ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

$Mn_2(CO)_{10}$ BASED VISIBLE-LIGHT PHOTO INITIATING SYSTEMS FOR DISTINCT MACROMOLECULAR STRUCTURES

Ph.D. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

FARKLI MAKROMOLEKÜLER YAPILARIN SENTEZİ İÇİN $Mn_2(CO)_{10}$ TEMELLİ GÖRÜNÜR BÖLGE FOTOBAŞLATICI SİSTEMLER

DOKTORA TEZİ

Mustafa ÇİFTÇİ
(509112005)

Kimya Anabilim Dalı

Kimya Programı

Tez Danışmanı: Prof. Dr. Yusuf YAĞCI

MART 2017

Mustafa Ciftci, a Ph.D. student of ITU Graduate School of Science Engineering and Technology student ID 509122005, successfully defended the thesis entitled "$Mn_2(CO)_{10}$ BASED VISIBLE-LIGHT PHOTO INITIATING SYSTEMS FOR DISTINCT MACROMOLECULAR STRUCTURES", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor: **Prof. Dr. Yusuf YAĞCI**
İstanbul Technical University

Jury Members: **Prof. Dr. Gürkan HIZAL**
Istanbul Technical University

Prof. Dr. Amitav SANYAL
Boğazici University

Prof. Dr. Nergis ARSU
Yıldız Technical University

Assoc. Prof. Dr. Bünyamin KARAGÖZ
Istanbul Technical University

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To my parents and my wife

FOREWORD

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Mustafa ÇİFTÇİ
(M.Sc. Chemist)

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ABBREVIATIONS

ADMET : Acyclic Diene Metathesis
ATRP : Atom Transfer Radical Polymerization
$CDCl_3$: Deuterated Chloroform
COE : *Cis*-cyclooctene
CMRP : Cobalt-Mediated Radical Polymerization
Conv : Conversion
CuAAC : Copper Catalyzed Azide-Alkyne Cycloaddition
$Cu^{I}Br$: Copper(I) Bromide
$Cu^{II}Br$: Copper(II) Bromide
$Ph_2I^+Br^-$: Diphenyl Iodonium Bromide
$Ph_2I^+PF_6^-$: Diphenyliodonium Hexafluorophosphate
DMF : *N*, *N*-Dimehthylformamide
EtBP : Ethyl 2-Bromopropionate
FT-IR : Fourier Transform Infrared Spectrophotometer
GPC : Gel Permeation Chromatography
^1H NMR : Hydrogen Nuclear Magnetic Resonance Spectroscopy
ITP : Iodine Transfer Polymerization
IBVE : Isobutyl Vinyl Ether
M_n : Number Avarage Molecular Weight
$Mn_2(CO)_{10}$: Dimanganese Decacarbonyl
MA : Methyl Acrylate
MMA : Methyl Methacrylate
NMP : Nitroxide-Mediated Polymerization
OMIP : Organoiodine-Mediated Radical Polymerization
PDI : Polydispersity
PE-*g*-PAA : Polyethylene-*graft*-poly(acrylic acid)
PE-*g*-P*t*BA : Polyethylene-*graft*-poly(*tert*-butylacrylate)
PMDETA : *N, N, N',N'', N''*- Pentamethyldiethylenetriamine
PMMA : Poly(methyl methacrylate)
PROAD : Photoinduced Radical Oxidation/Addition/Deactivation
PVC : Poly(vinyl chloride)
RAFT : Reversible Addition Fragmentation Chain Transfer
ROMP : Ring-Opening Metathesis Polymerization
ROP : Ring-Opening Polymerization
THF : Tetrahydrofuran
***t*BA** : *Tert*-Butyl Acrylate
TFA : Trifluoroacetic Acid
UV : Ultraviolet
TGA : Thermogravimetric Analysis
DSC : Differential Scanning Calorimetry
SEM : Scanning Electron Microscope

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$Mn_2(CO)_{10}$ BASED VISIBLE-LIGHT PHOTO INITIATED SYSTEMS FOR MACROMOLECULAR ARCHITECTURES

SUMMARY

Light is a particularly fascinating stimulus because it can be precisely modulated in terms of wavelength, polarization direction and intensity, allowing spatial and temporal of the chemical reactions. Photochemical reactions involve the absorption of light to create an excited species that may undergo a number of different reactions such as dissociation, isomerization, abstraction, electron or energy transfer, and bond formation. These reactions have been studied quite extensively in various fields including organic chemistry, molecular biology and electronics etc. Photoinduced chemical reactions can advantageously be utilized in the field of polymer chemistry. Among them, photoinitiated polymerization which is a process that transforms monomers into polymers under light irradiation, has many advantages over other polymerization methods. It is fast, uses little energy, and readily occurs at room temperature. It has been estimated that energy costs can be reduced 30% by switching from thermal polymerization to photoinitiated polymerization. Therefore, it has been the basis of numerous conventional applications in surface coatings, printing inks, adhesives, microelectronics, printing plates and three dimensional imaging and micro-fabrication processes. Additionally, there is a huge number of photoinitiators for such photo-induced systems. Among them, dimanganese decacarbonyl ($Mn_2(CO)_{10}$) in conjunction with organic halides appears as an ideal photoinitiating system for the preparation of polymers with various topologies. Additional attractive features of the transition metal carbonyl compound include efficient light absorption in the visible region and solubility in a wide variety of reactive monomers. Many different applications of $Mn_2(CO)_{10}$ chemistry including initiation of free radical polymerization, promotion of cationic polymerization, mechanistic transformation, graft copolymerization, iodine degenerative transfer polymerization, preparation of telechelics and hyperbranched polymers have been reported and reviewed.

Taking account of the unique advantages of $Mn_2(CO)_{10}$ photochemistry, in this thesis, we focused on the development of new $Mn_2(CO)_{10}$ based photochemical approaches for the synthesis of macromolecular structures with various architectures.

In the first part of the thesis, polyolefin graft copolymers were prepared by combining ring-opening metathesis polymerization (ROMP), hydrobromination, and visible light-induced free radical polymerization. First, *cis*-cyclooctene (COE) was polymerized *via* ROMP in the presence of a chain transfer agent and quantitatively hydrobrominated to give bromo functional polyethylene (PE-Br). Subsequent irradiation of PE-Br in the visible range using dimanganese decacarbonyl ($Mn_2(CO)_{10}$) initiated free radical polymerization of *tert*-butyl acrylate (*t*BA) resulting in the formation of polyethylene-*graft*-poly(*tert*-butylacrylate) (PE-*g*-P*t*BA). The effect of $Mn_2(CO)_{10}$ concentration and irradiation time on the grafting density and efficiency was evaluated. Then, the *t*BA moieties of PE-*g*-P*t*BA were hydrolyzed into acrylic acid functionalities by acidolysis to obtain hydrophilic polyethylene-*graft*-poly(acrylic acid) (PE-*g*-PAA).

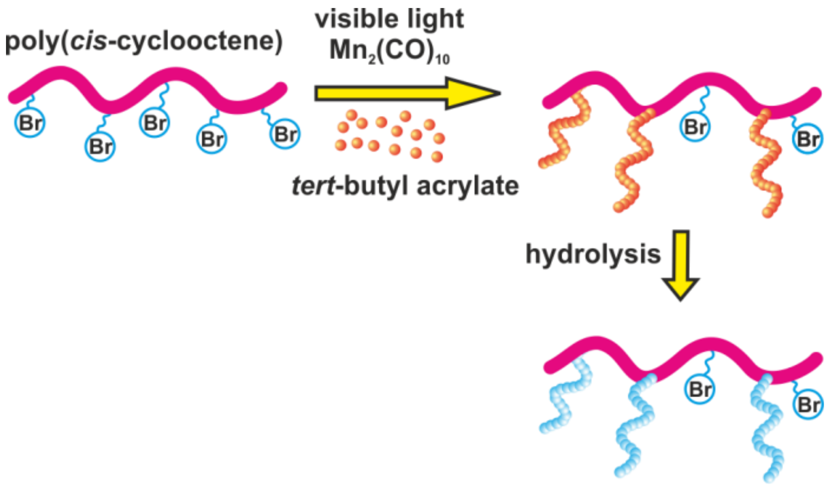


Figure 1 : Visible light induced graft copolymerization of *t*BA from Poly(COE-Br) by using $Mn_2(CO)_{10}$ and hydrolysis of resulted graft copolymer.

In the second part, a new photoredox catalyst system for Atom Transfer Radical Polymerization (ATRP) is developed on the basis of visible light photocatalysis using $Mn_2(CO)_{10}$ that initiates and controls the polymerization at ambient temperature. The polymerization was performed by $Mn_2(CO)_{10}$/alkyl halide system with visible- or sunlight in the presence of parts per million (ppm) copper catalysts. The photogenerated •$Mn(CO)_5$ radicals are not only able to abstract halogen atoms from alkyl halides to generate carbon centered radicals but also reduce the copper(II) bromide ($Cu^{II}Br_2$) to copper(I) bromide ($Cu^{I}Br$) directly, which was used as activator in the ATRP of vinyl monomers such as methyl methacrylate, methyl acrylate and styrene. The method was also used to synthesize graft copolymers from commercially available poly(vinyl chloride) without additional modification.

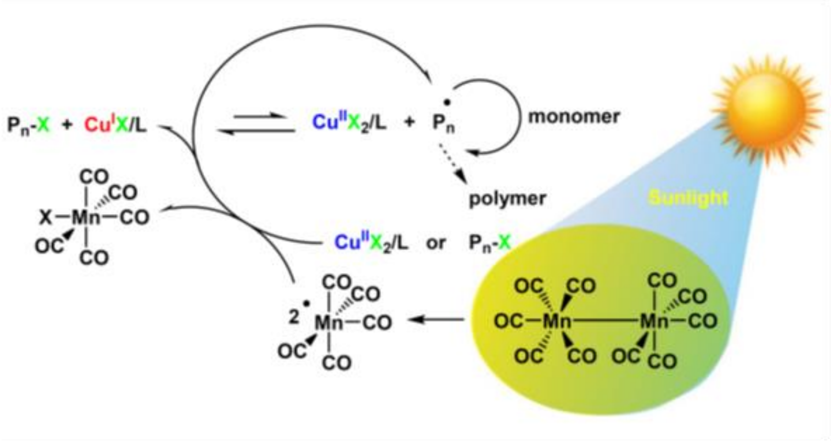


Figure 2 : Sunlight induced ATRP of methyl methacrylate catalyzed by dimanganese decacarbonyl with alkyl halide/$Cu^{II}Br_2$/PMDETA system.

Finally, a new photoinitiating system for living cationic polymerization of vinyl ethers is reported. In the current approach, visible-light irradiation of $Mn_2(CO)_{10}$ in the presence of an alkyl bromide results in the formation of carbon-centered radicals. The photochemically generated radicals were then oxidized by diphenyliodonium ions to the corresponding cations. These cations can add vinyl ether monomers, which are then rapidly deactivated by the bromide anions to give α-halide functional end groups. Poly(vinyl ether) chains are then grown through successive photoinduced radical oxidation/addition/deactivation (PROAD) in a controlled manner. The living nature of the system is evaluated through kinetics studies and block copolymer formation.

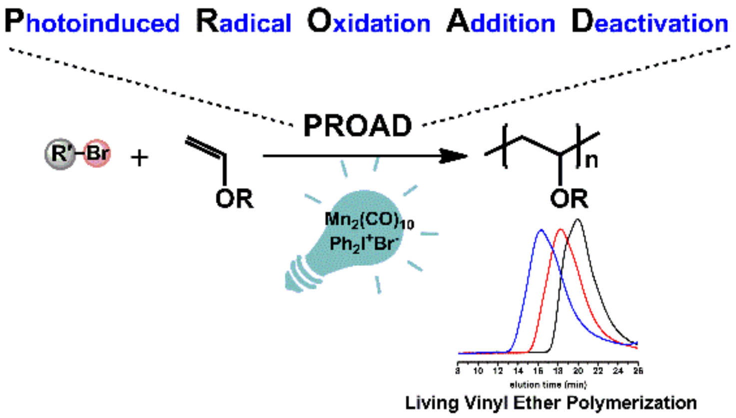


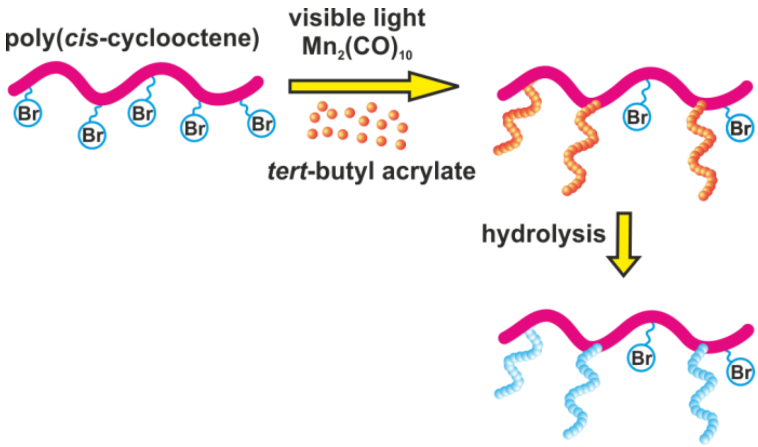
Figure 3 : Living Cationic Polymerization of Vinyl Ethers by Photoinduced Radical Oxidation Addition Deactivation Sequence.

MAKROMOLEKÜLER YAPILARIN SENTEZİ İÇİN $Mn_2(CO)_{10}$ TEMELLİ GÖRÜNÜR BÖLGE IŞIĞIYLA FOTOBAŞLATILMIŞ SİSTEMLER

ÖZET

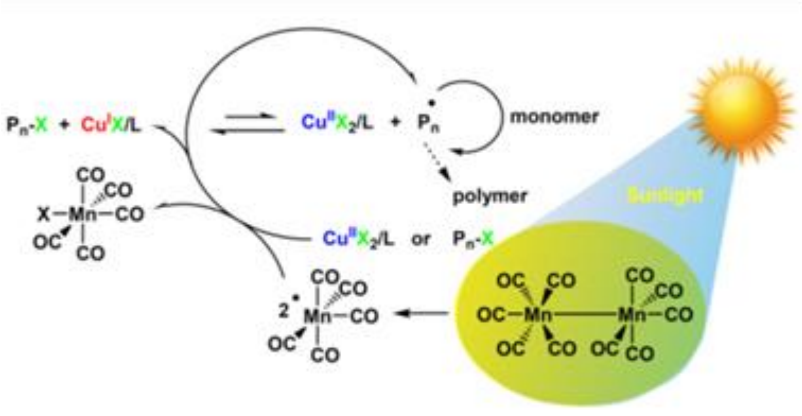
Işık, kimyasal tepkimelerin mekânsal ve zamansal kontrolüne imkan sağlayan dalga boyu, polarizasyon yönü ve yoğunluğu ayarlanabilmesi özellikleri sayesinde büyüleyici bir uyarıcıdır. Fotokimyasal reaksiyonlar, ayrışma, izomerleşme, elektron veya enerji transferi ve bağ oluşumu gibi birçok reaksiyonu vermek üzere, ışığın absorblanıp aktif türler yaratılmasını içerir. Bu reaksiyonlar organik kimya, moleküler biyoloji, elektronik gibi birçok alanda ayrıntılı olarak çalışılmıştır. Foto kimyasal başlatılmış reaksiyonlardan polimer kimyası alanında da faydalanılmaktadır. Özellikle, monomerlerin ışık etkisiyle polimerlere dönüştürüldüğü fotobaşlatılmış polimerizasyon tekniği diğer polimerizasyon tekniklerine göre birçok avantaja sahiptir. Isısal polimerizasyon yerine fotobaşlatılmış polimerizasyon tekniklerinin kullanımının %30 luk bir enerji tasarrufu sağlayacağı tahmin edilmektedir. Bu sebeple, yüzey kaplaması, mürekkep, yapıştırıcı, mikroelektronik, baskı levhaları ve üç boyutlu görüntüleme ile mikro-üretim gibi birçok klasik yöntemin temelini oluşturmaktadır. Ayrıca bu tür foto sistemler için birçok fotobaşlatıcı sistem geliştirilmiştir. Organik halojenler ile birlikte kullanılan $Mn_2(CO)_{10}$ sistemi farklı mimarideki polimerlerin sentezi için ideal bir sistem olarak ön plana çıkmaktadır. Görünür bölge ışığını absorplaması ve birçok farklı monomerdeki yüksek çözünürlük değerleri bu sistemin ilave avantajları olarak görülebilir. $Mn_2(CO)_{10}$ kimyasının, serbest radikal polimerzasyonu, katyonik polimerizasyon, mekanistik dönüşüm, aşı kopolimerizasyonu, dejeneratif iyot transfer polimerizasyonu, teleklik ve çok dallanmış polimer sentezi gibi birçok uygulaması literatürde mevcuttur. Bu tezde, tüm bu avantajlar dikkate alınarak, farklı mimarideki makromoleküler yapıların sentezi için $Mn_2(CO)_{10}$ temelli yeni fotokimyasal yöntemlerin geliştirilmesi üzerine odaklanılmıştır.

