

ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

**SYNTHESIS OF BLOCK COPOLYMERS BY TRANSFORMATION OF
DIFFERENT POLYMERIZATION METHODS USING VISIBLE LIGHT
PHOTOLYSIS**

**M.Sc. Thesis by
Gökhan AÇIK**

Department : Chemistry

Programme : Chemistry

JUNE 2011

**SYNTHESIS OF BLOCK COPOLYMERS BY TRANSFORMATION OF
DIFFERENT POLYMERIZATION METHODS USING VISIBLE LIGHT
PHOTOLYSIS**

**M.Sc. Thesis by
Gökhan AÇIK
(509091045)**

**Date of submission : 06 May 2011
Date of defence examination: 07 June 2011**

**Supervisor (Chairman) : Prof. Dr. Yusuf YAĞCI (ITU)
Members of the Examining Committee : Prof. Dr. Niyazi BIÇAK (ITU)
Ass. Prof. Dr. M. Atilla TAŞDELEN(YU)**

JUNE 2011

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**GÖRÜNÜR BÖLGE FOTOLİZİ KULLANILARAK FARKLI
POLİMERİZASYON YÖNTEMLERİNİN DÖNÜŞÜMLERİ İLE BLOK
KOPOLİMERLERİN SENTEZİ**

**YÜKSEK LİSANS TEZİ
Gökhan AÇIK
(509091045)**

**Tezin Enstitüye Verildiği Tarih : 05 Mayıs 2011
Tezin Savunulduğu Tarih : 07 Haziran 2011**

**Tez Danışmanı : Prof. Dr. Yusuf YAĞCI (İTÜ)
Diğer Jüri Üyeleri : Prof. Dr. Niyazi BIÇAK (İTÜ)
Yrd. Doç. Dr. M. Atilla TAŞDELEN (YÜ)**

HAZİRAN 2011

FOREWORD

I would like to thank all the people who support me and made this study possible. It is a pleasant opportunity that I express my gratitude to all of them.

First, I would like to thank my supervisor, Prof. Dr. Yusuf Yağcı, for his encouragement, guidance and support. More importantly, he also educated me how to well carry out a scientific research and he also contributed to develop myself in polymer science.

I would like to express deeply my special gratitude to Muhammet Ü. Kahveci, Ali Görkem Yılmaz and Asst. Prof. Dr. M. Atilla Taşdelen. This thesis would not have been possible without the support and encouragement of them. Everytime, they guided me in many issue and helped me with them kind patience.

I wish to deeply thank to all the members of Yagci Lab for all their help, support and friendship. In particular, Yasemin Yüksel Durmaz, Kübra Demir, Mustafa Uygun, Manolya Kukut, Binnur Aydoğan, Burçin Gacal, Demet Göen Çolak, Mustafa Çiftçi, Faruk Oytun, Gamze Karagactı, Dilek Okuş, Hande Çelebi, Alev Tüzün, Halime Cengiz, Zeynep Beyazkılıç, Bahadır Gacal and Selim Beyazıt at with all of you, it has really been a great pleasure.

I also thank to my best friend Çağatay Altınkök for his kind support, help, encouragement and significantly always beeing next to me.

Finally, during all stages involved in the preparation of this thesis, I'm grateful to my family for their encouragement, understanding, patience and support all through my education.

Thank all of you very much...

May, 2011

Gökhan AÇIK

Chemist

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	vii
TABLE OF CONTENTS	vii
ABBREVIATIONS	ix
LIST OF TABLES	xi
LIST OF FIGURES	xiii
LIST OF SYMBOLS	xv
SUMMARY	xvii
ÖZET	xix
1. INTRODUCTION	1
2. THEORETICAL PART	3
2.1 Transformation Reactions	3
2.1.1 Direct transformation reactions	5
2.1.2 Indirect transformation reactions.....	6
2.2 Controlled Radical Polymerization Methods.....	7
2.2.1 Atom transfer radical polymerization (ATRP)	8
2.2.2 Nitroxide-mediated radical polymerization (NMRP).....	12
2.2.3 Reversible addition–fragmentation chain transfer process (RAFT).....	13
2.3 Photoinitiating Systems	16
2.3.1 <i>Type I</i> photoinitiators (Unimolecular photoinitiator systems)	17
2.3.2 <i>Type II</i> photoinitiators (Bimolecular photoinitiator systems).....	19
2.4 Photochemistry of Dimanganese Decacarbonyl	22
3. EXPERIMENTAL WORK	25
3.1 Materials and Chemicals	25
3.1.1 Reagents for synthesis of block copolymers	25
3.1.2 Solvents.....	25
3.1.3 Other chemicals and reagents.....	26
3.2 Equipments	26
3.2.1 Light Source	26
3.2.2 ¹ H-Nuclear magnetic resonance spectroscopy (¹ H-NMR)	26
3.2.3 Gel permeation chromatography (GPC).....	26
3.3 Preparation Methods	27
3.3.1 General procedure for atom transfer radical polymerization	27
3.3.2 General procedures for visible light radical polymerization.....	27
4. RESULTS AND DISCUSSION	29
5. CONCLUSION AND SUGGESTIONS	35
REFERENCES	37
CURRICULUM VITAE	45

ABBREVIATIONS

[Mn₂(CO)₁₀]	: Dimanganese Decacarbonyl
¹H-NMR	: Nuclear Magnetic Resonance Spectroscopy
GPC	: Gel Permeation Chromatography
CRP	: Controlled Radical Polymerization
ATRP	: Atom Transfer Radical Polymerization
VLRP	: Visible Light Radical Polymerization
RAFT	: Reversible Addition Fragmentation Chain Transfer
NMRP	: Nitroxide Mediated Radical Polymerization
SFRP	: Stable Free Radical Polymerization
PMDETA	: <i>N, N, N', N'', N''</i> -Pentamethyldiethylenetriamine
THF	: Tetrahydrofuran
DMF	: Dimethyl formamide
St	: Styrene
MMA	: Methyl methacrylate
MA	: Methyl acrylate
BA	: Butyl acrylate
VA	: Vinyl acetate
t-BMA	: <i>tert</i> -Butyl methacrylate
CL	: ε-Caprolactone
VL	: δ-Valerolactone
4-VP	: 4-Vinyl pyridine
PSt	: Polystyrene
TEMPO	: 2,2,6,6- Tetramethylpiperidine-N-oxyl
BP	: Benzophenone
AIBN	: 2,2'-Azobis-(isobutyronitrile)
PI	: Photoinitiator

LIST OF TABLES

	<u>Page</u>
Table 2.1 : Structures of typical <i>Type I</i> radical photoinitiators	18
Table 2.2 : Structures of typical <i>Type II</i> photosensitizers	20
Table 2.3 : Structures of typical <i>Type II</i> hydrogen donors.....	21
Table 4.1 : Visible light induced block copolymerization of various monomers (0.5 mL) using PSt-Br ($M_n=2090 \text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.12$, 16 mg, $7.7\times 10^{-6} \text{ mol}$) and $\text{Mn}_2(\text{CO})_{10}$ (9.2 mg, $2.3\times 10^{-5} \text{ mol}$) in toluene (0.25 mL) at $\lambda = \text{ca. } 430 \text{ nm}$	31

LIST OF FIGURES

	<u>Page</u>
Figure 2.1 : Mechanistic transformation in living and living/controlled polymerization methods.....	4
Figure 2.2 : Indirect mechanistic transformation	6
Figure 2.3 : Examples of ligands used in copper-mediated ATRP	12
Figure 2.4 : Examples of the different classes of thiocarbonylthio RAFT agents.	15
Figure 2.5 : General structure of dimanganese decacarbonyl.	22
Figure 2.6 : Visible light-induced reaction of dimanganese decacarbonyl with alkyl halide.	23
Figure 4.1 : Gel permeation chromatography(GPC) traces of block copolymers synthesized by visible light induced block copolymerization of various monomers (0.5 mL) using ω -bromo-functionalized polystyrene (PSt-Br, $M_n=2090 \text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.12$, 16 mg, $7.7\times 10^{-6} \text{ mol}$) and $\text{Mn}_2(\text{CO})_{10}$ (9.2 mg, $2.3\times 10^{-5} \text{ mol}$) in toluene (0.25 mL) at $\lambda = \text{ca. } 430 \text{ nm}$: PSt-Br (a); polystyrene by chain extension (PSt) (b); polystyrene-b-poly(methyl methacrylate) (PSt-b-PMMA) (c); polystyrene-b-poly(vinyl acetate) (PSt-b-PVAc) (d); polystyrene-b-poly(butyl acrylate) (PSt-b-PBA) (e).	32
Figure 4.2 : $^1\text{H-NMR}$ spectra of block copolymers of methyl methacrylate (b), vinyl acetate (c) and butyl acrylate (d) and their precursor polystyrene (a) in CDCl_3 (See Figure 4.1 for the block copolymerization conditions).	33

LIST OFSYMBOLS

PI	: Photoinitiator
M	: Monomer
λ	: Wavelength
$h\nu$: Radiation
R\cdot	: Radical
<i>l</i>	: Light path length
C	: Concentration
A	: Absorbance
ϵ	: Molar extinction coefficient
M_n	: The number average molecular weight
(c)	: Conversion
T	: Time

SYNTHESIS OF BLOCK COPOLYMERS BY TRANSFORMATION OF DIFFERENT POLYMERIZATION METHODS USING VISIBLE LIGHT PHOTOLYSIS

SUMMARY

A novel two-step procedure for the preparation of block copolymers by transformation of atom transfer radical polymerization (ATRP) and visible light radical photopolymerization (VLRP) methods is investigated.

In the first step of the procedure, ω -bromide functional polystyrene was synthesized by ATRP of styrene in toluene at 90 °C using ethyl-2-bromopropionate and copper bromide/*N,N,N',N'',N'''*-pentamethyldiethylenetriamine as initiator and ligand, respectively. Visible light irradiation of these polymers in the presence of dimanganese decacarbonyl [$Mn_2(CO)_{10}$] produced macroradicals at ω -chain ends capable of initiating radical polymerization of various monomers, namely methyl methacrylate, butyl acrylate and vinyl acetate. In this way, depending on the termination mode of the monomer involved AB or ABA type block copolymers consisting of polystyrene and respective segments were readily formed. The final polymers and intermediates at various stages were characterized by 1H -NMR spectroscopy and gel permeation chromatography.

The synthetic conditions of VLRP were mild compared to those of the conventional thermal methods. The facile synthetic method is expected to extend to the synthesis of other block copolymers via combination of ATRP with free radical promoted cationic polymerization.

GÖRÜNÜR BÖLGE FOTOLİZİ KULLANILARAK FARKLI POLMERİZASYON YÖNTEMLERİNİN DÖNÜŞÜMLERİ İLE BLOK KOPOLİMERLERİN SENTEZİ

ÖZET

Bu çalışmada atom transfer radikal polimerizasyonu (ATRP) ve görünür ışık radikal polimerizasyonunun (VLRP) transformasyonu ile blok kopolimerlerin elde edilmesi için yeni bir prosedür önerilmiştir.

Prosedürün ilk aşamasında ω -brom fonksiyonel uçlu polistiren 90 °C de toluen içinde etil-2-bromopiyonatın başlatıcı, bakır bromür/ N,N,N',N'',N''' -pentametildietilentriaminin ligand olarak kullanıldığı sistemde, stirenin ATRP reaksiyonuyla elde edildi. Brom uçlu polistiren dimanganez dekarbonil $[Mn_2(CO)_{10}]$ varlığında görünür bölge fotolizi ile bromürü kopartmak suretiyle makroradikaller oluşturur. Bu makroradikallerde metilmetakrilat, bütül akrilat, vinil asetat gibi radikalik polimerleşen monomerlerin polimerleşmesini sağlar. Bu konseptte, sırasıyla polistiren ve diğer polimerlerden oluşan kopolimerler reaksiyon sonundaki durumuna göre AB veya ABA tipinde blok kopolimerler olarak elde edildi. En son elde edilen polimerlerin yapıları 1H -NMR spektroskopisi ve jel geçirgenlik kromatografisi yardımıyla aydınlatıldı.

