10)}$$

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.

2.2.1.3 Type I photoinitiators (Unimolecular photoinitiator systems)

Photoinitiators termed unimolecular are so designated because the initiation system involves only one molecular species interacting with the light and producing free-radical active centers. These substances undergo a homolytic bond cleavage upon absorption of light (reaction 2.11). The fragmentation that leads to the formation of radicals is, from the point of view of chemical kinetics, a unimolecular reaction (Eq:2.3).

$$\mathbf{PI} \xrightarrow{h\nu} \mathbf{PI^*} \xrightarrow{k} R_1^\bullet + R_2^\bullet \qquad \mathbf{(2.11)}$$

$$\frac{d[R_1^\bullet]}{dt} = \frac{d[R_2^\bullet]}{dt} = k\,[PI^*] \qquad \mathbf{(Eq.2.3)}$$

The number of initiating radicals formed upon absorption of one photon is termed as quantum yield of radical formation ($\Phi_{R\bullet}$) (Eq:2.4).

$$\Phi_{R^\bullet} = \frac{\text{Number of initiating radicals formed}}{\text{Number of photons absorbed by the photoinitiator}} \qquad \textbf{(Eq.2.4)}$$

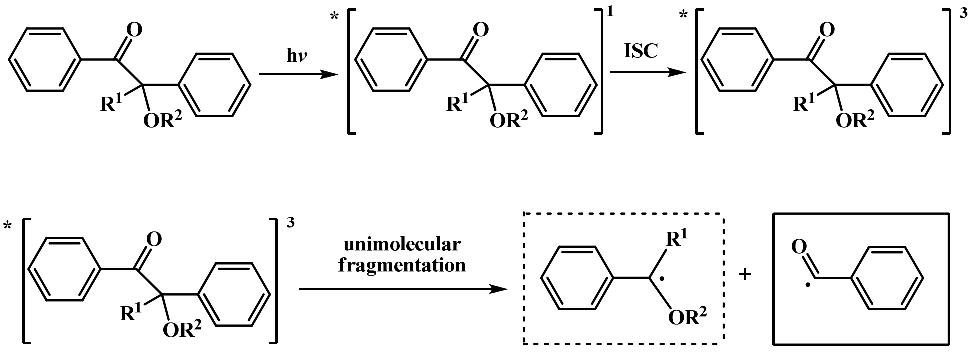
Theoretically, cleavage type photoinitiators should have a $\Phi_{R\bullet}$ value of two since two radicals are formed by the photochemical reaction. The values observed, however, are much lower because of various deactivation routes of the photoexcited initiator other than radical generation. These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

$$f_P = \frac{\text{Number of chain radicals formed}}{\text{Number of primary radicals formed}} \qquad \textbf{(Eq.2.5)}$$

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

$$\Phi_P = \Phi_{R\bullet} \text{ x } f_P \qquad \textbf{(Eq.2.6)}$$

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.



(2.12)

R^1 = H, Alkyl, substituted Alkyl, R^2 = H, Alkyl, substituted Alkyl

Type I photoinitiators which undergo a direct photofragmentation process (α or less common β cleavage) upon absorption of light and formation of initiating radicals capable of inducing polymerization. As illustrated in reaction 2.12, the photoinitiator is excited by absorption of ultraviolet light and rapid intersystem crossing to the triplet state. In the triplet state, the bond to the carbonyl group is cleaved, producing an active benzoyl radical fragment and another fragment. The benzoyl radical is the major initiating species, while, in some cases, the other fragment may also contribute to the initiation. The most efficient *Type I* initiators are benzoin ether derivatives, benzil ketals, hydroxylalkylphenones, α-aminoketones and acylphosphine oxides (Table 2.3) [73-76].

Table 2.3 : Structures of typical *Type I* radical photoinitiators

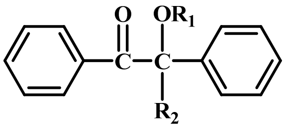
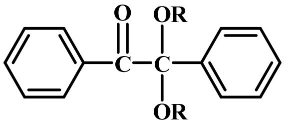
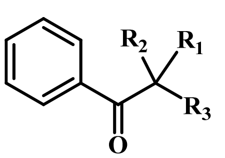
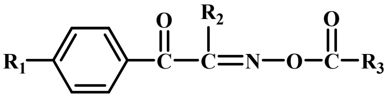
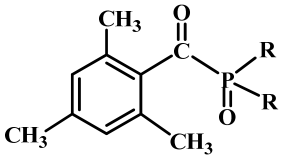
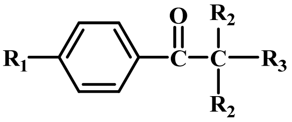
Photoinitiators	Structure	λ_{max} (nm)
Benzoin ethers	 R_1 = H, alkyl R_2 = H, substituted alkyl	323
Benzil ketals	 R = CH_3, C_3H_7, CH_2	365
Acetophenones	 R_1 = OCH_3, OC_2H_5 R_2 = OCH_3, H R_3 = C_6H_5, OH	340

Table 2.3 (Continued): Structures of typical *Type I* radical photoinitiators

Benzyl oximes	 $R_1 = H, SC_6H_5$ $R_2 = CH3, C_6H_{13}$ $R_3 = C_6H_5, OC_2H_5$	335
Acylphosphine Oxides	 $R = C_6H_5$ or OCH_3	380
Aminoalkyl phenones	 $R_1 = SCH_3$, morpholine $R_2 = CH3, CH_2Ph$ or C_2H_5 $R_3 = N(CH_3)_3$, morpholine	320

2.2.1.4 *Type II* photoinitiators (Bimolecular photoinitiator systems)

Bimolecular photoinitiators are so-called because two molecular species are needed to form the propagating radical: a photoinitiator that absorbs the light and a co-initiator that serves as a hydrogen or electron donor. These photoinitiators 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 co-initiator to produce initiating radicals (reaction 2.13). In this case, radical generation follows 2nd order kinetics (Eq:2.7).

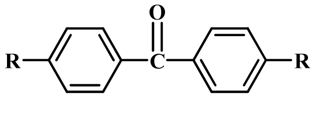
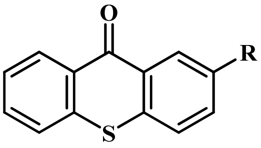
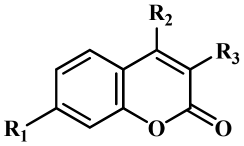
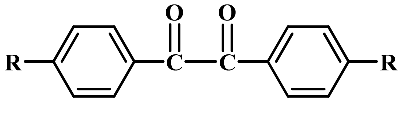
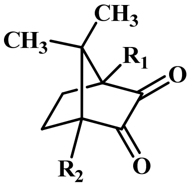
$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{PI}^* + \mathrm{COI} \xrightarrow{k} \mathrm{R}_1^{\bullet} + \mathrm{R}_2^{\bullet} \qquad \textbf{(2.13)}$$

$$\frac{d[\mathrm{R}_1^{\bullet}]}{dt} = \frac{d[\mathrm{R}_2^{\bullet}]}{dt} = k\,[\mathrm{PI}^*]\ [\mathrm{COI}] \qquad \textbf{(Eq.2.7)}$$

In these systems, photons are absorbed in the near UV and visible wavelengths. Free radical active centers are generated by hydrogen abstraction or photo-induced electron transfer process aforementioned.

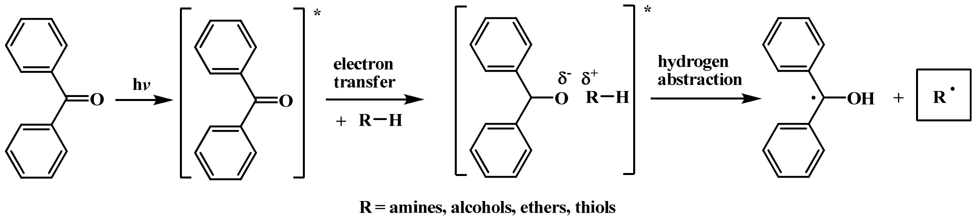
Photosensitizers of *Type II* system including benzophenones, thioxanthones, camphorquinones, benzyls, and ketocoumarins are listed in Table 2.4.

Table 2.4 : Structures of typical Type II photosensitizers

Photosensitizers	Structure	λ_{max} (nm)
Benzophenones	 R = H, OH, $N(C_2H_5)_2$, C_6H_5	335
Thioxanthones	 R = H, Cl, isopropyl	390
Coumarins	 $R_1 = N(C_2H_5)_2, N(CH_3)_2$ $R_2 = CH_3$, cyclopentane R_3 = benzothiazole, H	370
Benzils	 R = H, CH_3	340
Camphorquinones	 $R_1 = CH_3$, H $R_2 = H, CH_3$	470

Hydrogen abstraction

Photoinitiators that proceed via a hydrogen abstraction mechanism are exemplified by combination of benzophenone and a hydrogen donor (reaction 2.14). When R-H is an amine with transferable hydrogen, benzophenone undergoes an electron transfer followed by a hydrogen abstraction to produce an initiating species and semipinacol radical. The semipinacol radical does not efficiently initiate polymerization and typically react with other radicals in the system as a terminating species causing a reduction in the polymerization rate.



(2.14)

Photoinduced electron transfer reactions and subsequent fragmentation Photoinduced electron transfer is a more general process which is not limited to a certain class of compounds and is more important as an initiation reaction comprising the majority of bimolecular photoinitiating systems. The photoexcited compounds (sensitizer) can act as either an electron donor with the coinitiator as an electron acceptor or vice-versa. The radical ions obtained after the photoinduced electron transfer can generally undergo fragmentation to yield initiating radicals (reactions 2.15).

$$\mathbf{PS} \xrightarrow{h\nu} \mathbf{PS^*}$$

$$\mathbf{PS^*} + \mathbf{A} \longrightarrow \mathbf{PS^{\bullet +}} + \mathbf{A^{\bullet -}} \longrightarrow \mathbf{R_1^{\bullet}} + \mathbf{R_2^{\bullet}} \qquad \mathbf{(2.15)}$$

$$\mathbf{PS^*} + \mathbf{D} \longrightarrow \mathbf{PS^{\bullet -}} + \mathbf{D^{\bullet +}} \longrightarrow \mathbf{R_1^{\bullet}} + \mathbf{R_2^{\bullet}}$$

The electron transfer is thermodynamically allowed, if Gibbs Energy Change (ΔG) calculated by the Rehm-Weller equation (Eq:2.8) [77] is negative.

$$\Delta G = F\,[E\tfrac{1}{2}ox\,(D/D^{+\bullet}) - E_{\frac{1}{2}}^{red}\,(A/A^{-\bullet})] - E_{PS} + \Delta E_c \qquad \mathbf{(Eq.2.8)}$$

where, F = Faraday constant,

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

$E_{\frac{1}{2}}^{red}\,(A/A^{-\cdot})$ = 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. Dyes comprise a large fraction of visible light photoinitiators because their excited electronic states are more easily attained. Co-initiators, such as tertiary amines, iodonium salts, triazines, or hexaarylbisimidazoles, are required since dye photochemistry entails either a photo-reduction or photo-oxidation mechanism. Numerous dye families are available for selection of an appropriate visible initiation wavelength; examples of a thiazine dye (with an absorption peak around 675 nm), acridine dyes (with absorption peaks around 475nm), xanthene dyes (500–550 nm), fluorone dyes (450–550 nm), coumarin dyes (350–450 nm), cyanine dyes (400–750 nm), and carbazole dyes (400 nm) [78-81]. The oxidation or reduction of the dye is dependent on the co-initiator; for example, methylene blue can be photo-reduced by accepting an electron from an amine or photo-oxidized by transferring an electron to benzyltrimethyl stannane [78]. Either mechanism will result in the formation of a free-radical active center capable of initiating a growing polymer chain.

2.2.1.5 Monomers

Unsaturated monomers, which contain a carbon–carbon double bond (C=C), are used extensively in free radical photopolymerizations. The free-radical active center reacts with the monomer by opening the C=C bond and adding the molecule to the growing polymer chain. Most unsaturated monomers are able to undergo radical polymerization because free-radical species are neutral and do not require electron-donating or electron-withdrawing substituents to delocalize the charge on the propagating center, as is the case with ionic polymerizations. Commercial consideration in formulation development is therefore given to the final properties of the polymer system, as well as the reactivity of the monomer. Acrylate and methacrylate monomers are by far most widely used in free-radical photopolymerization processes. These monomers have very high reaction rates, with acrylates having an even faster reaction rate than their methacrylate counterparts [82]. This makes them especially amenable for high speed processing needed in the films and coatings industry.

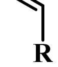
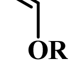
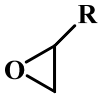
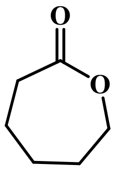
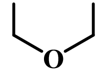
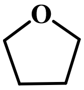
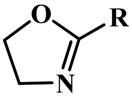
Multiacrylates increase the mechanical strength and solvent resistance of the ultimate polymer by forming cross-linked networks rather than linear polymer chains, whereas monoacrylates reduce the viscosity of the prepolymer mixture for ease of processing [82, 83]. One of the drawbacks of acrylate and methacrylate systems is their relatively large polymerization shrinkage. Shrinkage is caused by the formation of covalent bonds between monomer molecules. When a covalent bond is formed between two monomer molecules, the distance between them is approximately half as much as that between two molecules experiencing van der Waal’s forces in solution. This shrinkage causes stresses in the polymer parts, which can affect their ultimate performance, especially in applications such as stereo lithography, dentistry, and coatings. One way to overcome this disadvantage is to develop oligomeric acrylates. These oligomers contain 1 to 12 repeat units formed through step-growth polymerization; the ends are then capped with two or more (meth) acrylate functional groups.

Diallyldiglycolcarbonate has been used for many years in optical components such as lenses [84]. Acrylamide is used in stereo lithography and to prepare holographic materials [85, 86]. N-vinylpyrrolidinone is copolymerized with acrylates and methacrylates for cosmetic and biomedical applications [87]. Norbornene is copolymerized with thiols for optical fiber coatings [88].

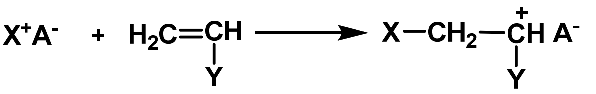
2.2.2 Photoinitiated cationic polymerization

Photoinitiated cationic polymerization is an important industrial processess widely used in different applications. For instance, coatings, inks, adhesives, and photolithography can be performed without the use of solvents, so a potential source of air and water pollution is eliminated [89, 90]. UV initiated cationic polymerization holds considerable promises in the fature, practically as a means of volatile emission, toxicity and molecular oxygen inhibition limitations. The type of general monomers, which may undergo photoinitiated cationic polymerization, are vinyl and alkoxy vinyl monomers, heterocyclic monomers involving sulphur, oxygen, and nitrogen atoms as summarized in Table 2.5. Most importantly, these monomers do not go decomposition and give side reactions at the wavelength of irradiation.

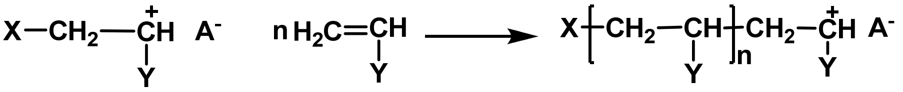
Table 2.5 : The type of general monomers, which may undergo photoinitiated cationic polymerization

 **vinyl monomer**	 **alkoxy vinyl**	 **cyclic sulphide**	 **epoxide**
 **caprolacton**	 **1,3,5-trioxane**	 **furan**	 **oxasine**

Onium salts such as diaryliodonium [91, 92] triarylsulphonium [93] and alkoxypyridinium [94-96] are the mostly used initiators mainly absorb the light in the region between 225 and 350 nm [92, 97-99] for photoinitiated cationic polymerization. Upon UV irradiation, reactive cations or Brønsted acids are produced by means of homolytic and heterolytic bond cleavages of these salts respectively.



$$X^+A^- + H_2C{=}\underset{Y}{CH} \longrightarrow X{-}CH_2{-}\underset{Y}{\overset{+}{C}H}\,A^- \tag{2.16}$$



$$X{-}CH_2{-}\underset{Y}{\overset{+}{C}H}\;A^- \quad n\,H_2C{=}\underset{Y}{CH} \longrightarrow X\left[CH_2{-}\underset{Y}{CH}\right]_n CH_2{-}\underset{Y}{\overset{+}{C}H}\;A^- \tag{2.17}$$

This reaction scheme holds for all types of cationic photoinitiators. Notably, the counter anion has to be nonnucleophilic in order to prevent the termination of a growing chain. Generally, molecular weights and percentage conversion increase in the order of $BF_4^- < PF_6^- < AsF_6^- < SbF_6^-$.

Chemical construction of the system used determines the photoinitiator which is suitable for the generation of the cations. In the case of onium salt, there are two acting systems, direct and indirect photolysis. In direct initiating systems, the energy is absorbed by the onium salt leading to decomposition. On the other hand, an additional component absorbs the energy in indirect systems. After absorbing energy, either the additives themselves or the species formed from additives can react with the onium salt thus producing initiating cations. Various wavelengths for specific applications can be tunned by altering the additional component. Photoinitiated cationic polymerization by direct irradiation of simple onium salts can be performed usually below 300 nm, so some limitations occur on the potential uses of cationic polymerization at high wavelength. Moreover, conventional light sources emit the light at a significant proportion at higher wavelengths. Therefore, limited absorption of the initiating system in a broad range causes waste of energy. One way to broaden the spectral sensitivity of the onium salts is substitution of chromophores onto aromatic groups of the salts. However, this method has some disadvantages such as multistep synthetic procedures, high cost and the failure in desired shift in the absorption characteristics of the salts. Several indirect ways to overcome this problem have been described [99]. All of these pathways involve electron transfer reactions either with photoexcited sensitizer [100-104], the electron donor compounds in the excited charge transfer complexes [105, 106] or with free radicals [107-109].

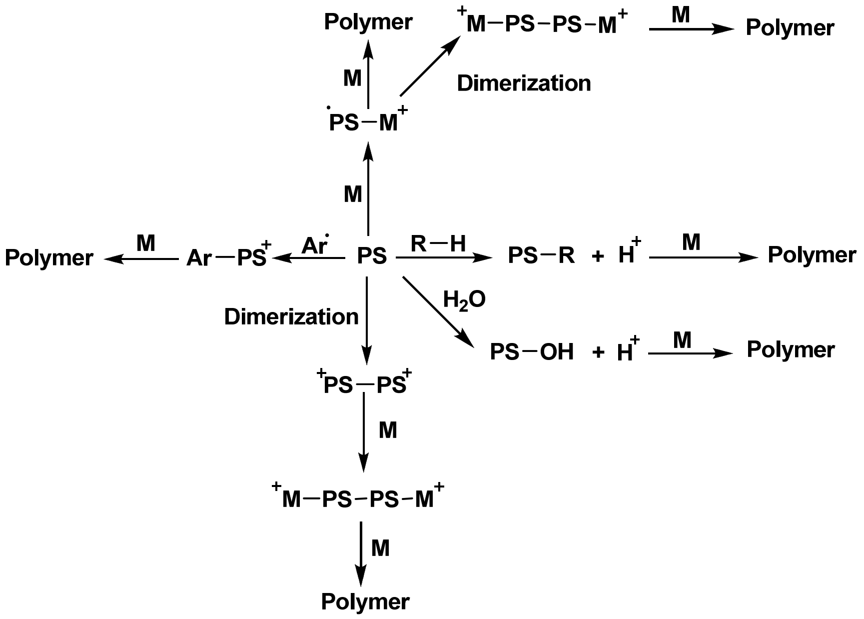
2.2.2.1 Photosensitized cationic polymerization

The absorption characteristics of the onium salts based photoinitiating systems can be adapted for particular applications requiring activation at wavelengths between 330-650 nm by the use of various photosensitizers. The photosensitizers enhance the sensitivity of the light source that used and accelerate the rate of polymerization by inducing onium salt decomposition with electron transfer (reaction 2.18).

Notably, aromatic carbonyl photosensitizers that undergo electron transfer via a radical route are not included [105-110].

$$(PS^*) + On^+ \longrightarrow PS^{\bullet +} + On^{\bullet} \tag{2.18}$$

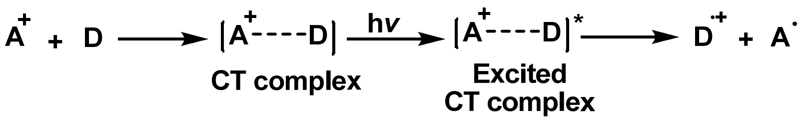
The photosensitizer radical cations initiate the cationic polymerization with the various mechanisms, which are depicted in reaction 2.19 [111].



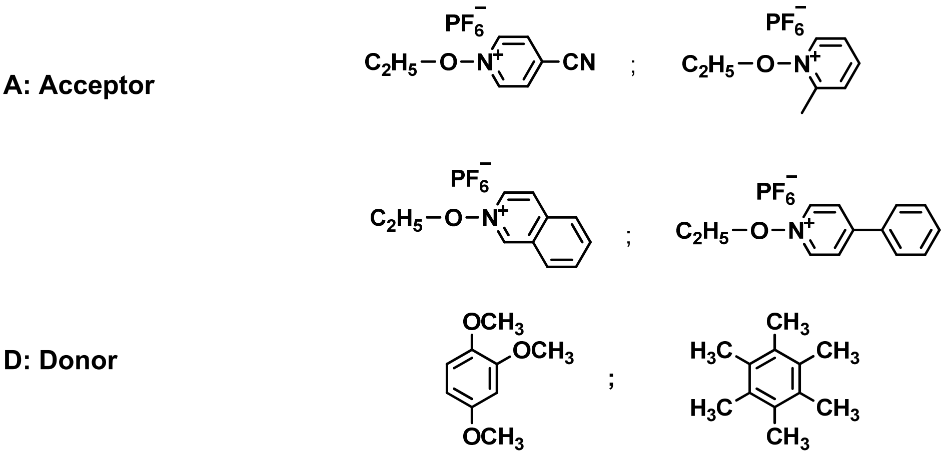
(2.19)

2.2.2.2 Photoinitiated cationic polymerization by charge transfer complexes

It has been reported [105, 106] that charge transfer complexes formed by mixing certain pyridinium ions with aromatic electron donors act as photoinitiators for cationic polymerization. It was suggested that radical cations of donors, formed by excitation of CT complex according to the following mechanism (reaction 2.20), are responsible for the polymerization.



$$\overset{+}{A} + D \longrightarrow \underset{\text{CT complex}}{[\overset{+}{A}\text{----}D]} \xrightarrow{h\nu} \underset{\text{Excited CT complex}}{[\overset{+}{A}\text{----}D]^{*}} \longrightarrow \overset{\cdot +}{D} + A^{\cdot} \qquad (2.20)$$



The radical cations formed initiate the cationic polymerization directly or they undergo hydrogen abstraction yielding Brønsted acid capable of initiating cationic polymerization. The absorption bands of the charge transfer complexes lie in the range between 350-650 nm depending on the structure of the electron donor compound and the acceptor pyridinium salt. Interestingly, CT initiation can be realized only with alkoxy pyridinium salts. The iodonium and sulphonium salts either do not form such complexes or their complexes absorb at lower wavelengths. 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 due to the strong electron donating power of the monomers.

2.2.2.3 Free radical promoted cationic polymerization

Onium salts are the most widely used for free radical promoted cationic photoinitiators. These salts are compounds containing heteroatoms, with a cationic center on the heteroatom and mostly inorganic metal complex anions as counterions (Table 2.6). Onium salts may be used to oxidize free radicals according to the reaction 2.21. The cations thus generated are used as initiating species for cationic polymerization. This process is usually termed as free radical promoted cationic polymerization.

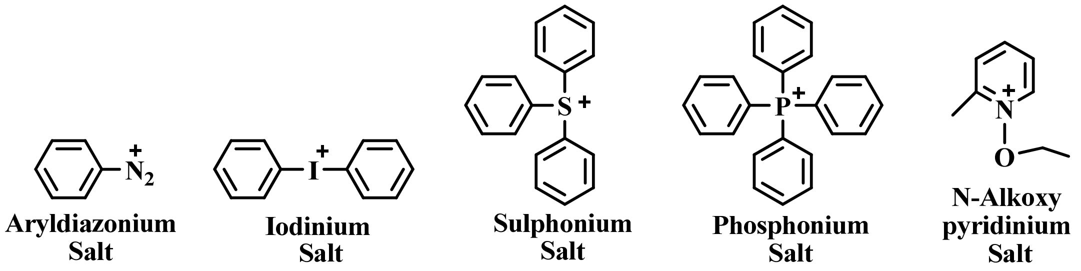
$$R \xrightarrow{On^{+}} R^{+} \qquad (2.21)$$

The efficiency of onium salts as oxidizing agents depends on their electron affinity. The higher the oxidation power of the onium salt, the higher is the reduction potential. Whether a radical can be oxidized by an onium salt or not is determined by using the Rehm-Weller Eqn. (Eq:2.9) providing oxidation and reduction potentials of the free radical and the onium ion are known.

$$\Delta G = F\,[\,E_{ox}^{1/2}(R^{\cdot}) - E_{red}^{1/2}(On^{+})\,] \qquad \textbf{(Eq. 2.9)}$$

However, the exact oxidation potentials of most radicals in radical polymerizations are unknown. Therefore, the calculation of ΔG in most cases is not feasible.

Table 2.6 : Onium salts for externally stimulated cationic polymerization

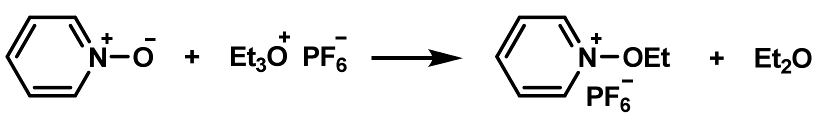


2.3 *N*-Alkoxy Pyridinium Salt Photoinitiators

N-Alkoxy pyridinium salts, together with iodonium and sulphonium salts are most widely used photoitiators for cationic polymerization. The objective of this part is to overview the photoactivity of *N*-alkoxy pyridinium salts in terms of direct and indirect photoinitiation for both cationic and free radical polymerizations.

2.3.1 Photochemistry of *N*-alkoxy pyridinium salts

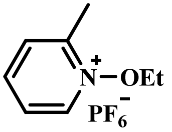
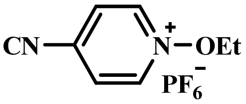
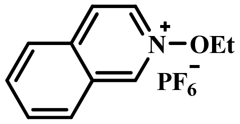
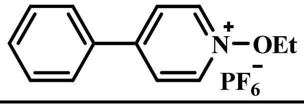
Several commercially available aromatic *N*-oxides can be reacted with triethyloxonium salts possessing non-nucleophillic counterions in dichloromethane or chloroform to yield their corresponding *N*- alkoxy pyridinium salts [112]. Since the triethyloxonium salt introduces a non-nucleophilic counterion, i.e. PF_6^-, an ion exchange is not necessary for their applications in cationic polymerization (reaction 2.22).



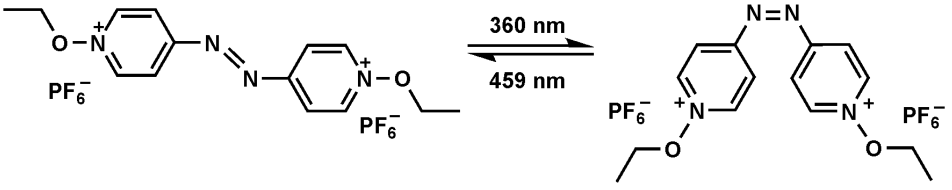
(2.22)

By derivating the structure via attaching different substituent on the aromatic ring, the absorption bands of the salts can be shifted to longer wavelengths [94]. Table 2.7 shows structure and optical properties of different *N*-alkoxy pyridinium salts.