Bu kapsamda tezin ilk bölümünde, polyolefin aşı kopolimerlerinin (Halka açılması metathesis polimerizasyonu (ROMP), hidrobromlama ve görünür bölge ışığıyla başlatışmış serbest radikal polimerizasyonu yöntemlerinin birleşimi ile sentezlenmesi incelenmiştir. İlk olarak cis-siklookten bir zincir transfer ajanının varlığında ROMP yöntemi ile polimerleştirilip, brom fonksiyonlu polietilen vermek üzere hidrobromlanmıştır. Elde edilen bu polimerin $Mn_2(CO)_{10}$ varlığında görünür bölgede aydınlatılması, PE-*g*-P*t*BA aşı kopolimerini vermek üzere, *t*BA monomerinin serbest radikal polimerizasyonu başlatmıştır. $Mn_2(CO)_{10}$ miktarının ve aydınlatma süresinin aşı yoğunluğu ve etkinliği üzerindeki etkisi incelenmiştir. Daha sonra PE-*g*-P*t*BA polimerinin *t*BA grupları akrilik asit fonksiyonu vermek üzere hidroliz edilip, hidrofilik PE-*g*-PAA aşı kopolimeri elde edilmiştir.



Şekil 4 : $Mn_2(CO)_{10}$ kullanarak *t*BA monomerinin Poly(COE-Br) üzerine aşı kopolimerizasyonu ve elde edilen polimerin hidrolizi.

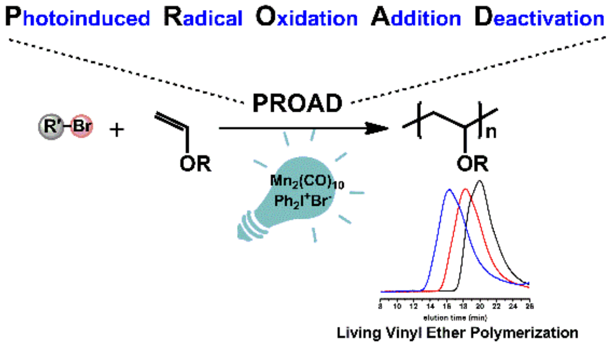
İkinci kısımda ise, $Mn_2(CO)_{10}$ kullanımı içeren yeni bir Atom Transfer Radikal Polimerizasyonu yöntemi geliştirilmiştir. Polimerizasyonlar $Mn_2(CO)_{10}$/alkil halojenür sisteminin, ppm mertebesindeki bakır katalizörü varlığında, güneş veya görünür bölge ışığı altında aydınlatılması ile gerçekleştirilmiştir. Sistemde fotokimyasal olarak oluşturulan $\bullet Mn(CO)_5$ radikalleri, alkil halojenürden halojen koparıp karbon merkezli radikaller oluşturmasının yanısıra aktivatör olarak görev yapan $Cu^{I}Br$ ün $Cu^{II}Br_2$ den doğrudan indirgenmesini sağlamaktadır. Ayrıca aynı yaklaşım kullanılarak, ticari polivinil klorür (PVC) nin aşı kopolimerlerinin sentezlenebileceğide gösterirlmiştir.



Şekil 5 : Metil metakrilatın, dimanganez dekakarbonil alkil halohenür/ $Cu^{II}Br_2$/PMDETA sistemiyle katalizörlüğünde, güneş ışığıyla başlatılmış Atom Transfer Radikal Polimerizasyonu.

Son olarak, vinil eterlerin yaşayan katyonik polimerizasyonu için yeni bir foto başlatıcı sistemi incelenmiştir. Bu bağlamda, alkil bromürün, $Mn_2(CO)_{10}$ varlığında aydınlatılması karbon merkezli radikal oluşumuna sebebiyet vermiştir. Daha sonra, bu radikaller vinil monomeri eklemek üzere difenilyodonyum iyonu yardımıyla ilgili katyonlara okside edilmiştir. Oluşan bu katyonlar vinil monomer eklenmesinin hemen ardından brom anyonu tarafından deaktive edilerek, halojen fonksiyonu ile sonlanır. Poli(vinil eter) zinciri ise benzer şekilde fotobaşlatılmış radikal oksidasyon/ekleme/deaktivasyon yöntemi ile kontrollü bir şekilde büyütülmüştür.

Sistemin yaşayan polimerizasyon doğası, kinetik çalışmalar ve blok kopolimerizasyon çalışmaları ile incelenmiştir.



Şekil 6 : Vinil eterlerin PROAD ile yaşayan katyonik polimerizasyonu.

1. INTRODUCTION

Every chemical reaction occurs only when a molecule is provided the necessary activation energy. When activation energy is provided in the form of light then the reaction is known as photochemical reaction. The application of photochemical reactions to the synthetic polymer science dates back to almost fifty years, although it recently gains higher priority as its advantages compared to other modes of syntheses have been noticed day by day. Most of the research on the utilization of photo-induced processes on polymer since is based on photoinitiated polymerization techniques in which monomers are transformed into polymers by light assistance. As it many has advantages over other polymerization processes, it has been widely used for the synthesis of various macromolecular structrures including branched polymers, hydrogels, cryogels, as well as metal and clay nanocomposites. Additionally, it has been the basis of numerous conventional applications in coatings, adhesives, inks, printing plates, optical waveguides, and microelectronics. Some other less traditional but interesting applications, including production of laser videodiscs, curing of acrylate dental fillings, and fabrication of 3D objects are also available.

In addition, there is a great number of photoinitiators with broad spectral sensitivities. Many photoinitiators having wide range of absorption characteristics have been developed and their mechanisms were investigated. These systems offer several advantages such as rapid reaction rates, reduced energy consumptions, mild temperatures and generation of reactive species at definite position of the macromolecular chains. In this context, manganese decacarbonyl ($Mn_2(CO)_{10}$) in conjunction with organic halides is an ideal photoinitiating system providing macromolecular design flexibility for the preparation of polymers with various topologies. In $Mn_2(CO)_{10}$, the Mn-Mn single bond is very weak (bond dissociation energy ~ 94-154 kJ mol^{-1}) and light-sensitive (λ_{max} = 345 nm in cyclohexane, which is assigned to the electron transition from σ to $\sigma*$ orbitals in the Mn-Mn bond). Upon UV or visible light irradiations, this bond easily decomposes to $MnCO_5^{\bullet}$ metalloradicals, which are readily undergo hydrogen or halogen atom abstraction reactions from alkyl halides or hydrogen donors. The formation of much stronger H-Mn (BDE ~ 250-270 kJ mol^{-1}) or X-Mn (242-294 kJ mol^{-1}) bonds provides a thermodynamic driving force for the abstraction reactions. The halogen abstraction reactions of $MnCO_5^{\bullet}$ from alkyl halide produces alkyl radicals ($R^{\bullet}$) in conjunction with X-$Mn(CO)_5$ products. Due to the steric effects of CO ligands, the abstraction reaction from a primary alkyl halide is faster than the secondary or tertiary alkyl halides. On the other hand, a weaker carbon-bromide bond is more facile compared to carbon-chloride bond in the generation of alkyl radicals.

The $Mn_2(CO)_{10}$ may undergo for several reactions including Mn-Mn bond cleavage (i), oxidation and reduction reactions, carbonyl ligand substitution (ii) and metal insertion into Mn-Mn bond (iv). For example, thermal or photochemical reaction of $Mn_2(CO)_{10}$ with triphenylphosphine (PPh_3) leads to ligand exchange reactions (v), in which a mixture of $Mn_2(CO)_8(PPh_3)_2$ and $Mn_2(CO)_9(PPh_3)$ are formed. Another well-known procedure is the reduction of $Mn_2(CO)_{10}$ using sodium/amalgam (Na/Hg) in tetrahydrofuran into $MnCO_5^-$ anion (iii), which can be further utilized in the metal-late alkylation or acylation reactions. Recently, the photochemically generated radicals from $Mn_2(CO)_{10}$ in conjunction with alkyl halides have been successfully used radical-based reactions, such as cyclisation (vi), coupling (vii), intermolecular addition (viii) and polymerizations (Figure 1.1).

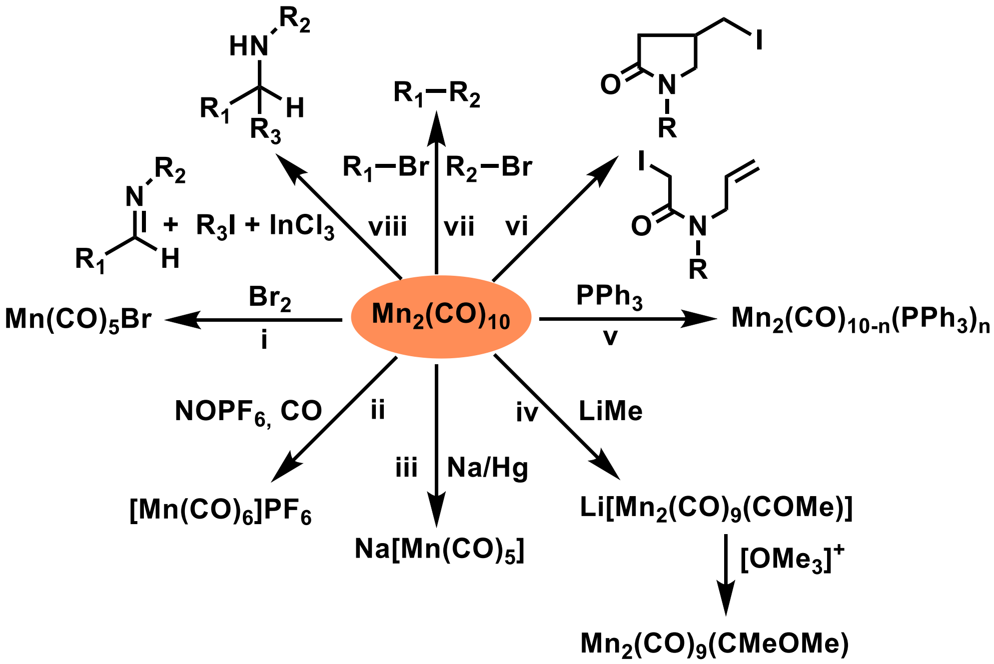


Figure 1.1 : Photochemical reactions of $Mn_2(CO)_{10}$.

These photoredox system involving both radical and cationic mechanisms has successfully been applied for macromolecular synthesis. A number different type of monomers including (meth)acrylates, styrenes, vinyl acetates, vinylidene fluorides, epoxides and vinyl ethers are effectively polymerized under ambient temperatures. From practical point of view, the most important feature of this initiating system is its optical characteristics, in particular the range and extent of light absorption (436 nm) with high quantum yield. Basically, radical production process involves a single electron transfer from transition metal to halide atom, which then decomposes to a halide ion and an alkyl radical (Figure 1.2). The produced alky radicals not only initiate the free radical polymerization of vinyl monomers, but also reduce the onium salts to generate ionic species for the cationic polymerization. Furthermore, this photoinitiating system has been perfectly adapted to the recently developed controlled radical polymerization (CRP) techniques, such as atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), iodine transfer polymerization (ITP) and reversible addition fragmentation chain transfer (RAFT) polymerization.

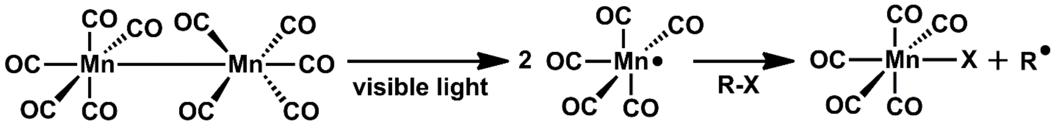


Figure 1.2 : Radical generation process by $Mn_2(CO)_{10}$ photochemistry.

Although the majority of industrial applications of photoinitiated polymerizations deal with free radical systems, the corresponding cationic mode is an important industrial process widely used in different applications such as coatings, inks, adhesives, varnishes, micro-electronics, microlithography and dyes. After the discovery of the living cationic polymerization, interest in such engineered macromolecular structures has been significantly increased. Among the living cationic polymerization techniques, the Lewis acid-catalyzed approach has been perfectly adapted to light-induced living cationic polymerization. In this methodology, photochemically generated cationic species (either carbocation or Brønsted acid) from photoinitiators containing halogen react with monomer (i.e., vinyl ether) and form a halide-monomer adduct required in the first stage of the propagation. Addition of new monomers to the adduct is catalyzed by Lewis acid, namely metal halides, by coordination of metal ion with the halogen of the adduct (Figure 1.3).

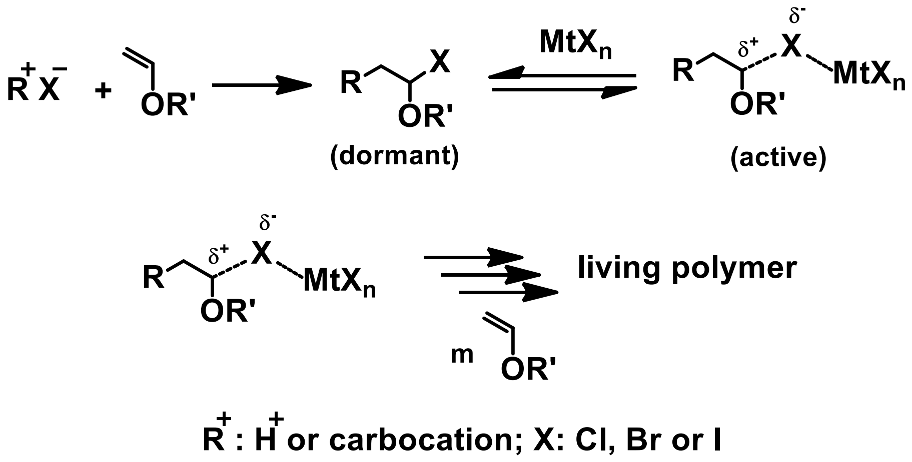


Figure 1.3 : Living cationic photopolymerization of vinyl ethers.

The well-known and the most widely used examples of cationic photoinitiators, are the onium-types such as iodonium, sulfonium and alkoxypyridinium salts due to their thermal stability, solubility in most of the cationically polymerizable monomers, and efficiency in generating reactive species upon photolysis. Since the spectral response of these photoiniators are usually below 300 nm, for their practical applications which require longer wavelengths, three modes of indirect activation are proposed. These include (a) oxidation of free radicals by oxidants (also called as free radical promoted cationic polymerization), (b) formation of charge transfer complexes, and (c) the use of photosensitizers in conjunction with onium salts.

1.1 Purpose of the Thesis

The objective of the thesis is to demonstrate the application of $Mn_2(CO)_{10}$ based photochemical routes for the synthesis of various macromolecular architectures. Different photo-initiating methods for both radical and cationic polymerizations are demonstrated. During the thesis, chromatographic (GPC), spectroscopic (^{1}H-NMR, UV, FT-IR) and thermographic (DSC) analyses are performed for the characterization of precursor and corresponding final polymers. Thesis is organized in such that each chapter has its own introduction, experimental, results and discussion sections.

Chapter 2 represents a novel photo-induced “grafting from” strategy for the synthesis of polyolefin based graft copolymers by using $Mn_2(CO)_{10}$ photochemistry. Thus, a bromo-functional polyolefin was used as macroinitiator in the presence of $Mn_2(CO)_{10}$ for the visible light induced free radical polymerization of *tert*-butyl acrylate (*t*BA) to give the corresponding graft copolymer (PE-*g*-P*t*BA).

Chapter 3 shows a simple and efficient photo-initiating system for ATRP of (meth)acrylates and St under visible light or sunlight irradiation by $Mn_2(CO)_{10}$ photochemistry. In the approach, $Mn_2(CO)_{10}$ not only initiates but also controls the polymerization. It was also proved that, the method was applicable for the synthesis of graft copolymers from commercially available poly(vinyl chloride) without additional modification.

Chapter 4 discusses a new photoinitiating system for living cationic polymerization of vinyl ethers by using $Mn_2(CO)_{10}$ in the presence of alkyl halide and oxidant.

Finally, concluding remarks are summarized in Chapter 5 along with recommendations for further work.