Görünür ışık radikal polimerizasyonunun reaksiyon koşulları termal polimerizasyona göre oldukça ılımlıdır. Bundan dolayı görünür ışık radikal polimerizasyonu serbest radikalle yükseltgenmiş katyonik polimerizasyonla birleştirilerek katyonik polimerleşen monomerlerle farklı blok kopolimerlerin sentezi içinde uygun olacağı beklenmektedir.

1. INTRODUCTION

Block copolymers have become increasingly important in recent years. This importance is not only due to their special chemical structures yielding unusual physical properties, but also due to the availability of various synthetic methods, including recently developed controlled/living polymerizations. Polymerization of two or more monomers in a sequential manner using controlled/living polymerization methods allows preparation of block copolymer with well-defined structures and chain lengths. However, depending on specific targeted applications it is often required to combine monomers polymerize by different mechanisms. The transformation polymerization appears to be an elegant method to combine diverse polymerization mechanisms. This way many monomers with different chemical structures can be polymerized to yield block copolymers with novel properties. Many different modes of transformation polymerization have been reported [1-11] and reviewed [12, 13]. The use of the transformation approach to demonstrate the possibility of producing block polymers by combinations of free radical polymerization with anionic insertion [14], activated monomer [14, 15], cationic [16-20], free radical promoted cationic [21-25], and condensation [26] polymerizations has been demonstrated previously. Transformations can be achieved not only between different polymerization methods, but also by the same mechanism using different initiating systems [27]. For example, atom transfer radical polymerization (ATRP) can be combined with nitroxide mediated radical polymerization (NMRP), both being controlled radical polymerization methods [28-31]. Transformation within the same polymerization process is not limited to controlled radical polymerization. The approach was easily adapted so that conventional free radical polymerization can be combined with controlled radical polymerizations. For example, Matyjaszewski and co-workers prepared block copolymers by the combination of ATRP and conventional radical polymerization using azo or redox initiators [32]. Boutevin and coworkers successfully used the same concept by employing trichloromethyl-terminated azo initiator [33]. In our laboratory, we demonstrated that ATRP could be combined with conventional photoinitiated radical polymerization [34]. There are

also numerous reports showing that a combination of two radically polymerized monomers leads to a block copolymer using conventional radical-radical transformation polymerization [35, 36]. In these examples, mostly initiators carrying two different radical forming sites were used as transformation agents, i.e., initiators containing groups of different thermal activity [37, 38], thermal and photochemical activity[39, 40], and redox and thermal activity [41]. Photochemical synthesis of block copolymers has a number of technical and theoretical advantages over other conventional methods. Because of the applicability at low temperatures, side reactions leading to the formation of homopolymers are minimized. Further, the reactive sites can be produced at definite positions of macromolecule due to the selective absorptivity of chromophores. Various methods for the photochemical synthesis of block copolymers have been treated by two review articles[42, 43]. In this thesis, a novel route for the synthesis of various AB and ABA type block copolymers has been reported by combination of atom transfer radical polymerization and visible light radical polymerization.

2. THEORETICAL PART

2.1 Transformation Reactions

Block copolymers are generally defined as macromolecules in which chemically different blocks (or segments) are connected together to combine their macroscopic properties and to design hybrid materials [12, 14]. Each segment exerts its character or function to the bulk of the copolymers. This way various properties that can be improved or combined to give possibility of using block copolymer compatibilizers, impact modifiers, surface modifiers, coating materials, antistatic agents and adhesives [15, 16]. These materials have attracted increasing attention because of their potential application as stabilizers, emulsifiers, dispersing agents, elastomeric materials and surfactants as well as in drug delivery, cosmetics and many other industrial applications. Traditionally, block copolymers can be synthesized by the sequential addition polymerization of different monomer units using the same chemistry. Living ionic polymerization is an elegant method for the controlled synthesis of block copolymers. However, besides high purity requirements this technique is limited to ionically polymerizable monomers and exclude monomers that polymerize by other mechanisms.

In fact, there exists some limitations even for the ionically polymerizable monomers. Carrying out the block copolymerization of two ionically polymerizable monomers depends critically on the structure and relative reactivity of the ionic species and the monomers [17, 18, 21]. Moreover, there is not yet a general acceptable polymerization method which is suitable for all monomers. Therefore, the application of a single mode polymerization technique for the synthesis of block copolymer is severely limited, and suffers from the requirement for care in the order of monomer addition.

In recent years, the development of polymerization processes for a high level of control over molar mass, polydispersity and end-group and molecular architecture has remained a major challenge. The rapid development of metallocene polymerization

of olefins and controlled radical polymerization strongly reflects this trend. In order to extend the range of monomers for the synthesis of block copolymers, a mechanistic transformation approach has been proposed, by which the polymerization mechanism could be changed from one to another which is suitable for the respective monomers. The pioneering work on the mechanistic transformation was originally reported by Burgess et al. three decades ago[19, 24, 44].

Transformation reactions are classified on the basis of interconversion between propagation mechanisms (Fig. 2.1). It can be seen that between the main living and controlled/living polymerization methods, transformations are accessible in both directions[45].

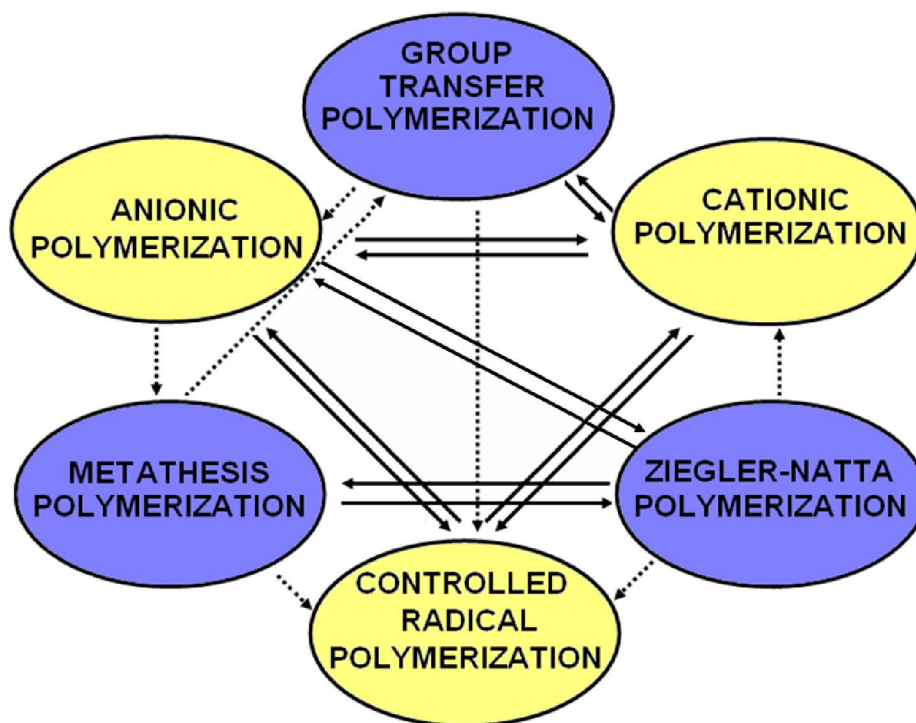


Figure 2.1: Mechanistic transformation in living and living/controlled polymerization methods.

All the research works performed in the area of mechanistic transformation could be outlined in two main categories which are divided in subcategories within themselves as well:

Direct transformation reactions

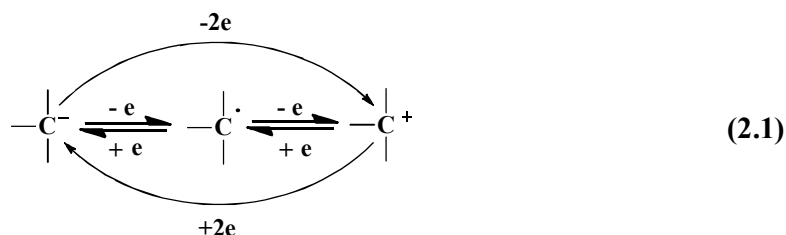
- Cation to Anion Direct Transformation
- Radical to Cation Direct Transformation

Indirect transformation reactions

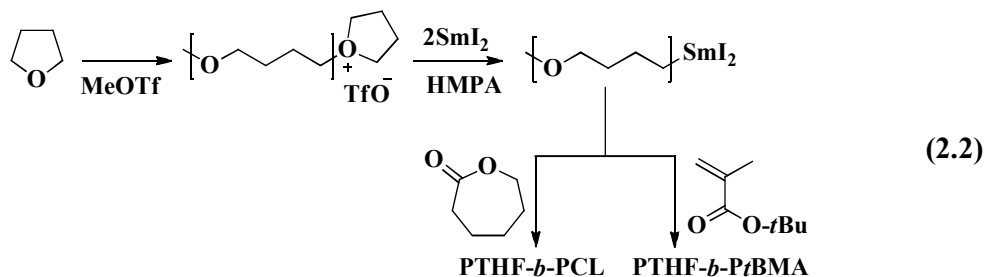
- Transformations of Anionic Polymerization to Radical Polymerization
- Transformations of Cationic Polymerization to Radical Polymerization
- Transformations of Radical Polymerization to Anionic Polymerization
- Transformations of Radical Polymerization to Cationic Polymerization
- Transformations Involving Anionic and Cationic Polymerization
- Transformations Involving Activated Monomer Polymerization
- Transformations Involving Metathesis Polymerization
- Transformation Involving Ziegler-Natta Polymerization
- Transformation Involving Group Transfer Polymerization

2.1.1 Direct transformation reactions

The transformation of a polymerization mechanism is carried out at the end of the first block segment in the polymerization mixture, which means that the species 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 shown below:



The shortcoming associated with the direct transformation, is the short lifetime 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 only successful example of direct transformation involving living polymerization methods was reported by Endo for the preparation of block copolymers of tetrahydrofuran (THF) with tert-butyl methacrylate (t-BMA), ϵ -caprolactone (CL)[22] and d-valerolactone (VL)[23] as shown in below:



2.1.2 Indirect transformation reactions

Indirect transformation is more attractive than direct transformations because it can be performed much more easily and uses various polymerization modes. As illustrated in Fig. 2.2. This type of transformation usually requires multistep reactions. The stable but potentially reactive functional group for the second polymerization mode is introduced at 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 species.

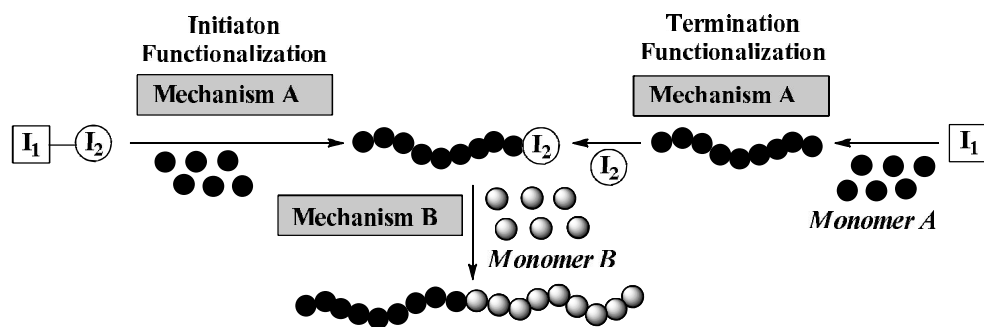
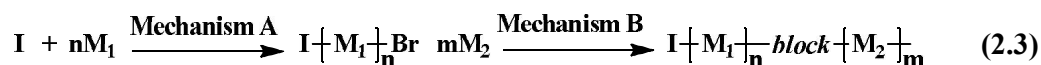


Figure 2.2 : Indirect mechanistic transformation

As a consequence; using transformation reactions, i.e., combining different polymerization mechanisms, novel polymeric materials may be synthesized from new and existing monomers. A full range of possible block and graft copolymers built from monomers with different chemical structure and accessible through transformation reactions. It is clear that the transformation reactions will continue to attract interest in the near future because of the possibility of the various newly developed living/controlled polymerization mechanisms. It would be possible to design and synthesize materials having precise structures with desired properties by combination of such mechanisms (2.3).