Table 2.7 : Structure and optical properties of *N*-alkoxy pyridinium salts and optical properties of *N*-alkoxy pyridinium salts

Detonation	**Structure**	**Wavelength (nm)**	**Extinction Coefficient (L mol^{-1} cm^{-1})**
$\mathrm{EMP^+\ PF_6^-}$		266	5927
$\mathrm{ECP^+\ PF_6^-}$		270	-
$\mathrm{EIQ^+\ PF_6^-}$		337	4218
$\mathrm{EPP^+\ PF_6^-}$		310	21440

As can be seen from Table 2.7, the spectral response of *N*-alkoxy pyridinium salts are varying from 260 to 340 nm. Upon irradiation in this range, these salts initiate polymerization through a mechanism called direct initiation. For practical applications, however, polymerizations need to be performed in lower energies, since the commercially available high pressure mercury lamps emit light with wavelengths longer than 350 nm. Different ways can be used to achieve this goal, which are generally called indirectly initiated polymerizations (*vide infra*). In indirectly initiated polymerizations, some additives need to be used to activate polymerizations. However, for industrial radiation curing applications, the use of one-component photoinitiators that have long wavelength absorption characteristics may still be advantageous because of the additional problems introduced by the co-initiator associated such as solubility, compatibility, migration, and cost problems. In this connection, it is worth to mention a recent report which concerns the use of azo-benzene type alkoxy pyridinium salt [113]. This new salt has absorption at around $\lambda =$ 459 and 360 nm and undergoes UV-induced *cis-trans* isomerization, which implies that the activation wavelength can be tuned without any additive, i.e., photosensitizer or free radical promoter (reaction 2.23).

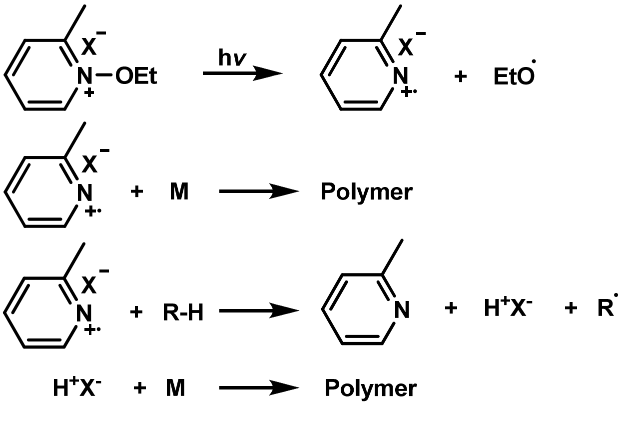


(2.23)

2.3.2 Photoinitiated cationic polymerization by using *N*-alkoxy pyridinium salts

2.3.2.1 Direct initiation

Pyridinium salts act directly as photoinitiators provided the irradiation is performed at wavelengths corresponding to their absorption bands [94]. Upon photolysis, pyridinium salts undergo a very rapid cleavage of the N-O bond to form pyridinium radical cation and alkoxy radical (reaction 2.24a). Both the initially formed radical cation and the proton are capable of initiating the reaction (reaction 2.24b-d). Laser flash photolysis studies were used for the detection of the nitrogen centered radical cations and the reactivity of these radical cations with various monomers were found be in the range of 10^6 to 10^9 L mol^{-1} s^{-1} [114].



(2.24a)

(2.24b)

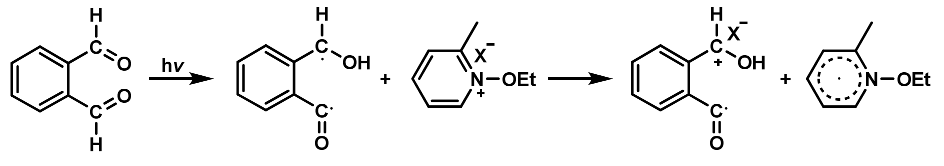
(2.24c)

(2.24d)

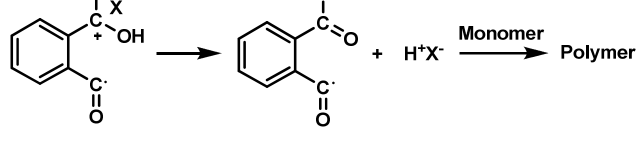
2.3.2.2 Indirect initiation

Free radical promoted cationic polymerization

An elegant method of generating carbocations capable of initiating the cationic polymerization of epoxides, cyclic ethers and alkyl vinyl ethers is based on electron transfer from free radicals to pyridinium salts. Electron-rich free radicals capable of undergoing this electron transfer reaction can be generated thermally or photochemically. It is known that benzoin derivatives and phenylazotriphenylmethane are effective to generate electron donating radicals directly by a photochemical process [95, 115]. Acylphosphine oxides were also used as free radical promoters for cationic polymerization in the presence of pyridinium salts. Laser flash photolysis studies showed that phosphonyl radicals are not oxidized even by much stronger oxidants such as iodonium ions [116-118]. Another interesting promoter, initially proposed by Scanio and co-workers [119], for cationic polymerization based on pyridinium chemistry was *o*-phthalaldehyde [120]. It was found that UV irradiation of *o*-phthalaldehyde leads to the formation of 1, 4-biradical transients via intramolecular hydrogen abstraction and the hydroxybenzyl radical formed is a good electron donor radical. It was also studied the effectiveness of such a redox process by series of flash photolysis experiments in which the biradical was trapped by 1,1'-dimethyl-4,4'-bipyridinium dications. Pyridinium ions such as *N*-ethoxy-2-methyl-pyridinium hexafluoroantimonate, ($EMP^+PF_6^-$) were also found to be powerful oxidizing agents for hydroxybenzyl radical to yield reactive species capable of initiating cationic polymerization (reactions 2.25a,b) [121].



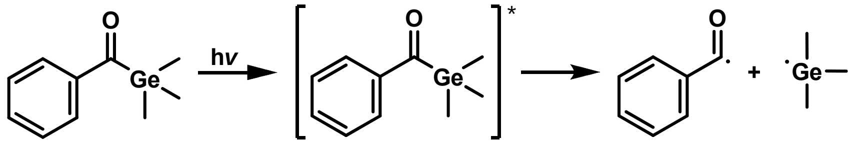
(2.25a)



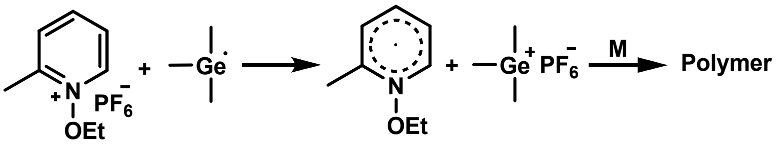
(2.25b)

Several vinyl and cyclic ether monomers were polymerized efficiently using *o*-phthalaldehyde and $EMP^+PF_6^-$.

Cationic polymerizations activated by free radical sources in the presence of alkoxy pyridinium salts can be performed also in the visible range. The reactivity of acylgermane based photoinitiators in free radical promoted cationic polymerization of appropriate monomers was recently tested [122]. Because of the fact that these photoinitiators exhibit long wavelength characteristics, (due to the well-known interaction of the lone pair of the carbonyl oxygen with the free *d*-orbitals of the germanium) the spectral sensitivity of cationic polymerization could easily be extended to the visible range (reactions 2.26a-b).



(2.26a)



(2.26b)

The oxidation of the germyl radicals is not limited to the alkoxy pyridinium salts and salts with appropriate reduction potentials such as iodonium salts can also be used [123]. The most striking advantage of this initiating system is its applicability to pigmented systems in the visible range.

Photosensitized cationic polymerization

It was previously reported that many aromatic hydrocarbons such as anthracene, phenothiazine, perylene and thioxanthone are able to sensitize the decomposition of pyridinium salts via electron transfer from the excited state sensitizer to the pyridinium salt [100]. The irradiation of the sensitizer (PS) is followed by the formation of a complex between excited sensitizer molecules and ground state pyridinium salt (reactions 2.27a). In this complex, one electron is transferred from the sensitizer to the pyridinium salt giving rise to the generation of sensitizer radical cation and pyridinyl radical (reaction 2.27b). The latter rapidly decomposes to give pyridine and an ethoxy radical as shown in reaction 2.27c. Proposed mechanism was revealed by laser flash photolysis studies of corresponding sensitizers and pyridinium salt. Although anthracene, perylene, phenothiazine and thioxanthone sensitized systems were found to be highly favorable, benzophenone and acetophenone seemed not to be suitable sensitizers.

Various mechanisms for the initiation of cationic polymerization are summarized in reaction 2.27. The radical cations themselves may initiate the polymerization of appropriate monomers (reaction 2.27d) or, alternatively, interact with hydrogen donor constituents of the polymerization mixture (such as solvent or monomer) resulting in the release of Brønsted acid (reactions 2.27e,f). Protons generated in this way are also capable of initiating the cationic polymerization (reaction 2.27g).

$$\mathrm{PS} \xrightarrow{h\nu} \left|\mathrm{PS}\right|^{*} \xrightarrow{\mathrm{EMP^{+}PF_6^{-}}} \left|\mathrm{PS{-}{-}EMP^{+}PF_6^{-}}\right|^{*} \qquad \textbf{(2.27a,b)}$$

$$\left|\mathrm{PS{-}{-}EMP^{+}PF_6^{-}}\right|^{*} \longrightarrow \mathrm{PS^{+\bullet}\,PF_6^{-}} + \left|\mathrm{EMP}\right|^{\bullet} \qquad \textbf{(2.27c)}$$

$$\mathrm{PS^{+\bullet}\,PF_6^{-}} + \mathrm{M} \longrightarrow \mathrm{Polymer} \qquad \textbf{(2.27d)}$$

$$\mathrm{PS^{+\bullet}\,PF_6^{-}} + \mathrm{R\text{-}H} \longrightarrow \mathrm{H\text{-}PS^{+}\,PF_6^{-}} + \mathrm{R^{\bullet}} \qquad \textbf{(2.27e)}$$

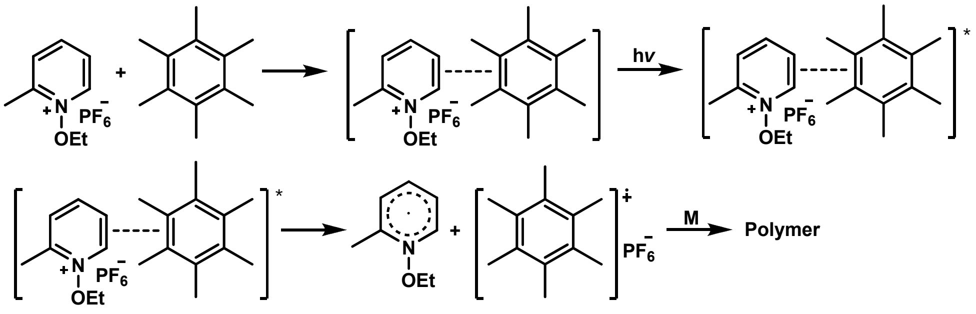
$$\mathrm{H\text{-}PS^{+}\,PF_6^{-}} \longrightarrow \mathrm{H^{+}\,PF_6^{-}} + \mathrm{PH2S} \qquad \textbf{(2.27f)}$$

$$\mathrm{H^{+}\,PF_6^{-}} + \mathrm{M} \longrightarrow \mathrm{Polymer} \qquad \textbf{(2.27g)}$$

There are also some other unique examples for sensitization of pyridinium salts which are based on the use of special sensitizers (dyes) [120, 124].

Photoinitiation by charge transfer complexes

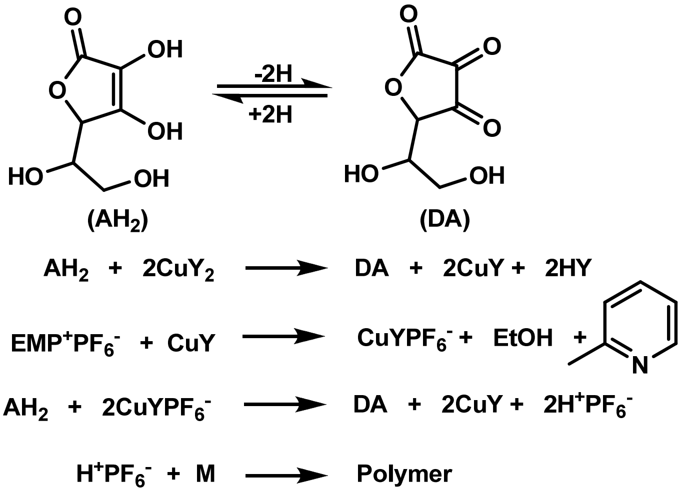
Alkoxy pyridinium salts were found to be capable of forming charge transfer (CT) complexes with electron rich donors such as methyl and methoxy-substituted benzene [105]. Notably, these complexes absorbed at relatively high wavelengths, where the components were virtually transparent. It was found that the CT complexes formed between pyridinium salts and aromatic electron donors act as photoinitiators for the cationic polymerization. The suggested mechanism is illustrated in reaction 2.28 [107].



(2.28)

Redox-initiated cationic polymerization

Crivello and Lam reported the diaryliodonium salt-ascorbate redox system as an alternative method for the initiation of cationic polymerization of appropriate monomers [125]. Following the same strategy, *N*-alkoxy pyridinium salts were also used in this redox process. However, the pyridinium salt redox system yielded lower polymer conversions [126]. The polymerization mechanism is quite similar to that described for the iodonium salts (reactions 2.29a-e).



(2.29a)

(2.29b)

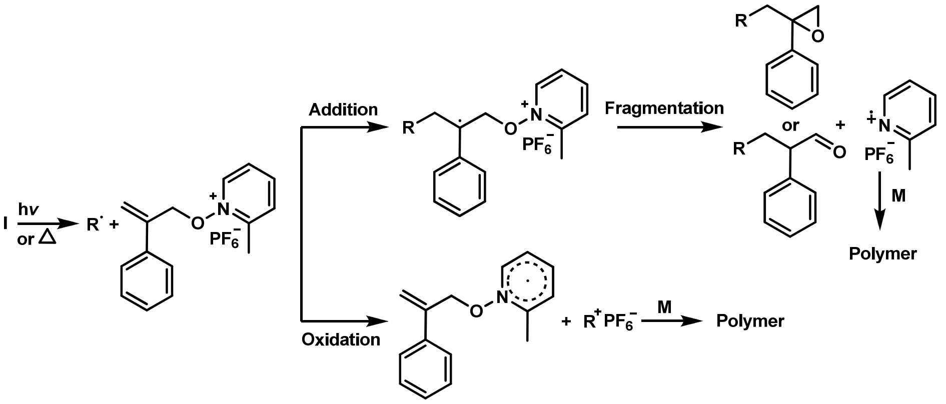
(2.29c)

(2.29d)

(2.29e)

Photoinitiation by addition-fragmentation reactions

When alkoxy pyridinium salts are equipped also with allylic groups, they present an additional initiation behaviour in the radical assisted reactions. Thus, allyloxy pyridinium salts were found to be efficient co-initiators for cationic polymerization in conjunction with free radical initiators [107, 125-127]. Either or both oxidation and addition-fragmentation mechanisms may be operative (reactions 2.30a,b). In the latter case, the experiments showed that fragmentation rather than addition is the rate determining step. It was also reported that initiation efficiency could be increased by choosing appropriate leaving groups and weak bonds in proximity to the allylic double bonds.

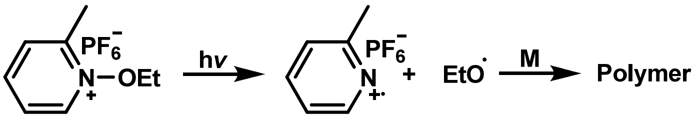


(2.30a)

(2.30b)

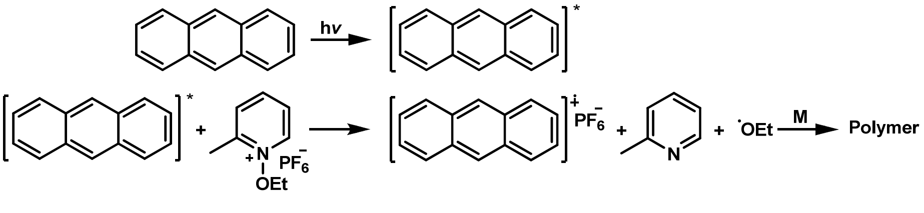
2.3.3 Photoinitiated free radical polymerization by using *N*-alkoxy pyridinium salts

The usage of *N*-alkoxy pyridinium salts is not restrained to cationic polymerization. As stated earlier, pyridinium radical cations and ethoxy radicals are formed concomitantly upon direct photolysis. Ethoxy radicals are able to initiate free radical polymerization (reaction 2.31) in accordance with the literature report [128-131].



(2.31)

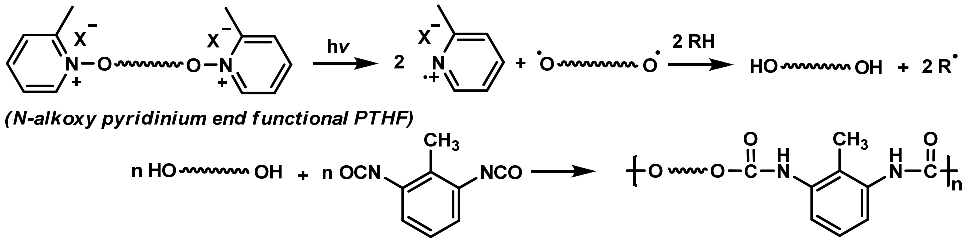
Furthermore, the radical generation can be achieved with the aid of photosensitizers such as anthracene. In this case, ethoxy radicals formed by electron transfer reaction initiate the polymerization (reaction 2.32).



(2.32)

2.3.4 The step-growth polymerization by using *N*-alkoxy pyridinium salts

The only attempt in this direction concerns in situ polyurethane formation upon photolysis of *N*-alkoxy pyridinium end functional polytetrahydrofuran (PTHF) in the presence of toluene diisocyanate [132]. Hydrogen abstraction of alkoxy radicals generated from the decomposition of the pyridinium ions results in the formation of hydroxyl groups capable of reacting with the isocyanates present in the solution (reaction 2.33). Polyurethane formation then proceeds in the classical manner.



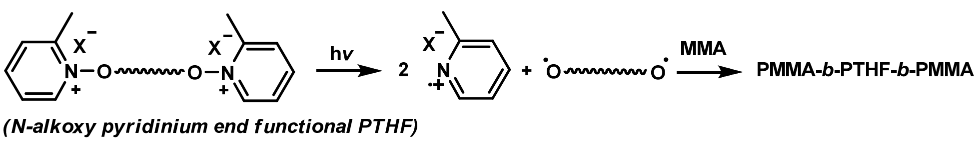
(2.33)

2.3.5 Block and graft copolymerization by using *N*-alkoxy pyridinium salts

The flexibility provided by the decomposition of *N*-alkoxy pyridinium salts via various methods gives possibility to prepare block and graft copolymers. For this purpose, direct, free radical promoted and photosensitized initiations were successfully combined with thermal, controlled/living radical and cationic polymerization techniques.

2.3.5.1 Direct block and graft copolymerization

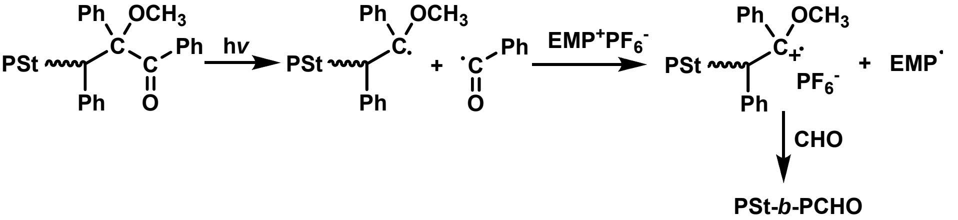
This synthetic approach based on pyridinium salt photochemistry involves the use of alkoxy radicals which are formed in both direct and sensitized decomposition of pyridinium ions in free radical polymerization. In a previous study, *N*-alkoxy pyridinium end functional PTHFs were prepared by deactivation of bifunctional living ends of tetrahydrofuran polymer chains by pyridinium *N*-oxides as precursors for block copolymers [131]. Upon direct and sensitized irradiation of these photoactive PTHFs, polymeric alkoxy radicals at both chain ends initiate the radical polymerization of methyl methacrylate (MMA) (reaction 2.34). Block copolymers of two monomers, which have quite different chemical nature, were thus prepared.



(2.34)

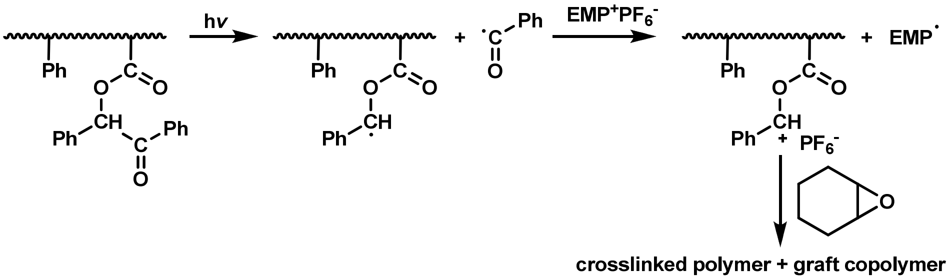
2.3.5.2 Indirect block and graft copolymerization

As mentioned earlier, electron donating free radicals can reduce pyridinium salts inducing their decomposition and formation of reactive carbocations [95, 121, 133-135]. For example; a polymer containing benzoin terminal groups can act as photochemical macroinitiator and is effective in photogenerating electron donor radicals. The initiation of polymerization by means of azo-benzoin initiators yields polymers with one or two benzoin end groups according to the termination mode of the particular monomer involved [136-138]. Irradiation of the resulting prepolymers caused α-scission, and benzoin and polymer bond electron donating radicals are formed in the same manner as described for low molar mass analogues. If the photolysis is carried out in the presence of cyclohexene oxide (CHO) and $EMP^+PF_6^-$ the polystyrene-attached radical is converted to the initiating cations to generate block copolymers (reaction 2.35) [139].



(2.35)

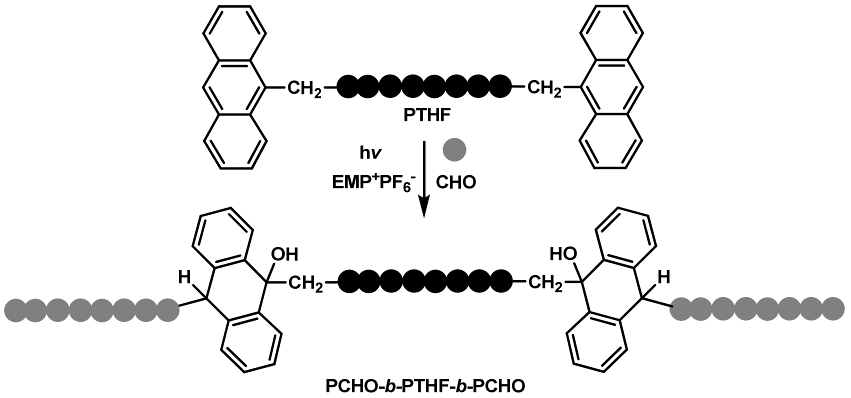
Similarly, side chain benzoin- containing polymers were also used as promoters to yield graft copolymers (reaction 2.36) [115].



(2.36)

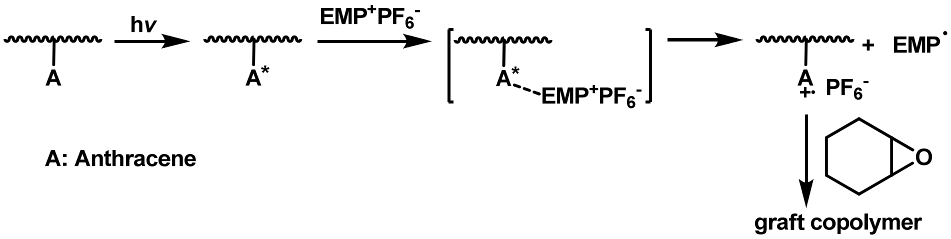
2.3.5.3 Photosensitized block and graft copolymerization

The reactivity of anthracene radical cations formed by photosensitization can provide elegant way to prepare block copolymers. First, anthracene terminated polymers were obtained by end-capping of living polytetrahydrofuran chains. In the second step, these polymers in CHO solutions were irradiated in the presence of the $EMP^+PF_6^-$ (reaction 2.37) leading to the formation of the corresponding block copolymer [101].



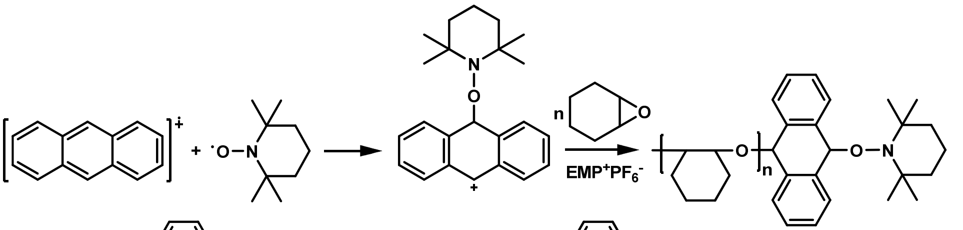
(2.37)

Obviously, if the anthryl groups are incorporated as the side chains, the same process yields graft copolymers (reaction 2.38). Typically side chain functional polymers were simply prepared by free radical copolymerization of 9-vinyl anthracene and styrene [140]. Upon irradiation at λ > 340 nm, photoexcited anthracene groups undergo internal electron transfer with the pyridinium salt to give initiating anthracene radical cations.

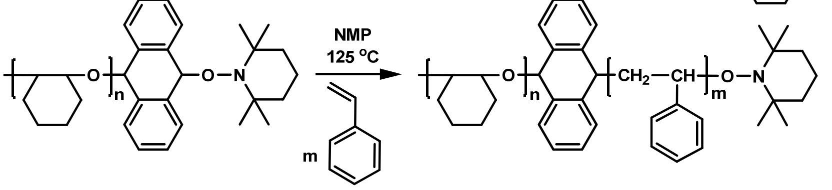


(2.38)

Interesting variation of mechanistic transformation between polymerization methods involves combination photoinitiated cationic polymerization and NMP. Anthracene-photosensitized cationic polymerization of CHO at λ = 350 nm in conjunction with $EMP^+PF_6^-$ (also with iodonium salts), in the presence of a stable radical, 2,2,6,6-tetramethylpiperidine-*N*-oxyl free radical (TEMPO) yielded polymers with alkoxyamine terminal groups. Electron transfer between anthracene and pyridinium ions yields anthracene radical cations which are quickly trapped by the nitroxide radicals to give, consequently, alkoxyamine functional dihydroanthryl cationic capable of initiating cationic polymerization of CHO (reaction 2.39a) [141].



(2.39a)



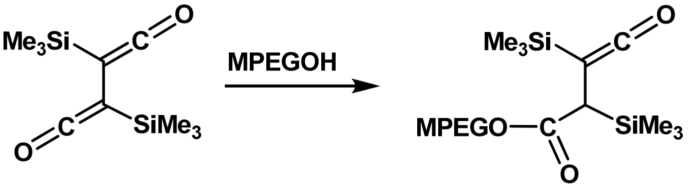
(2.39b)

These polymers were found to be efficient initiators for NMP of styrene (reaction 2.39b). Spectral analysis and molecular weight measurements of the obtained polymers showed that block copolymers are readily formed as a result of combination of photosensitized cationic and NMP mechanisms.