2. VISIBLE LIGHT-INDUCED GRAFTING FROM POLYOLEFINS[1]

Graft copolymers, a class of segmented copolymers, exhibit improved physical and chemical properties fulfilling endless demands of the industry for various applications. In many cases, such improvements can not be achieved by simple blending of respective homopolymers due to their incompatibility resulting in the formation of heterogeneous mixtures.[1, 2] In recent years, in need of preparing graft copolymers displaying improved physical and chemical properties, a number of strategies have been developed to solve that problem. Particularly, time and efforts have been devoted to the block and graft copolymers through recently developed controlled/living polymerization strategies and their combinations as summarized by our group.[3, 4]

Polyolefins have broad industrial utility on a huge scale as from packaging to building materials and automotive parts.[5, 6] Although they exhibit excellent resistance to harsh environment arising from the aliphatic nature, their relatively low compatibility and adhesion with other classes of polymers limits their broader applicability. Among the various strategies, the use of graft copolymers as compatibilizers is an elegant way to overcome these limitations by improving interfacial adhesion between two immiscible components. However, due to their inert chemical structure, grafting process can only be achieved by the incorporation of polar functionalities.[7-10] Radical polymerization at high temperature[11, 12], chemical-[13-15] and photo-grafting[16, 17], and ɤ-radiation functionalization[18, 19] are some of the methods used for fabricating polyolefins with polar functionalities. However, these processes either require severe conditions or the use of harsh reagents or give products without control of structure and compositions. For the obtainment of polyolefin graft copolymers with controlled structure and molecular weight, atom transfer radical polymerization (ATRP) seemed to be the most suitable route due to its simplicity and applicability to wide range of

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[1] This chapter is based on the paper " Ciftci M., Batat P., Demirel A.L., Xu G., Buchmeiser M. and Yagci Y., Visible light-induced grafting from polyolefins. Macromolecules, 2013, 46 (16), 6395-6401."

monomers.[20] Reports relating to the preparation of polyolefin graft copolymers by ATRP comprise in the first step the introduction of activated halide functionalities to the polyolefin. Recent studies focused on either acyclic diene metathesis (ADMET) or ring-opening metathesis polymerization (ROMP) using polar comonomers and post functionalization reactions.[21-26] In the approaches involving ATRP as the grafting method, the polyolefins should possess activated halides such as α-bromocarboxylic esters since their carbon-halide bonds are weaker and facilitates homolytic cleavage more easily in the presence of Cu(I) ligands.

Recently, Buchmeiser and co-workers[27, 28] reported a simple modification by ROMP derived poly(*cis*-cyclooctene), poly(COE), and poly(cyclopentene), poly(CPE), to yield a fully hydrobrominated intermediates, which were subsequently used as macroinitiators for the ATRP of *tert*-butyl acrylate (*t*BA) to yield polyethylene-*graft*-poly(*tert*-butylacrylate) (PE-*g*-P*t*BA). Notably, non-activated alkyl-halides, *i.e.* secondary alkyl bromides allowed for applying ATRP. The overall process for the preparation of poly(COE) is outlined in Figure 2.1.

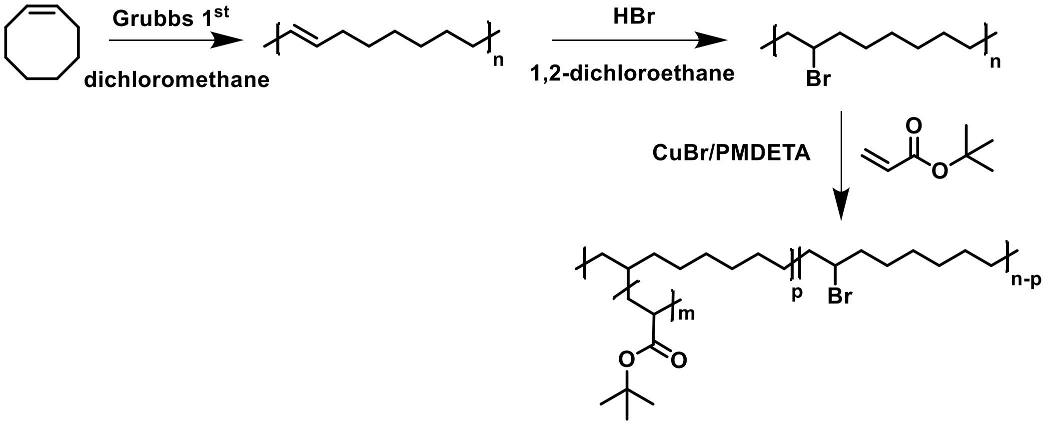

Figure 2.1 : Synthetic route to the poly(COE-Br) and PE-*g*-P*t*BA copolymer.

Photoinitiated free radical polymerization is an extensively used industrial process due to a number of technical and theoretical advantages.[29] Because of its applicability to most vinyl monomers at low temperatures, the availability of a wide range of photoinitiators acting in the UV-vis range and minimized side reactions, photoinitiated free radical polymerization has successfully been used for the preparation of both block[30-35] and graft copolymers[36, 37] for polymer-grafted surfaces[38, 39], hydrogels[40-42], cryogels[43], as well as for metal[44-52] and clay[53-57] nanocomposites. Although there exist a huge number of free radical photoinitiators with different solubility and absorption characteristics, dimanganese decacarbonyl ($Mn_2(CO)_{10}$) in conjunction with organic halides is ideal for use as a component of a photochemical free radical generation process[58-61] (Figure 2.2) since it absorbs light in the visible range and is soluble in a wide variety of reactive monomers.

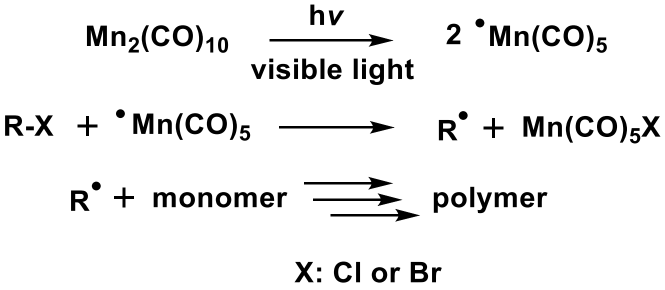

Figure 2.2 : Visible light-induced free radical polymerization of vinyl monomers using $Mn_2(CO)_{10}$ in the presence of an alkyl halide.

Earlier studies[62-64] from this laboratory showed that such a visible light-based radical generation process can be employed for the promotion of cationic polymerization and mechanism transformations involving different polymerization modes. In another related work from this laboratory, it was demonstrated that this chemistry can also be used as a simple and efficient method to prepare telechelics by visible-light-induced radical coupling.[65] Several other applications of $Mn_2(CO)_{10}$ chemistry including controlled radical polymerization process was also reported.[66-69]

On the basis of this background, we herein report a new visible light-induced "grafting from" method for the preparation of poly(ethylene)-based graft copolymers by using $Mn_2(CO)_{10}$ as the light absorbing component. Poly(*tert*-butyl acrylate) (P*t*BA) was chosen as the graft chains insuring a versatile platform for facile hydrolysis to yield amphiphilic polyolefin graft copolymers.

2.1 Experimental

2.1.1 Materials

$RuCl_2(PCy_3)_2(CHPh)$ (**G1**) (PCy_3=tricyclohexylphosphine), *cis*-cyclooctene (COE), hydrogen bromide (HBr) (33 wt.-% solution in acetic acid), and *cis*-4-octene was purchased from Aldrich. *cis*-COE was dried over CaH_2 and degassed by repeated freeze-pump-thaw cycles then distilled under N_2. *tert*-Butyl acrylate (*t*BA, 99%, Aldrich) was passed through basic alumina to remove any inhibitor and then vacuum distilled from CaH_2 prior to polymerization. Dimanganese decacarbonyl, ($Mn_2(CO)_{10}$, Aldrich), was purified by sublimation and stored in a refrigerator in the dark. Trifluoroacetic acid (TFA, 99%, Aldrich), dichloromethane (CH_2Cl_2, 99.5% Aldrich), toluene ($C_6H_5CH_3$, Aldrich, 99.5%) and pentane ($CH_3(CH)_2CH_3$, Aldrich, 98%) were used as recieved.

2.1.2 Synthesis of poly(cis-cyclooctene)

A solution of **G1** (8.3 mg, 0.010 mmol, 800 equiv.) in 1 mL of CH_2Cl_2 was added to a solution of COE (1.1 g, 10 mmol) and *cis*-4-octene (8.4 mg, 0.075 mmol) in 30 mL of CH_2Cl_2 under vigorous stirring. The reaction mixture was allowed to stir for 8 h at room temperature. After 8 h, the reaction was terminated by the addition of ethyl vinyl ether (2.0 mL), and the polymer was precipitated by the dropwise addition of the solution into methanol. The precipitated polymer was collected by filtration, washed with excess methanol and dried in vacuo. Yield: 0.83 g. ^{1}H NMR (400.133 Hz, $CDCl_3$) δ 5.39-5.32 (m, 2H), 1.97-2.02 (m, 4H), 1.29 (m, 8H) ppm. ^{13}C NMR (100.623 Hz, $CDCl_3$) δ 130.5, 130.0, 32.8, 29.9, 29.8, 29.3, 29.2, 27.4.

2.1.3 Hydrobromination poly(COE)

HBr (1.1 mL, 33 wt.-% solution in acetic acid, 5.9 mmol) was added to a solution of poly(COE) (0.50 g, 0.012 mmol) in 60 mL 1,2-dichloroethane in a pressure tube under nitrogen. The reaction solution was heated to 100 °C and refluxed for 48 h. After that the polymer was precipitated by the dropwise addition of the solution into methanol. The precipitated polymer was collected by filtration, washed with excess methanol and dried in vacuo. Yield: 0.62 g. ^{1}H NMR (400.133 Hz, $CDCl_3$) δ 3.97-4.07 (m), 1.72-1.81 (m), 1.29-1.53 (m). ^{13}C NMR (100.623 Hz, $CDCl_3$) δ 59.1, 39.1-39.3, 29.4-29.6, 29.1-29.2, 27.5-27.7.

2.1.4 Synthesis of polyethylene-*graft*-poly(*tert*-butyl acrylate)

Graft copolymerizations were carried out in a Pyrex tube. In a typical reaction, poly(COE-Br) (0.05 g, 0.0012 mmol) was placed in a Pyrex tube and 2 mL of toluene were added. The mixture was stirred vigorously to create a homogeneous solution. $Mn_2(CO)_{10}$ (0.017 g, 0,043 mmol) and *t*BA (2.20 g, 17 mmol) were then added and the tube was filled with dry nitrogen prior to irradiation by a Ker-Vis blue photoreactor equipped with 6 lamps (Philips TL-D 18 W) emitting light nominally at 400–500 nm at room temperature. At the end of the irradiation, the polymer was precipitated in a 10-fold excess of cold pentane and dried in vacuo. All other polymerizations were performed under identical experimental conditions. ^1H NMR (500 Hz, $CDCl_3$) δ 4.06-4.10 (m), 2.11-2.31 (m), 1.73-1.86 (m). ^{13}C NMR (125 Hz, $CDCl_3$) δ 176.2, 81.3, 59.1, 41.1-41.3, 39.1-39.3, 37.8-37.9, 27.6-29.2.

2.1.5 Synthesis of polyethylene-*graft*-poly(acrylic acid)

The *tert*-butyl acrylate groups of PE-*g*-P*t*BA, (0.300 g) were hydrolyzed using TFA (0.5 mL) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 24 h. Upon hydrolysis, the polymer precipitated in dichloromethane. It was separated by decantation, repeatedly washed with dichloromethane and finally dried in vacuo at room temperature. ^1H NMR (500 Hz, $CDCl_3$) δ 11.8-13.2, 4.06-4.10 (m), 2.11-2.31 (m), 1.64-1.82 (m). ^{13}C NMR (125 Hz, $CDCl_3$) δ 176.2, 59.1, 27.6-28.2.

2.1.6 Instrumentation

^1H and ^{13}C NMR spectra were recorded on an Agilent VNMRS 500 (500 MHz for proton and 125 MHz for carbon). Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer FTIR Spectrum One spectrometer. Gel-permeation chromatography (GPC) measurements were obtained from a ViscotekGPCmaxAutosampler system consisting of a pump module (GPCmax, Viscotek Corp., Houston, TX, USA), a combined light scattering (Model 270 Dual Detector, Viscotek Corp.), and a refractive index (RI) detector (VE 3580, Viscotek Corp.). The light scattering detector (λ_0 = 670 nm) included two scattering angles: 7° and 90°. The RI-detector was calibrated vs. polystyrene standards having narrow molecular weight distribution and so the quoted molecular weights of the polymers are expressed in terms of polystyrene equivalents. Two columns, i.e. a 7,8×300 mm LT5000L, Mixed, Medium Org and a 7,8×300 mm LT3000L, Mixed, Ultra-Low Org column equipped with a guard column 4.6×10 mm (Viscotek, TGuard) were used for the chloroform eluent at 35 °C (flow rate: 1mL.min^{-1}). Data were analyzed using ViscotekOmniSEC Omni-01 software. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Diamond DSC with a heating rate of 10 ^{o}C min^{-1} under nitrogen flow (20 mL min^{-1}).

For surface characterization, thin films of polymers were spin coated (Specialty Coating Systems, P67080 Spin Coater) on silicon wafers from 6 mg mL^{-1} solutions in dimethylacetamide at 2000 rpm for 1 min. The water contact angles (WCAs) were measured using the sessile drop method with a water drop volume of 3 μl on a contact angle system (Dataphysics, Contact Angle System OCA 20) at ambient temperature. 3 different positions were measured on a given sample and the average values were reported. The surface morphology of the coatings was characterized by Atomic Force Microscopy (AFM) (NTMDT, Solver P47) in tapping mode using Si cantilevers.

2.2 Results and Discussion

The possibility of generating radicals via the vis-light-triggered reaction of $Mn_2(CO)_{10}$ with alkyl halide prompted us to employ this initiating system for the synthesis of polyolefin-based graft copolymers. Accordingly, graft copolymers were obtained in two discrete steps. In the first step, a brominated polyolefin, *i.e.* poly(COE-Br) (M_n 41000 g·mol^{-1}, PDI 2.1), was synthesized *via* the ROMP of *cis*-cyclooctene (COE) (M_n 54000 g·mol^{-1}, PDI 1.6) followed by hydrobromination as described previously[11] (Scheme 1). In the second step, free radical polymerization of *t*BA in the presence of the fully hydrobrominated intermediate was initiated by the photolysis of $Mn_2(CO)_{10}$ under visible light resulted in the formation of the corresponding graft copolymer, PE-*g*-P*t*BA (Figure 2.3). Typical results are summarized in Table 2.1.

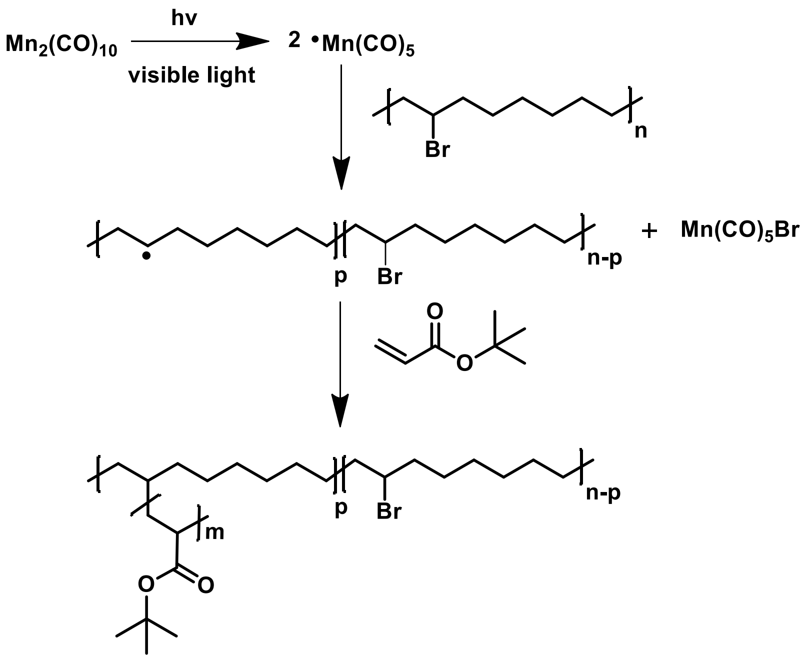

Figure 2.3 : Visible light induced graft copolymerization of *t*BA from Poly(COE-Br) by using $Mn_2(CO)_{10}$.

Table 2.1 : Visible light-induced grafting of *t*BA from poly(COE-Br)[a)] by using $Mn_2(CO)_{10}$.

Run	poly(COE-Br)$_0$/ (tBA)$_0$/$Mn_2(CO)_{10}$	t (h)	Conv. [%][b)]	M_n [g mol^{-1}]	PDI	Grafting [%][c)]
1	1/50/0.5	4	27	570 000	3.3	68
2	1/50/0.25	4	24	634 000	2.8	72
3	1/50/0.125	4	34	628 000	3.4	73
4	1/50/0.125	2	33	300 000	2.6	69
5	1/100/0.0125	2	31	265 900	1.46	71

[a)] M_n(poly(COE-Br)) = 41 000 g mol^{-1}, PDI = 2.11; [b)] Conversion of the monomer was determined gravimetrically; [c)] degree of grafting: percentage of bromoalkyl groups that started a *g*-polymer chain.