2.2 Controlled Radical Polymerization Methods

Nowadays, radical polymerization is a very useful 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) [46]. 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. Besides, rigorous process conditions are not needed for the polymerization. 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.

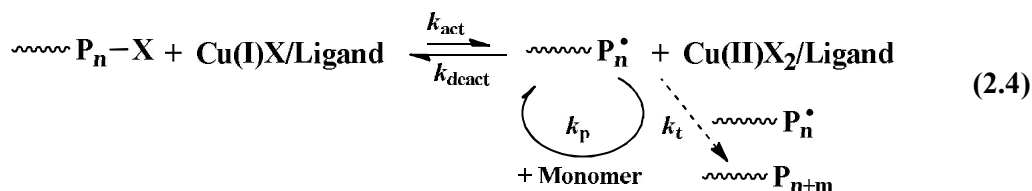
Advanced structures can be synthesized via living polymerization techniques. Moreover, living polymerization techniques allow preparation of macromonomers, macro initiators, functional polymers, block, graft copolymers, and star polymers. Well known example of these techniques is anionic polymerization [47], 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 radical polymerization without sacrificing the above-mentioned advantages, it was recognized that a living character had to be realized in conjunction with the free-radical mechanism. 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 radical polymerization (NMRP) 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 polydispersities, and predetermined (number-average) molar mass.

2.2.1 Atom transfer radical polymerization (ATRP)

Metal-catalyzed controlled radical polymerization, mediated by Cu, Ru, Ni, and Fe metal complexes, is one of the most efficient methods to produce polymers in the field of CRP [48]. Among aforementioned systems, copper-catalyzed ATRP in conjunction with organic halide initiator and amine ligand received more interest. The name ATRP comes from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of the polymeric chains. ATRP was developed by designing a proper catalyst (transition metal compound and ligands), using an initiator with an appropriate structure, and adjusting the polymerization conditions, such that the molecular weights increased linearly with conversion and the polydispersities were typical of a living process [49]. 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 [50, 51].

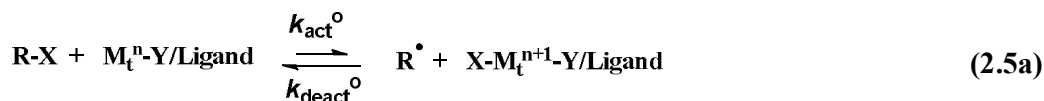


A general mechanism for ATRP is represented by (2.5). The radicals, i.e., the propagating species P_n^* , are generated through a reversible redox process catalyzed by a transition metal complex (activator, $\text{M}_t^n\text{-Y}$ / ligand, where Y may be another ligand or a counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, $\text{P}_n\text{-X}$. Radicals react reversibly with the oxidized metal complexes, X-M_t^{n+1} / ligand, the deactivator, to reform the dormant species and the activator. This process occurs with a rate constant of activation, k_a , and deactivation k_{da} , respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p . Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent

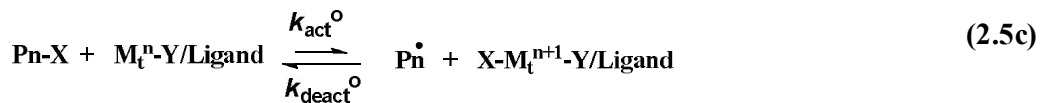
of the polymer chains undergo termination. Elementary reactions consisting of initiation, propagation, and termination are illustrated below (2.5a-e)[52].

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 [53]. A successful ATRP will have not only small contribution of terminated chains but also uniform growth of all the chains; this is accomplished through fast initiation and rapid reversible deactivation.

Initiation



Propagation



Termination



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

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 [50]. In fact, all vinyl monomers are susceptible to ATRP except for a few exceptions. Notable exceptions

are unprotected acids (eg (meth)acrylic acid). Some other monomers may be difficult to polymerize since they exhibit side reactions, which may be affected by the choice of reaction conditions, nature of the catalyst, etc. An example of such a monomer is 4-vinyl pyridine (4-VP), which can undergo quaternization by the (alkyl halide) initiator [54]. 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.

Initiators

The main role of the initiator is to determine the number of growing polymer chains. The initiation in ATRP may occur in one of two different ways. The common way to initiate is via the reaction of an activated (alkyl) halide with the transition-metal complex in its lower oxidation state. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, should rapidly and selectively migrate between the growing chain and the transition metal complex. Thus far, when X is either bromine or chlorine, the molecular weight control is best. Iodine works well for acrylate polymerizations in copper-mediated ATRP and has been found to lead to controlled polymerization of styrene in ruthenium and ruthenium-based ATRP.

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” [55].

Catalysts

Perhaps the most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst.

1. The metal center must have at least two readily accessible oxidation states separated by one electron.

2. The metal center should have reasonable affinity toward a halogen.
3. The coordination sphere around the metal should be expandable on oxidation to selectively accommodate a (pseudo) halogen.
4. The ligand should complex the metal relatively strongly.
5. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system. To differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species [56].

A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. The majority of work on ATRP has been conducted using copper as the transition metal. Apart from copper-based complexes, Fe [57], Ni [58], Ru [59], etc have been used to some extent.

Ligands

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

The most common ligands for ATRP systems are substituted bipyridines, alkyl pyridylmethanimines and multidentate aliphatic tertiary amines such as *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA), and tris[2-(dimethylamino) ethyl]amine (Me₆-TREN) (Fig. 2.3). Examples of ligands used in copper-mediated ATRP are illustrated below [49, 60].

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 [61]. 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 [62].

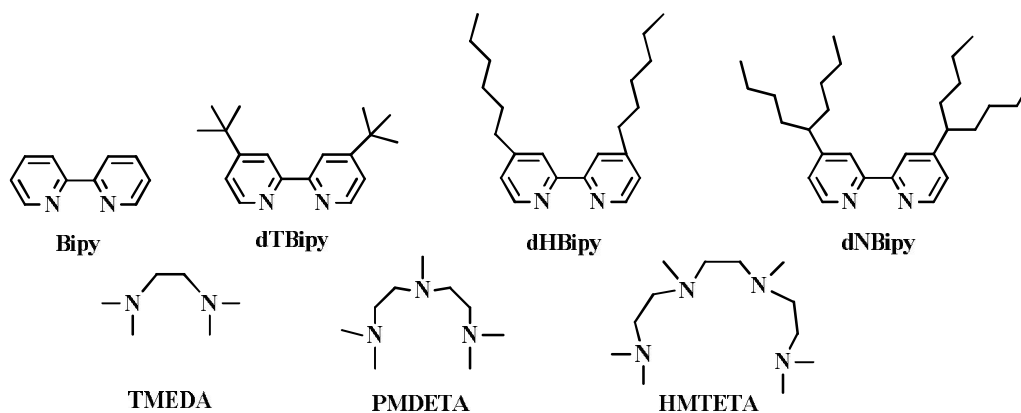


Figure 2.3 :Examples of ligands used in copper-mediated ATRP

Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used in the polymerization of different monomers. A solvent is sometimes necessary, especially when the polymer is insoluble in its monomer (e.g., polyacrylonitrile). ATRP has been also successfully carried under heterogeneous conditions in (mini)emulsion, suspension, or dispersion.

2.2.2 Nitroxide-mediated radical polymerization (NMRP)

Nitroxide-mediated radical polymerization (NMRP) belongs to a much larger family of processes called stable free radical polymerizations. In this type of process, the propagating species ($P_n\cdot$) reacts with a stable radical (X) as seen in reaction 2.5 [63]. 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.

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 NMRP 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 ($Z = \text{aryl or alkyl}$), (2) trithiocarbonates ($Z = \text{substituted sulfur}$), (3) dithiocarbonates (xanthates) ($Z = \text{substituted oxygen}$), and (4) dithiocarbamates ($Z = \text{substituted nitrogen}$ (Fig. 2.4).

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. 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 °C, which corresponds to the optimum decomposition temperature interval of the well-known initiator AIBN. However, even room temperature and high-temperature conditions can also be applied [73, 74]. Generally, a RAFT agent/free-radical ratio of 1:1 to 10:1 yields polymers with narrow molecular weight distributions.

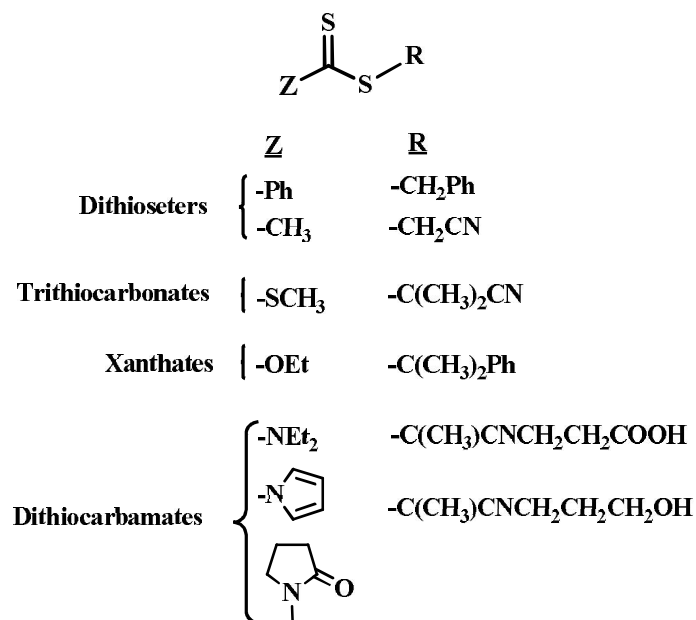
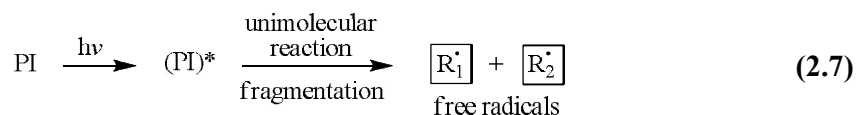


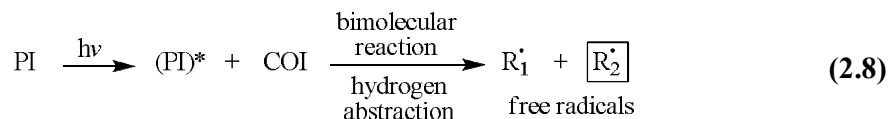
Figure 2.4 :Examples of the different classes of thiocarbonylthio RAFT agents.

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 ($\text{P}_n\cdot$) to the RAFT agent [$\text{S}=\text{C}(\text{Z})\text{SR}$] followed by fragmentation of the intermediate radical gives rise to a polymeric RAFT agent and a new radical ($\text{R}\cdot$). The radical $\text{R}\cdot$ reinitiates polymerization by reaction with monomer to form a new propagating radical ($\text{P}_m\cdot$). In the presence of monomer, the equilibrium between the active propagating species ($\text{P}_n\cdot$ and $\text{P}_m\cdot$) 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 $^1\text{H-NMR}$ and UV–vis spectroscopy [75]. 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 [76, 77].

Compounds which undergo unimolecular bond cleavage upon irradiation as shown in reaction 2.7 are termed as *Type I* photoinitiators [85].