2.4 Benzodioxinone Photochemistry in Polymer Synthesis

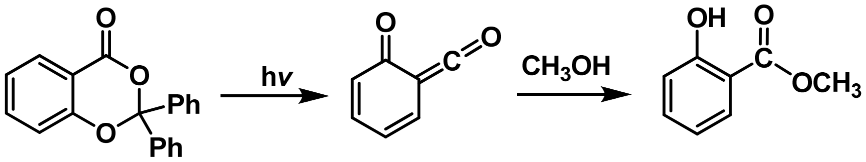
Majority of the reactions occurring from benzodioxinones are induced by the reactive ketene intermediates which are generated by thermolysis or photolysis of benzodioxinones. Existence of ketenes dates back 100 years ago and recently interest in these intermediates has been revitalized [142]. New methods for generating ketenes have been applied in the preparation of many valuable target molecules. Because of the carbonyl and alkenyl groups present in the structure and possibility of their transformation, ketenes are useful and versatile organic reactive intermediates. Ketenes have a middle sp carbon atom with an extra π bond (the C=O) at right angles to the C-C double and exhibit electrophilic character. Therefore, they can give various type of reactions. Asymetric synthesis by nuclephilic additions and [2+2] cycloadditions to ketenes yield β-lactams and lactones with high yields and stereoselectivities. In recent years, attention has also focused to another class of reactions ketenes, namely free radical chemistry and rearrangement reactions.

There are various types of ketenes such as haloketenes, bisketenes and α-oxoketenes. Highly variegated reactivity of ketenes makes them attractive candidates for polymer bound reactions. One of the most common starting compounds used in these types of reactions is bisketene. For example, the long-lived bisketene is readily reacted with a nuclophilic polymer such as poly(ethylene glycol) monomethylether (MPEGOH) to form polymer supported ketene (reaction 2.40) [143, 144].



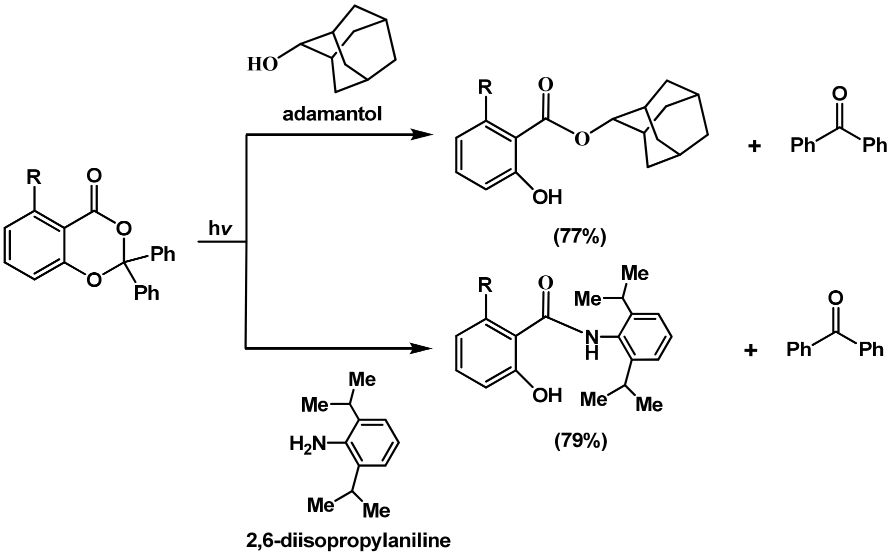
(2.40)

Another type of α-oxoketenes are quinoketenes generated from benzodioxinones. This highly reactive α-oxoketene can be formed in solution at room temperature and is identfied by using time-resolved infrared spectroscopy. The kinetics of the reaction of these intermediates towards water, methanol and diethylamine has been studied in detail. Obviously, the reaction product with methanol is a salicylate ester (reaction 2.41).



(2.41)

Photolysis of substituted benzodioxinones in the presence of sterically hindered alcohols, phenols and anilines which are inert to other acylation methods yields functionalized salicylic esters and amides. A wide range of salicylic ester and amides were synthesized by using this method [145]. Typical examples are demonstrated below (reaction 2.42a,b).



(2.42a)

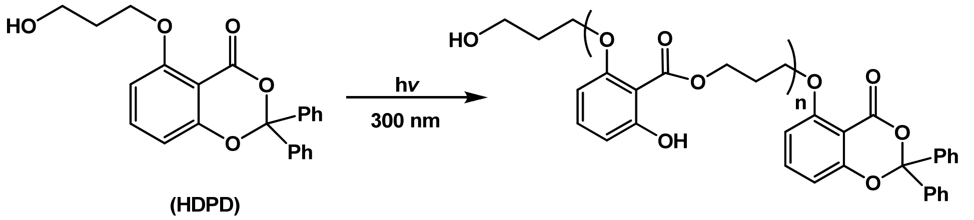
(2.42b)

2.4.1 The use of benzodioxinone photochemistry in step-growth polymerization

2.4.1.1 Photoiniduced synthesis of polyesters using benzodioxinones

For the first time, a true step-growth polymerization, i.e, polyesterification, was achieved by a photochemical means [146]. Thus, hetero bifunctional monomers namely, benzodioxinone and naphtodioxinone compounds possessing both chromophoric and aliphatic hydroxyl groups in the structure (5-(3-Hydroxypropoxy)-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one (HDPD) and 7-(3-Hydroxypropoxy)-2,2-diphenyl-4H-naphtho[2,3-d][1,3]dioxin-4-one (HDNP), respectively) were used in the process.

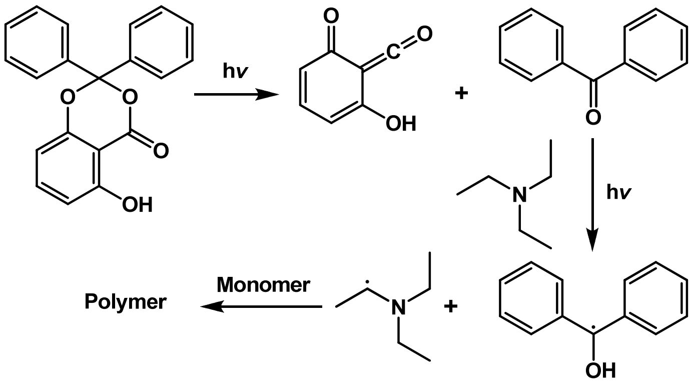
Photolysis of these compounds in CH_2Cl_2 at λ_{inc} = 300 nm yielded oligoesters with narrow molecular weight distribution (reaction 2.43). In the case of HDNP, photolysis can be performed at higher wavelengths, e.g., at λ_{inc} = 350 nm, because of the extended absorption introduced by the naphthalene ring.



(2.43)

2.4.2 Photoinitiated free radical polymerization using benzodioxinones

Benzophenone is widely used Type II photoinitiator in free radical polymerization and produced concomitantly together with ketene during the photolysis of benzodioxinones. Generation of benzophenone as photoinitiators from benzodioxinones may increase shelf life at the expense of initiation ability. In this system [147], benzophenone, actual photoinitiator, is formed only after photodecomposition of benzodioxinone (reaction 2.44a). The subsequent step is the usual radical formation by the hydrogen abstraction of photoexcited benzophenone from a hydrogen donor such as amines and ethers (reaction 2.44b). It has also been shown that functional groups of photolysis product can be used in self-cross-linking of monofunctional monomers.



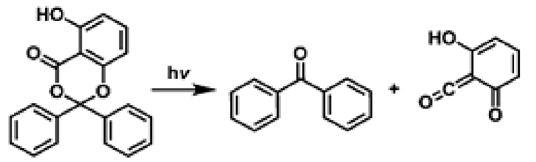
(2.42a)

(2.42b)

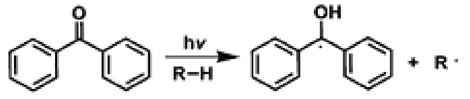
2.4.3 Photoinitiated cationic polymerization by using benzodioxinone via two-photon absorption

On the basis of the information gained from the free radical systems, it seemed appropriate whether benzodioxinone (HDPD) and naphthadioxinone (HDNP) can act as caged sensitizers for diphenyliodonium salt to generate acids for initiation of cationic polymerization. The first absorbed photon should uncage the sensitizer [148]. The released sensitizer absorbs the second photon to reduce the iodonium salt yielding in protonic acids for initiation of cationic polymerization.

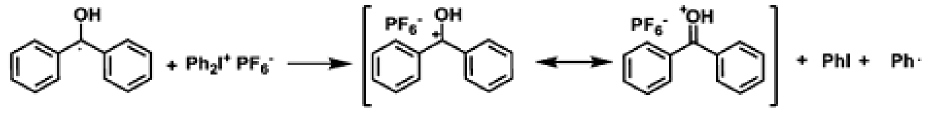
Experimentally, CHO was polymerized quite efficiently with benzophenone, benzodioxinone, and naphthadioxinone in the presence of iodonium salt. Upon absorption of light, benzodioxinone is photolyzed according to reaction 2.45a. The second photon absorbed by benzophenone leads to the formation of triplet benzophenone after intersystem crossing which readily abstracts hydrogen from solvent or monomer (reaction 2.45b). Laser flash photolysis experiments were performed to demonstrate that reaction 2.45d occurs under the experimental conditions. A bimolecular rate constant of $k_q = 1.2 \times 10^6$ M^{-1} s^{-1} was observed for hydrogen abstraction by benzophenone triplet states from. In this process, diphenylketyl radicals are generated, which are known to be powerful reducing agents ($E_{1/2}^{ox} \sim -0.7$ V (SCE)) [149]. Diphenylketyl radicals are reported to be able to reduce iodonium salts (reaction 2.45c) [150-152]. Back-electron-transfer reaction can be disregarded because the oxocarbenium ion decomposes into acid and benzophenone (reaction 2.45d) [153]. The ensuing protonic acid is capable of initiating cationic polymerization of CHO (reaction 2.45e).



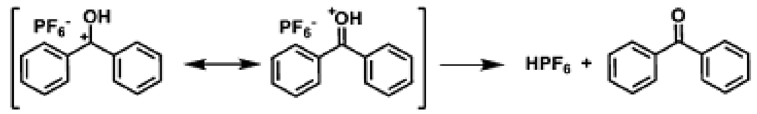
(2.45a)



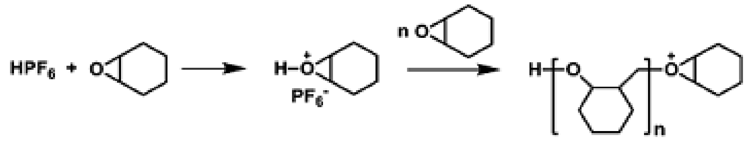
(2.45b)



(2.45c)



(2.45d)



(2.45e)

2.5 Copolymers

2.5.1 Statistical, gradient and alternating copolymers

When two or more comonomers are simultaneously copolymerized, either of statistical, gradient, or alternating copolymers can be obtained (Figure 2.2). 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.

Statistical Copolymer

Block Copolymer

Gradient Copolymer

Alternating Copolymer

Figure 2.2 : Schematic representation of miscellaneous copolymers of various compositions.

Choosing both reactivity ratios significantly higher than 1 result 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 2.2. 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 homopropogate 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 80ºC. 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 [154, 155].

2.5.2 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 [156, 157]. When two homopolymers are mechanically mixed, formation of an immiscible blend is often the case encountered. Microphase-separated heterogeneous mixtures arising from the incompatibility of the blended polymers can successfully be avoided by the latter strategy, which involves preparation of block and graft copolymers. Thus, engineering macromolecules of various block and graft structures appears to be an elegant approach in achieving polymers with improved physical and chemical properties. Preparation of block copolymers using living polymerization techniques has been known for quite a long time. Anionic polymerization [158], which provides end group control and permits the synthesis of polymers with a narrow polydispersity index, is a significant example of these techniques. Recently, advances in controlled polymerization techniques [159-161], such as radical, cationic, metathesis, and group transfer, have allowed for the synthesis of polymers with predetermined molecular weights and low polydispersities. A variety of block copolymers have been prepared by cationic, group transfer, metallocene, and metathesis routes. Among others, controlled radical polymerization routes have been studied extensively, because they can be employed for the polymerization of numerous vinyl monomers under mild reaction conditions.

The synthetic strategies to prepare block copolymers via radical polymerization routes will be discussed detail in following parts.

2.5.2.1 Block copolymer by conventional radical polymerization

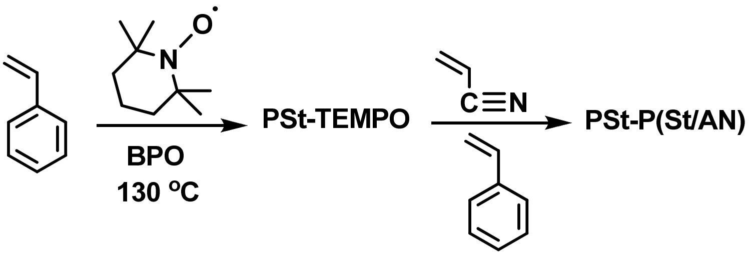
Normally, block copolymers cannot be synthesized by classical free radical copolymerization technique. Spontaneous block copolymer formation upon free radical copolymerization of A and B monomers would only occur when both reactivity ratios r_a and r_b are far larger than unity. Such a system has never been found. Generally, the most widely employed method for the preparation of block copolymers by using conventional radical polymerization routes is the macroinitiator technique. This technique has several advantages. First, macroinitiators can be fully characterized before their use in the free radical step to obtain block copolymers. Moreover, the macroinitiators can be prepared practically by all polymerization methods. In living polymerizations, it is possible to introduce the free radical initiating functionalities into polymers at both initiation and termination steps.

Azo or peroxy groups are incorporated into the free radical initiating sites of the polymers. Typical examples of such methodology by using living anionic [162] and cationic [163] polymerization were performed in the literature.

2.5.2.2 Block copolymers by controlled radical polymerization

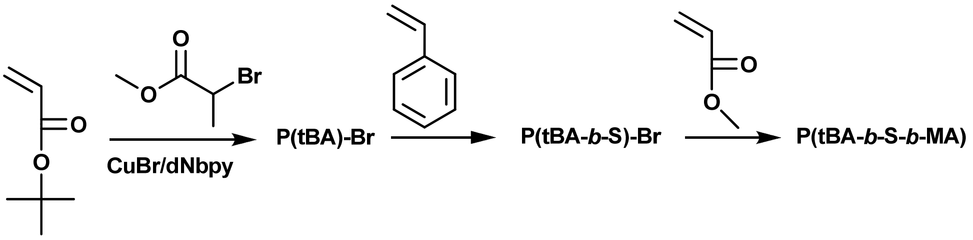
Well defined block copolymers can be synthesized by controlled radical polymerization with the technique of sequential monomer addition. In this technique, certain experimental conditions governing the growth of the first block should be handled carefully to increase the blocking efficiency. It is essentially important to stop the polymerization of the first monomer before it is used up completely because end functionalities might be lost, resulting in the formation of dead blocks. Another feature to be considered, as in all sequential monomer additions, is the order of introducing each monomer. Along with the rate constant of cross-addition k_a and the rate constant of propagation k_p of the second monomer, the equilibrium constants K_a and K_b between active and dormant species for the two kinds of monomer units should be taken into consideration. Apparently, the very active monomer should be polymerized first, which is valid for either of the controlled polymerization mechanisms.

NMP 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 [164]. 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 2.46).



(2.46)

A larger variety of block copolymers have been synthesized by ATRP due to the greater flexibility of the method, in terms of polymerizable monomers. The synthesis of triblock copolymers containing three different monomers is accomplished by a three-step sequential monomer addition. Matyjaszewski and coworkers [165] reported the synthesis of a P(*t*BA-*b*-St-*b*-MA) triblock using this method. *t*-BA was polymerized first using methyl 2-bromopropionate as the initiator, and the CuBr system followed by the addition of styrene and methyl acrylate (MA) (reaction 2.47).



(2.47)

Preparation of block copolymers comprising monomers of distinct reactivities requires that the monomers be introduced in a specific sequence if one desires to obtain good control over the polydispersities. The addition should be handled in a manner favoring the cross-propagation (i.e., the initiation of the second block by the first one) over propagation. For instance, a PMMA block should precede the growth of a PS block, and not the reverse. In this case, the cross-propagation is rather fast, because the equilibrium between active and dormant chains lies more to the active side. On the other hand, the rate of propagation of the St monomer is comparatively slow. As a result, nearly all the chains of the second PSt block are initiated before the propagation takes place. Evidently, this results in a low polydispersity.

Alternatively, a technique called the “halogen exchange” [166-171] can be employed to change this sequence of blocking. In this methodology, the first block (e.g., PSt) is formed using a bromine-functional initiator in combination with a copper (I) bromide catalyst. In the next step, the second monomer (e.g., MMA) is added together with copper (I) chloride. Here, the activation of bromine-functional chain is followed by deactivation with $CuCl_2$ (or CuClBr). Because the carbon-chlorine bond is stronger than that of carbon-bromine, formation of a carbon-chlorine bond predominates in this mixed halogen system, and thereby retards the propagation in comparison to the cross-propagation.

An ABCBA-type pentablock terpolymer was prepared using a bromo-terminated P*t*BA-*b*-PSt-*b*-P*t*BA triblock as a macroinitiator in the chain-extension with MMA [172]. The triblock copolymer with M_n = 13,600 and PDI = 1.23 was synthesized beforehand from a bifunctional PSt using the CuBr/PMDETA catalyst system. Subsequent chain-extension with MMA, using the system CuCl/HMTETA afforded the desired PMMA-*b*-P*t*BA-*b*-PSt-*b*-P*t*BA-*b*-PMMA terpolymer with M_n = 48,500 and PDI 1.21. An increase in the PDI was avoided due to the halogen exchange mechanism, which enhanced the rate of cross-propagation relative to the rate of propagation.

RAFT as a another controlled radical polymerization technique was used for the preparation of block copolymer of acrylonitrile (AN) and n-butylacrylate (n-BA) with low polydispersity and controlled moleculer weight using a novel RAFT agent, 2-cyanoethyl dithiobenzoate (CED) [173].

2.5.2.3 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 [174, 175]. Transformation reactions are classified on the basis of interconversion between propagation mechanisms (Figure 2.3). It can be seen that between the main living and controlled/living polymerization methods, transformations are accessible in both directions.

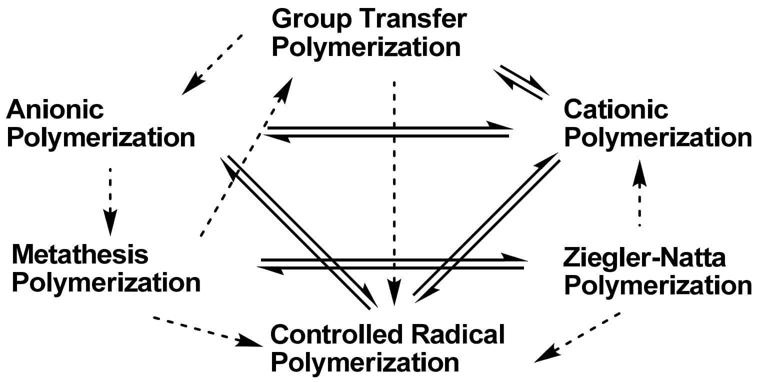
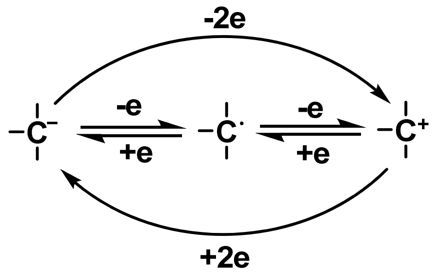


Figure 2.3 : Mechanistic transformations in living/controlled polymerization methods.

All the research works performed in the area of polymerization transformation mechanism could be outlined in two categories:

Direct transformation reactions

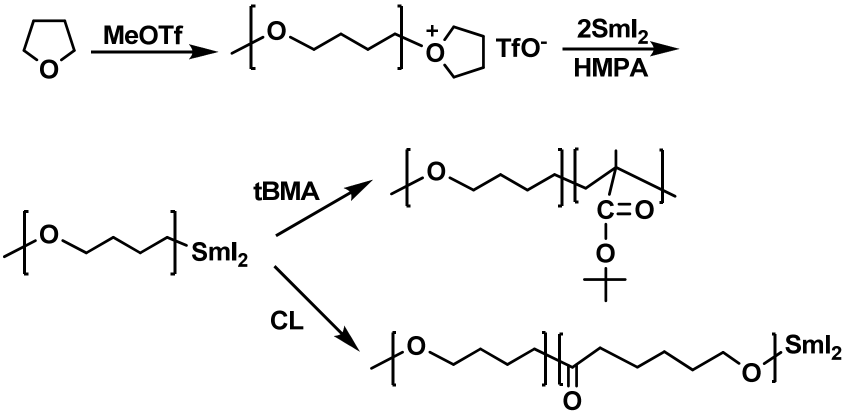
The transformation of a polymerization mechanism is carried out at the end of the first block segment in the polymerization mixture that means the species which initiated the polymerization mechanism of the first monomer by one mechanism was transformed to another mechanism by a redox process without termination and isolation as depicted below (reaction 2.48) In this case, propagating active centers are transformed directly to another active center with different polarity. This transfer occurs through an electron transfer for the transformation involving anionic and cationic systems.



(2.48)

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 [208]. This process involves the reduction of the cationic propagating end of polytetrahydrofuran (PTHF) to the anionic one by sumarinium (II) iodide/hexamethylphosphoramide (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 (*t*BMA) [176] *ε*-caprolactone (CL) [177] and σ-valerolactone (VL) [178] to yield a block copolymers of THF with respective monomers, as shown in reactions 2.49a-c.

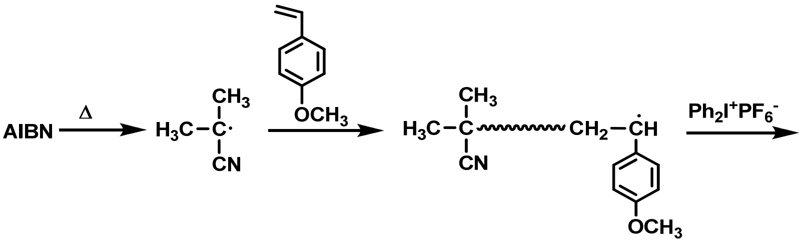


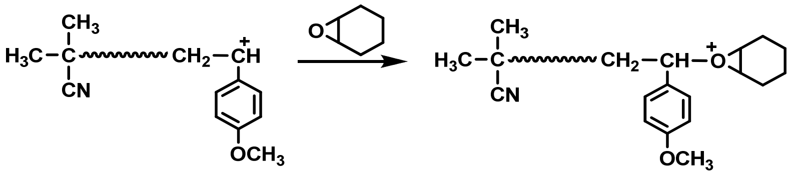
(2.49a)

(2.49b)

(2.49c)

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 [179]. 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 2.51a-c).


(2.50a)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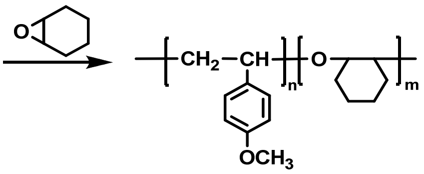

(2.50c)

Indirect transformation

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. 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 schematic representation of indirect transformation is shown in Figure 2.4.

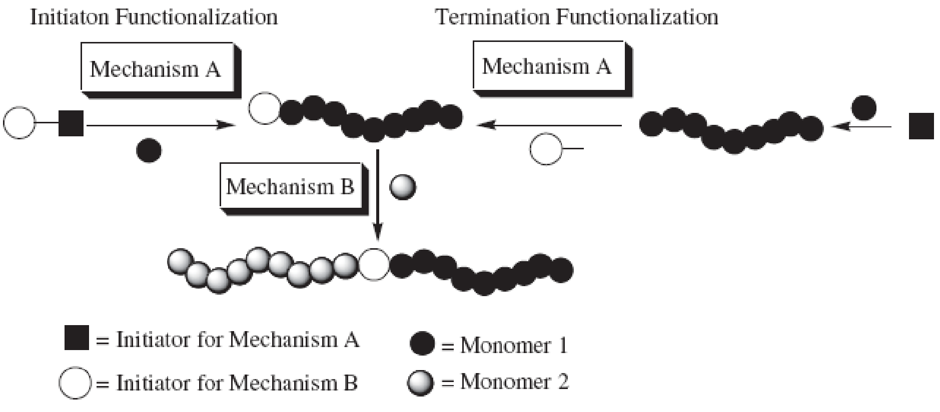


Figure 2.4 : Indirect mechanistic transformation.

In the following table, the methods will be classified according to the nature of the propagating centers involved in the transformation polymerization.

Table 2.8 : Transformation reactions used for block copolymer synthesis

Types of Transformation Reactions	*Reference*
1- Transformations Involving Condensation Polymerization	[180]
- Transformation of Condensation Polymerization to Radical polymerization	[181]
- Transformation of Condensation Polymerization to Living Radical Polymerization	[182]
- Transformation of Macrocyclic Polymerization to Condensation Polymerization	[183]
2- Transformation of Anionic Polymerization to Radical Polymerization	[184]
- Anionic to Photoinduced Radical Transformation	[185]
- Anionic to “Living” Radical Transformation	[186]
3-Transformation of Cationic Polymerization to Radical Polymerization	[187]
- Cationic to “Living” Radical Transformation	[188]
4- Transformation of Radical Polymerization to Anionic Polymerization	[189]
5- Transformation of Radical Polymerization to Cationic Polymerization	[139]
6- Transformations Involving Anionic and Cationic Polymerizations	[190]
7- Transformations Involving Activated Monomer Polymerization	[191]
8- Transformations Involving Metathesis Polymerization	[192]
9- Transformations Involving Ziegler-Natta Polymerization	[193]
10- Transformations Involving Group Transfer Polymerization	[194]

2.5.3 Synthesis of graft copolymers

2.5.3.1 Synthesis of graft copolymer by conventional radical polymerization methods

Graft copolymers are another class of segmented copolymers. As stated previously, no major difference exists between block copolymer synthesis and graft copolymer synthesis. The location of the sites and functions are at the chain ends or on the chains, respectively. Graft copolymers can be obtained with three general methods: (1) grafting-onto, in which side chains are preformed, and then attached to the backbone; (2) grafting-from, in which the monomer is grafted from the backbone; and (3) grafting-through, in which the macromonomers are copolymerized.

Graft copolymers by "grafting onto" method

Grafting onto methods involve reaction of functional groups (Y) located at the chain ends of one kind of polymer with other functional groups (X), which are distributed randomly on the main chain of the other polymer (Figure 2.5). By the use of a living mechanism, the molecular weight, molecular weight distribution, 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.

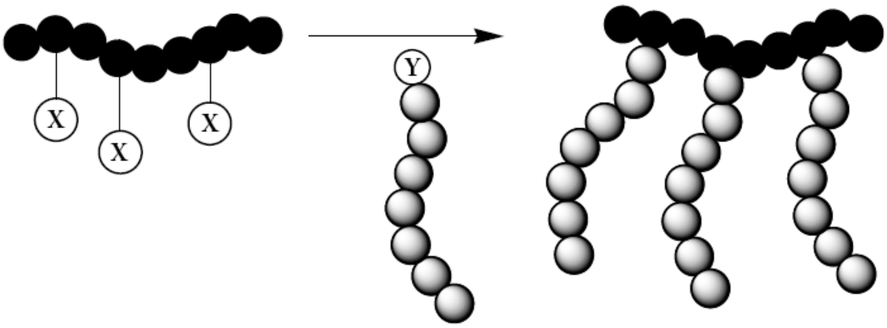


Figure 2.5 : Synthesis of graft copolymer by "grafting onto" method.