As can be seen from Table 2.1, neither the amount of $Mn_2(CO)_{10}$ nor the irradiation time did significantly affect the conversion of *t*BA or the degree of grafting. However, at low $Mn_2(CO)_{10}$ concentrations, comparably low molecular weight polymers with narrow polydispersity were obtained. Notably, compared to the ATRP route, the overall polydispersities of the graft copolymers obtained by photochemical means were broader. This can be expected since in the photochemical route, initiating free radicals are continuously formed by irradiation; growing polymer chains with large differences in chain lengths are present at the same time. However, the process is still attractive as it avoids any copper contamination and can be conducted at room temperature. Figure 2.4 shows GPC traces of the polymers before and after irradiation. Clearly, after photo-grafting the GPC trace shifts to higher molecular weights without indication of remaining unreacted precursor polymer. Notably, no free P*t*BA was observed.

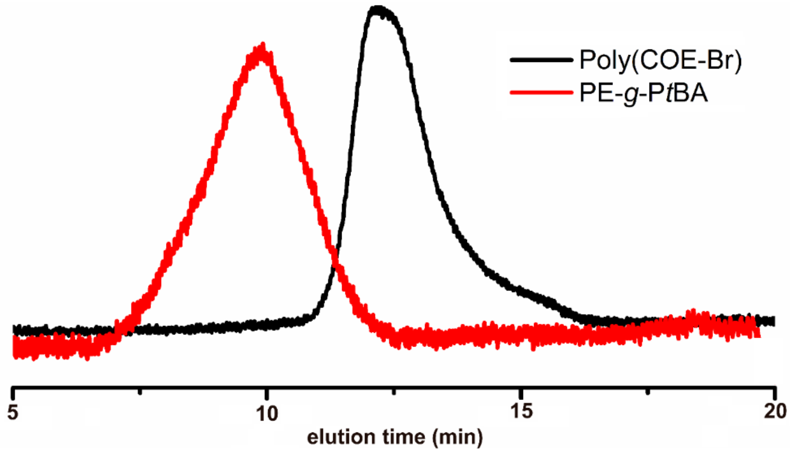

Figure 2.4 : GPC traces of poly(COE-Br) and PE-*g*-P*t*BA.

Successful grafting was confirmed by ^{1}H- and ^{13}C-NMR analyses. As can be deduced from the ^{1}H-NMR spectra of the precursor and the graft copolymers (Figure 2.5), the appearance of a new signal at δ=2.22 ppm corresponding to the –CH_2CH- moiety clearly indicates the presence of P*t*BA grafted chains. Notably, residual signals of the CHBr moieties between 4.06 - 4.10 ppm, confirm that some of the bromine atoms did not take part in the light induced radical generation process. Similar behavior was observed in the analogous ATRP approach.

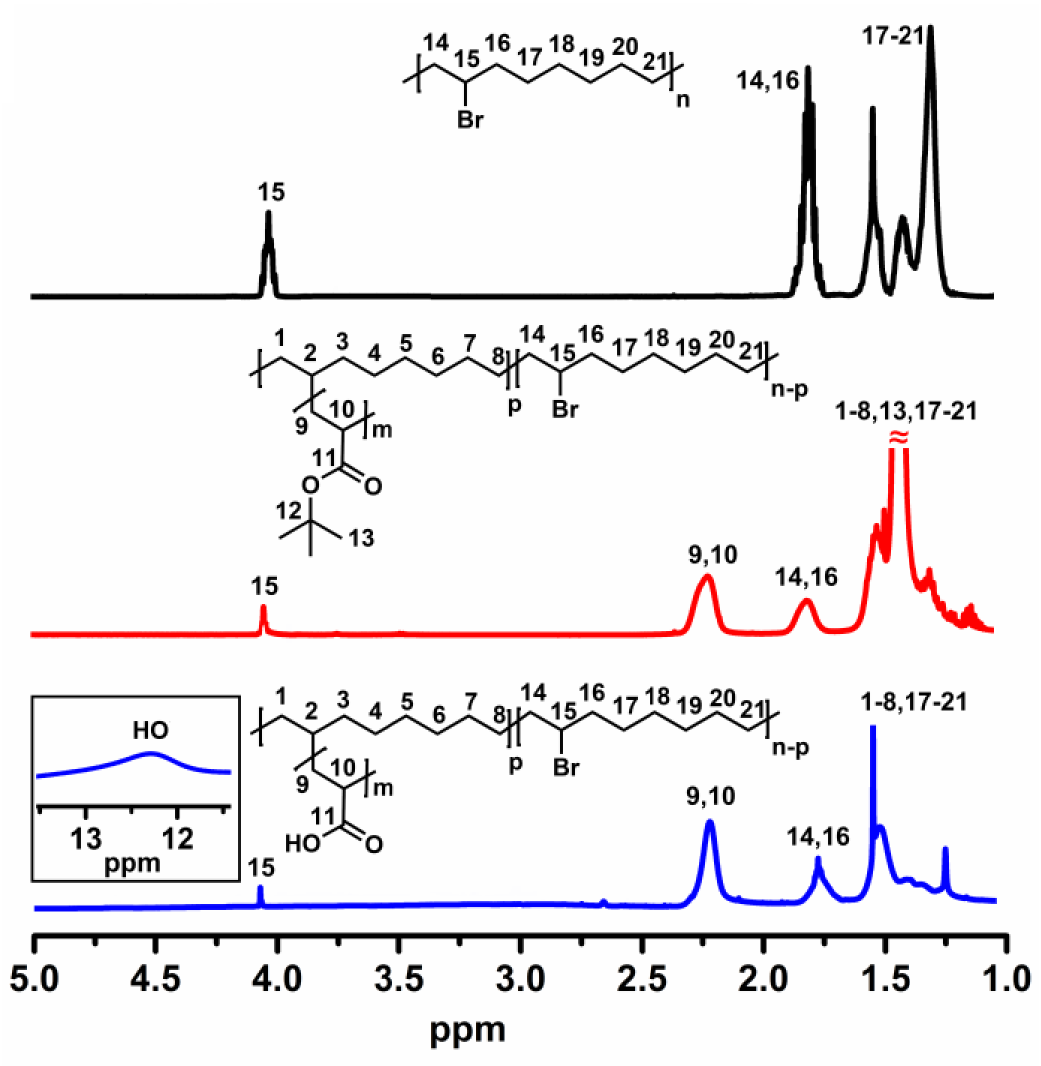

Figure 2.5 : ^{1}H-NMR spectra of poly(COE-Br), PE-*g*-P*t*BA and PE-*g*-PAA.

In the ^{13}C-NMR spectrum of the PE-*g*-P*t*BA, the signals for the carbonyl and tertiary carbon appear at δ = 176.2 and 81.3 ppm, respectively. A weak resonance of the alkyl halide at 59.1 ppm additionally confirms the grafting of P*t*BA from poly(COE-Br) (Figure 2.6).

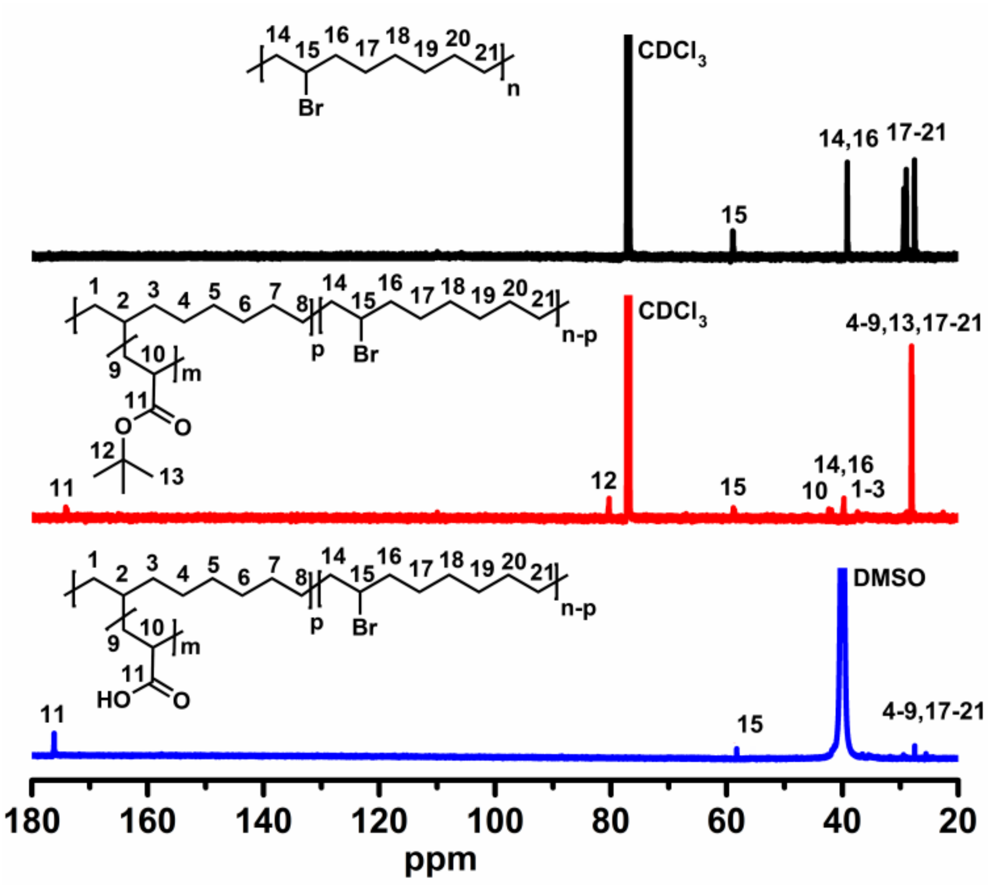

Figure 2.6 : ^{13}C-NMR spectra of poly(COE-Br) (top), and PE-*g*-P*t*BA (middle), PE-*g*-PAA (bottom).

The tBA content in the graft copolymer was calculated from the ^{1}H NMR spectra by using following equation:[70]

$$tBA\ (mol\%) = \frac{4(b+c)}{3a+4(b+c)}\ X\ 100\ \%$$

Where a represents the integrated peak area of the hydrogens at C-14 and C-16 at δ = 1.78 ppm, while b and c represent the total integrated peak area of the hydrogens at carbon-9 and carbon-10 at δ = 2.22 ppm.

The IR-spectra of the graft copolymers exhibit characteristic bands for both the PE backbone and the grafted P*t*BA chains (Figure 2.7). Thus, in addition to the polyolefin bands at around 2900 cm^{-1}, the spectrum shows the typical P*t*BA-derived carbonyl band at 1726 cm^{-1}.

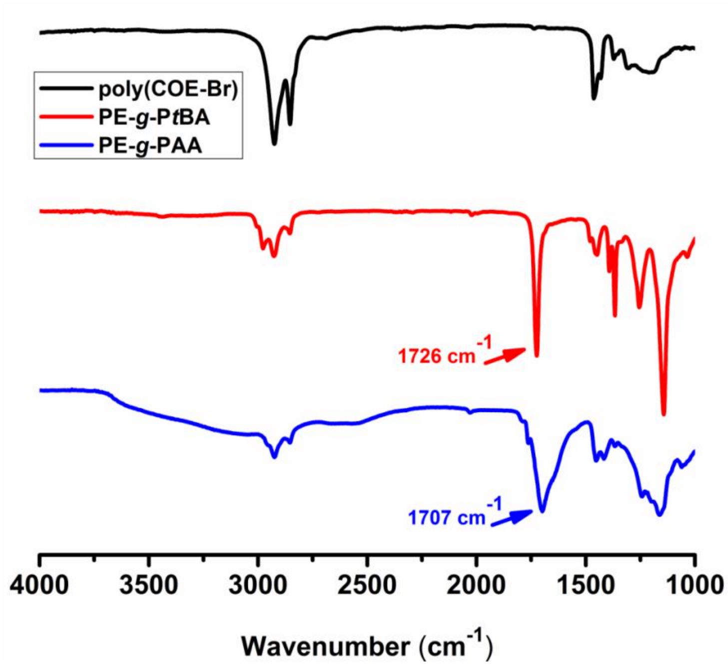

Figure 2.7 : FT-IR spectra of poly(COE-Br), and PE-*g*-P*t*BA, PE-*g*-PAA.

Next, the *t*BA moieties of PE-*g*-P*t*BA were converted into acrylic acid units through acidic hydrolysis to generate PE-*g*-PAA copolymers (Figure 2.8).

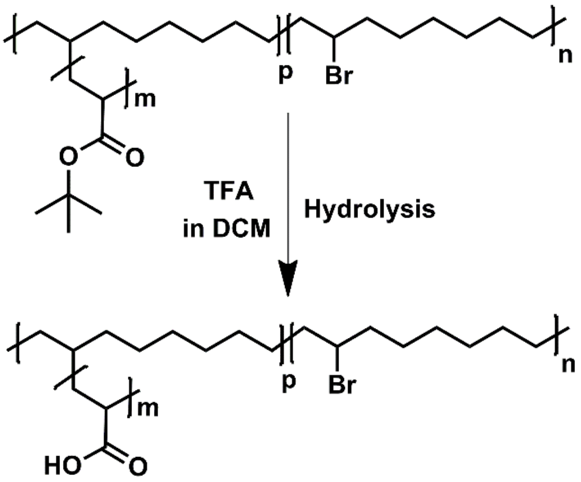

Figure 2.8 : Hydrolysis of PE-*g*-P*t*BA.

Hydrolysis was conducted by dissolving the polymer in dichloromethane (DCM) at room temperature followed by addition of excess trifluoroacetic acid (TFA).[71] It was previously reported [72] that PE-*g*-P*t*BA materials were insoluble in DCM. In our case, the remaining Br-groups initially present in poly(COE-Br) facilitated solubility of the graft copolymer in the halogenated solvent. Thus, we were able to realize successful hydrolysis by using TFA in DCM. In the ^{1}H-NMR spectrum of

PE-*g*-PAA, the disappearance of the C-CH_3 protons and appearance of the COOH-signals around δ=12.3 ppm, clearly confirm the hydrolysis process (Figure 2.5). Even more convincing evidence for successful hydrolysis was obtained from the ^{13}C-NMR spectrum of PE-*g*-PAA. Thus, after hydrolysis, the methine tertiary carbon (C-$(CH_3)_3$) at δ = 81.3 ppm disappeared (see Figure 3.6). The presence of the carboxylic acid functionality was also corroborated by IR analysis of the hydrolysis product with a broad O–H stretching band at around 3500 cm^{-1} and a strong carbonyl (C=O) stretching band at 1707 cm^{-1} (see Figure 2.7).

Thin films of PE-*g*-P*t*BA and PE-*g*-PAA were also characterized by water contact angle (WCA) measurements and atomic force microscopy (AFM). PE-*g*-P*t*BA was dissolved in $CHCl_3$ at a concentration of 6 mg/mL and thin films were spin-coated on silicon wafers. For all polymers (runs 1, 3 and 4, Table 2.1) uniform 20-25 nm thick films were obtained (Figure 2.9). As the molecular weight of the polymer increased, more aggregates were observed on the film surfaces.

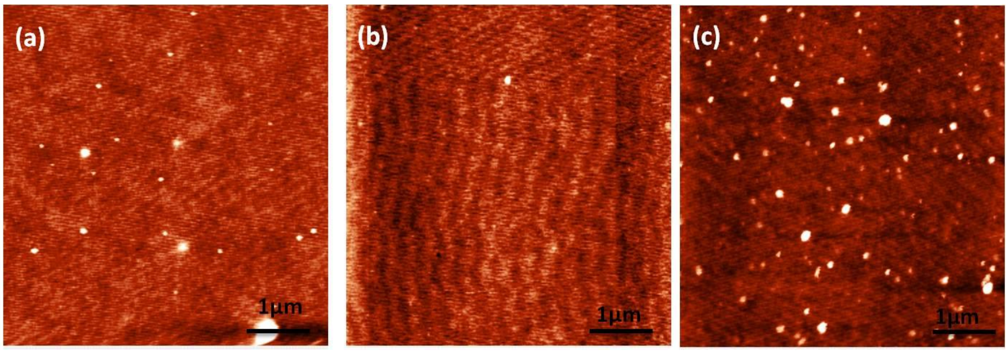

Figure 2.9 : AFM height images PE-*g*-P*t*BA. a) run 1, b) run 4, c) run 3.

The shapes of water droplets on these films are shown in Figure 2.10. WCAs were measured between 86-89°. These values indicate the presence of P*t*BA side groups on the surface and are consistent with previous measurements. The grafting density of 68-73 % resulted in WCAs of 86-89°.