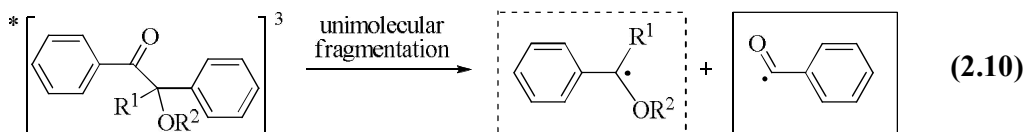
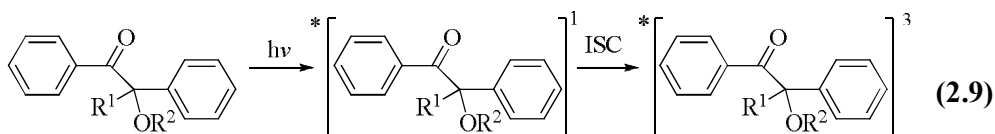
If the excited state photoinitiator interacts with a second molecule (a coinitiator) to generate radicals in a bimolecular reaction as shown in reaction 2.8, the initiating system is termed as “*Type II* Photoinitiator” [85].



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 systems and visible light photoinitiators belong almost exclusively to this class of photoinitiators.

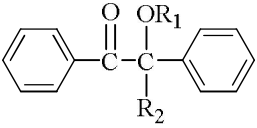
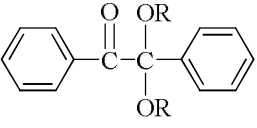
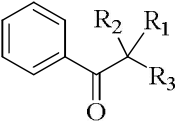
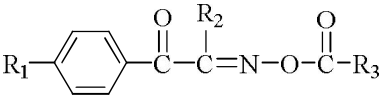
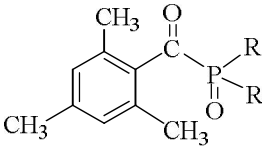
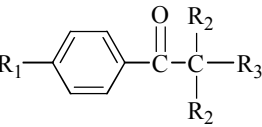
2.3.1 *Type I* photoinitiators (Unimolecular photoinitiator systems)

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. *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.



R¹ = H, Alkyl, substituted Alkyl, R² = H, Alkyl, substituted Alkyl

Table 2.1 : Structures of typical *Type I* radical photoinitiators

Photoinitiators	Structure	λ_{\max} (nm)
Benzoinethers	 $R_1 = \text{H, alkyl}$ $R_2 = \text{H, substituted alkyl}$	323
Benzilketals	 $R = \text{CH}_3, \text{C}_3\text{H}_7, \text{CH}_2$	365
Acetophenones	 $R_1 = \text{OCH}_3, \text{OC}_2\text{H}_5$ $R_2 = \text{OCH}_3, \text{H}$ $R_3 = \text{C}_6\text{H}_5, \text{OH}$	340
Benzoyloximes	 $R_1 = \text{H, SC}_6\text{H}_5$ $R_2 = \text{CH}_3, \text{C}_6\text{H}_{13}$ $R_3 = \text{C}_6\text{H}_5, \text{OC}_2\text{H}_5$	335
Acylphosphineoxides	 $R = \text{C}_6\text{H}_5 \text{ or } \text{OCH}_3$	380
Aminoalkylphenones	 $R_1 = \text{SCH}_3, \text{morpholine}$ $R_2 = \text{CH}_3, \text{CH}_2\text{Ph or C}_2\text{H}_5$ $R_3 = \text{N(CH}_3)_3, \text{morpholine}$	320

As illustrated in reactions 2.9 and 2.10, 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

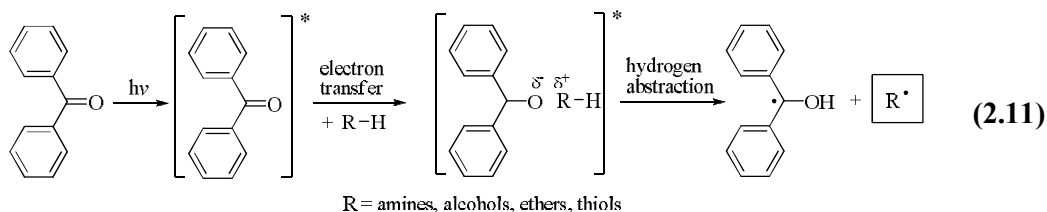
most efficient *Type I* initiators are benzoin ether derivatives, benzil ketals, hydroxylalkylphenones, α -aminoketones and acylphosphine oxides (Table 2.1) [86-89].

2.3.2 *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. In this case, radical generation follows 2nd order kinetics. 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.

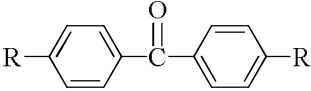
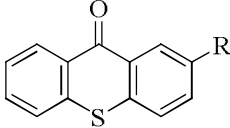
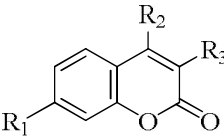
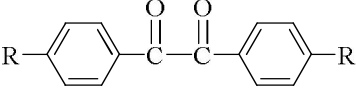
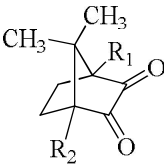
Hydrogen abstraction

Photoinitiators that proceed via a hydrogen abstraction mechanism are exemplified by combination of benzophenone and a hydrogen donor (reaction 2.11). 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.



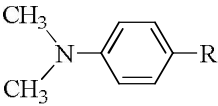
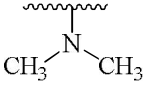
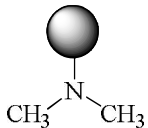
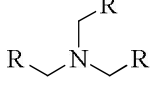
Photosensitizers of *Type II* system including benzophenones, thioxanthenes, camphorquinones, benzyls, and ketocoumarins are listed in Table 2.2.

Table 2.2 : Structures of typical *Type II* photosensitizers

Photosensitizers	Structure	λ_{max} (nm)
Benzophenones	 R = H, OH, N(C ₂ H ₅) ₂ , C ₆ H ₅	335
Thioxanthenes	 R = H, Cl, isopropyl	390
Coumarins	 R ₁ = N(C ₂ H 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

The co-initiators such as an amine, ether, thiol or alcohol with an abstractable α -hydrogen are also classified in Table 2.3.

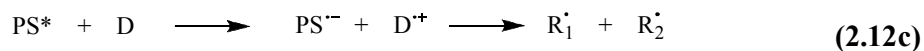
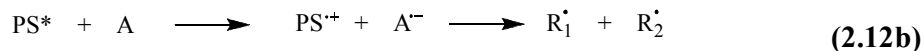
Table 2.3 : Structures of typical *Type II* hydrogen donors

Hydrogen Donors	Structure
Aliphatic Amines	$\begin{array}{c} \text{R}_1 \\ \\ \text{R}_2 - \text{N} - \text{R}_3 \end{array}$ <p> $\text{R}_1 = \text{C}_2\text{H}_5, \text{CH}_3, \text{CH}(\text{CH}_3)_2$ $\text{R}_2 = \text{C}_2\text{H}_5, \text{C}_2\text{H}_4\text{OH}, \text{CH}(\text{CH}_3)_2$ $\text{R}_3 = \text{C}_2\text{H}_5, \text{C}_2\text{H}_4\text{OH}, \text{CH}(\text{CH}_3)_2$ </p>
Aromatic Amines	 <p> $\text{R} = \text{H}, \text{COOH}, \text{COOCH}_2\text{CH}_3, \text{COOC}_8\text{H}_{17}$ </p>
Polymeric Amines	 <p> polymer = poly(methyl methacrylate)s, polyacrylates or polyurethanes </p>
Dendrimeric Amines	 <p> core = polyglycerols or poly(propylene imine)s </p>
Acrylated Amines	 <p> $\text{R} = \text{acrylates or methacrylates}$ </p>
Alcohols	$\text{R}-\text{OH}$ $\text{R} = \text{isopropyl},$ hydroxyethyl methacrylate
Ethers	$\text{R}-\text{O}-\text{R}$ $\text{R} = \text{tetrahydrofuran}, \text{benzodioxole}$ poly(ethylene oxide), poly(propylene oxide), poly(tetrahydrofuran)
Thiols	$\text{R}-\text{SH}$ $\text{R} = \text{benzimidazole}, \text{benoxazole},$ benzthiazole, thioxanthone

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 (reaction 2.12).



2.4 Photochemistry of Dimanganese Decacarbonyl

Metal carbonyl complexes are one of the most photoreactive transition metal complexes among known, and studies of the photochemistry of metal carbonyls and their derivatives acquaint to researcher. Reviews of metal carbonyls are numerous [90], but only a few deal specifically with excited-state processes [91-93]. All metal carbonyl photoprocesses include electronic absorption phenomena, luminescence, non-radiative decay, energy transfer, and chemical reaction. The use of light as a synthetic tool in this field became important in the late 1950's and early 1960's, and the last substantial review of the photochemistry appeared in 1969 [91]. The commercially available metal carbonyl complexes of manganese have the formula $[\text{Mn}_2(\text{CO})_{10}]$ with the structure shown in Figure 2.5.

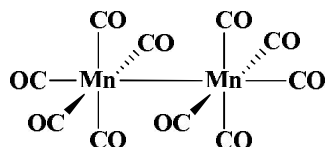


Figure 2.5 :Chemical structure of dimanganese decacarbonyl.

In recent years, for the use of photopolymerization systems in expanded and environmental-friendly applications, some disadvantages need to be overcome. The most important drawback is related to the limited availability of photoinitiators that can act in the low energy light emitted by the light sources. Photoinitiators that can produce active centers upon irradiation by the visible light can provide polymerizations to occur under sunlight without the need of an additional light source. In this respect, dimanganese decacarbonyl $[\text{Mn}_2(\text{CO})_{10}]$ metal complex provides many advantages since it photolysis easily upon sunlight irradiation to give intermediates that abstract halogenides to produce radical centers. The highly active,

versatile, and photoresponsive controlled/living radical polymerizations[94] were developed using $[\text{Mn}_2(\text{CO})_{10}]$ coupled with an alkyl halide initiator (R-X) under weak visible light according to Bamford pioneered to about dimanganese decacarbonyl studies (Figure 2.6).[95, 96]

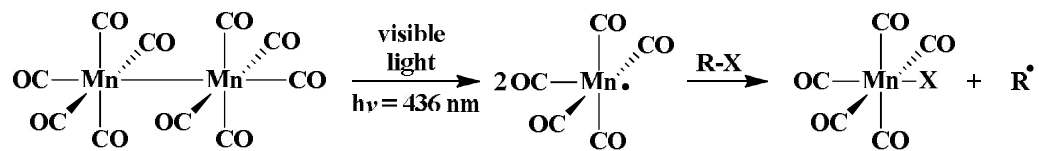
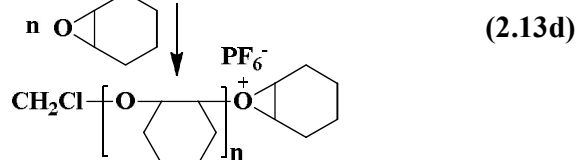
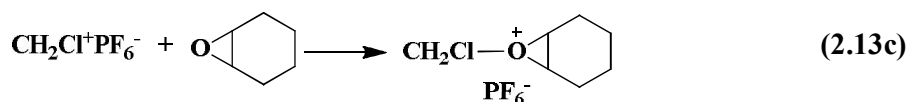
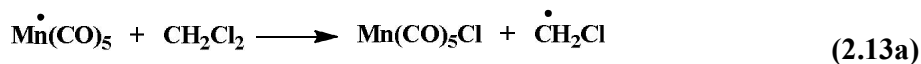


Figure 2.6 :Visible light-induced decomposition of dimanganese decacarbonyl with alkyl halide.