The method is most suited for the reaction of "living" anionic and cationic polymers with electrophilic and nucleophilic functions carried by a polymer backbone, respectively. A representative example is the preparation of poly(butadiene-g-styrene) and poly(butadiene-g-styrene) copolymers [195], 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.

Graft copolymers by “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. Initiating radicals can be formed on a polymer chain upon irradiation with γ-rays, electron beams [196, 197], and UV light [198-200]. Grafting is usually performed by irradiation of a polymer swollen by a monomer. The method has found a number of applications to modify the properties of the polymers for special uses. For example, surface modification, which is often required to broaden the applicability of plastics, can be achieved by photografting. Surface modification by photografting can bring about improvements in dyeability, adhesiveness, printability, paintability, biocompatibility, antifogging, antistatic, and antistainability properties. Regarding textiles, an increase in wrinkle and flame resistance of fibers may be of commercial importance. Chemical initiation has also been used in the grafting-from method. In this case, a polymer backbone contains some thermally cleavable bonds such as azo and peroxide linkages (Figure 2.6). If the polymers are heated in the presence of a second monomer, initiation takes place. In such systems, homopolymer formation is unavoidable because of the concomitant formation of low molar mass radicals. Side chain polymeric photoinitiators are also suitable precursors for this type of graft copolymerization. Both cleavage [201] and hydrogen abstraction [202] type photoinitiation have been successfully employed. In this connection, it should be emphasized that the hydrogen abstraction type photoinitiation has the advantage of producing graft copolymers free from the homopolymer contamination as the process yields only macroradicals.

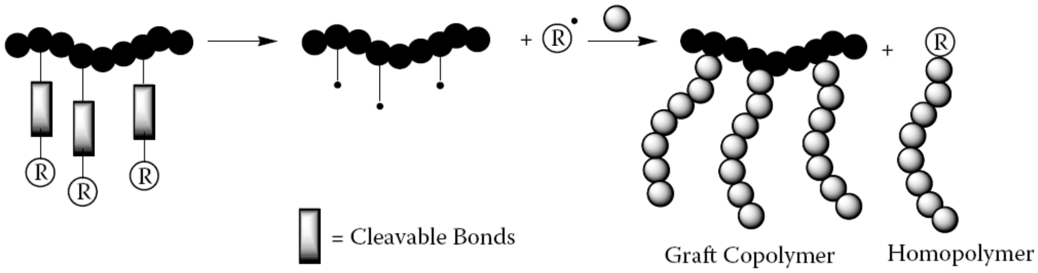


Figure 2.6 : Synthesis of graft copolymer by “grafting from” method.

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 [203].

Graft copolymer by “grafting through” method

Macromonomers are short polymer chains possessing a polymerizable group at one terminus. A great variety of methods involving living polymerization techniques, chain transfer reactions, and end chain modifications have been developed to synthesize such species. 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.

2.5.3.2 Synthesis of graft copolymer by controlled/living radical polymerization methods

Preparation of graft copolymers by using controlled/living radical polymerization methods also follows the same synthetic strategy that was described previously for the conventional radical polymerization. Obviously, graft copolymers obtained by using controlled/living radical polymerizations exhibit high structural control. Although earlier studies have only been concerned with ATRP and NMP, today it is possible to synthesize graft copolymers with all the controlled methods.

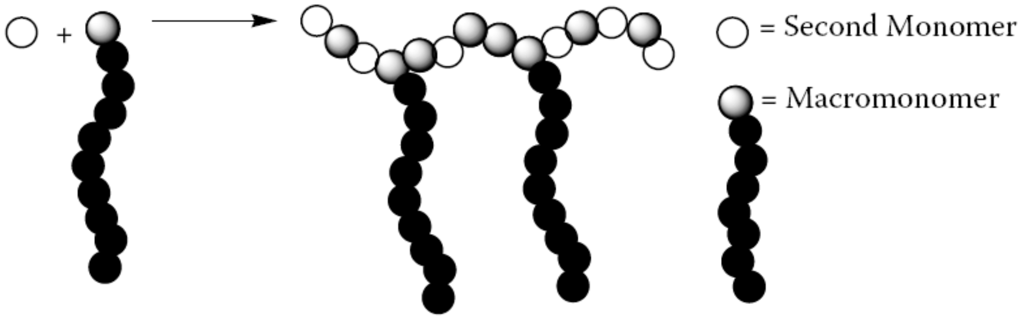
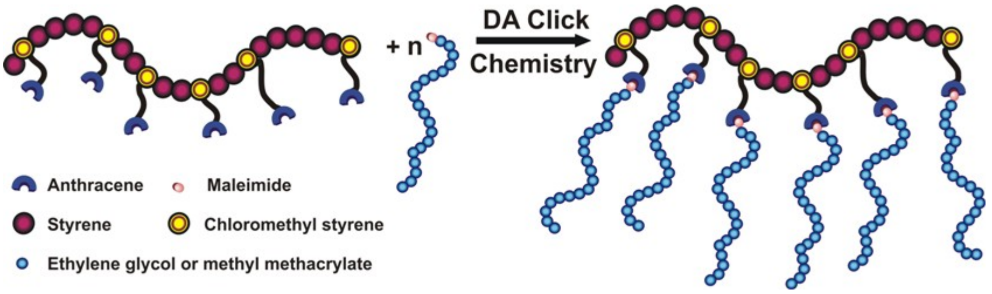


Figure 2.7 : Synthesis of graft copolymer by using macromonomer.

An interesting example which combines two different controlled radical polymerization methods, namely NMP and ATRP, via “Click Chemistry” strategy between anthracene and maleimide has been given in reaction 2.51. Using these Diels-Alder (DA) functional groups, well-defined polystyrene-*g*-poly(methyl methacrylate) (PSt-*g*-PMMA) copolymers were successfully prepared. The whole process was divided into two stages; first, random copolymers of styrene (St) and chloromethyl styrene (CMS) with various CMS contents were prepared by nitroxide mediated radical polymerization (NMP) process. Then, the chloromethyl groups were converted to anthryl groups via etherification with 9- anthracene methanol. The other component of the click reaction, namely protected maleimide functional poly(methyl methacrylate) (PMMA), obtained by atom transfer radical polymerization (ATRP) using the corresponding functional initiator. In the final stage, PMMA prepolymer was deprotected by *retro* Diels-Alder *in situ* reaction by heating at 110^{o}C in toluene. The recovered maleimide groups and added anthryl functional polystyrene underwent Diels-Alder reaction to form respective (PSt-*g*-PMMA) copolymers [204].



(2.51)

2.6 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 [159, 205].

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):

$$f = \frac{\text{number of functional groups}}{\text{number of polymer chains}} \qquad \textbf{(Eq.2.11)}$$

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 2.8.

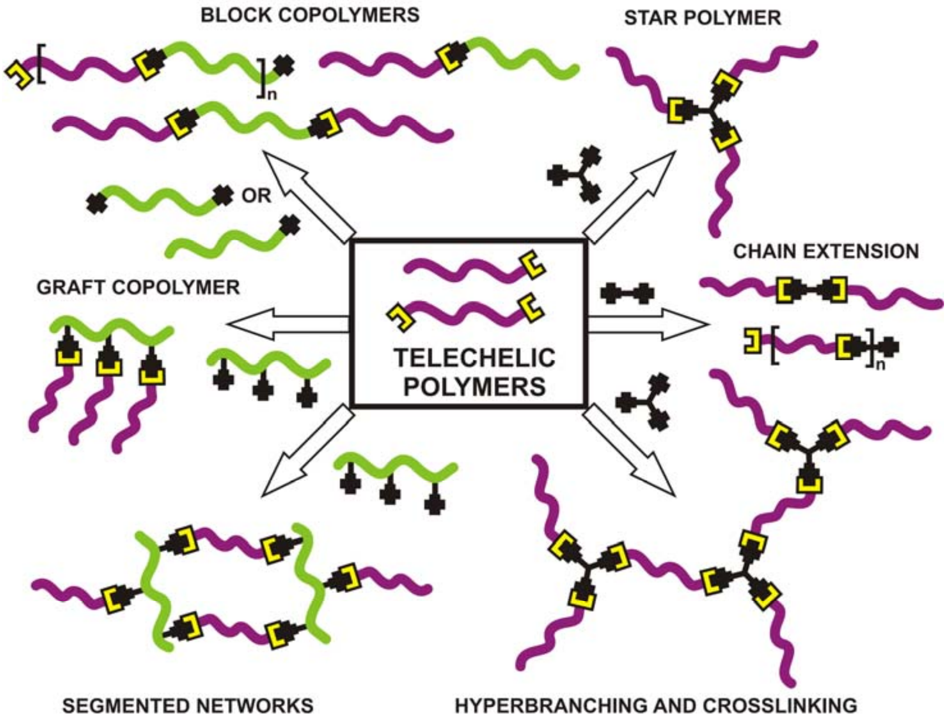


Figure 2.8 : Various architectures obtained by the reactions of telechelics.

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. Liquid telechelic polymers are the basis for reaction injection moulding. Liquid telechelics that can be used for network formation offer advanced processibility and may result in materials with improved properties [206].

2.6.1 Preparation of telechelics by using conventional 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) [207]. But, the first method has serious limitations because well-defined end groups can be observed only if not more than one type of primary radical is formed that does not cause side reactions such as transfer. Moreover, a propagating radical will readily react with another radical, primary or macroradical, either through disproportionation or through coupling reactions (termination) (Figure 2.9). The former will produce monofunctional telechelics with both a saturated and an unsaturated chain end, while only the latter will yield bifunctional telechelics.

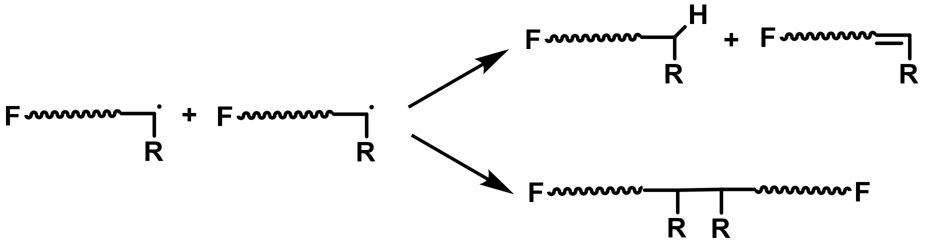


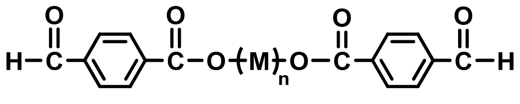
Figure 2.9 : Termination reactions.

Azo compounds use very frequently for the functional initiators technique. Upon heating the aliphatic azo compounds, nitrogen is evolved, and two carbon centered free radicals are formed (reaction 2.52).

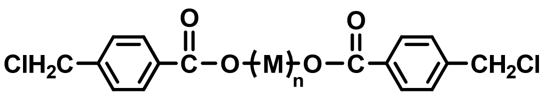
$$R^1{-}N{=}N{-}R^2 \xrightarrow{\Delta} R^1 + R^2 + N_2 \qquad \textbf{(2.52)}$$

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 [208-210].

Aroyl peroxides as another functional initiator give styryl telechelics [211]. When employing benzoyl peroxides *p*-substituted with formal groups (reaction 2.53) or chloromethyl (reaction 2.54), the telechelics require no further modification before being used as prepolymers.



(2.53)



(2.54)

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):

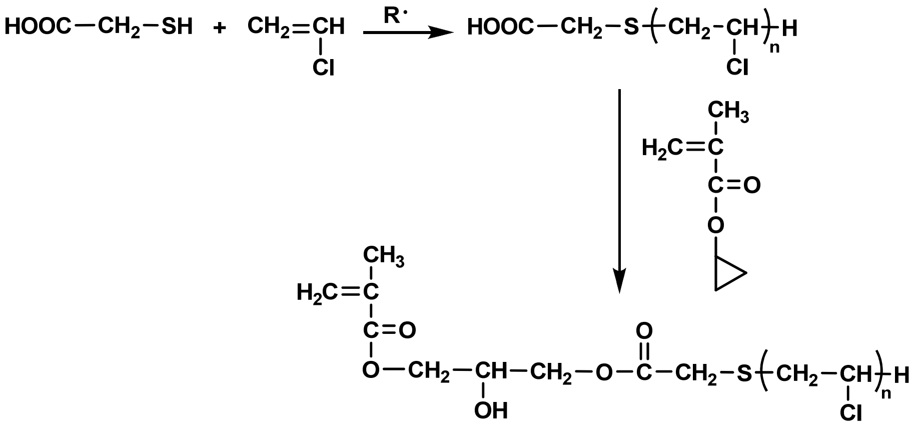
$$I \longrightarrow 2R\cdot \qquad (2.55a)$$

$$R\cdot + n\,M \longrightarrow RM_n^{\bullet} \qquad (2.55b)$$

$$RM_n^{\bullet} + \textcircled{F}{-}SH \longrightarrow RM_n{-}H + \textcircled{F}{-}S\cdot \qquad (2.55c)$$

$$\textcircled{F}{-}S\cdot + n\,M \longrightarrow \textcircled{F}{-}S{-}M_n^{\bullet} \qquad (2.55d)$$

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 [212] 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 2.56a and 2.56b).



$$HOOC{-}CH_2{-}SH + CH_2{=}\underset{Cl}{CH} \xrightarrow{R\cdot} HOOC{-}CH_2{-}S{\left(CH_2{-}\underset{Cl}{CH}\right)_n}H$$

(2.56a)

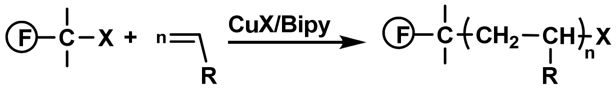
(2.56b)

Moreover, telechelics with certain functional groups can be prepared directly from the precursor initiators or, alternatively, via modification of the available telechelics. For instance, hydrolysis of nitrile groups yields carboxyl-terminated oligostyrene while isocyanate end groups are obtained directly from the azide telechelics or by treatment of amino-terminated polymers with phosgene [213]. The functional group approach to synthesize amino telechelics causes some complications since amino compounds participate in chain-transfer reactions.

2.6.2 Preparation of telechelics by using controlled radical polymerization methods

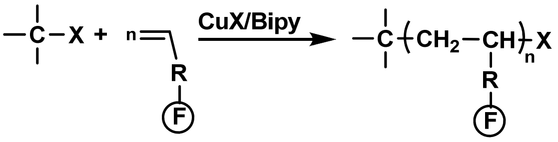
Polymer functionalization by ATRP can be achieved by using functional initiators and monomers and the chemical transformation of the halogen end groups. These routes are summarized in reactions 2.57-2.59.

Through Initiator Functionality



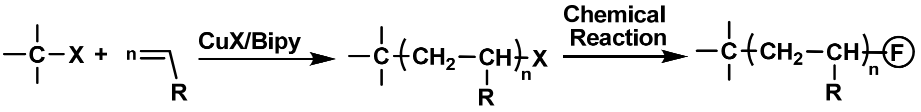
(2.57)

Through Monomer Functionalty



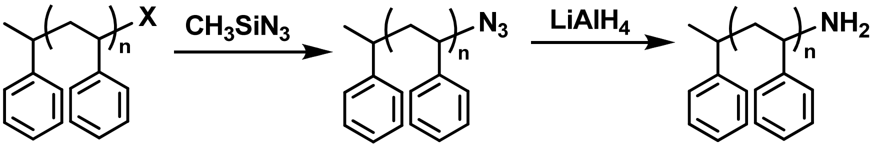
(2.58)

Through Chemical Reaction of Halide End Group



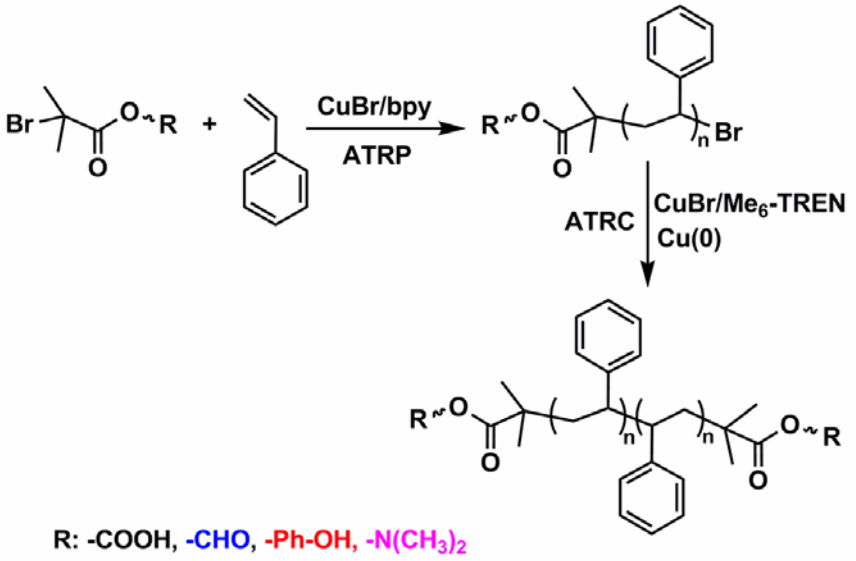
(2.59)

Quite a number of functional initiators were successfully used in ATRP to prepare functional styrene and acrylate type polymers [214]. For this purpose initiators should be equipped with the desired functional groups as well as with a radical stabilizing group on the α-carbon atom such as aryl, carbonyl, nitrile, and multiple halogens to ensue successful ATRP. Notably, direct bonding of halogen to aryl or carbonyl group does not facilitate radical generation. In this connection, it should also be pointed out that any functionalities in the initiator should not interfere with ATRP, ie, should be inert to catalyst. Obviously, ATRP leads to the formation of monofunctional telechelics since the other chain always contains halogen as a result of the fast deactivation process. These polymers could be called heterotelechelic since halogen is also a functional group. Therefore, α,ω-telechelics can only be prepared by transformation of the halide end group by means of nucleophilic substitution, free radical chemistry, or electrophilic addition catalyzed by Lewis acids [215]. Typical example of such displacement is represented in reaction 2.60, which illustrates the reactions used to replace the halogens with azides and consequently leading to amino-functional telechelics [216-218].



(2.60)

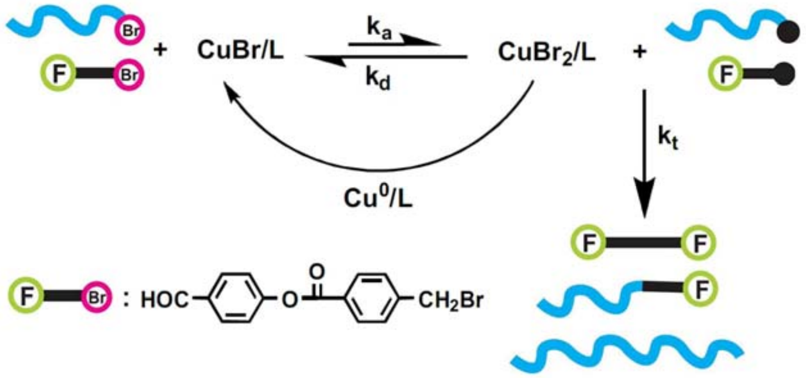
Bifunctional telechelics can be synthesized via atom transfer coupling process. In a recent work [219], polymers monofunctionalized with aldehyde, aromatic hydroxyl, dimethyl amino groups were obtained by ATRP of styrene using functional initiators in the presence of the CuBr/bpy catalytic complex. Bifunctional 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 (Me_6TREN) as ligand, Cu(0) as reducing agent and toluene as solvent. The overall process is depicted below (reactions 2.61a and 2.61b).



(2.61a)

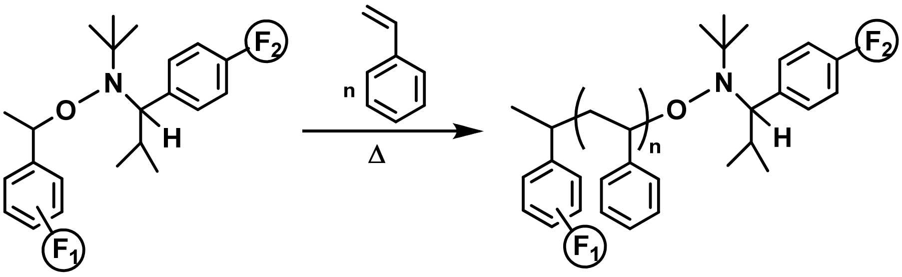
(2.61b)

Moreover, telechelic polymers werealso prepared by ATRCC [220]. The concept is based on the activation of the dormant species at the chain ends of polystyrene (PS-Br) prepared by ATRP and also functional ATRP initiator (***F***-R-Br) in the absence of a monomer. Depending on the number of functionality of the polymer used in the system, ATRCC yields ω-polystyrene and α,ω-polystyrene telechelics. However, at least in principle, not only the desired functional polymers but also various side products may be formed due to the self coupling reactions of macroradicals generated from PS-Br, and low–molecular weight radicals from ***F***-R-Br. The possible reactions of the model system are depicted in reaction 2.62.



(2.62)

It is also possible to prepare telechelic polymers by NMP procedure since it tolerates a wide variety of functional groups [8]. For the synthesis of telechelics by NMP there are two general methods, i.e., functional groups can be placed at the initiating chain end, F_1, or the nitroxide mediated chain end, F_2 (reaction 2.63).



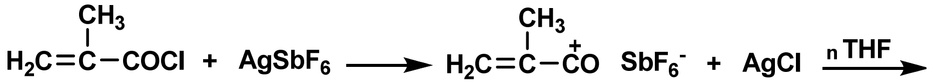
(2.63)

Telechelics with a variety of functional groups can essentially be prepared by using functional nitroxides [57, 221, 222].

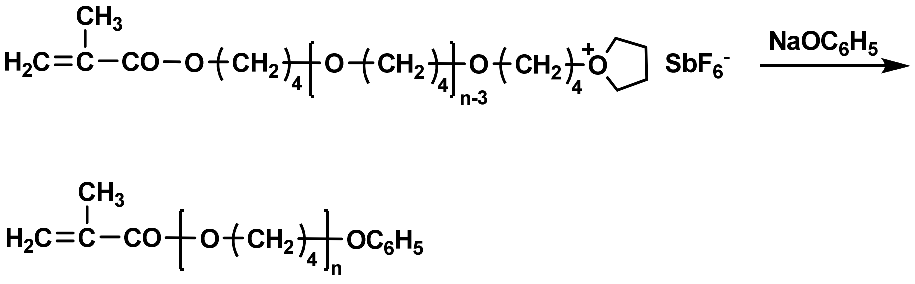
2.6.3 Preparation of telechelics by using macromonomers

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 [223-225]. 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. First one is 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. Second, 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. 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 reaction 2.64a,b.



$$H_2C{=}\overset{CH_3}{\overset{|}{C}}{-}COCl + AgSbF_6 \longrightarrow H_2C{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{+}{C}O\ SbF_6^- + AgCl \xrightarrow{n\,THF} \qquad \textbf{(2.64a)}$$



$$H_2C{=}\overset{CH_3}{\overset{|}{C}}{-}CO{-}O{-}(CH_2)_4{-}\left[O{-}(CH_2)_4\right]_{n-3}{-}O{-}(CH_2)_4{-}\overset{+}{O}\square\ SbF_6^- \xrightarrow{NaOC_6H_5} \qquad \textbf{(2.64b)}$$

$$H_2C{=}\overset{CH_3}{\overset{|}{C}}{-}CO{-}\left[O{-}(CH_2)_4\right]_n{-}OC_6H_5$$

Termination of the cationic ring-opening polymerization of *N*-*t*-butylaziridine with methacrylic acid yields macromonomers [226], which is the case of functionalization of growing chains through end-capping reactions.

As for macromonomers derived by post-functionalization, an example was described by Haddleton and colleagues [227]. 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.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Styrene (St, 99%, Aldrich):

It was passed through a basic alumina column to remove the inhibitor before use.

Chloromethyl styrene (CMS, ca.60/40 meta/para-isomer mixture; 97%; Aldrich):

It was distilled under reduced pressure before use.

Methyl methacrylate (MMA, 99%, Aldrich):

It was passed through a basic alumina column to remove the inhibitor before use.

Methyl acrylate (MA, 99%, Aldrich):

It was passed through a basic alumina column to remove the inhibitor before use.

2-Hydroxyethyl methacrylate (HEMA, 96%, Acros):

It was passed through a basic alumina column to remove the inhibitor before use.

Divinyl benzene (DVB55, 55% mixture of isomers, technical grade, Aldrich):

It was used as received.

3.1.2 Solvents

Diethyl ether (J.T. Baker):

It was dried with calcium chloride and distilled over sodium wire.

Dichloromethane (J.T. Baker):

It was dried with calcium chloride and distilled over P_2O_5. It was stored over molecular sieves for use as a solvent in the photopolymerization experiments.

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

(a) It was used as eluent for chromatography as received (High Performance Liquid Chromatography Grade).

(b) For use in the chemical reactions, it was dried and distilled over benzophenone/sodium.

n-Hexane (95%, Aldrich):

It was used without further purification.

Acetonitrile (98%, Aldrich):

It was used as received.

N,N-Dimethyl formamide (99.8%, Merck):

It was used as received.

Methanol (Technical):

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

3.1.3 Other chemicals

N, N, N',N'', N''-Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich):

It was distilled before use.

2,2 Dipyridyl (bpy, 99% Acros):

It was used as received.

CuBr (98 %, Acros):

It was used as received.

CuCl (≥ 99 %, Acros):

It was used as received.

2,2,6,6-Tetramethylpiperidine-N-oxyl free radical (TEMPO, 99%, Aldrich):

It was used without further purification.

2,2’-Azobis-(isobutyronitrile) (AIBN, 98%, Aldrich):

It was recrystallized from ethanol.

Ethyl-2-bromopropionate (99 %, Aldrich) (1):

It was used as received.

Ethyl-2-bromoisobutyl bromide (98 %, Aldrich):

It was used as received.

Ethylene glycol (95 %, Aldrich)

It was used as received.

Triethylamine (99.5 %, Fluka):

It was used as received.

Silver hexafluoroantimonate (AgSbF6, 98%, Aldrich):

It was used as received.

Isoquinoline N-oxide (IQ, 98 %, Aldrich):

It was used as received.

4-Phenylpyridine N-oxide (PP, 98 %, Aldrich):

It was used as received.

Carbon Disulfide (99.5 %, Merck):

It was used as received.

(2, 4, 6-Trimethylbenzoyl)diphenylphosphine oxide (TMDPO, Ciba):

It was used as received

Morpholine (99 %, Merck):

It was stored over metallic sodium under nitrogen atmosphere for 24 h and finally distilled under reduced pressure.

2,6-Dihydroxybenzoic acid (97 %, Acros):

It was used as received.

N',N'-Dimethylpyridine-4-amine (DMAP, 99 %, Acros):

It was used as received.

Benzophenone (≥ 99 %, Aldrich):

It was 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)

^{1}H NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument.

3.2.3 Infrared spectrophotometer (FT-IR)

FT-IR spectra were recorded on a Perkin Elmer FTIR Spectrum One B spectrometer.

3.2.4 UV-Visible spectrophotometer

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

3.2.5 Gel permeation chromatography (GPC)

(a) 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 ultrastyragel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate 0.3 mL/min. Molecular weights were calculated on the basis of a calibration curve recorded with mono disperse polystyrene standards.

(b) Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL GPC columns (G2000H_{HR}, G3000H_{HR} and G4000H_{HR}), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were 456–42,800, 1050–107,000, and 10,200–2,890,000, respectively. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 30°C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Molecular weights were calculated with the aid of polystyrene standards.