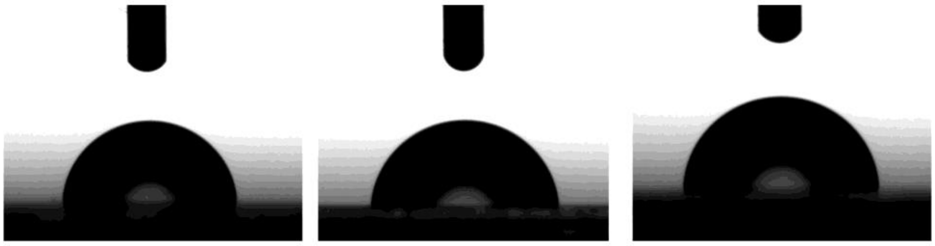

Figure 2.10 : Shapes of water drops on thin films of PE-*g*-P*t*BA: run 3 - WCA ~87±1° (left); run 4 – WCA ~86±1° (middle); run 1 – WCA ~ 89±1° (right).

After hydrolysis, the obtained PE-*g*-PAA polymers were dissolved in hot (~110 °C) DMAc at a concentration of 6 mg/mL and were spin-coated on silicon wafers. The resulting thin films contained large holes in some parts. The thickness of the uniform regions was ~20 nm. WCA measurements were done on the uniform regions. Figure 2.11 shows the shapes of the equilibrated water droplets on the thin films. WCAs of ~45° (run 3), ~46° (run 4) and ~40° (run1) were measured. As water droplet was put on the thin film, the contact angle decreased over time and stabilized around 40-45° after 15 sec. We attribute this decrease to the diffusion of water into the film (or spreading of water on the film) through the regions having high PAA density. The equilibrated WCAs of 40-45° were much smaller than those on PE-*g*-P*t*BA (~86-88°) indicating the successful conversion of P*t*BA to PAA by hydrolysis. Previously, WCA was measured as 62° on PE-*g*-PAA having grafting density of ~20%. WCA of 40-45° is consistent with the significantly larger grafting densities of 68-73% in our case.

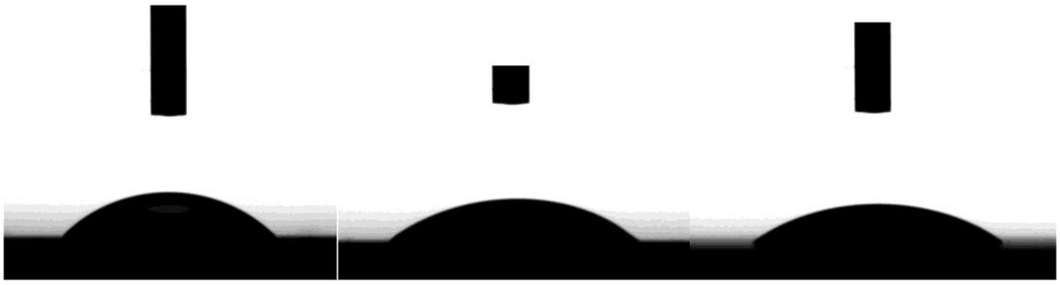

Figure 2.11 : Shapes of water drops on thin films of PE-*g*-PAA: run 3 - WCA ~45±2° (left); run 4 – WCA ~46±2° (middle); run 1 – WCA ~ 40±2° (right).

Meanwhile, the introduction of P*t*BA segments into poly(COE-Br) could play important role in the chain relaxation and thermal behaviors of the polymer (Figure 2.12). The poly(COE-Br) possessed a glass transition peak at -28 °C.[73] After grafting, the resultant graft copolymer (PE-*g*-P*t*BA) did not exhibit notable glass transitions corresponding to poly(COE-Br) segments, but it has a melting peak at 50 °C. After hydrolysis, the graft copolymer (PE-*g*-PAA) also exhibits a glass transition peak at 115 °C. This change in thermal behavior is an additional evidence for the successful hydrolysis of the *t*BA group on the graft copolymer.[74]

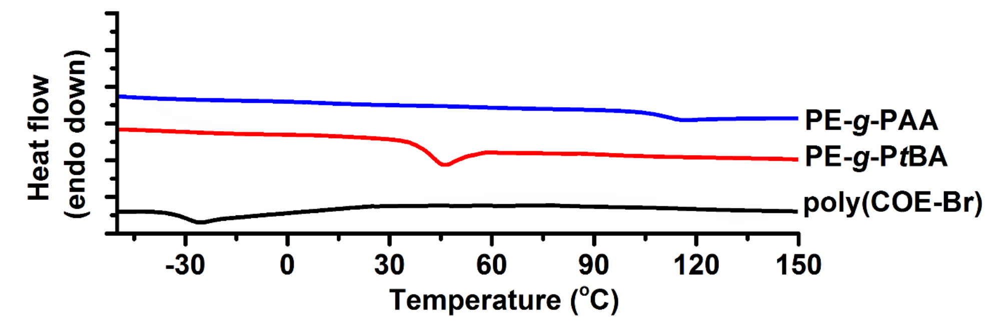

Figure 2.12 : DSC thermograms of poly(COE-Br), and PE-*g*-P*t*BA, PE-*g*-PAA.

2.3 Conclusion

In conclusion, we have shown that PE-*g*-P*t*BA copolymers can be prepared by combining ROMP of COE, subsequent hydrobromination and visible light-induced polymerization of *t*BA. First, ROMP was accomplished, and subsequent hydrobromination gave a polyolefin-based macroinitiator. Visible light-induced free radical polymerization of *t*BA in the presence of bromo-functional polyolefin using $Mn_2(CO)_{10}$ resulted in the formation of copolymers possessing polar and nonpolar segments in the side and main chain, respectively. Although controlled side chain lengths and molar masses were not attained, this strategy has relevance in simplicity in the fabrication and purification steps and can be expected to be applicable to a wide range of monomers that are susceptible to free radical polymerizable. The *t*BA esters of the graft copolymers were hydrolyzed into acrylic acid functionalities by acidolysis to obtain hydrophilic polyolefins. Structural evidence for the precursor, graft and transformed polymer were provided by ^{1}H and ^{13}C-NMR, FT-IR, AFM and WCA measurements.

3. SUNLIGHT INDUCED ATOM TRANSFER RADICAL POLYMERIZATION BY USING DIMANGANESE DECARBONYL[1]

Sunlight covers a broad energy band including infrared, visible light, ultra-violet, X-rays and gamma rays.[75] Since ancient times, it has been used to create hardened and insoluble wood, bamboo, and cotton as building and clothing materials. It would appear that this process involved the action of light became of great importance in the production of thermosetting plastics. The advantages of light-induced reactions include the effective, mild and easy process.[76, 77] Light can also be used as external stimuli to switch the reactions "on" and "off" and can trigger the reactions locally at specific positions and spaces.[78-80] Light-induced polymerization has been widely employed in conventional radical polymerization as a key technique in various applications, such as coatings, adhesives, medicine, optics and microelectronics.[48, 29] The use of light in controlled radical polymerization also brings several distinct advantages, including temporal and spatial control over chain growth, easy preparation of well-defined polymers at room temperature and minimization of possible higher temperature side reactions.[81, 82] Although extensive efforts have been made in this area, it is still crucial to explore an effective light-induced controlled radical polymerization (CRP) method in synthetic polymer chemistry. The commonly used light-induced CRP methods are adapted from thermal counterparts including iniferter[83], nitroxide-mediated radical polymerization (NMRP)[84-87], atom transfer radical polymerization (ATRP)[88-99], cobalt-mediated radical polymerization (CMRP)[100-102], organoiodine-mediated radical polymerization (OMIP)[66-69, 103], organotellurium-mediated radical polymerization (TERP)[104, 105] and reversible addition-fragmentation chain transfer polymerization (RAFT)[106-110] etc. Among them, light-induced ATRP has been studied extensively because of the broad range of monomers and mild polymerization conditions. The light-induced ATRP is based on photoredox

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[1] This chapter is based on the paper " Ciftci M., Tasdelen M.A. and Yagci Y., Sunlight induced atom transfer radical polymerization by using dimanganese decacarbonyl. Polymer Chemistry, 2014, 5, 600-606."

reactions of copper catalysts under various radiation sources with or without various photoinitiators.[88-95, 97, 99] Many UV and visible light free radical photoinitiators were reported to be powerful promoters for light-induced ATRP. Recently, Hawker et al. reported the light-induced ATRP of methacrylates regulated by visible light using iridium based photoredox catalyst.

Dimanganese decacarbonyl ($Mn_2(CO)_{10}$) has a weak Mn−Mn linkage (20−40 kcal/mol) and visible light photolysis provides the $\bullet Mn(CO)_5$ metalloradical with good quantum efficiency.[58, 59, 111] It abstracts halides from a variety of organohalogen compounds, generating the corresponding carbon centered radicals.[62, 112, 65, 63, 113-115] A visible light-induced degenerative iodine transfer polymerization using $Mn_2(CO)_{10}$ in conjunction with alkyl iodides (R-I) was recently developed by Kamigaito and coworkers.[67-69] Since the reverse reaction between R• radical and $I\text{-}Mn(CO)_5$ regenerating R-X and $Mn(CO)_5\bullet$ is less likely due to the strength of the Mn-I bond, the contribution of the reversible termination mechanism must be quite limited. This system was applicable to not only unconjugated monomer, vinyl acetate, but also conjugated monomers such as acrylate and styrene derivatives with the use of appropriate initiators (Figure 3.1).[66-69]

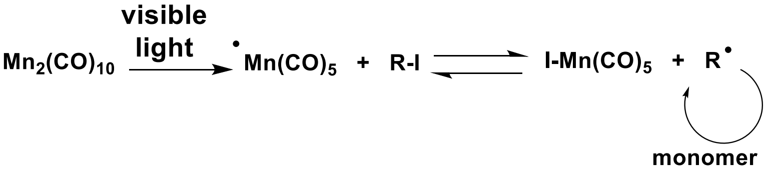

Figure 3.1 : Proposed mechanism of light-induced degenerative iodine transfer polymerization with $Mn_2(CO)_{10}$/alkyl iodide system.

In the frame of our continuous interest in developing ultraviolet- and visible-light-induced CRP, we herein report a new light-induced ATRP of methyl methacrylate under the sun by using $Mn_2(CO)_{10}$ as the light absorbing component. The polymerization activators, Cu(I)−ligand, can be continuously generated by both $Mn(CO)_5\bullet$ and R• radicals during the polymerization. The mechanism of the light-induced ATRP was studied using a photoreactor emitting light nominally at 400–500 nm at room temperature.

3.1 Experimental

3.1.1 Materials

Methyl methacrylate (MMA, Aldrich, 99%), methyl acrylate (MA, 99%, Aldrich) and styrene (St, 99%, Aldrich) were passed through a basic alumina column to remove the inhibitor. N, N, N', N'', N'- Pentamethyldiethylenetriamine (PMDETA, 99%; Aldrich) was used as a ligand and was distilled prior to use. Dimanganese decacarbonyl, ($Mn_2(CO)_{10}$, 98%; Aldrich), was purified by sublimation and stored in a refrigerator in the dark. Ethyl 2-bromopropionate (EtBP, 98%; Aldrich), methanol (CH_3OH, 99.9%; Merck), copper (II) bromide ($Cu^{II}Br_2$, 99%; Acros) were used as received.

3.1.2 Polymerizations

A series of visible light induced ATRP reactions, using MMA, were carried out under different experimental conditions at room temperature. An example detailing a typical procedure was as follows: MMA (2 mL, 18.6 mmol), PMDETA (4 μL, 1.9×10^{-2} mmol), $Cu^{II}Br_2$ (4.2 mg, 1.9×10^{-2} mmol), EtBP (12.2 μL, 9.4×10^{-2} mmol), $Mn_2(CO)_{10}$ (1.8 mg, 4.7×10^{-3} mmol) and methanol (0.1 mL, 2.5 mmol) were put into a Schlenk tube (i.d= 9 mm) equipped with a magnetic stirring bar and the reaction mixture was degassed by three freeze-pump-thaw cycles and left in vacuum. The mixture was irradiated by a Ker-Vis blue photoreactor equipped with six lamps (Philips TL-D 18 W) emitting light nominally at 400–500 nm at room temperature. The light intensity was 45 mW cm^{-2} as measured by Delta Ohm model HD-9021 radiometer. The sun-light ATRP was carried out under sunny weather in April in Istanbul (Turkey); an absolute irradiance measurement leads to an estimated incident energy <60 mW/cm^2 in the 400-500 nm range. After given time the resulted polymers were precipitated in ten-fold excess methanol and then dried under reduced pressure. Conversion of the monomer was determined gravimetrically.

3.1.3 Characterization

Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax autosampler system consisting of a pump, a Viscotek UV detector, and a Viscotek differential refractive index (RI) detector. Three ViscoGEL

GPC columns ($G_{2000}HHR$, $G_{3000}HHR$, and $G_{4000}HHR$, 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 polystyrene standards having narrow-molecular- weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. The resulting molecular weight distributions were reassessed by universal calibration using Mark-Houwink parameters for poly(methyl methacrylate) ($K = 7.56 \times 10^{-5}$ dLg^{-1}, $\alpha = 0.731$)[116] and for polystyrene ($K = 14.1 \times 10^{-5}$ dLg^{-1} and $\alpha = 0.70$).[117]

3.2 Results and Discussion

The visible-light-mediated photoredox catalysis is an attractive tool to initiate organic reactions because of its low cost, easy availability and almost infinitely available source of energy (e.g. sunlight, household fluorescence or LED bulbs, Xe lamp).[118-120] For example, Stephenson et al. reported a visible-light-mediated Appel-type reaction, which converts alcohols into halides in good yields, with exceptional functional group tolerance.[121, 122] Recently, the radical polymerization of methacrylates was also controlled by visible light using an iridium-based photoredox catalyst.[88, 91] In order to take advantage of visible-light-mediated photoredox process, first, optical properties of reaction mixture, dimanganese decacarbonyl, ($Mn_2(CO)_{10}$) and their combination in the visible range were investigated by UV-vis spectroscopy. As can be seen in Figure 3.2., only $Mn_2(CO)_{10}$ strongly absorbs visible light where the other components of the reaction mixture were completely transparent. Thus, all irradiations were performed at ambient temperature under visible light irradiation using either a photoreactor equipped with six lamps emitting light nominally at 400–500 nm or sunlight.

Initially, the polymerization of methyl methacrylate (MMA) was examined by using the $Cu^{II}Br_2$/PMDETA as the catalyst, ethyl 2-bromopropionate (EtBP) as the initiator and $Mn_2(CO)_{10}$ as the photosensitive compound.

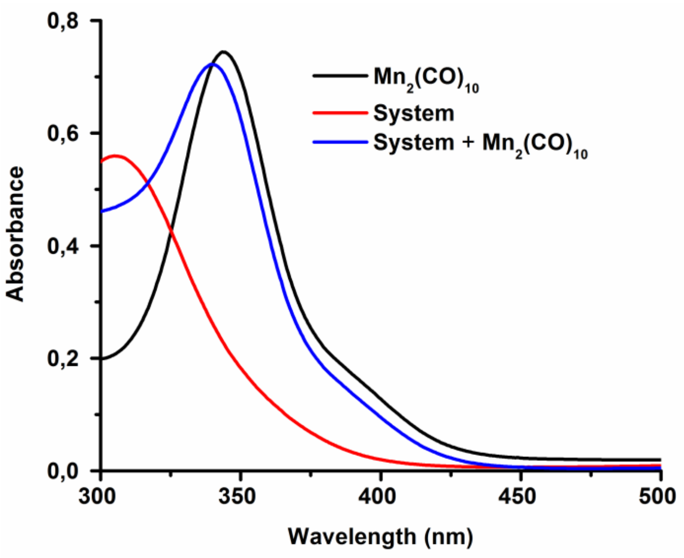

Figure 3.2 : UV–Vis spectra of $Mn_2(CO)_{10}$, reaction mixture and both of them in methanol. The concentration of all components was 2.3 x 10^{-3} M.