Dimanganese decacarbonyl is also used various photopolymerization applications. For example, Yagci reported the cationic polymerization of cyclohexene oxide on photolysis of $\text{Mn}_2(\text{CO})_{10}$ in halogenated solvents, in combination with an onium salt, which resulted in a new method for initiating cationic polymerization (reaction 2.13)[27]. In this concept, photoinitiated cationic polymerization yielded low molecular weight polymer and relatively narrow polydispersity but this was coupled with low conversion. The resulting cations can directly react with the monomer.

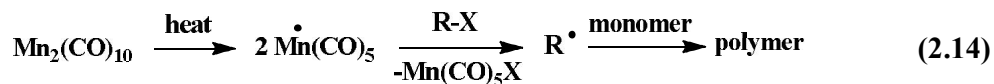


Hudson and co-workers have also investigated a heterogeneous graft copolymerization using $\text{Mn}_2(\text{CO})_{10}$ as the initiator [97].

The controlled/living radical polymerization of vinyl acetate (VAc) and its copolymerization with methyl acrylate (MA) were investigated by Kamigaito and coworkers in bulk or fluoroalcohols using dimanganese complex $[\text{Mn}_2(\text{CO})_{10}]$ in

conjunction with an alkyl iodide (R-I) as an initiator under weak visible light. The dimanganese complex induced the controlled/ living radical polymerization of vinyl acetate even in the fluoroalcohols without any loss of activity[94]. The R-I/Mn₂(CO)₁₀ system was also effective for the copolymerization of methyl acrylate and vinyl acetate, in which methyl acrylate was consumed faster than vinyl acetate, and then the remaining vinyl acetate was continuously and quantitatively consumed after the complete consumption of methyl acrylate.

Dimanganese decacarbonyl has been also used in thermolysis process (2.14). In this concept, for example [Mn₂(CO)₁₀] initiates the radical polymerization of methyl methacrylate in the presence of a variety of organic halides including C₆H₅CH₂Br, Me₂C(Br)-CO₂Et, BrCH₂C(Br)=CH₂, and ClCH₂C(Cl)=CH₂ in toluene at 60-90 °C[34].



As a result of these applications, various macromolecular architectures can successfully be synthesized in the presence of the highly active, photoresponsive and thermoresponsive dimanganese decacarbonyl with alkyl halide complexes.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Reagents for synthesis of block copolymers

Dimanganese decacarbonyl (Aldrich): It was purified by sublimation and stored in a refrigerator in the dark.

Styrene (St; 99%, Aldrich): Styrene was passed through a basic alumina column to remove the inhibitor prior to use.

Butyl acrylate (BA; $\geq 99\%$, Aldrich): Butyl acrylate was passed through a basic alumina column to remove the inhibitor prior to use.

Vinyl acetate (VAc; $\geq 99\%$, Acros): Vinyl acetate was distilled under reduced pressure and stored under nitrogen.

Methyl methacrylate (MMA, 99%, Aldrich): Methyl methacrylate was passed through a basic alumina column to remove the inhibitor.

Methyl acrylate (MA, 99%, Aldrich): Methyl acrylate was passed through a basic alumina column to remove the inhibitor.

3.1.2 Solvents

Toluene (Aldrich 99%): Toluene was dried with calcium chloride and distilled over sodium wire.

Methanol (Technical): Methanol was used for the precipitation of polymers without further purification.

Tetrahydrofuran (THF) (99.8%, J.T.Baker): Tetrahydrofuran was used as received.

Dichloromethane (99.8%, J.T.Baker): It was first washed with conc. sulfuric acid until the acid layer remained colorless, and then with water, followed by another washing with 5% sodium hydroxide (aq.) and finally with water again. It was dried with calcium chloride and distilled over calcium hydride. It was stored over molecular sieves for use as a solvent in the photopolymerization experiments.

3.1.3 Other chemicals and reagents

Ethyl-2-bromopropionate (>99%, Aldrich): It was used as an initiator, was used as received.

N, N, N', N'', N''' -Pentamethyldiethylene triamine (PMDETA, Aldrich): PMDETA was used as a ligand, was distilled before used.

Copper bromide (CuBr, 98%, Acros): It was used as received.

3.2 Equipments

3.2.1 Light Source

Dental LED lamp (Bluephase) supplied by Ivoclar Vivadent Company. The wavelength range is 430–490 nm and maximum light performance is 1110 mW cm⁻² ±10%.

3.2.2 ¹H-Nuclear magnetic resonance spectroscopy (¹H-NMR)

¹H-NMR spectra of 5–10 % (w/w) solutions in CDCl₃ with Si(CH₃)₄ as an internal standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer.

3.2.3 Gel permeation chromatography (GPC)

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 PSt standards having narrow molecular weight distribution. Data were analyzed using ViscotekOmniSEC Omni-01 software. Molecular weights of polymers were calculated with the aid of polystyrene standards.

3.3 Preparation Methods

3.3.1 General procedure for atom transfer radical polymerization

Monomer (St, 87.3 mmol), ligand (PMDETA, 0.87 mmol), catalyst (CuBr, 0.87 mmol), initiator (ethyl-2-bromopropionate, 0.87 mmol) and deoxygenated solvent (toluene) were added, consecutively, to a Schlenk tube equipped with a magnetic stirring bar. The tube was degassed by three freeze-pump-thaw cycles, left under vacuum, and placed in a thermostated oil bath (110 °C) for 25 minutes. After the polymerization, the reaction mixture was diluted with tetrahydrofuran (THF) and then passed through a column of neutral alumina to remove metal salt. The excess of THF and unreacted monomer were evaporated under reduced pressure. The resulted polymer, bromo ω -end-functionalized polystyrene (PSt-Br), was dissolved in a small amount of THF, and precipitated in ten-fold excess methanol. The polymer was dried under vacuum at room temperature (Yield % = 17.0; $M_{n, GPC} = 2090 \text{ g}\cdot\text{mol}^{-1}$; $M_w/M_n = 1.12$).

3.3.2 General procedures for visible light radical polymerization

A typical photopolymerization procedure is as follows. $\text{Mn}_2(\text{CO})_{10}$ (9.2 mg, 2.3×10^{-5} mol) and 0.5 mL of MMA (4.7×10^{-5} mol) were added to a solution of PSt-Br (16 mg, 7.7×10^{-6} mol) in 0.25 mL of deoxygenated toluene in a Pyrex tube. The solution was flushed with nitrogen for 4-5 min. The reaction tube was sealed off and irradiated with a dental LED lamp (Bluephase) supplied by Ivoclar Vivadent Company. The wavelength range is 430–490 nm and maximum light performance is $1110 \text{ mW cm}^{-2} \pm 10\%$. At the end of one-hour irradiation, the polymerization solution was poured into cold methanol. The precipitated polymer was filtered off and dried in vacuo (Yield % = 5.8; $M_{n, GPC} = 5530 \text{ g}\cdot\text{mol}^{-1}$; $M_w/M_n = 1.64$). Similarly, VLRP of BA, VAc and St were also carried out using $\text{Mn}_2(\text{CO})_{10}$ and PSt-Br under same conditions (See Table 4.1 for details).

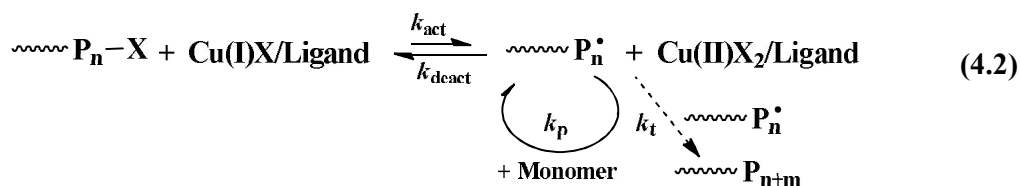
4. RESULTS AND DISCUSSION

About four decades ago, Bamford demonstrated that carbon-centered radicals were formed upon irradiation ($\lambda = \text{ca. } 436 \text{ nm}$) of organic halides in the presence of dimanganese decacarbonyl, $\text{Mn}_2(\text{CO})_{10}$. [98-101] Upon absorption of light, $\text{Mn}_2(\text{CO})_{10}$ decomposes to $\text{Mn}(\text{CO})_5$ (4.1). The latter reacts with the terminal halide group yielding initiating alkyl radicals. Both bromine and chlorine compounds are found to be effective, and there is no initiation when no halide is present.

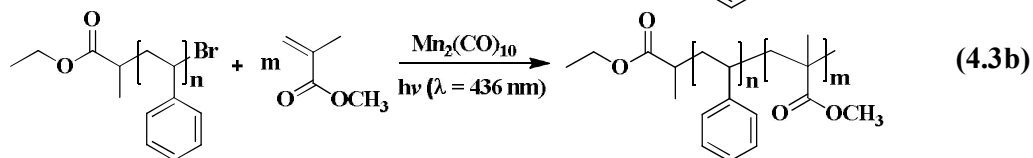
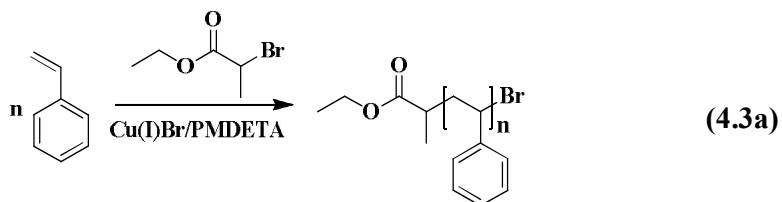


Such visible light initiation was successfully employed in the synthesis of various graft and block [102, 103] copolymers even in heterogeneous conditions [97] by using prepolymers possessing suitable side- and end-chain halide functionality. Recently, this system in conjunction with certain additives has been used as an initiating system for controlled/living radical polymerizations. [94, 104-106] Due to the possibility of generation of electron donor radicals, this system was also used for visible light free radical promoted cationic polymerization of structurally different monomers such as vinyl ethers and epoxides [27].

Among various controlled radical polymerization methods, ATRP seems to be the most versatile method because of its simplicity and applicability to a wide range of monomers. [50, 107] Moreover, it provides many possibilities in structural and architectural design and allows the development of new products with monomers currently available. ATRP involves reversible homolytic cleavage of a carbon-halogen bond by a redox reaction between an organichalide (Pn-X) and a transition metal, such as copper(I) salts (4.2) [108].



Polymers obtained by ATRP contain terminal halide groups, which can be activated by the $\text{Mn}_2(\text{CO})_{10}$. Thus, ATRP of styrene initiated by ethyl-2-bromopropionate, using CuBr/PMDETA catalytic system was performed. As the bromide functional polystyrene (PSt-Br) was intended to be used in the subsequent photoinitiation process, the conditions of ATRP (high concentration of initiator – $0.09 \text{ mol}\cdot\text{L}^{-1}$ and short reaction time - 25 minutes) were deliberately selected so as to obtain a low molecular weight polymer, combined with a satisfactory conversion and polydispersity. The low molecular weight polymer would also provide better spectral characterization, particularly for the halide end group that is crucial for the photoinitiating system described. Accordingly, in this reaction stage the macroinitiator (PSt-Br, $M_n=2090 \text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.12$) possessing one reactive bromide group at the chain end was obtained. Subsequently, this macroinitiator was used to initiate the free radical polymerization of vinyl monomers through visible light irradiation at room temperature. Since PSt-Br does not absorb at the irradiation wavelength, $\lambda = 436 \text{ nm}$, all the light is absorbed by $\text{Mn}_2(\text{CO})_{10}$. $\text{Mn}(\text{CO})_5$ formed from the photodecomposition of the excited state of $\text{Mn}_2(\text{CO})_{10}$ abstracts bromine atom from the macroinitiator, PSt-Br, to generate polymeric radicals capable of initiating the polymerization of the second monomer. The overall process is represented in 4.3 on the example of the preparation of styrene-methyl methacrylate block copolymer.