3.2.6 Differential scanning calorimeter (DSC)

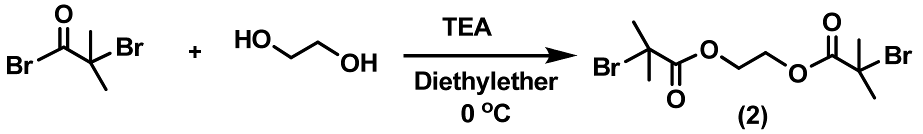
Differential scanning calorimeter (DSC) was performed on a Perkin Elmer Diamond DSC with a heating rate of 10 ^{o}C min^{-1} under nitrogen flow.

3.2.7 Atomic force microscopy (AFM)

For Atomic Force Microscopy (AFM) measurements, films were spin coated on silicon oxide substrates from 10 mg/ml solutions in $CHCl_3$. Height and phase images were taken by NT-MDT Solver P47 in tapping mode with ultra sharp Si cantilevers having force constant of 48 N/m.

3.3 Preparation Methods

3.3.1 1,2-Bis(bromoisobutryloxy)ethane (2)

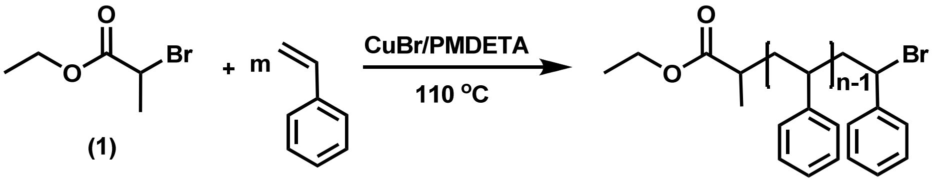


(3.1)

Initiator 2 was synthesized by dropwise addition of 2-bromoisobutyryl bromide (2.25 mL, 42 mmol) to ethylene gylcol (1.25 mL, 21.15 mmol) and triethylamine (TEA, 6.3 mL, 45.05 mmol) solution in diethylether (50 mL) at 0 °C under an nitrogen atmosphere. After addition, the reaction mixture was stirred overnight at room temperature. The reaction mixture extracted with $NaHCO_3$ and NaCl solution and organic phase was dried with Na_2SO_4. The solution was concentrated and the crude product was purified by column chromatography over silica gel eluting with

Hex/EtOAc (10/1) to give the product as white solid (yield: 4.5 g, 65 %). ^{1}H NMR ($CDCl_3$): 4.43 (s, 4H, CO-O-*CH_2*-*CH_2*-O-CO) 1.94 (s, 6H, O-CO-C-*$CH_3)_2$*) [228].

3.3.2 Preparation of monobrominated polystyrene (PSt-Br) by ATRP



(3.2)

CuBr (0.124g, 0.86 mmol), PMDETA (181 μL 0.86 mmol), ethyl-2-bromopropionate (**1**) as an initiator (112 μL, 0.86 mmol), and styrene (10 mL, 86 mmol) were were introduced in a Schlenk tube, and the reaction mixture was degassed by three freeze–pump–thaw cycles and left in vacuo. The tube was heated at 110°C in an oil bath and stirred for a certain time. Then the mixture was diluted with THF, and passed through an alumina column to remove the complex salts. Precipitation of the polymer was performed in a ten-fold volume of methanol. The solid was then collected after filtration and drying at 40 °C in vacuum for overnight. ^{1}H NMR ($CDCl_3$): δ= 7.08-6.57 (m, 5H, Ar), 4.40 (bs, 1H, Ph-*CH*-Br), 3.94 (m, 2H, CH_3-*CH_2*-O-CO), 1.85-0.92 (m, 9H, *CH_2*-*CH*Ph, *CH_3*-CH_2-O-CO, CO-*CH*-*CH_2*).

3.3.3 Preparation of dibrominated polystyrene (Br-PSt-Br) by ATRP

Dibrominated polystyrene (Br-PSt-Br) was synthesized using the same methodology described above except using **2**, as an initiator instead of using **1**. CuBr (0.03 g, 0.22 mmol), PMDETA (45.5 μL 0.22 mmol), (**2**) as an initiator (0.04g, 0.11 mmol), and styrene (5 mL, 44 mmol) were introduced in a Schlenk tube, and the reaction mixture was degassed by three freeze–pump–thaw cycles and left in vacuo. The tube was heated at 90°C in an oil bath and stirred for 1 h. Then the mixture was diluted with THF, and passed through an alumina column to remove the complex salts. Precipitation of the polymer was performed in a ten-fold volume of methanol. The solid was then collected after filtration and drying at 40 °C in vacuum for overnight. ^{1}H NMR ($CDCl_3$): δ= 7.07-6.58 (m, 5H, Ar), 4.39 (bs, 1H, Ph-*CH*-Br), 3.37 (m, 2H, CO-O-*CH_2*-*CH_2*-O-CO), 1.85-1.45 (m, 3H, *CH_2*-*CH*Ph), 0.85 (bs, 6H, O-CO-C-*$CH_3)_2$*).

3.3.4 Synthesis of *N*-alkoxy isoquinolinium ion terminated polystyrene (PSt-IQ)

A three-necked flask equipped with an N_2 inlet and a rubber septum was connected to a vacuum line. Dichloromethane (15ml) polystyrene (1 equiv.), isoquinoline N-oxide (10 equiv) and $AgSbF_6$ (1.1 equiv.) is added to the flask equipped with a magnetic stirrer under N_2 atmosphere, respectively. The flask was then connected to a condenser and placed into a thermostatically controlled bath at 40 ^{0}C. The mixture was filtered after stirred for overnight, poured into ten-fold excess of cold methanol. The precipitated polymer was filtered off and dried in *vacuo.* ^{1}H NMR ($CDCl_3$): δ= 8.81 (s, 1H, Ar), 8.55 (bd, 1H, Ar), 8.15 (bd, 1H, Ar), 8.04 (s, 1H, Ar) 7.89 (bd, 1H, Ar), 7.16 (bd, 1H, Ar), 7.07-6.58 (m, 5H, Ar), 5.09 (bs, 1H, Ph-*CH*-O-N), 3.94 (m, 2H, CH_3-CH_2-O-CO), 1.85-0.9 (m, 6H, CH_2-*CH*Ph, O-CO-CH_2-CH_3).

3.3.5 *N*-Alkoxy 4-phenylpyridinium ion terminated polystyrene (PSt-PP)

Dichloromethane (15ml) polystyrene (1 equiv.), 4-phenylpyridine *N*-oxide (10 equiv.) and $AgSbF_6$ (1.1 equiv.) were introduced in a three-necked dried flask equipped with an N_2 inlet, respectively. The flask was stirred at 40 ^{0}C for overnight. After that time, the mixture was filtered and precipitated into ten-fold excess of cold methanol. The precipitated polymer was filtered off and dried in *vacuo.* ^{1}H NMR ($CDCl_3$): δ= 8.32 (bm, 2H, Ar), 8.09 (bm, 2H, Ar), 7.71 (bm, 2H, Ar), 7.54 (bm, 3H, Ar), 7.07-6.58 (m, 5H, Ar), 5.09 (bs, 1H, Ph-*CH*-O-N), 3.94 (m, 2H, CH_3-CH_2-O-CO), 1.85-0.9 (m, 6H, CH_2-*CH*Ph, O-CO-CH_2-CH_3).

3.3.6 Synthesis of *N*-alkoxy isoquinolinium ion terminated bifunctional polystyrene (IQ-PSt-IQ)

The same procedure was applied by using respective bifunctional precursor polymers. A three-necked flask equipped with an N_2 inlet and a rubber septum was connected to a vacuum and dried under vacuum. After cooling to room temperature dichloromethane (15mL) bifunctional polystyrene (1 equiv.), isoquinoline *N*-oxide (20 equiv.) and $AgSbF_6$ (2.2 equiv.) is added to the flask equipped with a magnetic stirrer under N_2 atmosphere, respectively. The flask was then connected to a condenser and placed into a thermostatically controlled bath at 40 ^{0}C. The mixture was filtered after stirred for overnight, poured into ten-fold excess of cold methanol. The precipitated polymer was filtered off and dried in *vacuo.* ^{1}H NMR ($CDCl_3$): δ=

8.75 (s, 1H, Ar), 8.34 (bd, 1H, Ar), 8.04-8.01 (bd, 1H, Ar), 8.01 (s, 1H, Ar) 7.88 (bd, 1H, Ar), 7.66-7.62 (bd, 1H, Ar), 7.09-6.60 (m, 5H, Ar), 5.05 (bs, 1H, Ph-*CH*-O-N), 3.37 (m, 2H, CO-O-CH_2-CH_2-O-CO), 1.85-1.45 (m, 3H, CH_2-*CH*Ph), 0.85 (bs, 6H, O-CO-C-$CH_3)_2$).

3.3.7 Synthesis of *N*-alkoxy 4-phenylpyridinium ion terminated bifunctional polystyrene (PP-PSt-PP)

Dichloromethane (15mL) bifunctional polystyrene (1 equiv.), 4-phenylpyridine *N*-oxide (20 equiv.) and $AgSbF_6$ (2.2 equiv.) is added to the flask equipped with a magnetic stirrer under N_2 atmosphere, respectively. After the stirring at 40 ^oC for overnight, the mixture was filtered and poured into ten-fold excess of cold methanol. The precipitated polymer was filtered off and dried in *vacuo.* ^1H NMR ($CDCl_3$): δ= 8.32 (bm, 2H, Ar), 8.09 (bm, 2H, Ar), 7.71 (bm, 2H, Ar), 7.54 (bm, 3H, Ar), 7.07-6.58 (m, 5H, Ar), 5.05 (bs, 1H, Ph-*CH*-O-N), 3.38 (m, 2H, CO-O-CH_2-CH_2-O-CO), 2.16-1.24 (m, 3H, CH_2-*CH*Ph), 0.85 (bs, 6H, O-CO-C-$CH_3)_2$).

3.3.8 Photoinduced block copolymerizations of methyl methacrylate using *N*-alkoxy isoquinolinium or *N*-alkoxy 4-phenylpyridinium ion terminated polystyrenes as a macrophotoinitiator

MMA (1.5 ml, 3.92M) was added to a solution of CH_2Cl_2 (2 ml) containing one of the pyridinium ion terminated polystyrene (12.5 mM). The tube was degassed under high vacuum and sealed under N_2. Irradiations were carried out using a Rayonet photoreactor equipped with lamps which emitted light at nominally 350 nm for 60 min. At the end of the photolysis, the reaction mixture was poured into cold hexane. The precipitate was filtered off and dried. The obtained polymers were extracted with cyclohexane to remove polystyrene. ^1H NMR ($CDCl_3$): δ= 7.08-6.57 (m, 5H, Ar), 3.58 (bs, 3H, CO-O-CH_3), 1.86-0.83 (m, 8H, CH_2-*CH*Ph, CH_2-C(CH_3)-CO, CO-*CH*-CH_3).

3.3.9 Preparation of poly(styrene-*co*-chloromethyl styrene) P(St-co-CMS) precursors

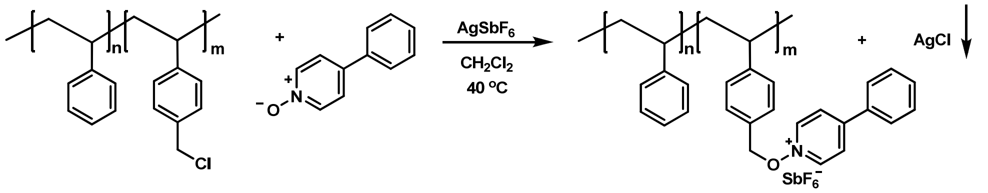
P(St-*co*-CMS) copolymers containing various amounts of CMS moieties were prepared via NMP of St and CMS at 125 ^oC. Following procedure described for copolymer which consist of 10 % CMS unit in feed: CMS (0.46 ml, 3.27 mmol), St (3.38 mL, 29.48 mmol), AIBN (0.05g, 0.32 mmol) and TEMPO (0.10g, 0.64 mmol) were introduced in a Schlenk tube, and the reaction mixture was degassed by three freeze–pump–thaw cycles and left in vacuo. The tube was stirred at 125 ^{o}C for 24 h. Then the mixture was diluted with THF, and precipitated in methanol. After the reprecipitation from methanol polymer was dried in *vacuo.* ^{1}H NMR ($CDCl_3$): δ= 7.08-6.58 (m, 9H, Ar), 4.52 (bs, 2H, Ph-CH_2-Cl), 3.97 (bs, 1H, Ph-*CH*-O-N), 2.35-0.9 (m, 6H, CH_2-*CH*Ph,) 0.39-0.19 (bs, 12H N-(C-$(CH_3)_2)_2$).

3.3.10 Preparation of poly(chloromethyl styrene) PCMS precursors

The same methodology described above was also used for the preparation homo poly(chloromethylstyrene) PCMS except using only CMS as the monomer. CMS (10 ml, 0.32 mol), AIBN (0.26g, 1.60 mmol) and TEMPO (0.65g, 4.01 x 10^{-2} mmol) were introduced in a Schlenk tube, and the reaction mixture was degassed by three freeze–pump–thaw cycles and left in vacuo. The tube was stirred at 125 ^{o}C for 20 h. Then the mixture was diluted with THF, and precipitated in methanol. After the reprecipitation from methanol polymer was dried in *vacuo.* ^{1}H NMR ($CDCl_3$): δ= 7.04-6.47 (m, 4H, Ar), 4.50 (bs, 2H, Ph-CH_2-Cl), 3.97 (bs, 1H, Ph-*CH*-O-N), 2.05-0.86 (m, 3H, CH_2-*CH*Ph,) 0.39-0.19 (bs, 12H N-(C-$(CH_3)_2)_2$).

3.3.11 Preparation of 4-phenylpyridinium-*N*-oxyl functional polystyrenes P(St-co-PPMS)

A three-necked flask equipped with an N_2 inlet and a rubber septum was connected to a vacuum and dried at 130 ^{o}C under vacuum. After cooling to room temperature dichloromethane (15 ml), precursor polymers (1 equiv. Cl unit), 4-phenylpyridine *N*-oxide (10 equiv.) and $AgSbF_6$ (1.1 equiv.) is added to the flask equipped with a magnetic stirrer under N_2 atmosphere, respectively. The flask was then connected to a condenser and placed into a thermostatically controlled bath at 40 ^{0}C. The mixture was filtered after stirred for overnight, poured into ten-fold excess of cold methanol. The precipitated polymer was filtered off and dried in *vacuo.* ^{1}H NMR ($CDCl_3$): δ= 9.43 (bm, 2H, Ar), 8.56 (bm, 2H, Ar), 8.04 (bm, 2H, Ar), 7.65 (bm, 3H, Ar), 7.05-6.51 (m, 9H, Ar), 5.54 (bs, 1H, Ph-*CH*-O-N), 2.08-0.86 (m, 3H, CH_2-*CH*Ph,).



(3.2)

3.3.12 Photoinduced grafting reactions of methyl methacrylate using 4-phenylpyridinium-*N*-oxyl functional polystyrenes

MMA (1.5 ml, 3.92M) was added to a solution of CH_2Cl_2 (2 ml) containing one of the pyridinium ion functional polystyrene (12.5 mM). The tube was degassed under high vacuum and sealed under N_2. Irradiations were carried out using a Rayonet photoreactor equipped with 16 lamps and emitting light nominally at 350 nm with the light intensity of 1.04 10^{-3} mW cm^{-2} as measured by Delta Ohm model HD-9021 radiometer. At the end of the photolysis, the reaction mixture was poured into cold hexane. The precipitate was filtered off and dried. ^1H NMR ($CDCl_3$): δ= 7.05-6.55 (m, 9H, Ar), 5.58 3.58 (bs, 3H, CO-O-*CH_3*), 2.08-0.86 (m, 3H, *CH_2-CH*Ph, CH_2-C(CH_3)-CO).

3.3.13 Photoinduced modification of 4-phenylpyridinium-*N*-oxyl functional polystyrenes

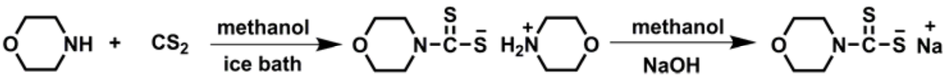
The experimental procedure applied for grafting process was also used for photoinduced modification. In this case, however, photolysis was performed in dry THF (5 ml) in the absence of monomer. After the irradiation polymer was precipitated in methanol. ^1H NMR ($CDCl_3$): δ= 7.03-6.54 (m, 9H, Ar), 4.51 (bs, 2H, Ph-*CH_2*-OH), 2.06-0.86 (m, 6H, *CH_2-CH*Ph,). FT-IR: 3430, 2949, 1724, 1638, 1485, 1435, 1247, 1147, 1065, 964, 841, 748 cm^{-1}.

Morpholine-4-dithiocarbamate sodium salt was kindly synthesized by Bunyamin Karagoz. Their synthesis procedures are given below.

3.3.14 Synthesis of morpholine-4-dithiocarbamate sodium salt (MDC^- Na+)

To a 100 mL of Erlenmeyer flask there were added (17.40 g, 0.20 mol) morpholine and 20 mL methanol. The solution was cooled to 0 °C in ice bath. Carbon disulfide (7.60 g, 0.10 mol) was introduced by drop wise addition through a pressure equalizing dropping funnel over 30 min under vigorous stirring. Then the solution of

(4.00 g, 0.10 mol) NaOH in 20 mL methanol was added and the mixture was stirred at 60 ^{o}C for 1h. About ¾ of methanol was removed by rotavapor. The mixture was chilled and poured into 40 mL diethyl ether. The white precipitate (sodium salt of morpholine dithiocarbamic acid) was filtered and dried at 40 ^{o}C for 2 h under vacuum. The yield was 15.70 g (84.90 %).



(4.2)

3.3.15 Synthesis of morpholine-4-dithiocarbamate terminated polystyrenes (MDC-PSt-MDC)

Dibrominated polystyrene (Br-PSt-Br) (0.50g, 7.9 x 10^{-2} mmol), morpholine-4-dithiocarbamate sodium salt (MDC$^-$ Na$^+$) (0.15 g, 7.9 x 10^{-1} mmol) and dimethyl formamide (7 mL) were added to the flask. The reaction mixture was degassed by three freeze–pump–thaw cycles and left in vacuo. The tube was then placed in a stirrer at room temperature for 48 h. The mixture was precipitated in methanol and the precipitated polymer was filtered off and dried in *vacuo.* ^{1}H NMR ($CDCl_3$): δ= 7.09-6.58 (m, 5H, Ar), 4.40-3.66 (m, 10H, Ph-*CH*-S-CS, CS-N-CH_2-CH_2-O), 3.38 (m, 2H, CO-O-CH_2-CH_2-O-CO), 2.16-1.44 (m, 3H, CH_2-*CH*Ph), 0.85 (bs, 6H, O-CO-C-$CH_3)_2$).

3.3.16 Photoinduced block copolymerization of methyl acrylate using morpholine-4-dithiocarbamate terminated polystyrenes as a macrophotoiniferter

The solution MDC-PSt-MDC (0.10 g, 1.5 x 10^{-2} mmol) and MA (0.80 mL, 9 mmol) in CH_2Cl_2 (1.7 mL) was irradiated a Rayonet merry-go-round photoreactor equipped with 16 lamps emitting light nominally at $\lambda > 300$ nm at room temperature. The light intensity was 6 x 10^{-3} mW cm^{-2} as measured by Delta Ohm model HD-9021 radiometer. After given time, the resulted polymers were precipitated in the methanol and then dried under reduced pressure. Conversion of monomer was determined gravimetrically. ^{1}H NMR ($CDCl_3$): δ= 7.07-6.57 (m, 5H, Ar), 3.94-3.23 (b, 25H, CO-O-CH_3,, CO-O-CH_2-CH_2-O-CO, CO-*CH*-S-CS, CS-N-CH_2-CH_2-O), 2.31-1.19 (m, 6H, CH_2-*CH*Ph, CH_2-*CH*-CO,), 0.85 (bs, 6H, O-CO-C-$CH_3)_2$).

3.3.17 Photoinduced block copolymerization of methyl acrylate using morpholine-4-dithiocarbamate terminated polystyrenes as a macrophotoiniferter in the presence of TMDPO

TMDPO (3.10 x 10^{-3} g, 0.8 x 10^{-2} mmol) and monomer (MA, 1.19 mL, 13.3mmol) with MDC-PS-MDC, (0.10 g, 2.2 x 10^{-2} mmol) solution in CH_2Cl_2 (2.6 mL) were put into Pyrex tubes that flushed with dry nitrogen. The mixtures were irradiated as described above except that a cupric sulfate aqueous solution was used as the photofilter in order to avoid the absorption of MDC-PSt-MDC. The thickness of saturated solution of $CuSO_4$ was 1 cm. Conversion of monomer was determined gravimetrically. ^{1}H NMR ($CDCl_3$): δ= 7.07-6.57 (m, 5H, Ar), 3.94-3.23 (b, 25H, CO-O-*CH_3,,* CO-O-*CH_2-CH_2*-O-CO, CO-*CH*-S-CS, CS-N-*CH_2-CH_2*-O), 2.31-1.19 (m, 6H, *CH_2-CH*Ph, *CH_2-CH*-CO,), 0.85 (bs, 6H, O-CO-C-*CH_3)$_2$*).

Benzodioxinone and derivatives were kindly synthesized by Volkan Kumbaracı. Their synthesis procedures are given below.

3.3.18 Synthesis of 7-hydroxy-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one (HDPD)

The precursor compound was synthesized according to the literature procedure [229]. Thus, to an ice-cold suspension of 2,4-dihydroxybenzoic acid (2.5 g, 16.23 mmol) in trifluoroacetic acid (13 mL) were added trifluoroacetic anhydride (14 mL) and benzophenone (4.43 g, 24.37 mmol). The mixture was warmed slowly to room temperature and then stirred for 24 h. The mixture was then concentrated on the rotary evaporator, poured into a saturated solution of aqueous $NaHCO_3$, and extracted with three portions of diethyl ether. Collected extracts were washed with water and brine, dried (MgSO4), and concentrated to leave yellow solids. Chromatography over silica using EtOAc/Hex (30/70) as the eluent afforded 0.9 g (17 %) of HDPD as yellow solid. m.p.; 63-65 °C. ^{1}H NMR ($CDCl_3$): δ= 10.43 (s, 1H, OH), 7.60-7.54 (dd, *J=7.4*, *J=1.4*, 4H, Ar), 7.35-7.31 (m, 6H, Ar), 7.71 (d, *J=8.7*, 1H, Ar), 6.63 (s, 1H, Ar), 6.52 (d, *J=8.6*, 1H, Ar). FT-IR: 3230, 2975, 1687, 1612, 1594, 1491, 1447, 1240, 1121, 960, 750 cm^{-1}. UV (CH_2Cl_2): λ_{max}., nm (ε, l mol^{-1} cm^{-1}); 303 (8932), 263(18470), 229 (21869). MS (EI) *m/z* (%): 318(60), 273(7), 241(8), 183(80), 136(100), 105(67), 77(47), 71(42), 43(27).

3.3.19 Copolymerization of hydroxyethyl metacrylate and methyl metacrylate by ATRP (P(HEMA-co-MMA))

CuCl (0.09 g, 0.91 mmol), bpy (0.357 g 2.28 mmol), ethyl-2-bromopropionate (118 μL, 0.91 mmol) as an initiator HEMA (2 mL, 16.4 mmol), MMA (7.22 mL 67.5 mmol) and 6 mL dried methanol were introduced in a Schlenk tube, and the reaction mixture was degassed by three freeze–pump–thaw cycles and left in vacuo. The tube was stirred at 10°C for certain time. Then the mixture was diluted with THF, and passed through a silica column to remove the complex salts. The resulting copolymers was precipitated in hexane and collected by filtration. Conditions and results are summarized in Table 1. ^{1}H NMR ($CDCl_3$): δ= 4.08 (br. s, 2H, CO-O-*CH₂*-), 3.81 (br. s, 4H, -CH_2-OH, CH_3-CH_2-O-CO), 3.57 (br. s, 3H, CO-O-CH_3), 1.86-0.81 (m, 17H, CH_2-CCH_3, CH_3-CH_2-O-CO, CO-*CH*-CH_3). FT-IR: 3513, 3002, 2950, 2843, 1727, 1484, 1449, 1387, 1271, 1243, 1148, 1069, 988, 750 cm^{-1}.

3.3.20 Preparation of benzodioxinone terminated polystyrene (PSt-B)

A solution of HDPD (0.19 g, 0.6 mmol) and anhydrous potassium carbonate (1.24 g, 9 mmol) in acetone (25 mL) were stirred for 3 h. After that time, PS-Br (0.83 g, 0.24 mmol) was added and the mixture was heated at reflux temperature for 16 h. The reaction mixture was filtered to remove the salt. Then, the mixture was concentrated on the rotary evaporator and precipitated in methanol. The functional polymer was collected by filtration. (0.8 g ; yield: 96 %).^{1}H NMR ($CDCl_3$): δ= 7.51 (s, 1H, Ar), 7.25-6.51 (m, 15H, Ar), 6.20-6.05 (m, 2H, Ar), 4.50 (s, 1H, Ph-*CH*-O), 3.94 (m, 2H, CH_3-CH_2-O-CO), 1.85-0.92 (m, 10H, CH_2-*CH*Ph, CH_3-CH_2-O-CO, CO-*CH*-CH_3). ^{13}C NMR ($CDCl_3$): δ=176.7, 176.6, 162.8, 161.6, 146.0, 145.7, 145.3, 145.3, 129.7-127.4, 115.4, 107.1, 96.5, 59.9, 46.4, 45.9, 43.8, 40.4, 37.3, 37.2. FT-IR: 3513, 3026, 2981, 2912, 1731, 1680, 1601, 1492, 1452, 1370, 1181, 1072, 1028, 908, 756 cm^{-1}.

3.3.21 Graft copolymerization by photoinduced click chemistry process

A solution of PSt-B (1.2 eqiv.) P(HEMA-*co*-MMA) copolymers (1 hydroxyl eqiv.) in 2 mL CH_2Cl_2 were introduced in a quartz tube and irradiated at 300 nm for 20 h. After this time, graft copolymer firstly precipitated in hexane then reprecipitated in diethyl ether for the removing of excess polystyrene. Conversion determined by gravimetrically. Conditions and results are summarized in Table 2. ^{1}H NMR ($CDCl_3$): δ= 7.55 (br. s, 1H, Ar), 7.25-6.51 (m, 5H, Ar), 6.08 (m, 2H, Ar), 4.52 (s, 1H, Ph-*CH*-O), 4.10 (s, 4H, Ph-CO-O-CH_2, CO-O-CH_2), 3.83 (s, 4H, CH_2-OH, CH3-CH_2-O-CO), 3.58 (s, 3H, CO-O-CH_3), 1.85-0.82 (m, 24H, CH_2-CCH_3, CH_2-CCH_3, CH_3-$\mathrm{CH_2}$-O-CO, CO-*CH*-CH_3). FT-IR: 3513, 3026, 2982, 2880, 1725, 1660, 1625, 1484, 1451, 1382, 1269, 1240, 1147, 1065, 988, 840, 756 cm^{-1}.

4. RESULTS AND DISCUSSION

The main objective of this thesis is to describe novel synthetic routes for the preparation of various macromolecular structures such as block and graft copolymers. As it will be shown below, the methodology employed here is to obtain photofunctional polymeric metarials via a range of controlled polymerization methods. This strategy provides benefit of controlling molecular weight and functionality. After direct or postfunctionalization of the polymers yielded photoactive polymers with suitable chromophoric groups. In the following subsection the individual polymerization, functionalization and final photoinduced processes will be described in detail.