The reactants typically consisted of $[MMA]_0/[EtBP]_0/[Cu^{II}Br_2]_0/[PMDETA]_0/[Mn_2(CO)_{10}]_0$ = 200/1/0.2/0.2/0.2 with a small amount of methanol (0.1 mL, 2.5 mmol) to facilitate better dissolution of the Cu^{II} complex. Several control experiments were carried out with removing an essential component one-by-one, and the results were shown in Table 3.1 (entries 1 and 2). Notably, when the polymerizations were conducted in the absence of either light, or $Mn_2(CO)_{10}$ or $Cu^{II}Br_2$, the experiments failed to produce any polymer at the end of irradiation and each component was required for successful controlled radical polymerization. Irradiation of the mixture without $Cu^{II}Br_2$ resulted in free radical polymerization (entry 3, Table 3.1), most likely due to photogenerated radicals from alkyl halides via classical halogen abstraction reaction.[59] A series of polymerization reactions were carried out with changing the molar ratio of $Mn_2(CO)_{10}$ (entries 4-6, Table 3.1). Encouragingly, initial results employing 0.2 mol% $Mn_2(CO)_{10}$ did afford polymer; however, the reaction displayed little to no control, with a molecular weight distribution value of 1.82. The irreversible radical termination occured at high $Mn_2(CO)_{10}$ concentration and to gain control over this system the radical concentrations needed to be lowered, which could be achieved by simply reducing the catalyst loading. Compared with the reference condition of entry 4, reducing the concentration of the $Mn_2(CO)_{10}$ significantly decreased the yield of PMMA and molecular weight distribution of resulting polymers as well ($M_{n,GPC}$ = 8100, M_w/M_n = 1.16). Furthermore, the experimental molecular weight of polymer was in good agreement with the theoretical value using 0.05 mol % $Mn_2(CO)_{10}$. Decreasing the catalyst amount to ppm level resulted in slightly a slower polymerization while preserving good control over the molar mass and narrow molecular weight distribution (entries 7, Table 3.1). Since the light-induced ATRP system only requires photons to drive the reaction, the sunlight can be utilized as an inexpensive, abundant, clean and renewable energy source. Therefore, sunlight was used to drive the polymerization of MMA in both high and low catalyst concentrations (entry 8 and 9, Table 3.1). When the sunlight used as light source, the polymerization proceed with a relatively smaller rate (entry 6, Table 3.1) than that in the reference process (entry 8, Table 3.1). Apparently, the low catalyst loadings with sunlight resulted in a polymer with a higher molar mass than what was theoretically calculated and a molecular weight distribution of ~1.43, thus indicating loss of control (entry 9, Table 3.1). The applicability of this method was extended to other vinyl monomers such as methyl acrylate and styrene (entry 10 and 11 Table 3.1). In both cases, the control over the polymerization is good, with low polydispersity values and good correlation between experimental and theoretical molecular weights.

Table 3.1 : Visible light- or sunlight induced ATRP of vinyl monomers at room temperature.

No	**$[M]_0/[RX]_0/[MtX]_0/[L]_0/[Mn_2(CO)_{10}]_0$**	**Mon.**	**Conv. (%)**	**$M_{n,theo}$[a] ($g.mol^{-1}$)**	**$M_{n,GPC}$[a] ($g.mol^{-1}$)**	**M_w/M_n[b]**
1[c]	200/1/0.2/0.2/0.2	MMA	-	-	-	-
2[d]	200/1/0.2/0.2/0.0	MMA	-	-	-	-
3[d]	200/1/0.0/0.2/0.2	MMA	93	18600	74800	2.65
4[d]	200/1/0.2/0.2/0.2	MMA	82	16400	34500	1.82
5[d]	200/1/0.2/0.2/0.1	MMA	54	8500	16500	1.48
6[d]	200/1/0.2/0.2/0.05	MMA	35	7000	8100	1.16
7[d]	200/1/0.01/0.01/0.05	MMA	29	5800	6200	1.21
8[e]	200/1/0.2/0.2/0.05	MMA	28	6200	5600	1.28
9[e]	200/1/0.01/0.01/0.05	MMA	23	4600	5500	1.43
10[d]	200/1/0.2/0.2/0.05	MA	21	3600	4100	1.19
11[d]	200/1/0.2/0.2/0.05	St	17	3500	3800	1.23

[a]$M_{n,th}$ = $[Monomer]_0/([RX]_0$ x $Mw_{monomer}$ x conversion; [b]Molecular weight ($M_{n,GPC}$) and distribution (M_w/M_n) were determined by gel permeation chromatography; [c] Polymerization was performed under dark, time = 180 min.; [d]Polymerization was performed at visible light irradiation, time = 180 min., light intensity = 45 mW cm^{-2}. [e]Polymerization was performed with sunlight, time = 180 min., light intensity = 60 mW cm^{-2}.

Overall, the control experiment results support that the polymerization proceeds through the photocatalytic initiation mechanism that we have proposed in Figure 3.3. The primary photochemical reaction involves the homolysis of $Mn_2(CO)_{10}$, which affords the metal-centered $\bullet Mn(CO)_5$ radicals. This radical was not only able to abstract halogen atoms from alkyl halides to generate carbon centered radicals but also reduced the $Cu^{II}Br_2$ to $Cu^{I}Br$ directly, which was used as activator in the ATRP. Subsequently, polymerization was started by the activation of an R-X initiator by the $Cu^{I}X/L$ activator.

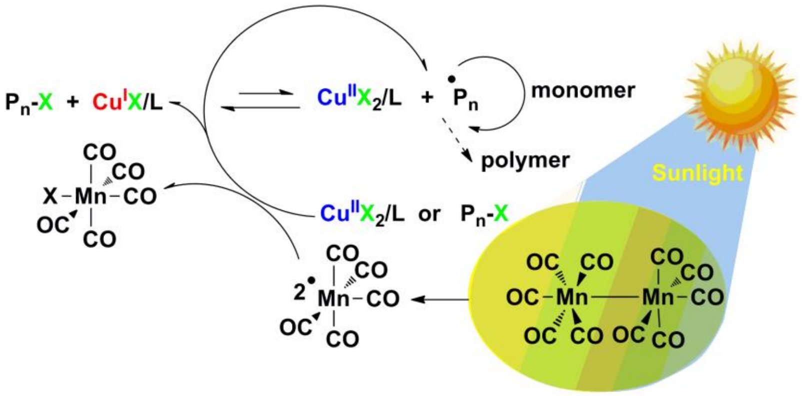

Figure 3.3 : Mechanistic scheme for sunlight induced ATRP using $Mn_2(CO)_{10}$.

In order to gain more insight into the initiation mechanism, the change in the optical absorption spectrum of the polymerization solution was recorded as a function of irradiation time (Figure 3.4). The photoredox reaction of $Mn_2(CO)_{10}$ with Pn-X or $Cu^{II}X_2/L$ was confirmed experimentally by UV/Vis-spectroscopy as the absorption spectra of $Mn_2(CO)_{10}$ significantly decreased. Although, the maximum absorption spectrum at 345 nm decreased gradually, it was still observable throughout the polymerization period. As formation of Cu^{I} ions cannot be observed directly in solution, it was detected indirectly through its catalytic activity in the polymerization.

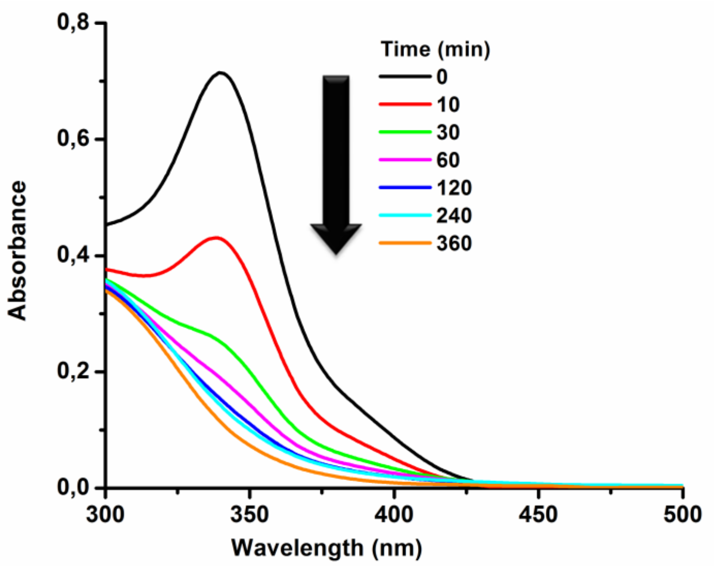

Figure 3.4 : Typical UV/vis spectral changes of the initiating system on visible light irradiation λ = 400-500 nm under nitrogen.

To further investigate the exact role of $Mn_2(CO)_{10}$, visible light irradiation of the reaction mixture without alkyl halide was monitored by UV-Vis spectroscopy. In this case, a new weak band centred on 455 nm was appeared (Figure 3.5). This absorption corresponding to the ligand-to-metal charge-transfer transition of copper metal was responsible for the photoreduction of Cu^{II} to Cu^{I}.[123, 124] The result implies that photogenerated •$Mn(CO)_5$ radicals may directly reduce the Cu^{II} to Cu^{I} under visible light irradiation.

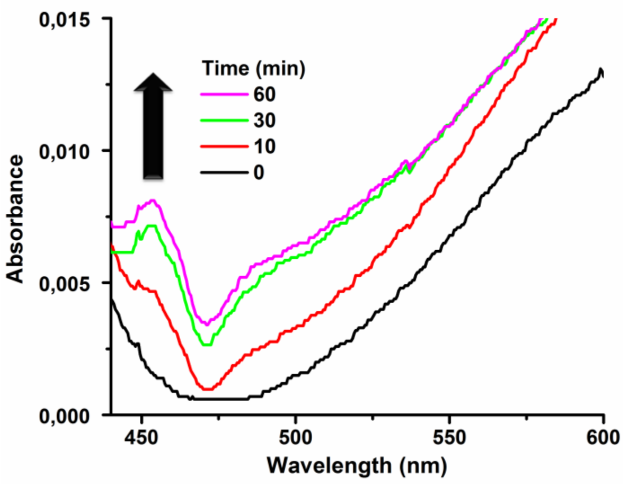

Figure 3.5 : Typical UV spectral changes of the initiating system in the absence of alkyl halide under visible light irradiation λ = 400-500 nm under nitrogen.

Kinetic studies of the visible- and sun-light induced polymerization revealed that the reaction proceeded with first-order kinetics, indicating a constant concentration of growing radicals during polymerization. The linear relationship between monomer consumption, ln($[M]_0/[M]$) and the polymerization time indicated that the termination reaction was suppressed (Figure 3.6a). Evolution of the molar mass and molecular weight distribution (M_w/M_n) (Figure 3.6b) shows that during visible- and sun-light ATRP of MMA with $[MMA]_0/[RX]_0/[MtX]_0/[L]_0/[Mn_2(CO)_{10}]_0$ = 200/1/0.2/0.2/0.05 ratio, the polydispersity indexes in both cases were slightly broader (1.13−1.33), and the obtained molar masses were in good agreement with the theoretical values, indicating high initiation efficiency.

Low catalyst concentrations and mild reaction condition are desirable to reduce the environmental impact of ATRP. Therefore, Cu catalyst concentrations were reduced to 100 ppm and instead of previous condition sunlight was used as the irradiation source.

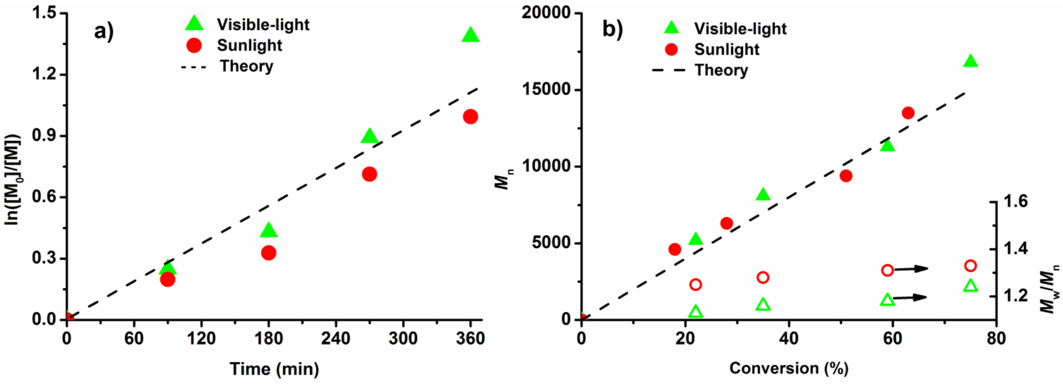

Figure 3.6 : Visible light- or sunlight-induced ATRP of methyl methacrylate ($[MMA]_0/[Cu^{II}Br_2]_0/[PMDETA]_0$ = 200/1/0.2/0.2/0.05), a) kinetic plot and b) molecular weights and distributions of the resulting polymers as a function of degree of conversion.

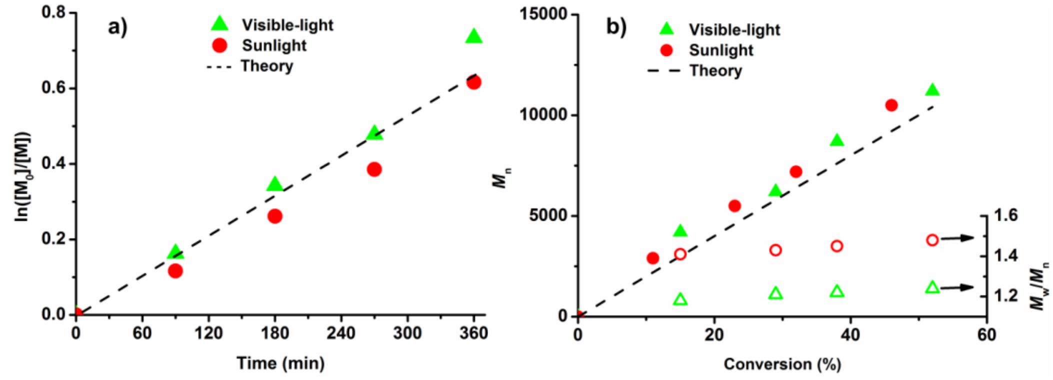

Figure 3.7 : Visible light- or sunlight-induced ATRP of methyl methacrylate with low copper catalyst loading ($[MMA]_0/[Cu^{II}Br_2]_0/[PMDETA]_0$ = 200/1/0.01/0.01/0.05), a) kinetic plot and b) molecular weights and distributions of the resulting polymers as a function of degree of conversion.

Similar to the previous case, the rate of polymerization was higher using the visible light than when using the sunlight. As was shown in Figgure 3.7a, a linear dependence was again observed in the kinetic plots, indicating a constant concentration of growing radicals during polymerization. Evolution of the molar mass and molecular weight distribution (Figure 3.7b) shows that the experimental molecular weight values close to the theoretical ones in both cases. In addition, the molecular weight distributions were relatively high, ranging from 1.41-1.48 and reasonable control was observed under sunlight irradiation.

The effect of visible light irradiation on the polymerization of MMA was further studied by employing a periodic light on-off process (Figure 3.8). The reaction mixture was exposed to visible light for a two-hour period to afford approximately 30% conversion. Thereafter, the light source was periodically turned-off and the polymerization proceeded at a much lower rate during this period, indicating a negligible concentration of the active radical present under dark conditions.

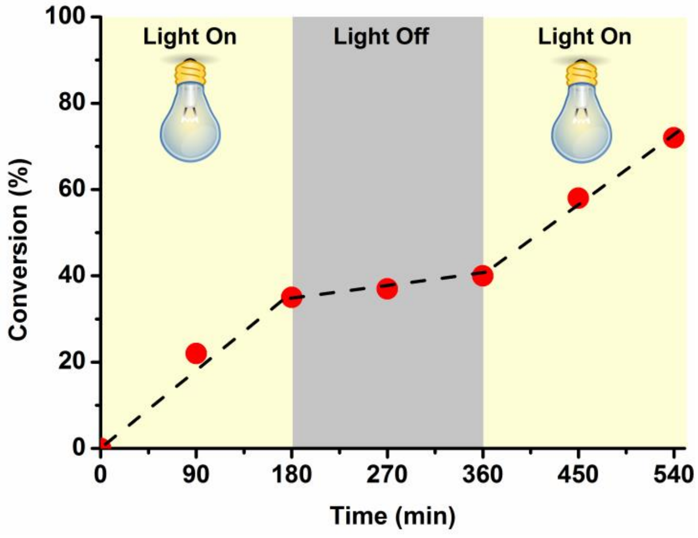

Figure 3.8 : Effect of visible light during the polymerization of MMA at room temperature: $[MMA]_0/[Cu^{II}Br_2]_0/[PMDETA]_0$ = 200/1/0.2/0.2/0.05.

Exposure to visible light for a second two-hour period ‘‘woke up’’ the polymerization, which proceeds with the same kinetic character as that observed in the former light-on process. This indicates that light stimulus not only controlled the initiation steps, but also efficiently regulated the chain growth during the polymerization process.

The “living” nature of the system was further confirmed by treating the macroinitiator made by this technique with a same monomer for chain extension using visible light-induced ATRP conditions. For example, a macroinitiator ($M_n = 6\,200$ g.mol^{-1}, $M_w/M_n = 1.21$) prepared by visible light-induced ATRP was employed in chain extension reaction. The GPC trace of the final polymer was clearly shifted to higher molecular weight (conversion= 45%, $M_n = 9\,800$ g.mol^{-1}, $M_w/M_n = 1.26$) comparing to the precursor macroinitiatorand and there was no detectable amount of the unreacted initial block (Figure 3.9).