All of the monomers were polymerized effectively yielding the corresponding block copolymers (Table 4.1). As seen in Figure 4.1, unimodal GPC traces with a small

shoulder are observed. Shifts to higher molar mass for all polymers are also found. The conversions, molecular weights and distributions are strongly related to the structure and reactivity of polystyryl radical to the monomers employed in the photoinitiated polymerization step. Similar dependency was also observed by Kamigaito and coworkers [105]. Generally, molecular weight distributions were higher than those obtained by controlled radical polymerization methods. However, due to the room temperature conditions, except butyl acrylate (BA) polymerization, these values are still low compare to that obtained by conventional thermally induced free radical polymerization. Under certain conditions[34], $Mn_2(CO)_{10}$ based initiating systems yield polymers with relatively low molecular weight distributions. Much higher molecular weight and its distribution observed in the case of BA may be attributed the high propagation rate constant of this particular monomer [109]. In order to confirm the efficiency of the photoinitiating system we also used St monomer in the second stage. After the photolysis, the molecular weight of polystyrene doubled as a result of successful chain extension via VLRP.

Table 4.1 : Visible light induced block copolymerization of various monomers (0.5 mL) using PSt-Br ($M_n=2090$ g·mol⁻¹, $M_w/M_n = 1.12$, 16 mg, 7.7×10^{-6} mol) and $Mn_2(CO)_{10}$ (9.2 mg, 2.3×10^{-5} mol) in toluene (0.25 mL) at $\lambda =$ ca. 430 nm.

Polymer ^a	Monomer (mol·L ⁻¹)	k_p ^b (L·mol ⁻¹ ·s ⁻¹)	Conv. (%)	M_n ^c (g·mol ⁻¹)	PDI ^c	Comp. (mol % PSt)
PSt	St ^d (5.83)	187	6.0	4850	1.15	100
PSt- <i>b</i> - PMMA	MMA (6.03)	450	5.8	5530	1.64	61
PSt- <i>b</i> - PVAc	VAc (7.24)	117	6.7	2990	1.13	57
PSt- <i>b</i> -PBA	BA (4.68)	679	7.7	22500	3.36	14

^a Polymer acronyms: PSt; polystyrene, PMMA; poly(methyl methacrylate), PVAc; poly(vinyl acetate), PBA; poly(butyl acrylate).

^b From Polymer Handbook.[109]

^c Number-average molecular weights (M_n) and polydispersities (PDIs) were ^determined using gel permeation chromatography.

^d Chain extension.

Conventional free-radical polymerization of methacrylate monomers terminates mainly by a disproportionation process[42], which in the present polymerization system results in the formation of AB block copolymers, PSt-*b*-PMMA.[110] However, any preference for a combination termination mechanism would [12]eventually yield ABAblock structure. The structure of the block copolymers was confirmed by ¹H-NMR analysis. As shown in Figure 4.2, the ¹H-NMR spectra of the block copolymers exhibit characteristic resonances of both PSt and the block segments.

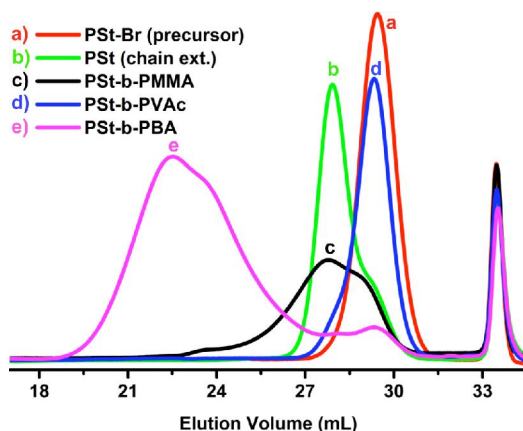


Figure 4.1 : Gel permeation chromatography traces of block copolymers synthesized by visible light induced block copolymerization of various monomers (0.5 mL) using ω -bromo-functionalized polystyrene (PSt-Br, $M_n=2090 \text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.12$, 16 mg, $7.7\times 10^{-6} \text{ mol}$) and $\text{Mn}_2(\text{CO})_{10}$ (9.2 mg, $2.3\times 10^{-5} \text{ mol}$) in toluene (0.25 mL) at $\lambda = \text{ca. } 430 \text{ nm}$: PSt-Br (a); polystyrene by chain extension (PSt) (b); polystyrene-*b*-poly(methyl methacrylate) (PSt-*b*-PMMA) (c); polystyrene-*b*-poly(vinyl acetate) (PSt-*b*-PVAc) (d); polystyrene-*b*-poly(butyl acrylate) (PSt-*b*-PBA) (e).

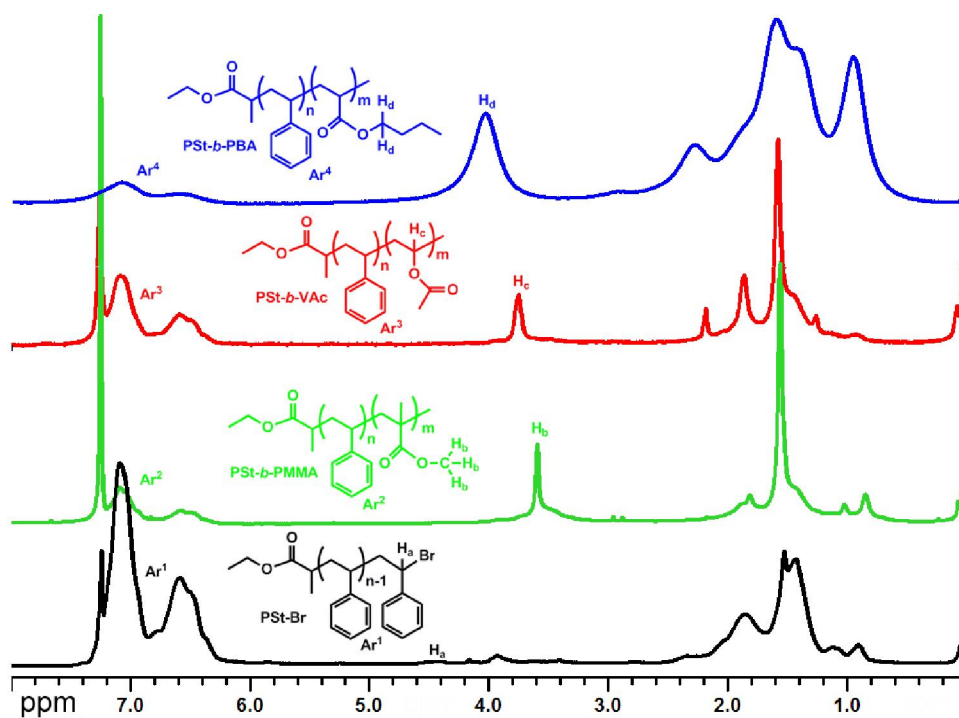


Figure 4.2 : ^1H -NMR spectra of block copolymers of methyl methacrylate (b), vinyl acetate (c) and butyl acrylate (d) and their precursor polystyrene (a) in CDCl_3 (See Figure 4.1 for the block copolymerization conditions).

5. CONCLUSION AND SUGGESTIONS

In conclusion, although these results are preliminary in nature, they clearly indicate that block copolymers can successfully be synthesized by combination of ATRP and VLRP processes. The synthetic approach described here was quite facile, since at least in principle, any polymer obtained by ATRP could be used as macroinitiator for the VLRP of a second monomer to yield corresponding block copolymers. The synthetic conditions of VLRP were mild compared to those of the conventional thermal methods. The facile synthetic method is expected to extend to the synthesis of other block copolymers via combination of ATRP with free radical promoted cationic polymerization. It is well established that the radicals stemming from the photolysis of organic halides in the presence of $Mn_2(CO)_{10}$ can readily be oxidized to the corresponding cations by suitable oxidants. The described method can also be used for the VLRP of bifunctional monomers using polymers obtained by ATRP leading to the formation of networks with dangling chains. Further studies in these lines are now in progress.

REFERENCES

- [1] **Feng, X.S. and Pan, C.Y.**, 2002. Block and star block copolymers by mechanism transformation. 7. Synthesis of polytetrahydrofuran/poly(1,3-dioxepane)/polystyrene abc miktoarm star copolymers by combination of crop and atrp, *Macromolecules*, **35**, 2084-2089.
- [2] **Lai, R.F., Guo, H.Q., and Kamachi, M.**, 2009. Synthesis of a graft polymer pvac-g- p(an-r-bve)-b-pcho in "one-step" by radical/cationic transformation polymerization and coupling reaction, *Polymer*, **50**, 3582-3586.
- [3] **Guo, H.Q., Kajiwara, A., Morishima, Y., and Kamachi, M.**, 1996. Radical cation transformation polymerization and its application to the preparation of block copolymers of p-methoxystyrene and cyclohexene oxide, *Macromolecules*, **29**, 2354-2358.
- [4] **Acar, M.H. and Matyjaszewski, K.**, 1999. Block copolymers by transformation of living anionic polymerization into controlled/"living" atom transfer radical polymerization, *Macromolecular Chemistry and Physics*, **200**, 1094-1100.
- [5] **Coca, S. and Matyjaszewski, K.**, 1997. Block copolymers by transformation of "living" carbocationic into "living" radical polymerization .2. Aba-type block copolymers comprising rubbery polyisobutene middle segment, *Journal of Polymer Science Part a-Polymer Chemistry*, **35**, 3595-3601.
- [6] **Coca, S. and Matyjaszewski, K.**, 1997. Block copolymers by transformation of "living" carbocationic into "living" radical polymerization, *Macromolecules*, **30**, 2808-2810.
- [7] **Coca, S., Paik, H.J., and Matyjaszewski, K.**, 1997. Block copolymers by transformations of living ring-opening metathesis polymerization controlled/"living" atom transfer radical polymerization, *Macromolecules*, **30**, 6513-6516.
- [8] **Kajiwara, A. and Matyjaszewski, K.**, 1998. Formation of block copolymers by transformation of cationic ring-opening polymerization to atom transfer radical polymerization (atrp), *Macromolecules*, **31**, 3489-3493.
- [9] **Bernaerts, K.V., Schacht, E.H., Goethals, E.J., and Du Prez, F.E.**, 2003. Synthesis of poly(tetrahydrofuran)-b-polystyrene block copolymers from dual initiators for cationic ring-opening polymerization and atom transfer radical polymerization, *Journal of Polymer Science Part a-Polymer Chemistry*, **41**, 3206-3217.
- [10] **Erdogan, T., Bernaerts, K.V., Van Renterghem, L.M., Du Prez, F.E., and Goethals, E.J.**, 2005. Preparation of star block co-polymers by combination of cationic ring opening polymerization and atom transfer radical polymerization, *Designed Monomers and Polymers*, **8**, 705-714.