4.1 Macromolecular Design Based on *N*-Alkoxy Pyridinium Salts by Combination of ATRP and Photopolymerization

The posibility of incorporation of a wide range radical generating photosensitive groups into polymers has led most studies to focus on free radical polymerization. It was shown that certain alkoxy pyridinium and isoquinolinium salts as mentioned previously can act as photoinitiators for both cationic and free radical polymerization. It was demonstrated that upon exposure to ultraviolet light, these photoactive groups yield alkoxy radicals capable of initiating polymerization of a vinyl monomer such as MMA and thus forming block and graft copolymers. As it will be shown below, UV-induced process can also be used for polymer modification. When the photolysis is performed in the presence of a non-polymerizable hydrogen donor such as THF, the alkoxy radicals abstract hydrogen to give hydroxyl functions at the side chains.

4.1.1 Synthesis of block copolymer using *N*-alkoxy pyridinium ion terminated polymers

The halide chain ends of polystyrenes prepared by ATRP can easily be converted into photoactive alkoxy pyridinium and isoquinolinium salts (4-phenylpyridinium *N*-

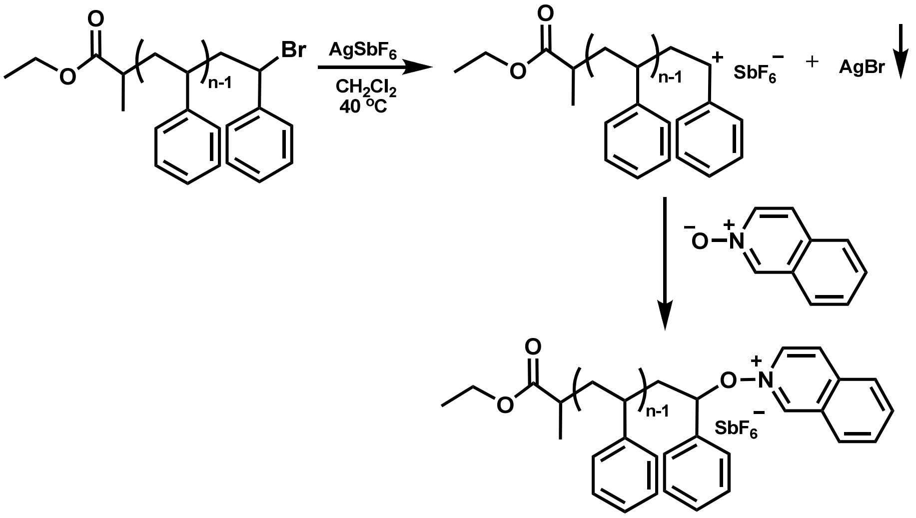
oxide (PP), isoquinolinium *N*-oxide (IQ)) with a non-nucleophilic counterion such as hexafluoroantimonate. For this purpose, mono- and dibrominated polystyrenes were prepared via ATRP in a usual manner by using mono and bifunctional ATRP initiators, respectively. The results are collected in Table 4.1.

Table 4.1 : Conditions and results of ATRP of styrene using initiators 1 and 2 in the presence of CuBr/PMDETA complex

Initiator	**[I] (mol.L^{-1})**	**Conv. (%)**	**$M_{n,theo}$ (g.mol^{-1})**	**$M_{n,GPC}$ (g.mol^{-1})**	**$M_{n,NMR}$ (g.mol^{-1})**	**M_w/M_n**	**Polymer**
1[a]	0.086	64	6850	5750	7130	1.14	PSt_1-Br
2[b]	0.043	25	2960	1830	1940	1.13	Br-PSt_2-Br

[a] In Bulk, [M]:[I]:[CuBr]:[PMDETA] = 100:1:1:1, Temperature: 110°C, Time: 55 min.
[b] In Toluene, [M]:[I]:[CuBr]:[PMDETA] = 200:1:2:2, Temperature: 90°C, Time: 60 min.
[CuBr] = 0.086M.

Benzylic salts with complex metal halide anions like SbF_6^- can easily be prepared by mixing corresponding halides with Lewis acids and using silver salt technique [230, 231]. The preparation of photoactive salts was achieved *in situ* to avoid difficulties arising from handling of the isolated polymeric benzylic salts. The reaction was accompanied with the precipitation of AgBr. The overall reaction is illustrated below for the example of polymeric *N*-alkoxy isoquinolium salt (reaction 4.1).



(4.1)

The structure of polystyrenes, carrying *N*-alkoxy pyridinium ions, was investigated by spectral methods (^{1}H NMR and UV). As can be seen from Figure 4.1, the characteristic protons originating from the polystyrene chains appear in both spectra. The molecular weights of starting polystyrenes were calculated by using the ratio between proton at the chain end (a proton in Figure 4.1a) to aromatic protons from ^{1}H NMR spectra. The shifting of the peak from 4.38 ppm (a proton in Figure 4.1a) to

5.09 ppm (c proton in Figure 4.1b) of the proton located in the α-position of the chain end is a clear indication of the functionalization. The aromatic protons of isoquinolinium group appeared at 7.61-8.81 ppm (Figure 4.1b).

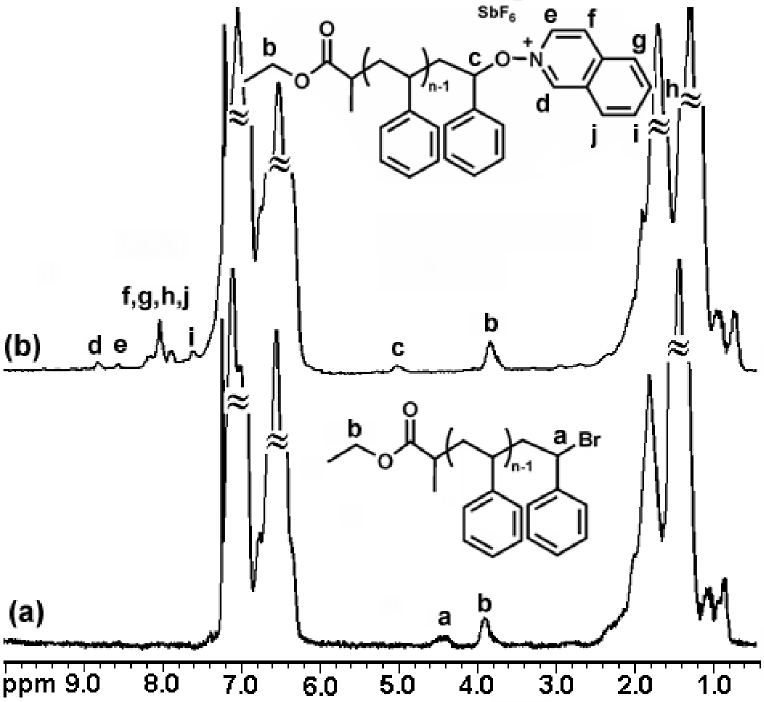


Figure 4.1 : ^{1}H NMR spectra of PSt$_1$-Br (a) and its polymeric *N*-alkoxy isoquinolinium salt (b).

More evident changes appear in UV spectra of pyridinium ion terminated polymers as compared to the precursor polymers. All salts possess similar absorption spectra characteristic to the corresponding low molar mass analogous with maximum at 314 and 342 nm for 4-phenylpyridinium and isoquinolinium ions, respectively. In this connection, it should be pointed out that the respective *N*-oxides in the functionalization step was deliberately chosen so as to achieve an absorption at wavelengths where the polymer itself is transparent, i.e., at λ>310 nm. For example, polystyrene with simple alkoxy pyridinium terminal group would have absorbed at much lower wavelengths and as consequence, in addition to the decomposition of the salt, irradiation would have resulted in degradation of the polystyrene backbone. Alkoxy pyridinium salts undergo an irreversible photolysis leading to decomposition of the salt. This was further confirmed for all the polymeric salts by the spectral changes on UV irradiation. Representative result for the decomposition of 4-phenylpyridinium ion terminated polystyrene (PSt$_1$-PP) is shown in Figures 4.2. UV spectra were recorded after the solution had been exposed to the light of the UV lamp for subsequent intervals of 4 min each.

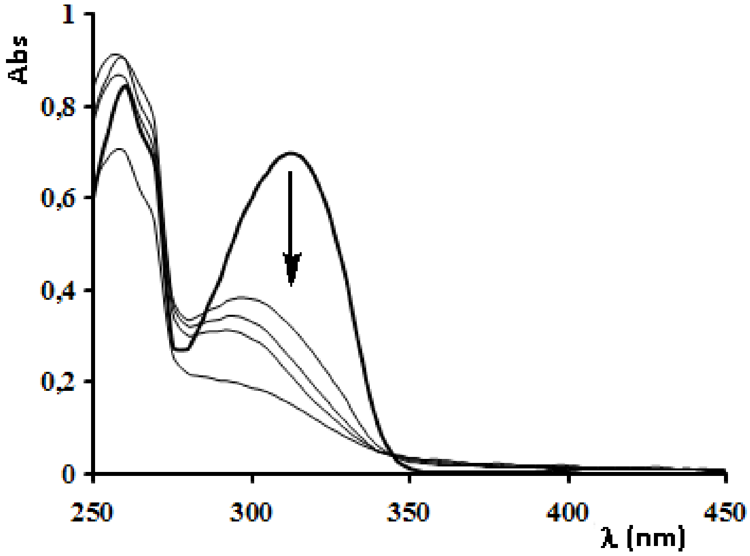


Figure 4.2 : Typical UV spectral change of PS_1-PP on irradiation at λ = 350 nm under nitrogen in CH_2Cl_2: UV spectra were taken at every 4 minute.

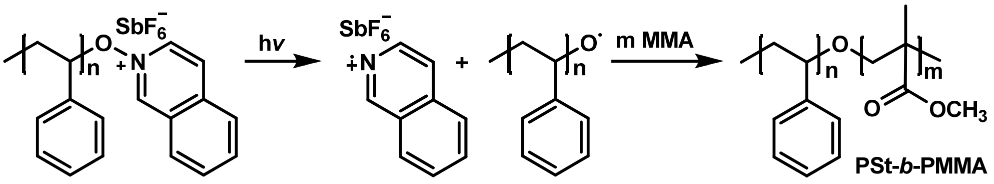
The salts were used as photoinitiators for polymerization of MMA and the results are compiled in Table 4.2.

Table 4.2 : Photoinduced block copolymerization of MMA with PSt

Macroinitiator ($M_{n,initial}$, g.mol^{-1})	Conv. (%)	$M_{n,GPC}$^{a} (g.mol^{-1})	$M_{n,NMR}$^{a} (g.mol^{-1})	Copolymer composition	
				PSt (%)	PMMA (%)
PSt_1-IQ (5890)	2.5	21190	18650	34	66
PSt_1-PP (5760)	8.1	21830	28180	22	78
IQ-PSt_2-IQ (2640)	5.5	27160	20440	7.5	92.5
PP-PSt_2-PP (1350)	5.6	45170	52040	3	97

[Macroinitiator]: 12.5mM, [MMA]: 3.92M, Time: 60 min.
[a] After irradiation.

As can be seen from Table 4.2, all salts readily initiate the polymerization. It is interesting to note that 4-phenylpyridinium ions appear to initiate the polymerization more efficiently than isoquinolinium ions. We consider that the same mechanism implies for the initiation by all of the salts, since they are structurally similar. Based on the previous studies and present results, the following mechanism for the initiation of the polymerization of MMA is suggested as illustrated for the example of isoquinolinium ion terminated polystyrene (PSt_1-IQ) (reaction 4.2).



(4.2)

In this process, the type of block copolymer greatly depends on the number of functionality of the particular salt involved in the photoinitiation step. Initiation of MMA polymerization by means of mono-functional salts is expected to yield AB type block copolymers, while bi-functional initiators give ABA type three block copolymers. By GPC analysis, the formation of block copolymer was evident as shown in Figure 4.3**,** where GPC traces recorded with the prepolymer (PSt_1-Br), PSt_1-PP and block copolymer (PSt_1-PMMA) are shown. The chromatogram of the block copolymer shows a unimodal molecular weight distribution and does not possess a peak at high elution volume corresponding to homopolymers.

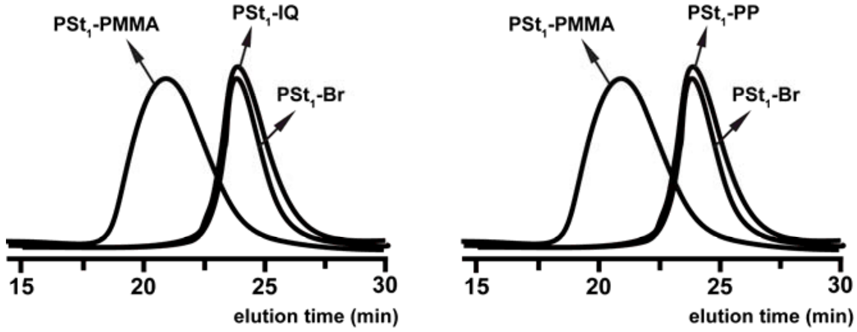


Figure 4.3 : GPC traces of intermediate products and block copolymers.

The ^{1}H NMR spectrum of the block copolymer shows the characteristic bands of both St and MMA segments and the signals corresponding to the pyridinium moiety were disappeared. Similarly, in the UV spectrum of the block copolymer the characteristic absorption band was not detected.

Although these results are preliminary in nature, they serve to indicate the efficiency and convenience of using polystyrenes obtained by simple ATRP process to introduce photochemically active chain ends into polymers. The results obtained are entirely consistent with the usual photochemical behavior of the alkoxy pyridinium salts. In addition to their use as precursors for block copolymers via a photoinduced free radical process, these salts can also initiate cationic polymerization of appropriate monomers as was demonstrated for low molar mass analogous.

Moreover, photoinduced destruction of the terminal salt structure may be useful tool to investigate chain-end interactions of polymers.

4.1.2 Synthesis of graft copolymer using *N*-alkoxy pyridinium ion functionalized polymers

Poly(styrene-*co*-chloromethylstyrene) P(St-*co*-CMS) was selected as the precursor polymer for photoactive functionalization through chloromethyl groups [232]. Thus, P(St-*co*-CMS) copolymers containing 11 and 26 mol % CMS units and PCMS were prepared via NMP of St and CMS at 125°C. Copolymer compositions of polymers were determined using ^{1}H NMR spectroscopy. The mole fractions of CMS and St were calculated from the ratio of the peak areas around 4.51 ppm, corresponding to two side-chain methylene protons of CMS to the total area between 6.58-7.42 ppm, which was attributed to the total aromatic protons. Similar method was applied for all random copolymers to calculate the mole fractions of CMS and St. The molar compositions of copolymers and number average molecular weights of P(St-*co*-CMS) and PCMS were determined by GPC which are presented in Table 4.3. It should be noted that the composition of the resulting copolymer is close to the feed composition which is in accordance to the reactivity of the monomers reported in the literature [233].

Table 4.3 : Preparation and characterization of precursor polymers

CMS content in feed (mol %)	$M_{n,GPC}$ (g/mol)	M_w/M_n	CopolymerComposition^a (mol%)		Code
			CMS	St	
10	3700	1.34	11	89	P(St-*co*-CMS)$_{11}$
25	8200	1.30	26	74	P(St-*co*-CMS)$_{26}$
100	4700	1.41	100	0	PCMS

[AIBN]= 0.0836M, [TEMPO] = 0.167M, T= 125 ^{0}C, t= 24h.
^{a}Determined by ^{1}H NMR spectra.

Phenyl pyridinium ions were successfully introduced into the preformed P(St-*co*-CMS) copolymer backbone through nucleophilic substitution of CMS units. In this connection, it should be pointed out that the 4-phenylpyridinium *N*-oxide in the functionalization step was deliberately chosen for two reasons. First, unsubstituted structure of PP, particularly at the carbon atom adjacent to nitrogen, sterically favors the nucleophilic substitution reaction. Secondly, as far as the ultimate use of the polymers is considered, it is desirable to achieve an absorption at wavelengths where the polymer itself is transparent, i.e., at λ>310 nm. For example, polystyrene with simple alkoxy pyridinium such as those derived from picoline-*N*-oxide would have absorbed at much lower wavelengths and as consequence, in addition to the decomposition of the salt, irradiation would have resulted in degradation of the polystyrene backbone. Indeed, significant changes appear in UV spectra of pyridinium ion terminated polymers as compared to the precursor polymers and the polymeric salts possess similar absorption spectra characteristic to the corresponding low molar mass analogs with maximum at 314 nm (Figure 4.4).

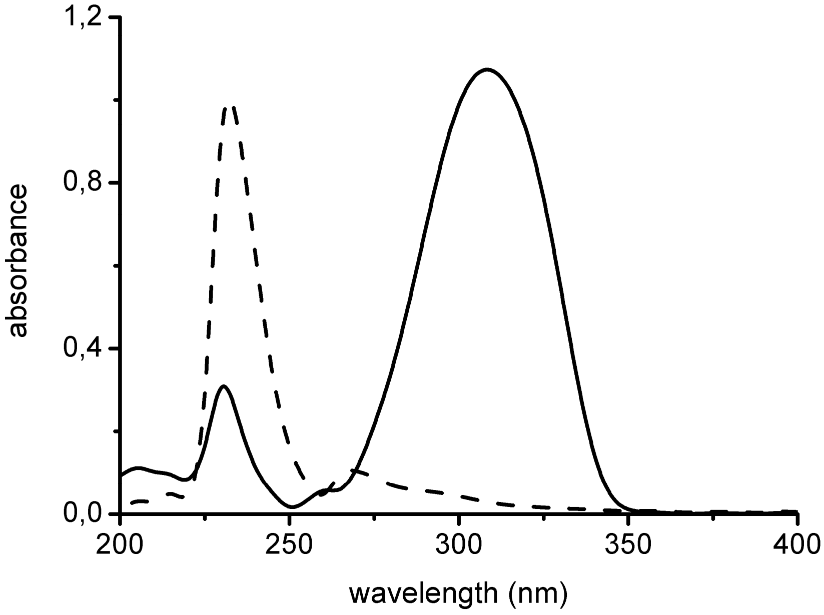


Figure 4.4 : Optical absorption spectra of P(St-*co*-CMS)$_{26}$ (dash), and (PP) (solid) in CH_2Cl_2.

Further confirmation of structural changes was obtained from ^{1}H NMR studies. As can be seen from Figure 2, the characteristic protons originating from the polystyrene chains appear in both spectra. The shifting of the peak from 4.51 ppm (a proton in Figure 4.5a) to 5.54 ppm (b proton in Figure 4.5b) of the pendant methylene protons of the chain is a clear indication of functionalization. The aromatic protons of pyridinium group appeared at 7.65-9.43 ppm. Notably, methylene protons adjacent to chloro functions were disappeared indicating a complete functionalization.

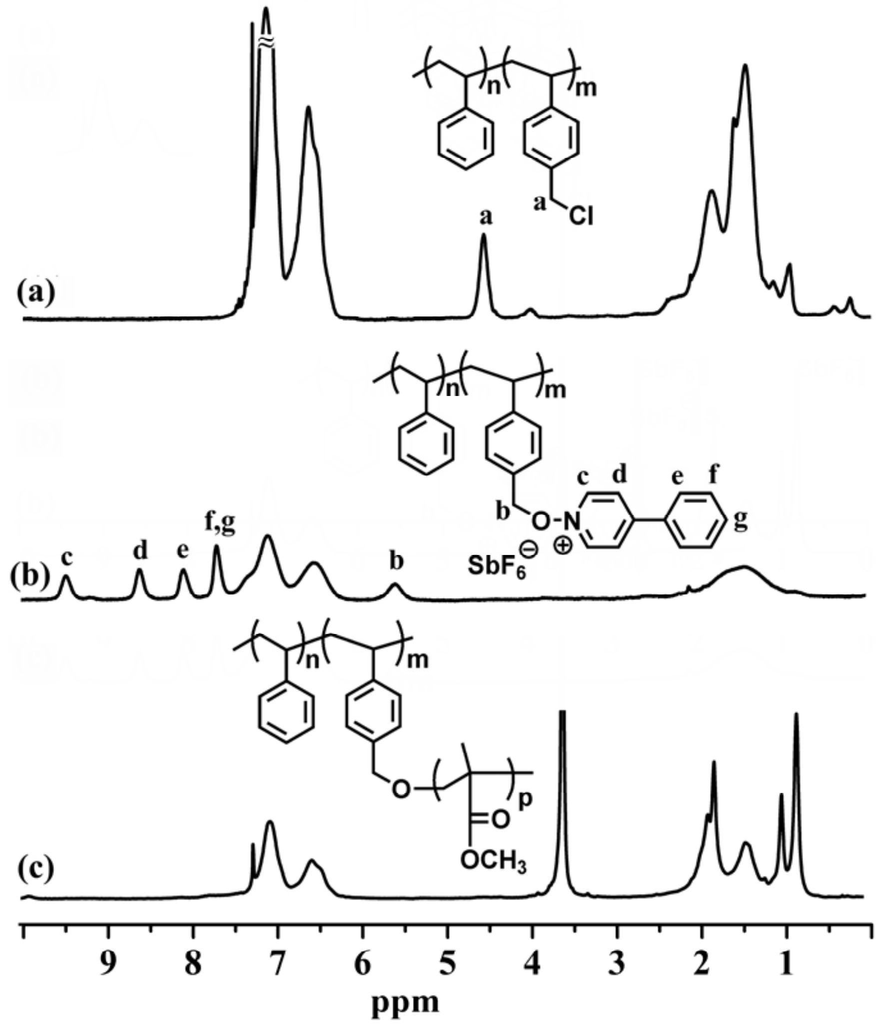
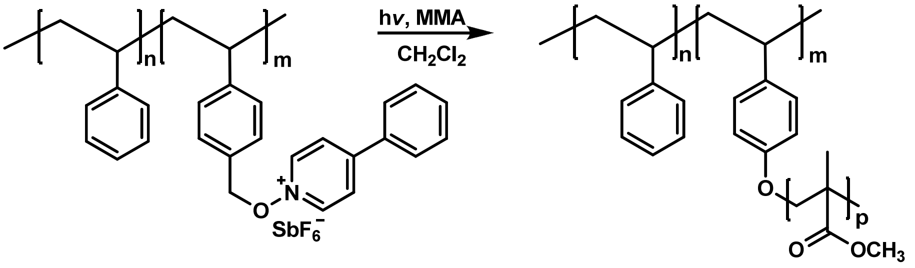


Figure 4.5 : ^{1}H NMR spectra of P(St-*co*-CMS)$_{26}$ (a), P(St-*co*-PPMS) (b) and P(St-*g*-MMA) (c) in $CDCl_3$.

In the photochemical functionalization step, precursor polymers with 11 and 26 mol % choloromethyl contents were used. Polymers with higher chloromethyl content, for example homo PCMS, were functionalized with lower efficiency and the resulting polymers were hardly soluble in common solvents. This is expected since the chemical reactivity of a function in a polymer is influenced by different factors such as steric hindrance, electrostatic, polarity and solvation effects, and specific interactions [234].

Using these polymers, graft copolymerization was then carried out by photoiniated polymerization of MMA by the side chain alkoxy radicals formed from the decomposition of pyridinium ions present in the parent copolymers (reaction 4.3). The phenylpyridinium radical cations formed concomitantly during photolysis are unreactive towards MMA as detailed laser flash photolysis studies revealed that these species can only act as cationic initiators for highly nucleophilic monomers. The radical cations undergo abstraction and consequently form phenylpyridine and protonic acid [108, 114].



(4.3)

As can be seen from Table 4.4, conversion of MMA, the molecular weights and the PMMA content of the resulting graft copolymers increased with the increasing content of the pyridinium ion in the prepolymer. It is also noted that the copolymers have broader molecular weight distributions. This is in accordance with nature of the photointiated polymerization since initiating species are generated continuously; growing polymer chains with some differences in chain lengths are present at the same time.

Table 4.4 : Photoinduced grafting of MMA

Macroinitiator	**Conv. (%)**	**Copolymer Composition**[b]		**$M_{n,GPC}$**[a] **(g.mol^{-1})**	**$M_{n,NMR}$**[b] **(g.mol^{-1})**	**M_w/M_n**[a]
		St %	**MMA %**			
P(St-*co*-PPMS)$_{11}$	56	44	56	8500	8400	1.48
P(St-*co*-PPMS)$_{26}$	79	14	86	45900	59000	1.50

[MMA] = 2.47 M, λ = 350nm, t = 1h, in 5 ml CH_2Cl_2.
[a] Determined by GPC based on polystyrene standards.
[b] Determined by ^{1}H NMR spectra.

GPC analysis of the graft copolymers compared to the P(St-*co*-CMS) starting material confirms the grafting reaction has occurred (Figure 4.6). The molar mass of the product was clearly shifted toward to a lower elution volume. This shows an increase in the molecular weight of the graft copolymers compared with those of the starting materials. Unfortunately, it was very difficult to compare with the molecular weights of the pyridinium ion functionalized polymers under identical conditions because of the unreliable retentions of the polymers arising from the interactions of the ionic groups themselves as well as with the column material. The ^{1}H NMR spectrum of the graft copolymers shows the characteristic bands of both St and MMA segments and the signals corresponding to the pyridinium moiety were disappeared (Figure 4.5c). Graft copolymer compositions were calculated from the ratio of the peak areas around 3.58 ppm corresponding to methyl protons of the MMA to the total area between 6.5 and 7.5 ppm related to the aromatic protons of St and CMS units.

Moreover, in the UV spectra of the graft copolymer the characteristic bands were not detected.

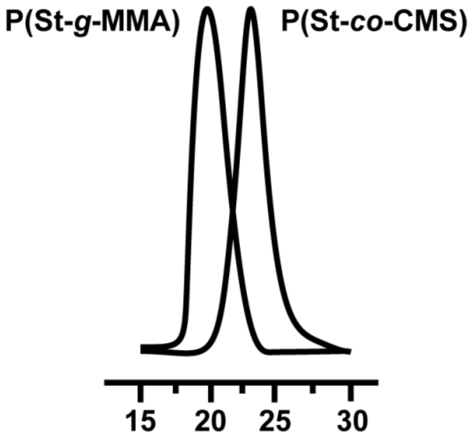


Figure 4.6 : GPC traces of P(St-*co*-CMS)$_{26}$ and P(St-*g*-MMA).

The thermal properties of the precursors and graft copolymers were investigated by DSC. As can be seen from Figure 4.7, the incorporation of ionic and bulky pyridinium functionality into the copolymer causes an increase in the glass transition temperature (T_g) from 106 ^oC to 146 ^oC. However, T_g at 137 ^oC is evident for the graft copolymer. This value is expected since the ionic groups were decomposed and PMMA segments were incorporated as a consequence of the photoinduced grafting process. An increase of T_g compare to that of the precursor polymer is probably due to the lowering of mobility.