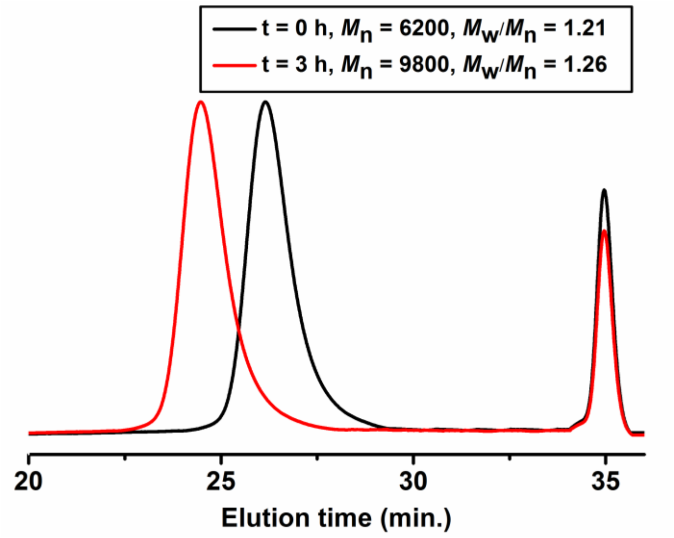

Figure 3.9 : GPC traces of PMMA-Br macroinitiator before and after chain extension via visible light-induced ATRP using $Mn_2(CO)_{10}$. Experimental conditions:$[M]_0/[PMMA\text{-}Br]_0//[MtX]_0/[L]_0/[Mn_2(CO)_{10}]_0$ = 200/1/0.01/0.01/0.05 ratio

One of the key advantages of $Mn_2(CO)_{10}$ chemistry over ATRP is its ability to abstract halogen atom from primary alkyl halides. Hence, when using alkyl halides, primary carbon-centred radicals were generally easier to form than secondary radicals, while tertiary radicals were even more difficult to prepare and this usually requires iodide precursors.[125] From this point, chlorine atoms of commercially available poly(vinyl chloride) (PVC, M_n = 63 000, M_w/M_n = 2.20) can act as initiation sites for the direct grafting of MMA by visible light induced ATRP.[126, 127] The graft copolymerization was carried out 24 h under the similar conditions. The GPC results illustrate an efficient grafting reaction of the PVC and formation of a graft copolymer (conversion= 30%, $M_n = 135\ 000\ g \cdot mol^{-1}$, M_w/M_n = 1.91). Their GPC traces show a monomodal molecular weight distribution and a significant shift of the peak value toward higher molecular weights (Figure 3.10). This suggests that graft copolymerization occurred without detectable free homopolymer formation.

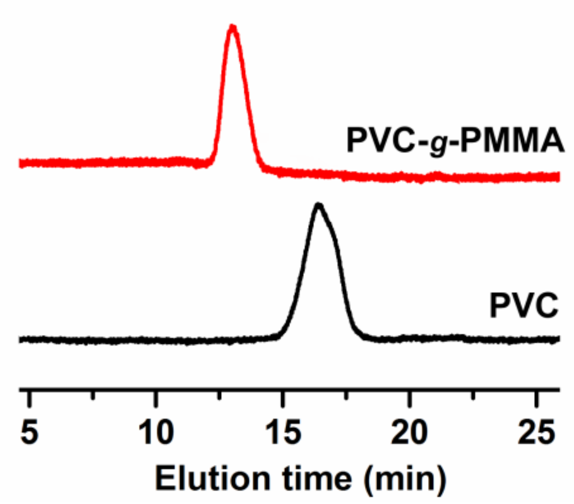

Figure 3.10 : GPC traces of PVC and PVC-*g*-PMMA. Experimental conditions: $[MMA]_0/[PVC]_0/[MtX]_0/[L]_0/[Mn_2(CO)_{10}]_0$ = 200/1/0.2/0.2/0.3 ratio

3.3 Conclusion

In the present article, a new initiating systems based on dimanganese decacarbonyl chemistry are proposed for the light-induced ATRP of methyl methacrylate. The advantages of this method are its highly responsive nature, facile reaction setup, use of only ppm level of catalyst, and commercially available and inexpensive catalysts. The growth of polymer chain can be manipulated by either varying of the $Mn_2(CO)_{10}$ concentration or adjusting light intensity, which changes the concentration of Cu^I catalyst. Moreover, a simple modification of commercially available PVC by visible light-induced ATRP of MMA forms a corresponding graft copolymer. The present sunlight induced ATRP can be used as an easy, convenient and inexpensive process as an alternative to traditional thermal or photochemical controlled radical polymerization.

4. LIVING CATIONIC POLYMERIZATION OF VINYL ETHERS THROUGH A PHOTOINDUCED RADICAL OXIDATION/ADDITION/DEACTIVATION SEQUENCE[1]

Since the discovery of classical living anionic polymerization sixty years ago,[128] living polymerizations have been the most powerful tool for synthetic polymer chemistry providing control over molecular weight and functionality, and also facilitating design and synthesis of complex macromolecular architectures such as block, graft,[129] star[130] and telechelic polymers.[131] In recent years, there has been a tremendous interest to develop new controlled/living polymerization (CLP) methods involving almost all modes of polymerization processes. Most successful approaches to CLP have emerged from the radical mode and several CLPs, namely atom transfer radical polymerization (ATRP),[132-134] nitroxide mediated radical polymerization (NMRP)[135, 136] and radical addition-fragmentation transfer (RAFT) polymerization,[137] have witnessed remarkable developments. More recently, the interest was directed towards photoinduced processes allowing not only control over the polymerization, but also spatial and temporal control. Most of these approaches are based on photoinduced electron transfer reactions. For example, various photoactive compounds such as photoinitiators,[138, 89, 139, 95, 140, 141] dyes,[92] mesoporous structures,[142] nanoparticles[143] were successfully employed to affect the electron transfer and Cu(II)'s reduction to Cu(I) which in turn catalyzes ATRP process. Similar photoinduced redox strategy has been conveyed to azide-alkyne click reactions also utilizing Cu(I) species.[144, 80] Photoinduced electron transfer promoted ATRP was also reported for Ir(ppy)$_3$ based systems by Hawker and co-workers.[145] Boyer group elegantly extended this concept to RAFT process.[146] It was recently demonstrated that photoinduced ATRP methodology can also be achieved in completely organic systems by using phenothiazines[147-149] and dyes[150] as photoreductants. Mechanistic details evaluated by

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[1] This chapter is based on the paper "Ciftci M., Yoshikawa Y. and Yagci Y., Living Cationic Polymerization of Vinyl Ethers through a Photoinduced Radical Oxidation/Addition/Deactivation Sequence Angewandte Chemie International Edition, 2017,56, 519–523."

experimental and computational studies using several phenothiazine derivatives revealed that control of the polymerization is strongly related to the structure of the phenothiazine compounds. Promising field of photoiniated controlled polymerization is further extended to the ring-opening metathesis polymerization by Boydston et al.[151, 152]

Although photoinitiated cationic polymerization has been known and industrially applied for decades,[153-156] possibilities to develop the new variations to adapt this process to CLP have scarcely been investigated. The photoinitiated cationic living polymerization of tetrahydrofuran proceeding in a quasi-living fashion dates back as early as late 1970s.[157, 158] In a recent study, metal-free, visible light-initiated, living cationic polymerization of *p*-methoxystyrene was achieved by regulating cationic chain end in a manner similar to RAFT process.[159] The Lewis acid-catalyzed living cationic polymerization of vinyl ethers developed by Sawamato and Higashimura was also adapted to a photochemical process.[160] In this methodology, the halide-monomer adduct that is required for the initiation in the first stage was formed by photochemical means. In the subsequent step, the monomer addition to the adduct is catalyzed by Lewis acids, namely metal halides, by coordination interaction. Propagation and the rest of the polymerization proceed in the same manner in conventional living cationic polymerization to that described by Sawamoto et al.[161, 162]

Dimanganese decacarbonyl ($Mn_2(CO)_{10}$) in combination with organic halides is known to generate free radicals in the visible range with good quantum efficiency through halide abstraction. As the low-molar mass and polymeric halides are readily available, the process is widely used for various synthesis purposes.[163] In the authors' laboratory, a broad range complex macromolecular structures including block[62, 63] and graft copolymers,[164-166] and hyper-branched polymers[167] were prepared by either selective photochemical generation of radicals or converting them into carbocations[115] which were used in bio applications such as drug delivery.[168, 169] We have also reported $Mn_2(CO)_{10}$ based photoredox system for copper catalyzed ATRP under visible- and sunlight.[138] In this approach, manganese compound has a dual action; (i) photogeneration of radicals by halide abstraction from alkyl halide, and also (ii) reduction $Cu^{II}Br_2$ to $Cu^{I}Br$ to activate ATRP process. Kamigaito and coworkers applied $Mn_2(CO)_{10}$ photochemistry to degenerative iodine transfer polymerization of both unconjugated and conjugated monomers.[67, 170] The approach was further extended to controlled radical polymerization[171] and block copolymerization of vinylidene fluoride monomers.[172, 173]

These results prompted us to investigate whether photochemically formed radicals by halide abstraction can be oxidized to the corresponding carbocations capable of adding to vinyl ether monomers leading to the living polymerization in the absence of Lewis acid. In this study, photoinitiated living cationic polymerization of vinyl ethers by using $Mn_2(CO)_{10}$ in the presence of alkyl halide and oxidant is presented. This system features elimination of Lewis acids catalysts, under benign conditions, irradiation with visible light at room temperature in metal free media, so it can be easily adapted to bio applications.

In view of manganese carbonyl promoted photoinduced radical generation and electron transfer reactions of electron donor radicals with onium salts, similar abstraction and redox reactions were envisaged to involve between $Mn_2(CO)_{10}$, benzyl bromide (BB), diphenyl iodonium bromide ($Ph_2I^+Br^-$) and vinyl ethers. Initially, the changes in the optical absorption spectrum of the radical generating photoactive components in the presence of $Ph_2I^+Br^-$ were recorded as a function of irradiation time. It should be pointed out that at the irradiation wavelength, the light is absorbed only by the manganese compound as the other components are transparent. As can be seen from Figure 4.1, the change in the optical absorption spectrum of the initiating system was recorded as a function of irradiation time and gradual photo-bleaching was observed.

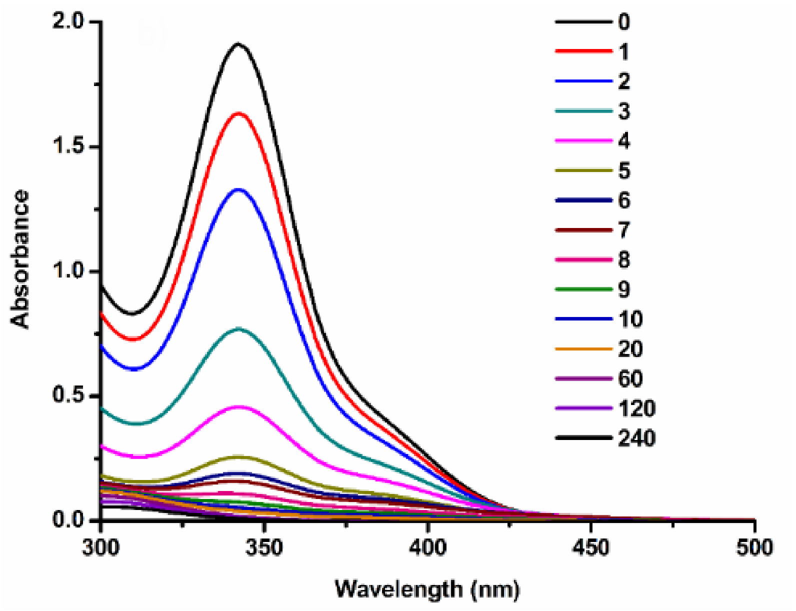

Figure 4.1 : Typical UV-vis spectral changes of the initiating system (BB/ $Mn_2(CO)_{10}$/ $Ph_2I^+Br^-$) on visible light irradiation, **λ** = 400–500 nm.

The polymerizations of isobutyl vinyl ether (IBVE) were conducted under various experimental conditions and typical results are collected in Table 4.1. As can be seen, the three components of the initiating system are indispensable for the polymerization to occur; no polymerization occurred in the absence of one or more compounds under our reaction conditions. Expectedly, with the iodonium salt having non-nucleophilic counter anion, polymerization proceeded via free ion mechanism and the resulting polymers had a broad molecular weight distribution (MWD) (Table 4.1, entry 4). In the presence of the oxidant with bromide anion, the photoctalytic system induced a controlled reaction to produce polymers with relatively narrow MWDs (Table 4.1, entry 5). Since, upon irradiation the carbon centered radicals are oxidized by the iodonium salt, it is reasonable to predict that the corresponding carbocations add to IBVE monomer which are rapidly deactivated by the bromide anions according to the mechanisms displayed in Figure 4.2. Poly(isobutyl vinylether) (PIBVE) chains were then grown via successive Photoinduced Radical Oxidation Addition Deactivation (PROAD) steps. In order to prove that PIBVE chain ends can be activated with the system described, HBr adduct of the monomer is formed by the irradiation of IBVE in the presence of $Ph_2I^+Br^-$ at UV region for a short time. Rapid addition of manganese compound and further irradiation at the visible range resulted in the successful polymerization with conversion and molecular weight characteristics quite similar to the benzyl bromide used system.

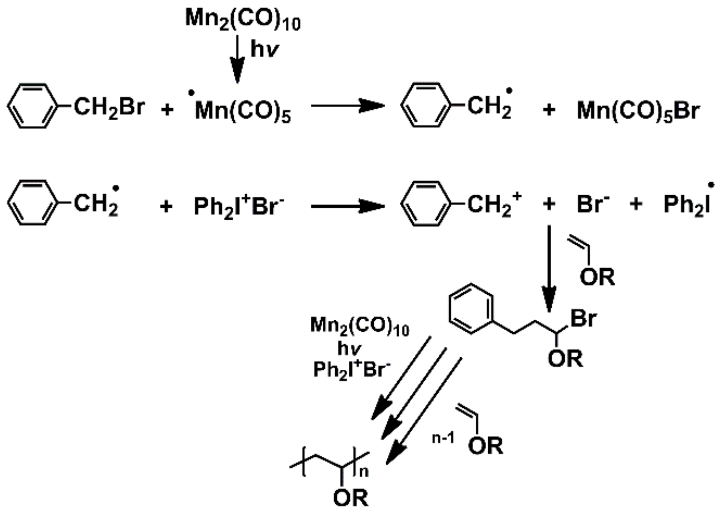

Figure 4.2 : Proposed mechanism for the photoinitiated living cationic polymerization of vinyl ethers.

Table 4.1 : Visible Light-Induced Cationic Polymerization of IBVE.

Run	[M]/[BB]/[$Mn_2(CO)_{10}$]/ [Oxidant]	[Oxidant]	Time (min)	Conv.[a] (%)	M_n (g mol^{-1})	M_w/M_n
1 [b]	2000/10/0/0	—	90	—	—	—
2 [b]	2000/10/0/1	$Ph_2I^+Br^-$	90	—	—	—
3 [b]	2000/10/1/0	—	90	—	—	—
4 [b]	2000/10/1/1	$Ph_2I^+ PF_6^-$	90	81	72900	2.97
5 [b]	2000/10/1/1	$Ph_2I^+Br^-$	90	75	103100	1.81
6 [c]	2000/10/10/10	$Ph_2I^+Br^-$	90	52	8400	1.50
7 [b]	2000/10/1/1	$Ph_2I^+Br^-$	45	48	72000	1.77
8 [b]	2000/10/1/1	$Ph_2I^+Br^-$	135	81	121000	1.86
9 [b]	2000/10/1/1	$Ph_2I^+Br^-$	180	93	153000	1.91

[a] Conversion of the monomer was determined gravimetrically. [b] Hexane as solvent. [c] Propylene carbonate was used as solvent.

To investigate the effects of the solvent on the polymerization, propylene carbonate was also used as reaction medium which resulted in a slower polymerization, better control over the molar mass and narrower molecular weight distribution (Table 4.1, entry 6). However, kinetic studies of the system showed that there was not a perfect linear relationship between M_n of the produced polymers and polymerization time. Furthermore, M_n remained almost stable after 70 % monomer conversion. These effect might be attributed to the low solubility of the formed polymer at relatively higher M_n values in the reaction medium.

The kinetic plot and the evolution of molecular weight and distribution with conversion for photoinduced living cationic polymerization of IBVE in hexane are summarized in Figure 4.3. The observed two important features of controlled/living polymerizations; (i) the linear increase of molecular weights with monomer conversion and the low polydispersities of the polymer chains (<1.9), indicate that the number of chains was constant which means chain transfer reactions are negligible and nearly all the chains start to grow simultaneously. The small but some tailing in GPC curves suggests slow initiation from benzyl bromide (Figure 4.4).