- [11] **Yenice, Z., Tasdelen, M.A., Oral, A., Guler, C., and Yagci, Y.**, 2009. Poly(styrene-b-tetrahydrofuran)/clay nanocomposites by mechanistic transformation, *Journal of Polymer Science Part a-Polymer Chemistry*, **47**, 2190-2197.
- [12] **Matzner, M., Noshay, A., and McGrath, J.E.**, 1977. Effect of hard segment chemical-structure on processibility of organo-siloxane block copolymers, *Transactions of the Society of Rheology*, **21**, 273-290.
- [13] **Acik, G., Kahveci, M.U., and Yagci, Y.**, 2010. Synthesis of block copolymers by combination of atom transfer radical polymerization and visible light radical photopolymerization methods, *Macromolecules*, **43**, 9198-9201.
- [14] **Goodman, I.**, *Developments in block copolymers. 2.* 1985, London; New-York: Elsevier applied science publ.
- [15] **Galli, G., Chiellini, E., Laus, M., and Angeloni, A.S.**, 1994. Hybrid liquid-crystalline block copolymers with polystyrene and polyester blocks, *Molecular Crystals and Liquid Crystals*, **254**, 429-443.
- [16] **Fischer, H. and Poser, S.**, 1996. Liquid crystalline block and graft copolymers, *Acta Polymerica*, **47**, 413-428.
- [17] **Szwarc M.**, 1956. Living Polymers and Mechanism of Anionic- Polymerization, *Advances in Polymer Science* **49**, 1-177.
- [18] **Hsieh, H.L. and Quirk, R.P.**, *Anionic polymerization : Principles and practical applications.* 1996, New York [u.a.]: Dekker.
- [19] **Burgess, F.J., Cunliffe, A.V., Maccallum, J.R., and Richards, D.H.**, 1977. Reaction to effect transformation of anionic-polymerization into cationic polymerization .1. Synthesis and reactivities of anionically generated bromine terminated polymers, *Polymer*, **18**, 719-725.
- [20] **Yildirim, T.G., Hepuzer, Y., Hizal, G., and Yagci, Y.**, 1999. Synthesis of block copolymers by transformation of photosensitized cationic polymerization to stable free radical polymerization, *Polymer*, **40**, 3885-3890.
- [21] **Matyjaszewski, K.**, *Cationic polymerizations : Mechanisms, synthesis, and applications.* 1996, New York: Marcel Dekker.
- [22] **Nomura, R. and Endo, T.**, 1995. One-pot transformation of living cationic polymerization into a living anionic one by samarium(ii) iodide - synthesis of poly(tetrahydrofuran-b-epsilon-caprolactone) block-copolymer, *Macromolecules*, **28**, 1754-1757.
- [23] **Nomura, R., Shibasaki, Y., and Endo, T.**, 1996. Block copolymerization of tetrahydrofuran with delta-valerolactone by the samarium iodide-induced transformation, *Polymer Bulletin*, **37**, 597-601.
- [24] **Burgess, F.J., Cunliffe, A.V., Dawkins, J.V., and Richards, D.H.**, 1977. Reaction to effect transformation of anionic-polymerization into cationic polymerization .3. Analysis of block copolymer formation by gel-permeation chromatography, *Polymer*, **18**, 733-740.
- [25] **Abel, E.W. and Moorhous, S.**, 1970. Utilization of hexamethylditin in synthesis of organotin-transitional metal complexes, *Journal of Organometallic Chemistry*, **24**, 687-690.
- [26] **Hizal, G., Sarman, A., and Yagci, Y.**, 1995. Synthesis of hydroxy-terminated polytetrahydrofuran by photoinduced process, *Polymer Bulletin*, **35**, 567-573.

- [27] **Yagci, Y. and Hepuzer, Y.**, 1999. A novel visible light initiating system for cationic polymerization, *Macromolecules*, **32**, 6367-6370.
- [28] **Miura, Y., Narumi, A., Matsuya, S., Satoh, T., Duan, Q., Kaga, H., and Kakuchi, T.**, 2005. Synthesis of well-defined ab(20)-type star polymers with cyclodextrin-core by combination of nmp and atp, *Journal of Polymer Science Part a-Polymer Chemistry*, **43**, 4271-4279.
- [29] **Celik, C., Hizal, G., and Tunca, U.**, 2003. Synthesis of miktoarm star and miktoarm star block copolymers via a combination of atom transfer radical polymerization and stable free-radical polymerization, *Journal of Polymer Science Part a-Polymer Chemistry*, **41**, 2542-2548.
- [30] **Durmaz, H., Aras, S., Hizal, G., and Tunca, U.**, 2005. Synthesis of a(3)b(3)-type polystyrene-poly(methyl methacrylate) miktoarm star polymers via combination of stable free radical and atom transfer radical polymerization routes, *Designed Monomers and Polymers*, **8**, 203-210.
- [31] **Shi, Y., Fu, Z.F., Li, B.Y., and Yang, W.T.**, 2006. Synthesis of diblock copolymers by combining stable free radical polymerization and atom transfer radical polymerization, *Journal of Polymer Science Part a-Polymer Chemistry*, **44**, 2468-2475.
- [32] **Paik, H.J., Teodorescu, M., Xia, J.H., and Matyjaszewski, K.**, 1999. Block copolymerizations of vinyl acetate by combination of conventional and atom transfer radical polymerization, *Macromolecules*, **32**, 7023-7031.
- [33] **Destarac, M. and Boutevin, B.**, 1999. Use of a trichloromethyl-terminated azo initiator to synthesize block copolymers by consecutive conventional radical polymerization and atp, *Macromolecular Rapid Communications*, **20**, 641-645.
- [34] **Gilbert, B.C., Harrison, R.J., Lindsay, C.I., McGrail, P.T., Parsons, A.F., Southward, R., and Irvine, D.J.**, 2003. Polymerization of methyl methacrylate using dimanganese decacarbonyl in the presence of organohalides, *Macromolecules*, **36**, 9020-9023.
- [35] **Degirmenci, M., Cianga, I., and Yagci, Y.**, 2002. Synthesis of well-defined polystyrene macrophotoinitiators by atom-transfer radical polymerization, *Macromolecular Chemistry and Physics*, **203**, 1279-1284.
- [36] **Erel, I., Cianga, I., Serhatli, E., and Yagci, Y.**, 2002. Synthesis of block copolymers by combination of photoinduced and atom transfer radical polymerization routes, *European Polymer Journal*, **38**, 1409-1415.
- [37] **Simionescu, C.I., Comanita, E., Pastravanu, M., and Druta, I.**, 1986. Azo peroxide initiators - synthesis and characterization of o-[4-(t-butylazo)-4-cyanovaleryl]-o'-acetyl peroxide, *Polymer Bulletin*, **16**, 235-241.
- [38] **Yagci, Y. and Reetz, I.**, in *Handbook of engineering polymeric materials*, N.P. Cheremisinoff, Editor. 1997, Marcel Dekker: New York. p. 735-753.
- [39] **Onen, A. and Yagci, Y.**, 1990. Bifunctional initiators - synthesis, characterization, and initiator properties of azo-benzoin initiators, *Journal of Macromolecular Science-Chemistry*, **A27**, 743-753.
- [40] **Onen, A. and Yagci, Y.**, 1990. Bifunctional initiators .2. Bulk-polymerization of styrene initiated by 4,4'-azobis(4-cyanopentanoyl)-bis(alpha-

- methylolbenzoin methyl-ether), *Angewandte Makromolekulare Chemie*, **181**, 191-197.
- [41] **Tunca, U., Serhatli, I.E., and Yagci, Y.**, 1989. Polymerization of acrylamide initiated by the redox system ce(iv)-4,4-azobis (4-cyano pentanol), *Polymer Bulletin*, **22**, 483-488.
- [42] **Yagci, Y. and Schnabel, W.**, 1990. Light-induced synthesis of block and graft-copolymers, *Progress in Polymer Science*, **15**, 551-601.
- [43] **Yagci, Y.**, 2000. Photoinitiating synthesis systems and their use in polymer, *Macromolecular Symposia*, **161**, 19-35.
- [44] **Burgess, F.J., Cunliffe, A.V., Maccallum, J.R., and Richards, D.H.**, 1977. Reactions to effect transformation of anionic-polymerization into cationic polymerization .2. Synthesis and reactivities of anionically generated xylene bromide-terminated polymers, *Polymer*, **18**, 726-732.
- [45] **Yagci, Y. and Tasdelen, M.A.**, 2006. Mechanistic transformations involving living and controlled/living polymerization methods, *Progress in Polymer Science*, **31**, 1133-1170.
- [46] **Matyjaszewski, K. and Gaynor, S.G.**, *In applied polymer science*, , ed. C.D. Craver and C.E. Carraher. 2000, Oxford: Pergamon Press. 929.
- [47] **Swarc, M.**, 1960. Termination of anionic polymerization, *Advances in Polymer Science*, **2**, 275-306.
- [48] **Kato, M., Kamigaito, M., Sawamoto, M., and Higashimura, T.**, 1995. Polymerization of methyl-methacrylate with the carbon-tetrachloride dichlorotris(triphenylphosphine)ruthenium(ii) methylaluminum bis(2,6-di-tert-butylphenoxide) initiating system - possibility of living radical polymerization, *Macromolecules*, **28**, 1721-1723.
- [49] **Wang, J.S. and Matyjaszewski, K.**, 1995. Controlled living radical polymerization - atom-transfer radical polymerization in the presence of transition-metal complexes, *Journal of the American Chemical Society*, **117**, 5614-5615.
- [50] **Patten, T.E. and Matyjaszewski, K.**, 1998. Atom transfer radical polymerization and the synthesis of polymeric materials, *Advanced Materials*, **10**, 901.
- [51] **Patten, T.E. and Matyjaszewski, K.**, 1999. Copper(i)-catalyzed atom transfer radical polymerization, *Accounts of Chemical Research*, **32**, 895-903.
- [52] **Matyjaszewski, K. and Xia, J.**, *Fundamentals of atom transfer radical polymerization*, in *Handbook of radical polymerization*, K. Matyjaszewski and T.P. Davis, Editors. 2002, John Wiley and Sons, Inc.: New York.
- [53] **Fischer, H.**, 1999. The persistent radical effect in controlled radical polymerizations, *Journal of Polymer Science Part a-Polymer Chemistry*, **37**, 1885-1901.
- [54] **Sonmez, H.B. and Bicak, N.**, 2002. Quaternization of poly(4-vinyl pyridine) beads with 2-chloroacetamide for selective mercury extraction, *Reactive & Functional Polymers*, **51**, 55-60.
- [55] **Xia, J.H. and Matyjaszewski, K.**, 1997. Controlled/"living" radical polymerization. Homogeneous reverse atom transfer radical polymerization using aibn as the initiator, *Macromolecules*, **30**, 7692-7696.
- [56] **Klumperman, B.**, *Living radical polymerization*, in *Encyclopedia of polymer science and technology*. 2004, John Wiley & Sons, Inc.: New York.