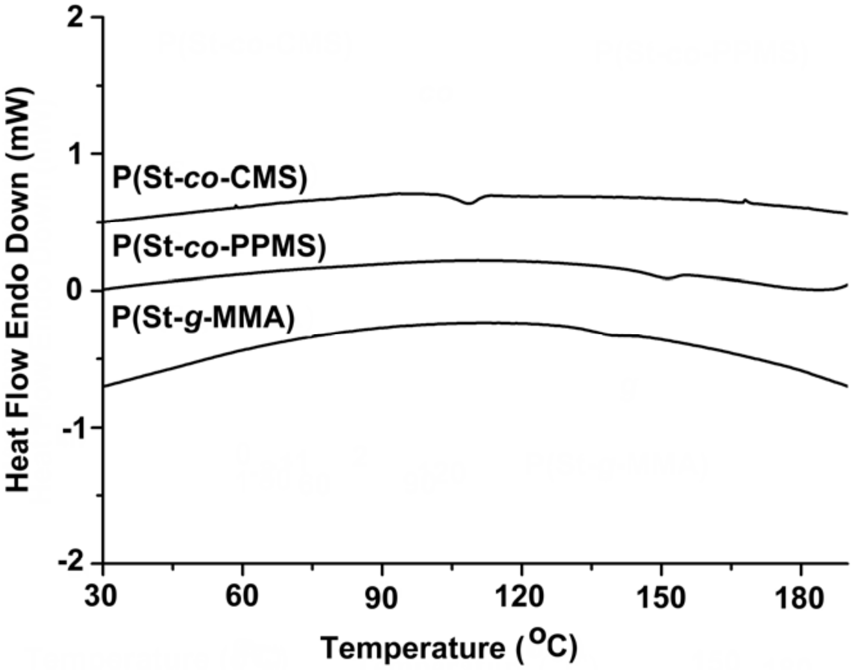
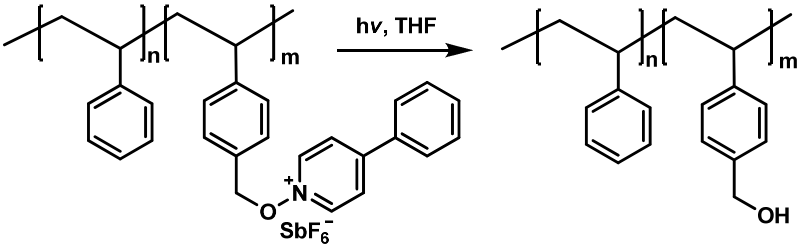


Figure 4.7 : DSC traces of P(St-*co*-CMS)$_{26}$, P(St-*co*-PPMS) and P(St-*g*-MMA).

These results serve to indicate the efficiency and convenience of using P(St-co-PCMS) obtained by simple NMP process to introduce photoactivity into the side-chains of the polymers. Photoinduced "grafting-from" technique through these groups leads to the graft copolymers. The method described here is a typical example of the mechanistic transformation approach which provides facile route to synthesis of block and graft copolymers that cannot be made by a single polymerization mode.

4.1.3 Side chain functionalization using *N*-alkoxy pyridinium ion functionalized polymers

The possibility of the use of photoinduced destruction of the salt structure for polymer modification was also considered. As has been shown earlier for in situ photoinduced polyurethane formation [132], the alkoxy radicals formed during the photolysis of *N*-alkoxy pyrdinium salts abstract hydrogen from hydrogen donors. When applied to side-chain pyridinium salts, similar hydrogen abstraction reaction is expected to occur. Indeed, upon irradiation of a solution containing P(St-co-PPMS) in THF as solvent and strong hydrogen donor, ionic groups were converted into hydroxyl groups (reaction 4.4).



(4.4)

The formation of hydroxyl functions at the side-chains was confirmed by FTIR analysis. In the spectrum of the irradiated polymer, a strong broad peak around at 3390 cm^{-1} was noted. Further evidence for the modification can be seen by the upfield shift of benzylic protons of the polymeric salt which appear at 5.54 ppm in the original polymer ^{1}H NMR spectrum (Figure 4.8a) and is shifted to 4.51 ppm in the photochemically modified polymer spectrum (Figure 4.8b). Interestingly, the addition of few drops of acetlychloride directly in the ^{1}H NMR tube facilitates the assignment of the photoinduced modification. Acetyl chloride reacts rapidly and quantitatively with hydroxyl side group to form derivatives that can be readily identified by ^{1}H NMR spectroscopy. The addition of this reagent causes a downfield shift of 0.44 ppm for the benzylic protons (Figure 4.8c).

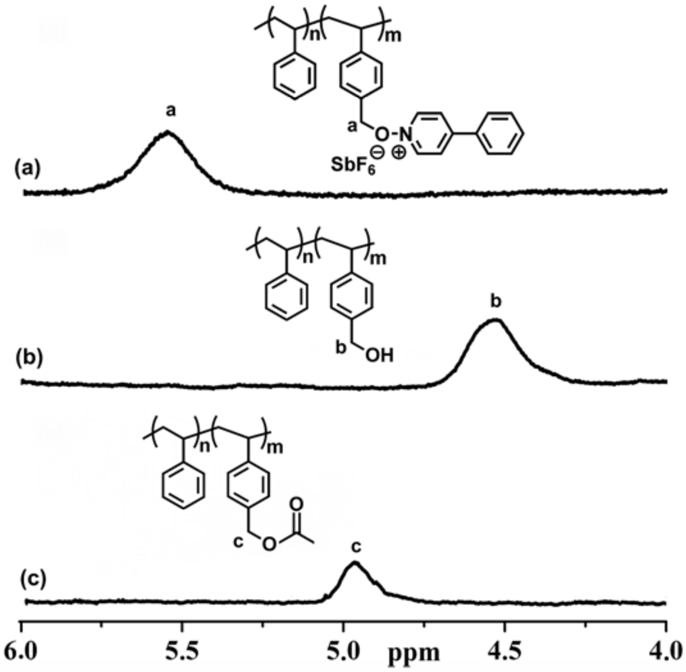


Figure 4.8 : ^{1}H NMR spectra of P(St-*co*-PPMS) (a) its irradiated form after photolysis in the presence of THF at 350 nm and (b) after addition of acetyl chloride (c).

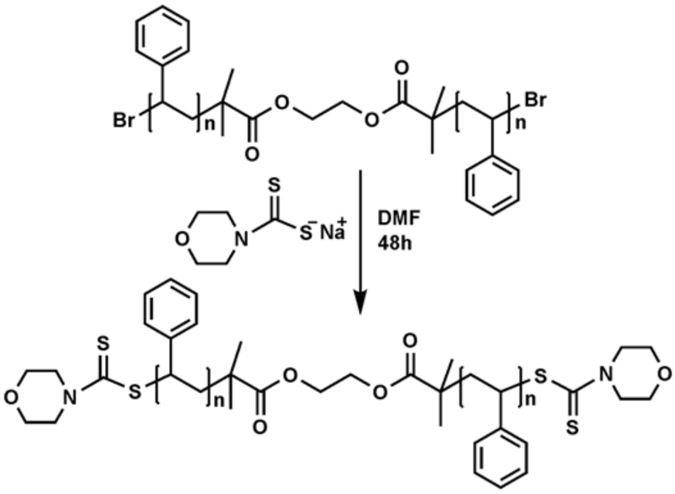
In addition to their use as precursors for graft copolymers, these polymeric salts can also yield polymers carrying hydroxyl functions at the side chain by a simple photoinduced process. The resulting structures are available for further chemical modification. For example *in situ* modification can simply be achieved by performing photolysis in the presence of functional isocyanates or acid chlorides which are known to be highly reactive towards hydroxyl groups. Thus, these novel photoactive polymers have the unique feature of being reactive not only for photoinduced grafting but also derivatization.

4.2 Macromolecular Design Based on Morpholine-4-Dithiocarbamate Sodium Salts by Combination of ATRP and Photoiniferter

Dithiocarbamates are kind of important control agents that have been widely used in controlled free radical polymerization, such as photoiniferters and RAFT agents in thermal conditions. Recently phenacyl ester of morpholino dithiocarbamate (PMDC) was designed and synthesized which acted as both photoiniferter and RAFT agent in controlled free radical polymerization [235]. Detailed polymerization and spectroscopic studies revealed that at early stages of the polymerizations, both reversible termination (iniferter) and RAFT mechanisms were operative. After PMDC is totally consumed, however, reversible termination was the dominant process in the polymerization.

4.2.1 Synthesis of block copolymers using morpholine-4-dithicarbamate terminated polymers

α-ω-Halogen end-groups of polymers, obtained by ATRP, may be altered to other functional groups by appropriate chemical reactions. Thus, polystyrene having bromine at both ends (Br-PSt-Br), obtained from ATRP by using bifunctional ATRP initiator can be converted into a photoactive morpholine-4-dithiocarbamate functional photoiniferter (MDC-PSt-MDC), by substitution reaction with morpholine-4-dithiocarbamate sodium salt ($MDC^- Na^+$) (reaction 4.5).



(4.5)

The structure of MDC-PSt-MDC was confirmed by ^{1}H NMR and UV-Vis spectral analysis. ^{1}H NMR spectrum of MDC-PSt-MDC exhibits the signals at 3.7- 4.1 ppm, attributed to methine proton next to sulfur atom and in morpholine moieties (Figure 4.9b). The disappearance of the peak corresponding to the proton located in the α-position of the chain end at 4.4 ppm (Figure 4.9a) is an additional evidence for the successful functionalization. Almost quantitative functionalization (*ca*. >96%) was attained as evidenced by the comparison of the intensities of integrals belonging to protons of initial ATRP initiator (c protons) to that of the methine proton next to sulfur and in morpholine group (a', d, e protons).

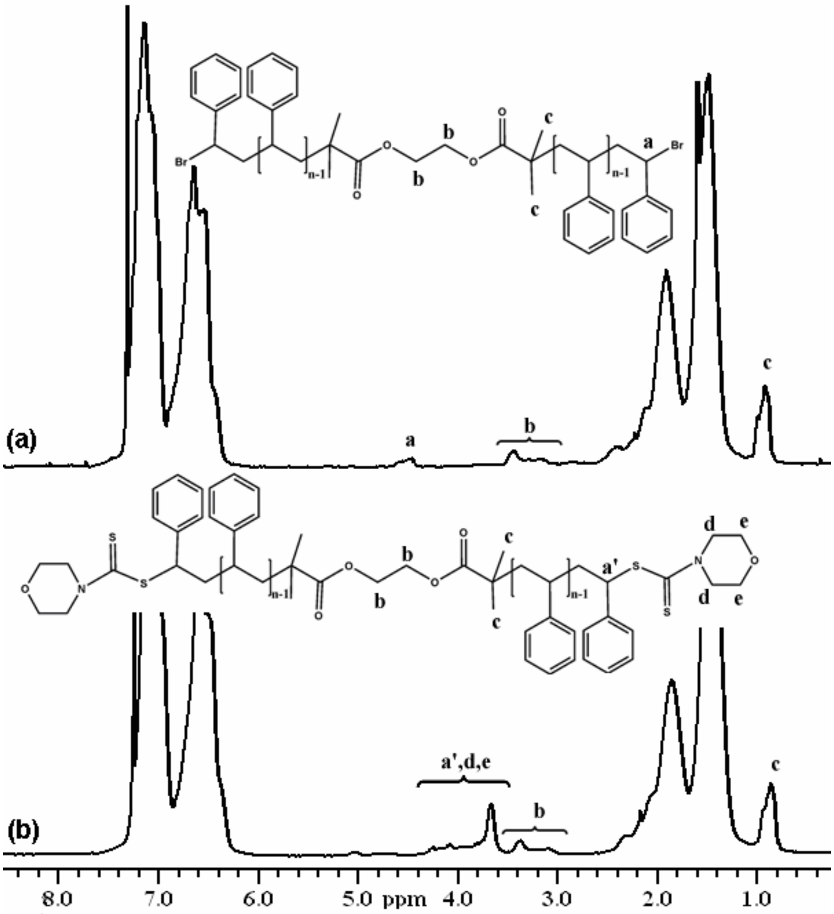


Figure 4.9 : ^{1}H NMR spectra of the Br-PSt-Br (a) and MDC-PSt-MDC (b) in $CDCl_3$.

The incorporation of morpholine-4-dithiocarbamate group at polymer chain ends was also evidenced by UV absorption measurements. Figure 4.10 shows the absorption spectra of the precursor bromo-terminated polymer and salt, $MDC^{-} Na^{+}$, and the final product, MDC-PSt-MDC. It can be seen that the polymeric photoiniferter contains the characteristic absorption band of morpholino-dithiocarbamate chromophore. In the IR spectrum of MDC-PSt-MDC, a weak absorption at 1067 cm^{-1} corresponding to a C=S group was also noted [236].

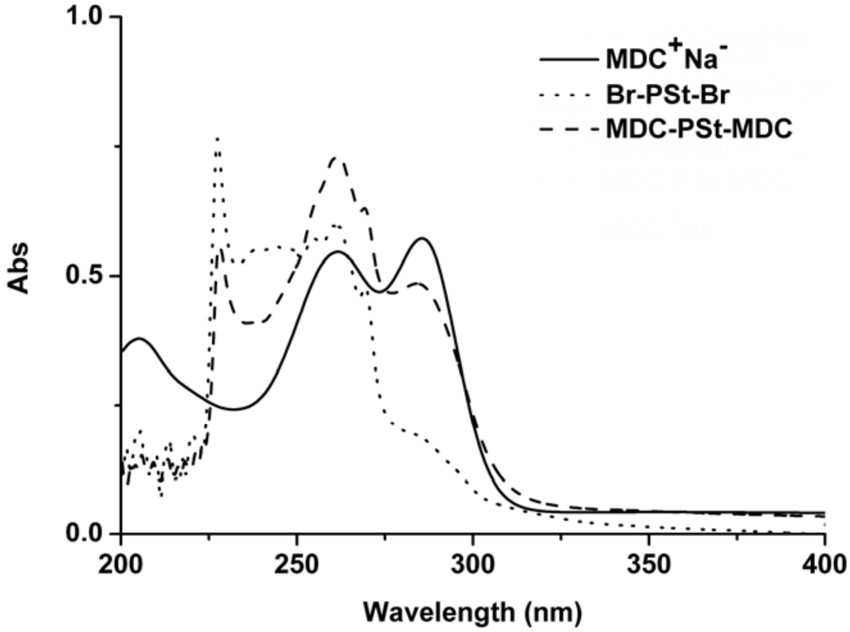


Figure 4.10 : Typical UV/vis spectra of MDC$^-$ Na$^+$, Br-PSt-Br and MDC-PSt-MDC.

Dithiocarbamate compounds are known to undergo decomposition in the absence of monomer [61]. Photoinduced decomposition of MDC-PSt-MDC was confirmed by the spectral changes on UV irradiation. Representative result for the decomposition of MDC-PSt-MDC is shown in Figure 4.11. UV spectra were recorded after the solution had been exposed to the light of the UV lamp for subsequent intervals during the 75 min.

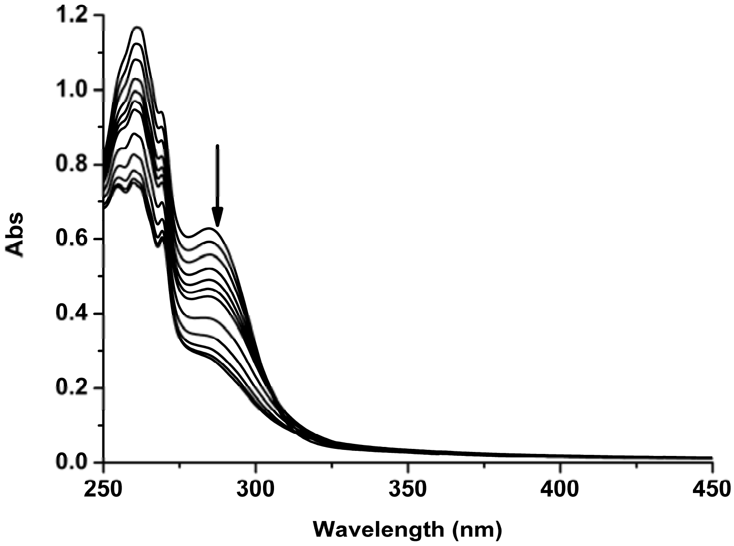
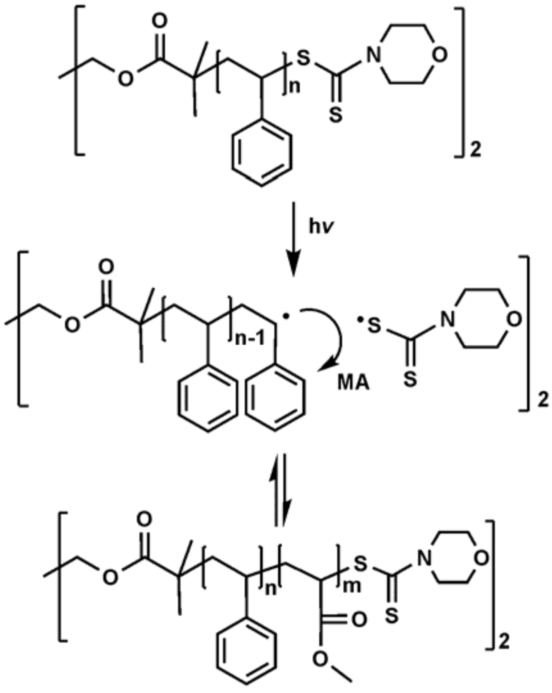


Figure 4. 11 : Typical UV/vis spectral changes of MDC-PSt-MDC on irradiation at above 300 nm under nitrogen in CH_2Cl_2: UV spectra were taken subsequent intervals during the 75 min.

The utilization of MDC-PSt-MDC as photoiniferter for block copolymerization with methyl acrylate was tested (reaction 4.6). The copolymerization of MA were performed by UV irradiation at different time intervals with MDC-PSt-MDC and $[MA]_0$ / $[MDC\text{-}PSt\text{-}MDC]_0$ mole ratio of 600:1.



(4.6)

Typical GPC profiles of these polymerization series are shown in Figure 4.12. All the GPC curves show a unimodal distribution and the elution peaks shift to the high-molecular weight-side increasing with reaction times.

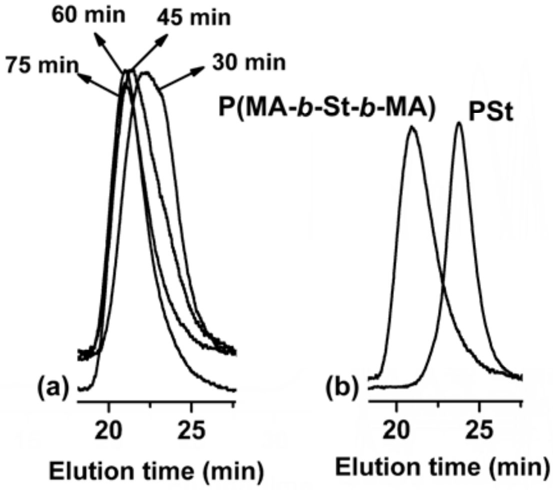


Figure 4. 12 : GPC traces for block copolymers obtained at different time interval ($[MDC\text{-}PSt\text{-}MDC]_0/[MA]_0 = 1/600$) (a) and comparision of resulting block copolymer after prufication with precursors (b).

Moreover, the copolymerization results are listed in Table 4.5. Theoretical number-average molecular weight, $M_{n,th}$, is calculated according to Equation 4.1.

$$M_{n,th} = \text{conv \%} \times ([MA]_0 / [MDC\text{-}PSt\text{-}MDC]_0) + M_{MDC\text{-}PSt\text{-}MDC} \qquad \textbf{(Eq:4.1)}$$

$M_{MDC\text{-}PSt\text{-}MDC}$ is the molecular weight of the polymeric photoiniferter. $M_{n,th}$ values are in good agreement with $M_{n,GPC}$ values, which further verifies the controlled character of the polymerization.

Table 4.5 : Polymerization conditions and results of MA polymerized under the UV irradiation using MDC-PSt-MDC as a macrophotoinitiator ($M_{n,th}$:5820, $M_{n,GPC}$:6330 M_w/M_n: 1.17)

No	Time (min)	Conv.[a] (%)	$M_{n,th}$[b]	$M_{n,GPC}$[c]	M_w/M_n[c]
1	30	7	9800	10100	1.53
2	45	20	16400	14800	1.48
3	60	26	19800	19800	1.42
4	75	25	19100	19700	1.41

[a] Determined by gravimetricaly.
[b] Calculated according to Equation (1).
[c] Determined by GPC based on polystyrene standard.

The controlled block copolymerization mechanism [61] is supported by the following evidences: first order kinetics up to 25 % of conversion shown in Figure 4.13 demonstrate that the concentration of chain radicals remains constant during polymerization, a linear relationship between molecular weight and conversion was observed (see Figure 4.14), and the molecular weight is controlled by the molar ratio of monomer consumed and photoiniferter used.

At the later stages of the polymerization, deviations from the first order kinetics and theoretical molecular weights increase take place. A possible reason for this observation might be the occurrence of the deactivation of chain-ends and termination reactions, which are more pronounced at higher monomer conversions.

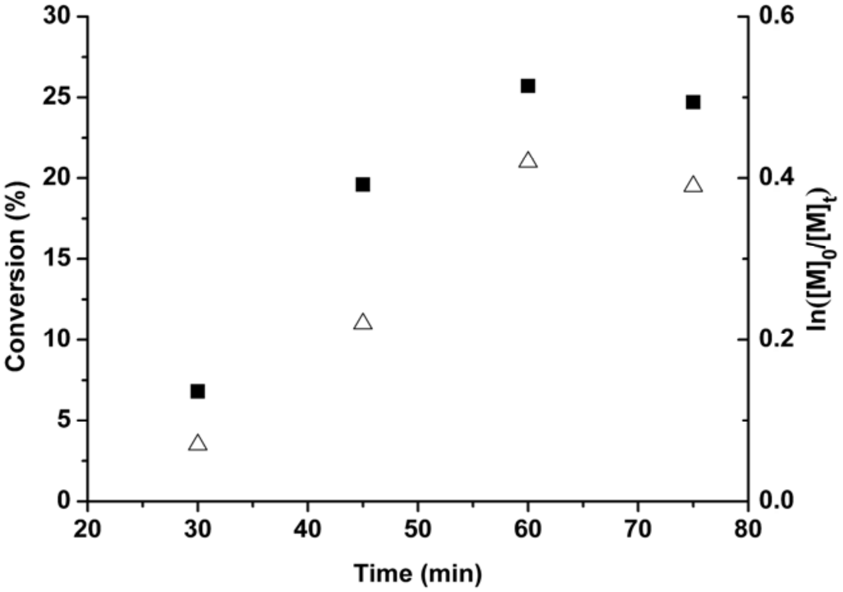


Figure 4.13 : Plots of (■) the monomer conversion and (Δ) ln($[M]_0/[M]_t$) versus the polymerization time ([MA] = 3.5 mol L-1, $[MA]_0$/$[MDC\text{-}PSt\text{-}MDC]_0$ = 600:1, λinc. > 300 nm, I = 6 x 10^{-3} mW cm^{-2}).

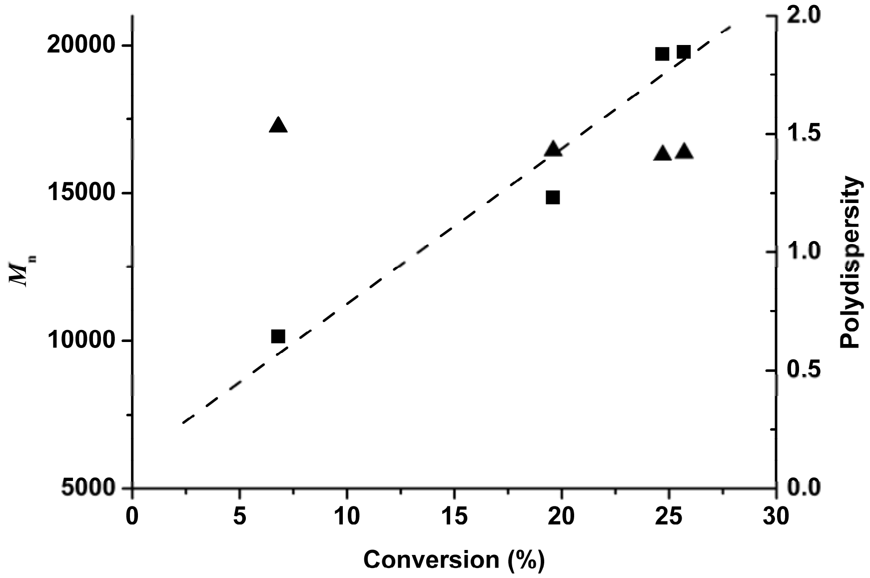


Figure 4.14 : Plots of GPC experimental (■) and theoretical (- -) polymer molecular weight (M_n) values and (▲) polydispersity (M_w/M_n) values versus the monomer conversion (experimental deteails are the same as given in Figure 4.13).

It was of interest whether polymerization proceeded also via RAFT mechanisms. We performed polymerization of MA using a conventional photoinitiator with MDC-PSt-MDC as a macro RAFT agent. In this case, initiating radicals are produced from the added photoinitiator and MDC-PSt-MDC was expected to act only as a RAFT agent. In the experiment, the absorbance of MDC-PSt-MDC was prevented by using a filter solution (see experimental). Thus, polymerization of MA by using 2, 4, 6-trimethylbenzoyl) diphenylphosphine oxide (TMDPO) as long wavelength absorbing photoinitiator in the presence of MDC-PSt-MDC under similar experimental conditions yields polymer with 30 % conversion and 1.7 polydispersity. The broader molecular weight distribution obtained indicates less controlled polymerization state when the light is absorbed by the added photoinitiator. These results indicate that either propagating radicals formed from the photoinitiator do not react with dithio groups in a manner similar to classical RAFT process or the propagating radicals are less reactive with MDC-PSt-MDC than with other RAFT agents.

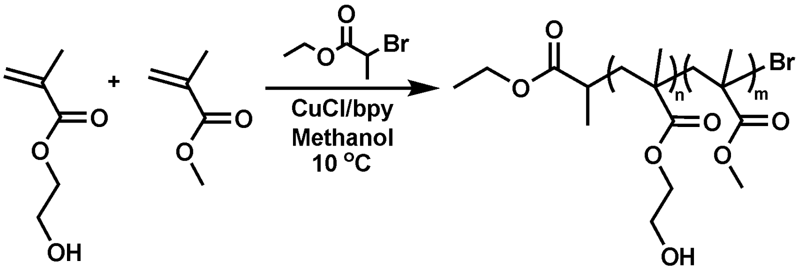
Mechanistic transformation from ATRP to photoiniferter process can be achieved by taking advantage of end-group modification of polymers obtained by ATRP. Well-defined block copolymers of St and MA were synthesized using polystyrene with morpholino-4-dithiocarbamate end-groups as a photoiniferter under UV irradiation at ambient temperature. The living character of this polymerization was confirmed by both the linear tendency of molecular weight evolution with conversion.

4.3 Macromolecular Design Based on Benzodioxinone by Combination of ATRP and Photopolymerization

Functionalized salicylate esters can be readily prepared by a photochemical acylation process by using benzodioxinones [237] in the presence of alcohols and phenols. Upon irradiation of benzodioxinones, ketene and the corresponding ketone are formed concomitantly. The intermediate ketene readily reacts with the alcohol present in the solution to yield salicylate ester. In here, this simple chemical reaction was used as an efficient synthetic methodology for the preparation of graft copolymers.

4.3.1 Synthesis of graft copolymer using poly(hydroxyethyl methacrylate-co-methyl methacrylate) and benzodioxinone terminated polystyrene

Benzodioxinone photochemistry for photoinduced grafting was used by taking advantage of chemoselective reactions of ketene intermediates towards hydroxyl groups. Thus, statistical linear copolymers of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) were prepared by ATRP at 10 °C in methanol by using ethyl-2-bromopropionate and CuCl/2,2'-bipyridine as initiator and catalyst, respectively (reaction 4.7). This monomer couple and feed ratio were selected because of the absorption characteristics and solubility of the resultant polymer. HEMA acted as the side chain functional monomer possessing antagonist hydroxyl functionality. The experimental conditions and results are presented in Table 4.6.