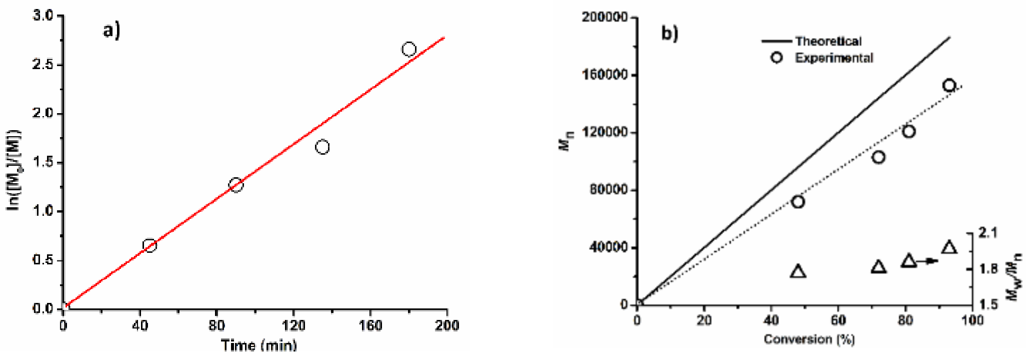

Figure 4.3 : (a) Kinetic plot and (b) molecular weights and distributions of the resulting polymers as a function of degree of conversion.

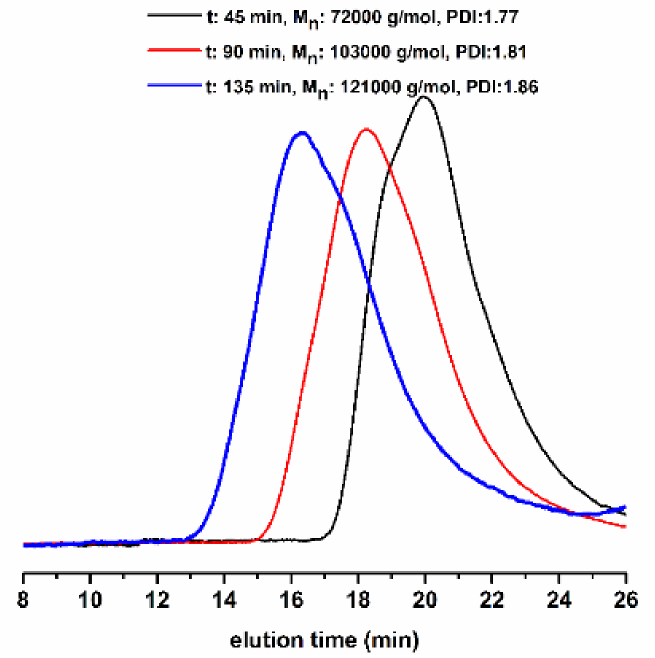

Figure 4.4 : GPC traces of the obtained PIBVE at different time intervals.

Furthermore, it was also demonstrated that the described approach can be employed not only for low molar mass halides but also polymeric halides which leads to the formation of block copolymers. Accordingly, a bromide functional polystyrene (PS), synthesized by conventional ATRP, was used as macroinitiator for the living cationic polymerization of vinyl ether resulting in the formation of PS-*b*-PIBVE. Successful block copolymerization was confirmed by spectral analyses of the precursor polymer and the resulting block copolymer. As can be seen from Figure 4.5, the NMR spectrum of the block copolymer represents $–OCH_2$ protons of isobutyl vinyl ether units between 3-3.7 ppm in addition to the characteristic aromatic peaks of PS segment indicating the successful block copolymerization.

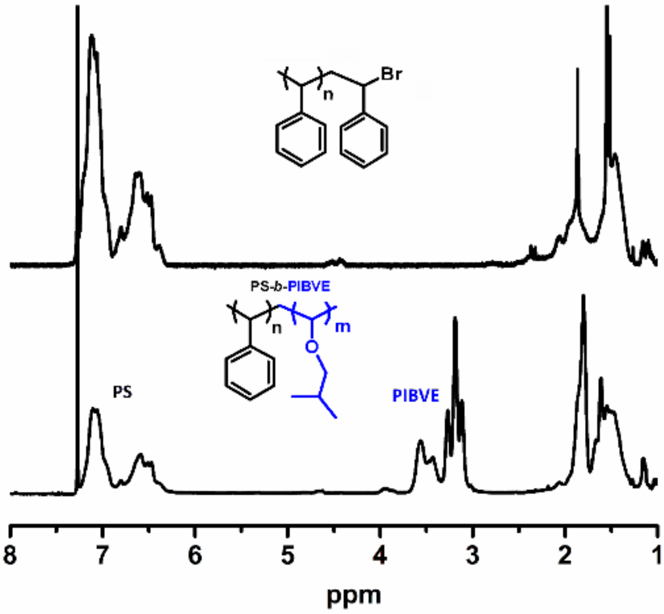

Figure 4.5 : ^{1}H NMR spectra of PS and PS-*b*-PIBVE.

FT-IR spectroscopy results also support the successful block copolymerization process. In the FT-IR spectrum of the precursor polymer characteristic bands for the PS were observed; while the spectrum of the block copolymer displays an additional band corresponding to a typical etheric C−O−C stretch band (Figure 4.6).

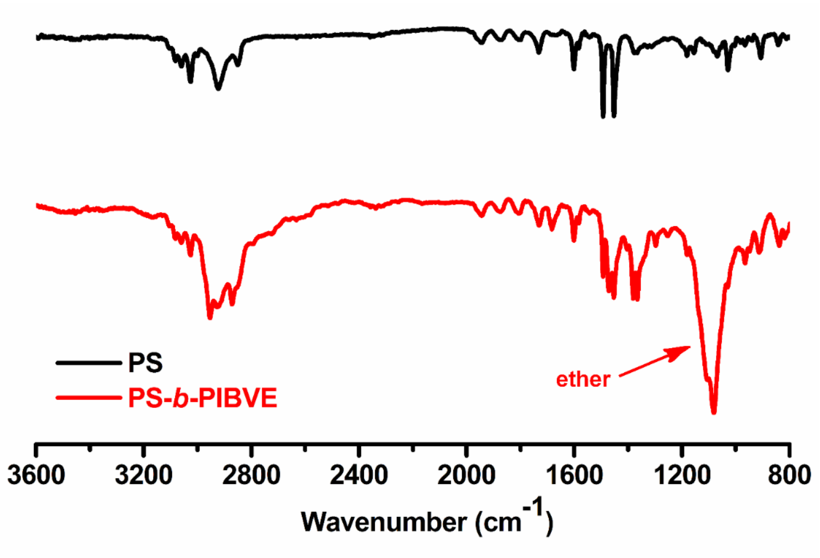

Figure 4.6 : FT-IR spectra of PS and PS-*b*-PIBVE.

Figure 4.7 shows the GPC curves of the precursor polymer and the final block copolymers. As can be seen, GPC trace of the block copolymer shifts to the higher elution volumes representing the increase in the molecular weight after the block copolymerization process.

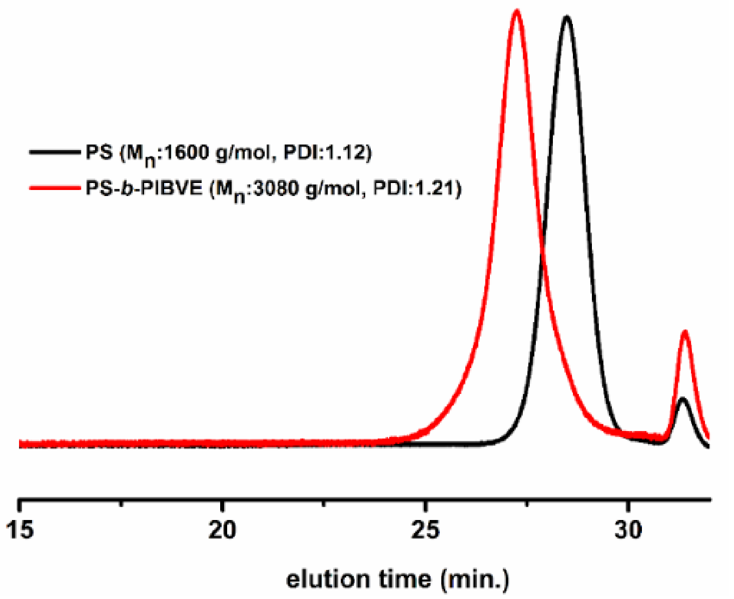

Figure 4.7 : GPC traces of PS and PS-*b*-PIBVE.

4.1 Experimental

4.1.1 Materials

Styrene (St; 99%, Aldrich) was passed through a basic alumina column to remove the inhibitor prior to use. Isobutyl vinyl ether (IBVE, 99%, Aldrich) was distilled from CaH_2 in vacuum. Dimanganese decacarbonyl ($Mn_2(CO)_{10}$, 99%, Aldrich) was purified by sublimation and stored in a refrigerator in the dark. N,N,N′,N″,N″-Pentamethyldiethylenetriamine (PMDETA; 99%, Aldrich) was distilled prior to use. Copper(I) bromide (CuBr, 98%, Acros), ethyl-2-bromo-propionate (>99%, Aldrich), diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$, 99%, Alfa Aesar), diphenyliodonium bromide (Ph_2I^+Br, 97%, Aldrich), benzyl bromide (BB, 98%, Aldrich), propylene carbonate (≥99.0%, Merck), hexane (95%, Sigma-Aldrich), tetrahydrofuran (THF, ≥99%, Aldrich) and methanol (99.9%, Merck) were used as received.

4.1.2 Instrumentation

All ^1H NMR spectra were recorded on an Agilent NMR System VNMRS 500 spectrometer at room temperature in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard. Gel permeation chromatography (GPC) measurements were performed on a Viscotek GPC max auto sampler system consisting of a pump, a Viscotek UV detector, and Viscotek a differential refractive index (RI) detector with three ViscoGEL GPC columns (G2000H HR, G3000H HR, and G4000H HR, 7.8 mm internal diameter, 300 mm length) in series. The effective molecular weight ranges were 456−42800, 1050−107000, and 10200−2890000, respectively. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 30 °C. Both detectors were calibrated with PS standards having narrow-molecular-weight distribution. Data were analyzed using ViscotekOmniSEC Omni-01 software. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer FTIR Spectrum One spectrometer.

4.1.3 PS

St (87.3 mmol), PMDETA (0.87 mmol), CuBr (0.87 mmol), 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 thermostatic oil bath (110°C) for 20 min. After polymerization, the reaction mixture was diluted with tetrahydrofuran (THF) and then passed through a column of neutral alumina to remove the copper salt. The excess THF and unreacted monomer were evaporated under reduced pressure. The resultant polymer, ω-bromo-end-functionalized polystyrene (PS), was dissolved in a small amount of THF, and precipitated in ten-fold excess of methanol.

4.1.4 PIBVE

In a typical photopolymerization procedure of IBVE, a Pyrex tube equipped with magnetic bar was heated in vacuum with a heat gun, and flushed with dry nitrogen. IBVE (1 mL, 7.7×10^{-3} mol), hexane (1 mL), BB (4.6 µL, 3.9×10^{-5} mol), $Ph_2I^+Br^-$ (1.4 mg, 3.9×10^{-6} mol) and $Mn_2(CO)_{10}$ (1.5 mg, 3.9×10^{-6} mol) were added to the Pyrex tube under vigorous stirring and the tube was sealed off under nitrogen atmosphere. Then, the mixture was irradiated at room temperature by a Ker-Vis blue photoreactor equipped with six lamps (Philips TL-D 18 W) emitting light nominally at 400–500 nm (light intensity 45 mW cm^{-2}). After given time, the reaction mixture was diluted with a small amount of THF and precipitated in excess of methanol. The polymer was dried under vacuum at room temperature.

4.1.5 PS-*b*-PIBVE

A pyrex tube equipped with magnetic bar was heated in vacuum with a heat gun, and flushed with dry nitrogen. PS (62 mg, 3.9×10^{-5} mol), IBVE (1 mL, 7.7×10^{-3} mol), propylene carbonate (2.5 mL), $Ph_2I^+Br^-$ (14 mg, 3.9×10^{-5} mol) and $Mn_2(CO)_{10}$ (15 mg, 3.9×10^{-5} mol) were added to the Pyrex tube under vigorous stirring and the tube was sealed off under nitrogen atmosphere. Then, the mixture was irradiated at room temperature by a Ker-Vis blue photoreactor equipped with six lamps (Philips TL-D 18 W) emitting light nominally at 400–500 nm (light intensity 45 mW cm-2). After given time, the reaction mixture was diluted with a small amount of THF and precipitated in excess of methanol. The polymer was dried under vacuum at room temperature.

4.2 Conclusion

In conclusion, the role of photoinduced electron transfer[174] reactions in macromolecular synthesis further confirmed and extended to living cationic polymerization. The experimental results presented here fully support the idea that suitable organic halides in conjunction with $Mn_2(CO)_{10}$ in the presence of one electron oxidants such as $Ph_2I^+Br^-$ may be used as promoters for living cationic polymerization of vinyl ethers. An important feature of this process is the addition and oxidation capabilities of the radicals under visible light irradiation and metal free conditions. Due to the high nuclephilic character, the bromide ions present as counter anions of the commercially available iodonium salt take part in the deactivation step of the approach. The described PROAD approach allows preparation of poly/vinyl ethers) with relatively narrow molecular weight distributions and may lead to new possibilities to prepare complex macromolecular structures and surface grafts either as continuous or patterned coatings providing appropriate halides are incorporated. Further studies in this line are now in progress.

5. CONCLUSIONS

The green and sustainable synthetic routes in polymer synthesis that result in more efficient chemical reactions and generate less waste and environmental emissions are priority in today’s polymer science. In this sense, photo-induced processes has received revitalized interest as it congregates a wide range of economic and ecological anticipations. Many studies involving various photopolymerization processes have been continuously conducted in different areas. In parallel to the extensive interest and publications in the photo-induced based systems, here in this thesis, three distinct applications of $Mn_2(CO)_{10}$ based photoinitiating strategies were deliberately selected in order to reflect their versatility and efficiency in macromoloecular syntheses.

First part of this thesis discusses overall background information to give more insight to basic principles of photopolymerization and $Mn_2(CO)_{10}$ chemistry.

Second part of this thesis describes utilization of $Mn_2(CO)_{10}$ compound for the operation of the photoinduced ATRP of (meth)acrylates and St under visible light or sunlight irradiation. In the process produced $MnCO_5^{\bullet}$ radicals not only abstract halogen atoms from alkyl halides to generate carbon centered radicals, but also regenerate the Cu(I) activators for the ATRP process. The main benefit of this process is temporal control of the growth of polymer chains; the process can be instantly stopped by turning off the light, and following turning on the light source restores the growth of polymer chains with the same kinetic character. Moreover, it was also proved that the process can be successfully utilized for the synthesis of poly(vinyl chloride)-*g*-poly(methyl methacrylate) graft copolymer from commercially available poly(vinyl chloride) (PVC) via grafting-from route.

In the third part, a new visible light-induced “grafting from” method for the preparation of poly(ethylene)-based graft copolymers is reported. In the first step of the method, cis-cyclooctene was polymerized via ROMP in the presence of a chain transfer agent and quantitatively hydrobrominated to obtain a pendant bromide containing linear poly(ethylene). The following polymerization of *t*BA using this polymer in conjunction with $Mn_2(CO)_{10}$ resulted in the graft copolymers possessing polar and nonpolar segments in the side and main chain, respectively. The ester groups of graft copolymer were subsequently converted into acrylic acid functionalities by acidolysis to obtain hydrophilic polyolefins.

In the last part of the thesis, we designed and demonstrated a facile photo-initiating system for living cationic polymerization of vinyl ethers, by using $Mn_2(CO)_{10}$ in the presence of alkyl halide and oxidant. The living nature of the polymerization was presented by the investigation of time dependence of logarithmic conversion and molecular weights. The capability of the system for the synthesis of block copolymers was also demonstrated.

It is believed that the concepts presented here will open new pathways to further developments of photochemical strategies for various applications.

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CURRICULUM VITAE

Name Surname: Mustafa ÇİFTÇİ

Place and Date of Birth: Elazığ-1986

E-Mail: mustafaciftcis@gmail.com

University and College Degrees Obtained:

2012 – 2017 Philosophy of Doctorate

Chemistry, Istanbul Technical University, Graduate School of Science Engineering and Technology

2009 – 2012 Master of Science

Chemistry, Istanbul Technical University, Graduate School of Science Engineering and Technology

2005 – 2009 Bachelor of Science

Chemistry, Faculty of Arts and Science, Uludag University

Professional Experience and Awards:

2013 - 2017 Research Assistant, Chemistry, Istanbul Technical University

2012 - 2017 National Ph.D. Fellowship Programme by Scientific and Technological Research Council of Turkey (TUBITAK)

2011 - 2013 Research Assistant, Chemistry, Bursa Technical University

Publications from thesis:

- **Ciftci M.,** Tasdelen M.A. and Yagci Y., Sunlight Induced Atom Transfer Radical Polymerization by Using Dimanganese Decacarbonyl, *Polymer Chemistry*, 2014, 5, 600-606.
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