- [57] **Teodorescu, M., Gaynor, S.G., and Matyjaszewski, K.**, 2000. Halide anions as ligands in iron-mediated atom transfer radical polymerization, *Macromolecules*, **33**, 2335-2339.
- [58] **Moineau, G., Minet, M., Teyssie, P., and Jerome, R.**, 2000. Synthesis of fully acrylic thermoplastic elastomers by atom transfer radical polymerization (atrp), 2 - effect of the catalyst on the molecular control and the rheological properties of the triblock copolymers, *Macromolecular Chemistry and Physics*, **201**, 1108-1114.
- [59] **Kato, M., Kamigaito, M., Sawamoto, M., and Higashimura, T.**, 1995. Polymerization of methyl-methacrylate with the carbon-tetrachloride dichlorotris (triphenylphosphine) ruthenium(ii) methylaluminum bis(2,6-di-tert-butylphenoxide) initiating system - possibility of living radical polymerization, *Macromolecules*, **28**, 1721-1723.
- [60] **Haddleton, D.M., Jasieczek, C.B., Hannon, M.J., and Shooter, A.J.**, 1997. Atom transfer radical polymerization of methyl methacrylate initiated by alkyl bromide and 2-pyridinecarbaldehyde imine copper(i) complexes, *Macromolecules*, **30**, 2190-2193.
- [61] **Acar, M.H. and Bicak, N.**, 2003. Synthesis of hexylated triethylenetetramine: New ligand for homogeneous atom transfer radical polymerization, *Journal of Polymer Science Part a-Polymer Chemistry*, **41**, 1677-1680.
- [62] **Bicak, N., Gazi, M., Tunca, U., and Kucukkaya, I.**, 2004. Utility of atom transfer radical polymerization for the preparation of poly(methyl methacrylate) beads in an aqueous suspension, *Journal of Polymer Science Part a-Polymer Chemistry*, **42**, 1362-1366.
- [63] **Catala, J.M., Bubel, F., and Hammouch, S.O.**, 1995. Living radical polymerization - kinetic results, *Macromolecules*, **28**, 8441-8443.
- [64] **Wang, D. and Wu, Z.**, 1998. Facile synthesis of new unimolecular initiators for living radical polymerizations, *Macromolecules*, **31**, 6727-6729.
- [65] **Miura, Y., Hirota, K., Moto, H., and Yamada, B.**, 1998. High-yield synthesis of alkoxyamine initiators carrying a functional group by reaction of ethylbenzenes with di-tert-butyl diperoxalate in the presence of nitroxides, *Macromolecules*, **31**, 4659-4661.
- [66] **Zink, M.O., Kramer, A., and Nesvadba, P.**, 2000. New alkoxyamines from the addition of free radicals to nitrones or nitroso compounds as initiators for living free radical polymerization, *Macromolecules*, **33**, 8106-8108.
- [67] **Benoit, D., Chaplinski, V., Braslau, R., and Hawker, C.J.**, 1999. Development of a universal alkoxyamine for "living" free radical polymerizations, *Journal of the American Chemical Society*, **121**, 3904-3920.
- [68] **Grimaldi, S., Finet, J.P., Le Moigne, F., Zeghdaoui, A., Tordo, P., Benoit, D., Fontanille, M., and Gnanou, Y.**, 2000. Acyclic beta-phosphonylated nitroxides: A new series of counter-radicals for "living"/controlled free radical polymerization, *Macromolecules*, **33**, 1141-1147.
- [69] **Benoit, D., Grimaldi, S., Robin, S., Finet, J.P., Tordo, P., and Gnanou, Y.**, 2000. Kinetics and mechanism of controlled free-radical polymerization of styrene and n-butyl acrylate in the presence of an

- acyclic beta-phosphonylated nitroxide, *Journal of the American Chemical Society*, **122**, 5929-5939.
- [70] **Baldovi, M.V., Mohtat, N., and Scaiano, J.C.**, 1996. Influence of acids on reaction rates of free radical scavenging by tempo. Relevance to "living" free radical polymerizations, *Macromolecules*, **29**, 5497-5499.
- [71] **Skene, W.G., Belt, S.T., Connolly, T.J., Hahn, P., and Scaiano, J.C.**, 1998. Decomposition kinetics, arrhenius parameters, and bond dissociation energies for alkoxyamines of relevance in "living" free radical polymerization, *Macromolecules*, **31**, 9103-9105.
- [72] **Tunca, U., Hizal, G., Acar, M.H., Tasdelen, M.A., Yagci, Y., and Mishra, M.K.**, *Controlled/living radical polymerization*, in *Handbook of vinyl polymers*, Y. Yagci and M.K. Mishra, Editors. 2009, CRC Press Taylor & Francis Group, : New York. p. 256-281.
- [73] **Convertine, A.J., Ayres, N., Scales, C.W., Lowe, A.B., and McCormick, C.L.**, 2004. Facile, controlled, room-temperature raft polymerization of n-isopropylacrylamide, *Biomacromolecules*, **5**, 1177-1180.
- [74] **Quinn, J.F., Rizzardo, E., and Davis, T.P.**, 2001. Ambient temperature reversible addition-fragmentation chain transfer polymerisation, *Chemical Communications*, 1044-1045.
- [75] **Chiefari, J. and Rizzardo, E.**, *Control of free radical polymerization by chain transfer methods*, in *Handbook of radical polymerization*, K. Matyjaszewski and T.P. Davis, Editors. 2002, John Wiley and Sons, Inc.: New York.
- [76] **Degee, P., Dubois, P., and Jerome, R.**, 1997. Bulk polymerization of lactides initiated by aluminium isopropoxide .3. Thermal stability and viscoelastic properties, *Macromolecular Chemistry and Physics*, **198**, 1985-1995.
- [77] **Johns, D., Lenz, R.W., and Luecke, A.**, *Lactones*, , in *Ring-opening polymerization*, I. K.J. and T. Saegusa, Editors. 1984, Elsevier: London. p. 464.
- [78] **Rabek, J.F.**, 1987. Mechanisms of photophysical and photochemical reactions in polymer: Theory and practical applications, wiley, new york.
- [79] **Wayne, R.P.**, 1988. Principles and applications of photochemistry, oxford univ. Press, oxford, uk.
- [80] **Calvert, J.G. and Pitts, J.N.**, 1966. Photochemistry, wiley & sons, new york.
- [81] **Rabek, J.F.**, *Mechanisms of photophysical and photochemical reactions*, in *Polymer: Theory and practical applications*. 1987, Wiley: New York.
- [82] **Wayne, R.P.**, *Principles and applications of photochemistry*. 1988, Oxford Univ. Press: Oxford UK.
- [83] **Calvert, J.G. and Pitts, J.N.**, *Photochemistry*,. 1966, Wiley & Sons, : New York.
- [84] **Silverstein, R.v., Bassler, G.C., and Morrill, T.C.**, *Spectrometric identification of organic compounds*. 1991, Wiley & Sons. 5th ed.: New York.
- [85] **Arsu, N., Reetz, I., Yagci, Y., and Mishra, M.K.**, *Photoinitiated radical vinyl polymerization* in *Handbook of vinyl polymers: Radical polymerization & technology*, Y. Yagci and M.K. Mishra, Editors. 2008, Taylor & Francis, Inc. p. 141-204.
- [86] **Hageman, H.J.**, 1985. Photoinitiators for free-radical polymerization, *Progress in Organic Coatings*, **13**, 123-150.

- [87] **Monroe, B.M. and Weed, G.C.**, 1993. Photoinitiators for free-radical-initiated photoimaging systems, *Chemical Reviews*, **93**, 435-448.
- [88] **Davidson, R.S.**, 1993. The chemistry of photoinitiators - some recent developments, *Journal of Photochemistry and Photobiology a-Chemistry*, **73**, 81-96.
- [89] **Gruber, H.F.**, 1992. Photoinitiators for free-radical polymerization, *Progress in Polymer Science*, **17**, 953-1044.
- [90] **Abel, E.W. and Stone, F.G.A.**, 1969. The chemistry of transition-metal carbonyls: Structural considerations, *Quarterly Reviews, Chemical Society*, **23**, 325-371.
- [91] **Becke-Goehring, M., Kettrup, A., Specker, H., Strohmeier, W., and Freund, F.**, 1968. Kinetik und mechanismus von austausch- und substitutionsreaktionen an metallcarbonylen, *Topics in Current Chemistry*, **10**, 306-346.
- [92] **Strohmeier, W.**, 1964. Photochemische substitutionen an metallcarbonylen und deren derivaten, *Angewandte Chemie*, **76**, 873-881.
- [93] **Koerner von Gustorf, E. and Grevels, F.W.**, 1969. Photochemistry of metal carbonyls, metallocenes, and olefin complexes, *Topics in Current Chemistry*, **13**, 366-450.
- [94] **Koumura, K., Satoh, K., and Kamigaito, M.**, 2008. Manganese-based controlled/living radical polymerization of vinyl acetate, methyl acrylate, and styrene: Highly active, versatile, and photoresponsive systems, *Macromolecules*, **41**, 7359-7367.
- [95] **Bamford, C.H. and Finch, C.A.**, 1963. Initiation of vinyl polymerization by manganese carbonyl and related compounds, *Transactions of the Faraday Society*, **59**, 540-547.
- [96] **Bamford, C.H. and Denyer, R.**, 1968. Initiation of free radical polymerization by manganese carbonyl and carbon tetrachloride, *Nature*, **217**, 59-60.
- [97] **Jenkins, D.W. and Hudson, S.M.**, 2002. Heterogeneous graft copolymerization of chitosan powder with methyl acrylate using trichloroacetyl-manganese carbonyl co-initiation, *Macromolecules*, **35**, 3413-3419.
- [98] **Bamford, C.H.**, in *Reactivity, mechanism and structure in polymer chemistry*, A.D. Jenkins and A. Ledwith, Editors. 1974, Wiley-Interscience: London; New York.
- [99] **Bamford, C.H.**, 1976. New photo-initiating systems and photoactive polymers and their applications, *Polymer*, **17**, 321-324.
- [100] **Bamford, C.H. and Paprotny, J.**, 1972. After effects in polymerizations photo-initiated by manganese carbonyl and halide systems, *Polymer*, **13**, 208-217.
- [101] **Bamford, C.H. and Mullik, S.U.**, 1973. Photosensitization of free-radical polymerization by $\text{Mn}(\text{CO})_5$, *Journal of the Chemical Society-Faraday Transactions I*, **69**, 1127-1142.
- [102] **Niwa, M., Higashi, N., and Okamoto, M.**, 1988. Synthesis of controlled block and graft copolymers .2. Block and graft-polymerization initiated by monohalo containing polymer manganese carbonyl systems, *Journal of Macromolecular Science-Chemistry*, **A25**, 1515-1525.
- [103] **Niwa, M., Katsurada, N., Matsumoto, T., and Okamoto, M.**, 1988. Synthesis of controlled block and graft-copolymers .1. Block

- polymerizations initiated asymmetric telechelic bromo-terminated polymer together with manganese carbonyl, *Journal of Macromolecular Science-Chemistry*, **A25**, 445-466.
- [104] **Koumura, K., Satoh, K., and Kamigaito, M.**, 2009. Mn-2(co)(10)-induced controlled/living radical copolymerization of methyl acrylate and 1-hexene in fluoroalcohol: High alpha-olefin content copolymers with controlled molecular weights, *Macromolecules*, **42**, 2497-2504.
- [105] **Koumura, K., Satoh, K., and Kamigaito, M.**, 2009. Mn-2(co)(10)-induced controlled/living radical copolymerization of vinyl acetate and methyl acrylate: Spontaneous formation of block copolymers consisting of gradient and homopolymer segments, *Journal of Polymer Science Part a-Polymer Chemistry*, **47**, 1343-1353.
- [106] **Koumura, K., Satoh, K., and Kamigaito, M.**, 2009. Mn-2(co)(10)-induced raft polymerization of vinyl acetate, methyl acrylate, and styrene, *Polymer Journal*, **41**, 595-603.
- [107] **Coessens, V., Pintauer, T., and Matyjaszewski, K.**, 2001. Functional polymers by atom transfer radical polymerization, *Progress in Polymer Science*, **26**, 337-377.
- [108] **Wang, J.S. and Matyjaszewski, K.**, 1995. Controlled living radical polymerization - halogen atom-transfer radical polymerization promoted by a cu(i)-cu(ii) redox process, *Macromolecules*, **28**, 7901-7910.
- [109] **Brandrup, J., Immergut, E.H., and Grulke, E.A.**, *Polymer handbook*. 1999, New York: Wiley.
- [110] **Alimoglu, A.K., Bamford, C.H., Ledwith, A., and Mullik, S.U.**, 1977. Synthesis and reactions of polymers with photoactive terminal groups .1. Kinetics and mechanisms of radical and anionic coupling of n-acetyldibenz b,f azepine units to polymer-molecules, *Macromolecules*, **10**, 1081-1085.



CURRICULUM VITA

Candidate's full name: Gokhan ACIK

Place and date of birth: Istanbul, 15.10.1987

Universities and Colleges attended:

2009-2011 Master of Science (Chemistry), Istanbul Technical University, Istanbul, Turkey

2005-2009 Chemistry, Trakya University, Edirne, Turkey

2001-2004 Bahcelievler High School, Istanbul, Turkey

Publications:

- **Acik G**, Kahveci MU, Yagci Y., Synthesis of Block Copolymers by Combination of Atom Transfer Radical Polymerization and Visible Light Radical Photopolymerization Methods. *Macromolecules*, 2010,43(21), 9198-9201.