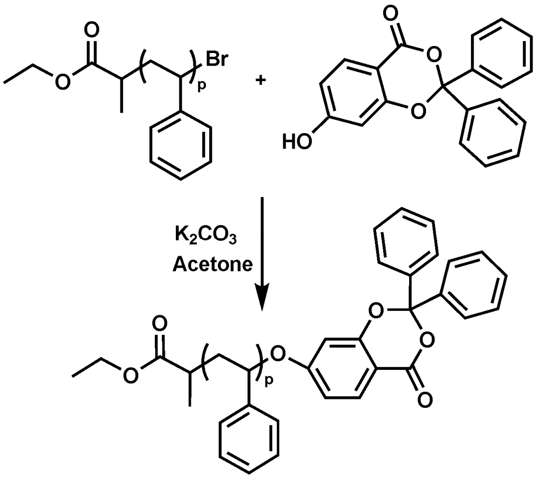
(4.7)

Table 4.6 : Conditions[a] and results for the synthesis of poly(hydroxyethyl methacrylate-co-methyl methacrylate) (P(HEMA-co-MMA))

Code	Time (h)	Conv.[b] (%)	$F_{HEMA/MMA}$[c] (mol %)	M_nGPC[d] (g/mol)	M_w/M_n[d]	N_{OH}[e]
P(HEMA-co-MMA)-1	15	66	19.6	8610	1.26	12.9
P(HEMA-co-MMA)-2	5	30	19.0	4290	1.30	6.3

[a] Feed ratio of HEMA/MMA : 2 mL / 7.22 mL (20/80 mol %) in methanol, [M]/[I]/[CuCl]/[bpy]: 90/1/1/2.5, Ethyl-2-bromopropionate was used as an initiator, temperature: 10°C.
[b] Determined by gravimetrically.
[c] Calculated by using ^{1}H NMR spectra.
[d] Determined from GPC measurements based on polystyrene standard. M_n: The number average molecular weight, M_w: The weight average molecular weight.
[e] Number of HEMA unit in copolymer was calculated by using ^{1}H NMR spectra and GPC results.

Photochemically active benzodioxinone functional polystyrene (PSt-B) was synthesized independently by a consecutive two-step procedure. The ATRP of styrene using the CuBr/PMDETA catalytic system provided a precursor polymer with a terminal halide group. As the functionalized polystyrene was intended to be used in a further photoinduced reaction, the conditions of ATRP (low temperature, high concentration of initiator - 0.85 M and short reaction time - 46 minutes) were chosen for obtainment a low molecular weight polymer, combined with a satisfactory conversion (32 %) and polydispersity (M_w/M_n : 1.08). Moreover, the agreement of the theoretical molecular weight ($M_{n,th}$: 3500) with the measured one ($M_{n,GPC}$: 3470) indicate the well-defined structure of the precursor polymer. Subsequent etherification with 7-hydroxy-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one (HDPD) in acetone by using K_2CO_3 yielded the desired polystyrene bearing terminal benzodioxinone group with 93% functionalization efficiency as determined by ^{1}H NMR analysis. The overall process is depicted in reaction 4.8.



(4.8)

The spectral data (NMR, FT-IR, UV spectroscopy) proved the presence of benzodioxinone functional group in the structure of polymer. The presence of aromatic protons belonging benzodioxinone moiety appear very clear at 6.05 and 7.51 ppm in the ^{1}H NMR of the polymer (Figure 4.15a). Successful functionalization was also evidenced by UV absorption measurements. Figure 4.16 shows the absorption spectra of PSt-B obtained, together with precursor PSt-Br and HDPD. It can be seen that PSt-B has spectra which is typical for benzodioxinone chromophore absorbing strongly in far UV and possessing an absorption maximum of the n $\rightarrow$ π^* transition around 320 nm. Thus, PSt-B is suitable for use in the subsequent photolysis at above 300 nm since the polystyrene itself does not absorb strongly in this region.

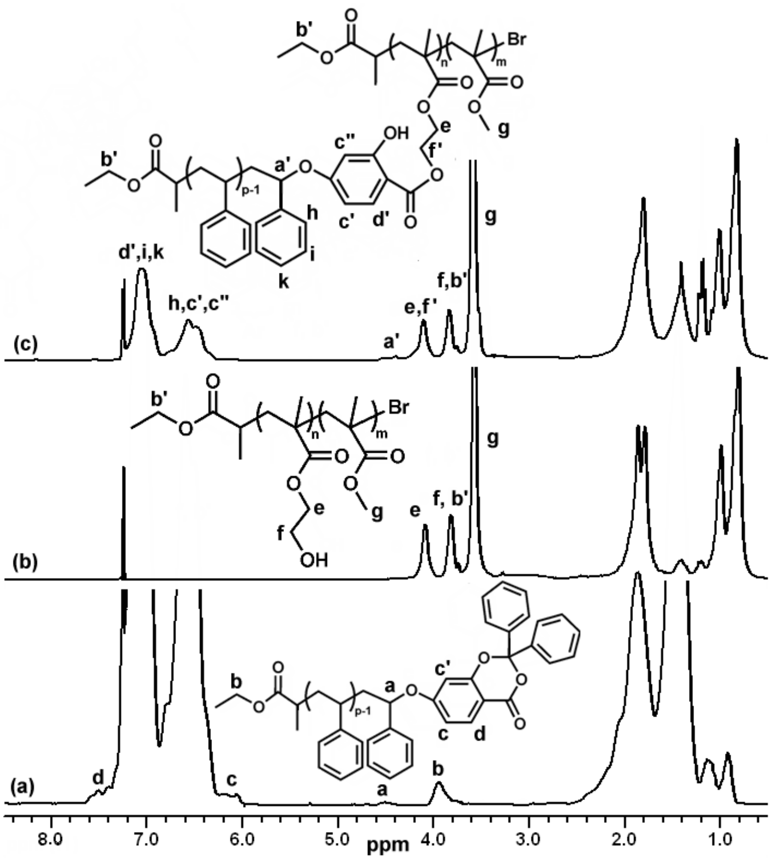


Figure 4.15 : ^{1}H NMR spectra of benzodioxinone terminated polystyrene (PSt-B) (a), poly(hydroxyethyl methacrylate-co-methyl methacrylate) (P(HEMA-co-MMA)-1) (b), and P(HEMA-co-MMA)-g-PSt graft copolymer (G1) (c) in $CDCl_3$.

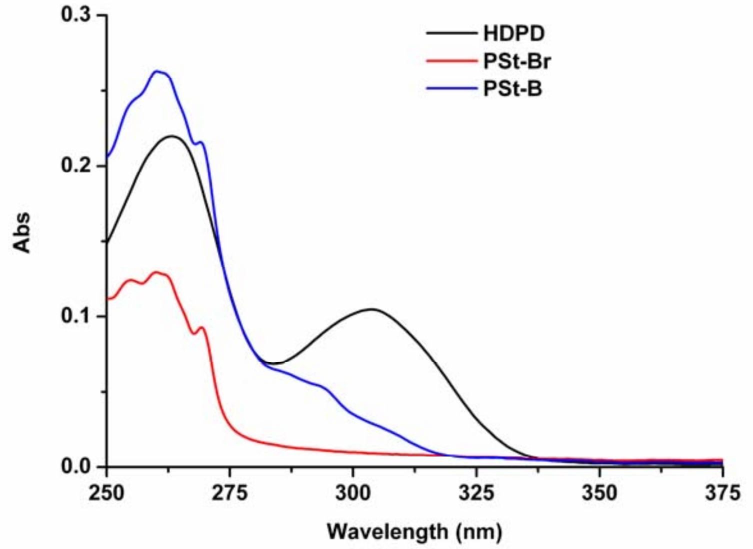
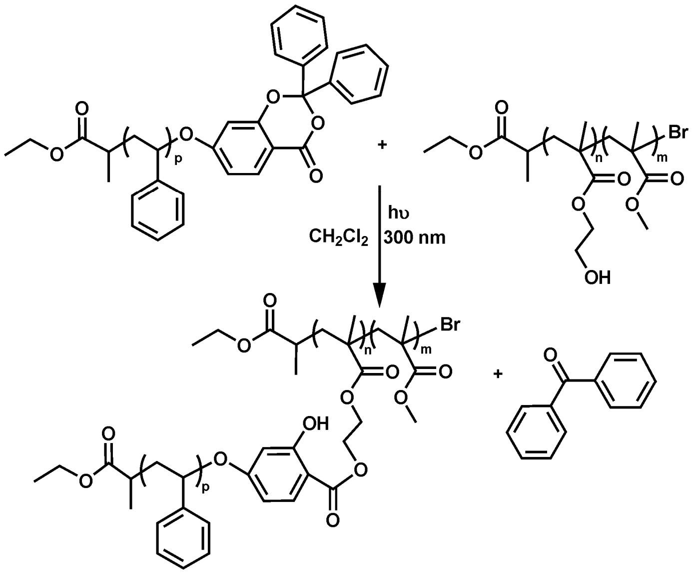


Figure 4.16 : Optical absorption spectra of benzodioxinone (HDPD), polystyrene (PSt-Br), and benzodioxinone terminated polystyrene (PSt-B) at same concentration (5.3 x 10^{-5} mol L^{-1}) in CH_2Cl_2.

As will be described below, the photoinduced esterification reaction utilizing polymers with antagonist functional groups, i.e., benzodioxinone and hydroxyl groups, leads to the formation of well-defined graft copolymers, with controlled chain lengths as both main- and side-chain segments were prepared by ATRP. The general process is presented in reaction 4.9.



(4.9)

In this process, first photoinduced decomposition of benzodioxinone proceeds via releasing of benzophenone to give ketene functionality at room temperature. Then, efficient nucleophilic reaction of the ketene and copolymers with pendant hydroxyl units resulted in the expected well-defined graft copolymers. The, byproduct, benzophenone is soluble in hexane, which is the precipitating solvent. The results are summarized in Table 4.7. Overall grafting efficiency ($X_{grafting}$) for the graft copolymer was calculated by a following equation:

$$X_{grafting} = (I_{aromatic} \times 3DP_{n,MMA} / I_{aliphatic\,(OCH3)} \times 5\ DP_{n,St}) / N_{OH} \times 100 \qquad \textbf{(Eq:4.2)}$$

where $I_{aliphatic}$ and $I_{aromatic}$ are integrated values of the sum of OCH_3 protons of P(HEMA-*co*-MMA) and the aromatic protons of PSt, respectively. N_{OH} is the number of the OH groups in the backbone polymer. Additionally, calculation from the ratio of aliphatic protons of HEMA moiety after grafting to that of unreacted ones (I_e+$I_{f'}$/I_e+$I_{f'}$+I_f+$I_{b'}$) gave the same grafting efficiency.

As can be seen from Table 4.7, the molecular weight of the precursor polymer (main chain) influenced the molecular weight of the resulting graft copolymer while the overall conversion and grafting efficiency did not change significantly. The moderate grafting efficiency could be attributed to the steric hindrance and the photoactivity of the benzophenone released from benzodioxinone. At the later stages of photolysis, the absorption of benzodioxinone moiety may be screened by benzophenone which absorbs the light at similar wavelengths. Attempts to prepare benzodioxinones releasing ketones either with no absorption or absorbing at different wavelengths than the initial benzodioxinone are under progress. The highest graft efficiency was about 58 % in our photoinduced system. However, this value should not be underestimated as only slightly higher graft efficiencies were attained with the well-known azide-alkyne click reaction [238-240]. Evidence for the formation of ester adduct of the resulting P(HEMA-*co*-MMA)-*g*-PSt graft copolymer was observed in the ^{1}H NMR spectra. In the ^{1}H NMR spectrum of the graft copolymer (Figure 4.15c), the resonance of terminal CH protons of polystyrene chain was observed 4.52 ppm and the presence of characteristic main chain PMMA and side-chain PSt provided direct evidence for the successful coupling. The broadening and shifting of the peaks corresponding to methylene protons was also noted. The GPC traces of the starting materials and the graft copolymer are presented in Figure 4.17. The shift of PSt-B and P(HEMA-*co*-MMA) precursors to higher molecular weight region revealed that the formation of P(HEMA-*co*-MMA)-*g*-PSt by photoinduced coupling reaction was achieved efficiently.

Table 4.7 : Conditions[a] and results for the synthesis of P(HEMA-co-MMA)-g-PSt graft copolymers

Code	**Initial Polymer**	**Yield[b] (%)**	**M_nGPC[c] (g/mol)**	**M_w/M_n[c]**	**$X_{grafting}$[e] (%)**	**Thermal Properties[f]**	
						$T_{g(HEMA\text{-}co\text{-}MMA)}$	**T_{ggraft}**
G1	**P(HEMA-*co*-MMA)-1**	52	19600	1.33	58	79.0	86.4
G2	**P(HEMA-*co*-MMA)-2**	40	11480	1.30	45	76.5	-[g]

[a] Polymerization carried out in CH_2Cl_2 at 300 nm for 20h at room temperature with [PS-B]/[OH] : 1.2/1 mol ratio; $M_{nGPC,PS\text{-}B}$: 4130, M_w/M_n:1.07.

[b] Yield was determined gravimetrically after purification.

[c] Determined from GPC measurements based on polystyrene standard. M_n: The number average molecular weight, M_w: The weight average molecular weight.

[e] Grafting efficiency was calculated from ^{1}H NMR spectra by using equation 1.

[f] The glass transition temperature (T_g) of polymers were determined by using DSC. T_g of PSt-B was determined as 92.0 °C.

[g] The glass transition temperature (T_g) of graft copolymer G2 was not determined.

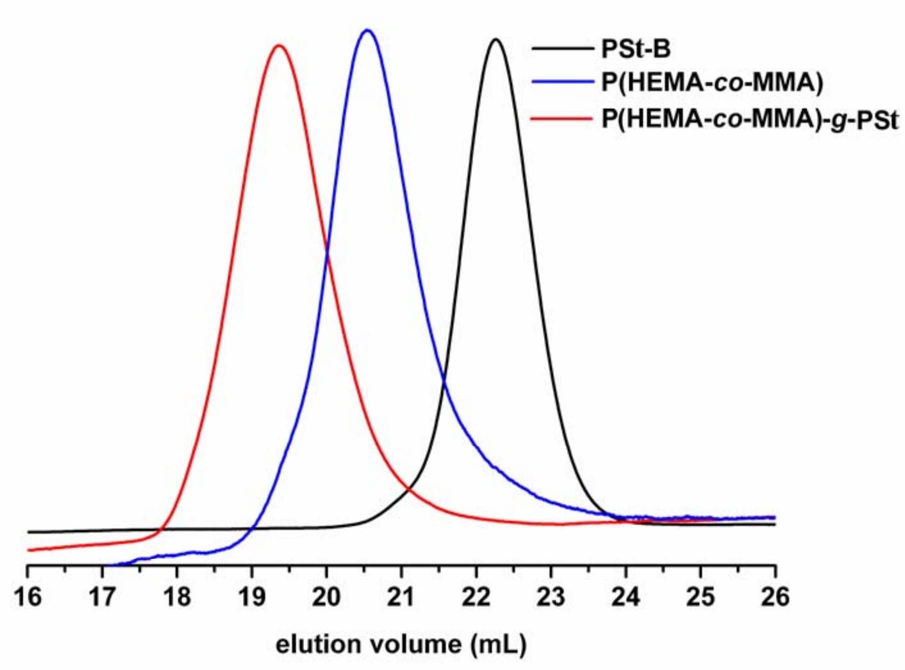


Figure 4.17 : GPC traces of benzodioxinone terminated polystyrene (PSt-B), poly(hydroxyethyl methacrylate-*co*-methyl methacrylate) (P(HEMA-*co*-MMA)-1), and P(HEMA-*co*-MMA)-*g*-PSt graft copolymer (G1).

The precursor polymers and the final graft copolymer were also analyzed by FT-IR spectroscopy and expected structures were confirmed. As can be seen from Figure 4.18, the carbonyl band at 1680 cm^{-1} corresponding to the dioxinone ring at the end of the polystyrene (Figure 4.18a) was detectable. After the photolysis, the graft copolymer exhibits new bands at 1625 and 1660 cm^{-1} attributed to intra-molecular hydrogen bonded carbonyl group (Figure 4.18c). Additionally, broadening of the band at about 3500 cm^{-1} belonging to both phenolic and aliphatic hydroxyl groups was noted.

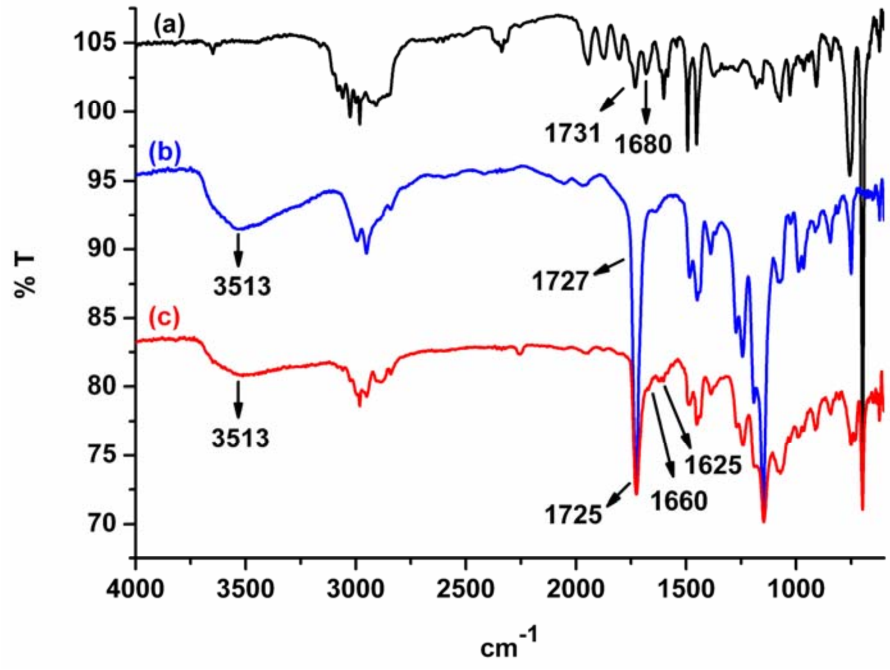


Figure 4.18 : FT-IR spectra of benzodioxinone terminated polystyrene (PSt-B) (a), poly(hydroxyethyl methacrylate-co-methyl methacrylate) (P(HEMA-*co*-MMA)-1) (b), and P(HEMA-*co*-MMA)-*g*-PSt graft copolymer (G1) (c).

Glass transition temperatures (T_g) of the polymers determined by DSC measurements are tabulated in Table 4.7. The parent polymers P(HEMA-*co*-MMA)-1 and P(HEMA-*co*-MMA)-2 showed T_g values at 79.0 ^oC and 76.5 ^oC, respectively. T_g of the pristine PS-B was determined to be at 92.0 ^oC. The graft copolymer G1 showed a single T_g at 86.4 ^oC between those of P(HEMA-*co*-MMA)-1 and PSt-B indicating miscibility at these low molecular weights. A control experiment with a blend of P(HEMA-*co*-MMA)-1 and PSt-B confirmed the miscibility. While the first heating showed two T_g values at 74.8 ^oC and 91.0 ^oC, there was only a single T_g at 86.3 ^oC after the second heating. The lower molecular weight graft polymer G2 similarly showed miscibility of parent polymer P(HEMA-*co*-MMA)-2 and PSt-B and it was not possible to determine a clear T_g value.

Figure 4.19 shows the AFM images of the parent polymers P(HEMA-*co*-MMA)-1 and P(HEMA-*co*-MMA)-2 together with the graft copolymers G1 and G2. The parent polymer P(HEMA-*co*-MMA)-1 (Figure 4.19a) had very smooth surface topography typical of single phase amorphous polymers. Any phase contrast could not be observed (Figure 4.19b) which indicates the same type of material throughout the film. The surface topography of the graft polymer G1 (Figure 4.19c) showed 2-3 nm high, 50-60 nm wide circular regions. These regions also showed contrast in the phase images (Figure 4.19d) and thus can be attributed to the grafted PSt side chains of the parent polymers. Although DSC measurements showed only a single glass transition in the bulk for the grafted polymer G1, the observed circular regions could be induced by the interface effects, namely the surface segregation of lower surface energy PS. The height of 2-3 nm is consistent with the molecular weight of the grafted PS chains. The PS regions persisted even after 18 hours of annealing at 110 ^{o}C. The films stayed stable after such long annealing indicating the favorable interaction of the parent polymer with the silicon oxide substrate. The parent polymer P(HEMA-*co*-MMA)-2 (Figure 4.19e) and the corresponding graft polymer G2 (Figure 4.19f) also showed similar behavior.

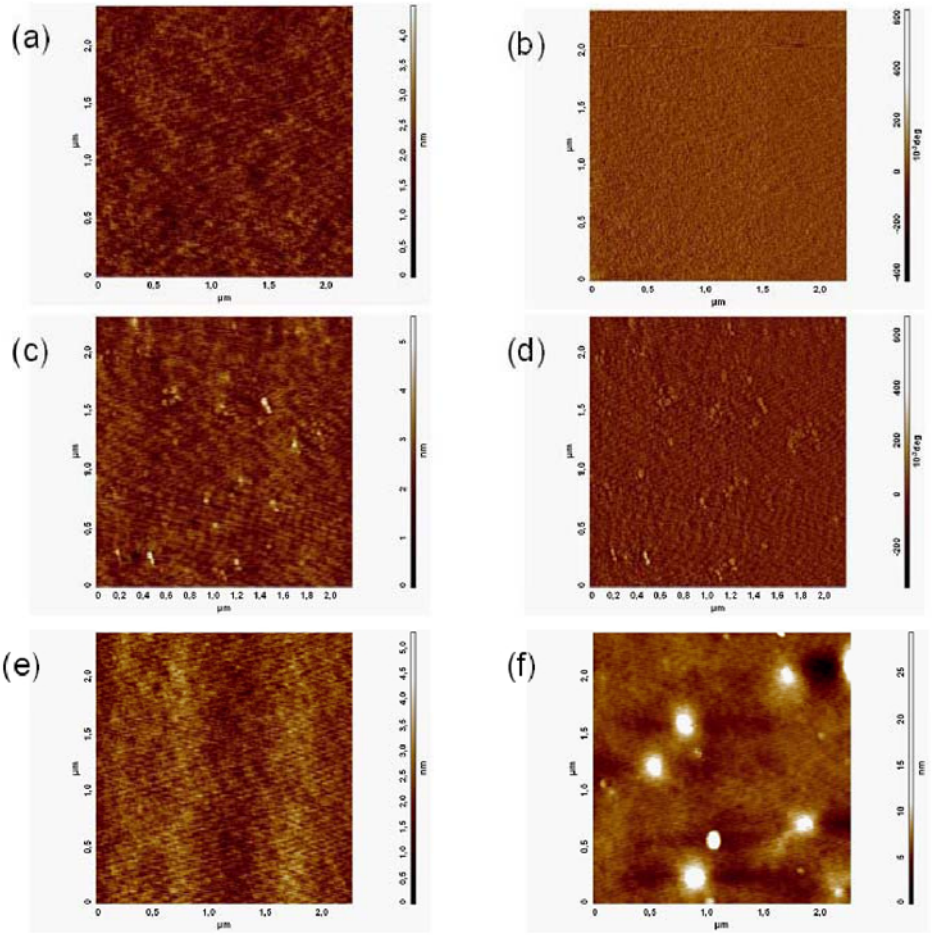


Figure 4.19 : AFM images of the polymer films on silicon oxide substrates: (a) height and (b) phase image of poly(hydroxyethyl methacrylate-co-methyl methacrylate (P(HEMA-co-MMA)-1); (c) height and (d) phase image of P(HEMA-co-MMA)-g-PSt graft copolymer (G1); (e) height image of poly(hydroxyethyl methacrylate-*co*-methyl methacrylate) (P(HEMA-*co*-MMA)-2); (f) height image of P(HEMA-*co*-MMA)-*g*-PSt graft copolymer (G2).

In summary, P(HEMA-*co*-MMA)-*g*-PSt graft copolymer with well-defined main and side chains was synthesized by the “grafting onto” method via combination of ATRP and photoinduced ester formation reaction of benzodioxinones. The hydroxyl group functionality of the main chain and the benzodioxinone functionality of the side chains were very high. The moderate graft efficiency in photoinduced click coupling reaction obtained may be due to the steric hindrance, as well as the photoactivity of the benzophenone produced concomitantly. The structure of target copolymer and intermediates were well characterized by ^{1}H NMR, GPC, UV, FT-IR, DSC and AFM. This work provided a new click route to prepare the graft copolymers which can be performed under mild conditions without requirement of any catalyst. The readily availability of the hydroxyl functionality in many synthetic and natural polymers makes this method particularly useful for polymer modification.

5. CONCLUSION

Novel synthetic routes for the preparation of various macromolecular structures such as block and graft copolymers were described in this thesis. The methodology employed here is to obtain photofunctional polymeric metarials via a range of controlled polymerization methods.

The first strategy consists of *N*-alkoxy pyridinium salts such as 4-phenylpyridinium N-oxide and isoquinolinium *N*-oxide in order to prepare blok and graft copolymer. Moreover, side chain functionalization was sucsesfully performed by using this strategy.

The halide chain ends of polystyrenes prepared by ATRP were converted into photoactive alkoxy pyridinium and isoquinolinium salts with a non-nucleophilic counterion such as hexafluoroantimonate. These photoactive polymeric salts were used as precursors for block copolymers via a photoinduced free radical process. In the photoinduced block copolymerization step, the type of block copolymer greatly depends on the number of functionality of the particular salt.

Furthermore, graft copolymers were sythesized by using *N*-alkoxy pyridinium side chain functional copolymers. Poly(styrene-*co*-chloromethylstyrene) P(St-*co*-CMS) was selected as the precursor polymer for photoactive functionalization through chloromethyl groups. It was demonstrated that upon exposure to ultraviolet light, these photoactive groups yield alkoxy radicals capable of initiating polymerization of a vinyl monomer such as MMA and thus forming graft copolymers.

Also, UV-induced process was used for polymer modification. Photolysis of photoactive precursors were performed in the presence of a non-polymerizable hydrogen donor such as THF and the alkoxy radicals abstracted hydrogen to give hydroxyl functions at the side chains.

In the second strategy, ABA type block copolymer was synthesized by combination of ATRP and photoiniferter processes. Thus, polystyrene having bromine at both ends (Br-PSt-Br), obtained from ATRP by using bifunctional ATRP initiator was converted into a photoactive morpholine-4-dithiocarbamate functional photoiniferter (MDC-PSt-MDC), by substitution reaction with morpholine-4-dithiocarbamate sodium salt ($MDC^- Na^+$).

The utilization of MDC-PSt-MDC as photoiniferter for block copolymerization with methyl acrylate was tested. The controlled block copolymerization mechanism was supported by first order kinetics up to 25 % of conversion. This results were demonstrated that the concentration of chain radicals remains constant during polymerization, and a linear relationship between molecular weight and conversion was also observed.

Synthesis of graft copolymer by combination of ATRP and photochemical acylation process by using benzodioxinone was the third strategy in this thesis. Benzodioxinone photochemistry for photoinduced grafting was used by taking advantage of chemoselective reactions of ketene intermediates towards hydroxyl groups. Thus, statistical linear copolymers of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) prepared by ATRP was used as a hydroxyl group sources.

Photochemically active benzodioxinone functional polystyrene (PSt-B) was synthesized independently by a consecutive two-step procedure. Subsequent etherification with 7-hydroxy-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one (HDPD) in acetone by using K_2CO_3 yielded the desired polystyrene bearing terminal benzodioxinone group with 93% functionalization efficiency.

Finally, by the photolysis of these two precursor polymer, P(HEMA-*co*-MMA)-*g*-PSt graft copolymer with well-defined main and side chains was synthesized by the “grafting onto” method via combination of ATRP and photoinduced ester formation reaction of benzodioxinones.

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