ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

VISIBLE LIGHT-INDUCED ATOM TRANSFER RADICAL POLYMERIZATION

M.Sc. THESIS

Mustafa ÇİFTÇİ

Department of Chemistry

Chemistry Programme

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GÖRÜNÜR BÖLGE ATOM TRANSFER RADİKAL POLİMERİZASYONU

YÜKSEK LİSANS TEZİ

Mustafa ÇİFTÇİ
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Mustafa Çiftçi, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID **509101067**, successfully defended the **thesis** entitled "**VISIBLE LIGHT-INDUCED ATOM TRANSFER RADICAL POLYMERIZATION**", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 4 May 2012
Date of Defense :   5 June 2012

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To my family,

FOREWORD

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

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

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

I wish to deeply thank to all the members of Yagci Lab for all their help, support and friendship. In particular, Gökhan Açık, Çağatay Altınkök , Ali Görkem Yilmaz, Faruk Oytun, Ömer Suat Taşkın, Muhammed Aydın, Emre Tunç, Cemil Dizman, Kübra Demir, Mustafa Uygun, Manolya Kukut, Binnur Aydoğan, Burçin Gacal, Barış Kışkan and Demet Göen Çolak at with all of you, it has really been a great pleasure.

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

This work is supported by ITU Graduate School of Science, Engineering and Technology.

May 2012   Mustafa ÇİFTÇİ
                                                                                        Chemist

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ABBREVIATIONS

^{1}H-NMR	**:** Nuclear magnetic resonance spectroscopy
AGET	**:** Activators generated by electron transfer
ARGET	**:** Activators regenerated by electron transfer
ATRP	**:** Atom transfer radical polymerization
BAPO	**:** Bis (2,4,6-trimethyl benzoyl) phenyl phosphine oxide
C/LRP	**:** Controlled/living radical polymerization
Cu(II)Cl$_2$	**:** Copper (II) chloride
EtBP	**:** Ethyl-2-bromopropionate
GPC	**:** Gel permeation chromatography
MMA	**:** Methyl methacrylate
Mn$_2$(CO)$_{10}$	**:** Dimanganase decarbonyl
NMRP	**:** Nitroxide mediated radical polymerization
PI	**:** Photoinitiator
PMDETA	**:** *N, N, N',N'', N''*-Pentamethyldiethylenetriamine
PMMA	**:** Poly(methyl methacrylate)
RAFT	**:** Reversible addition fragmentation chain transfer
SR&NI	**:** Simultaneous reverse and normal initiation
TEMPO	**:** 2, 2, 6, 6-Tetramethyl-1-piperidinyloxy
THF	**:** Tetrahydrofuran
UV	**:** Ultra-violet

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VISIBLE LIGHT-INDUCED ATOM TRANSFER RADICAL POLYMERIZATION

SUMMARY

Polymerization at lower temperature would provide several advantages. Firstly, monomers with low ceiling temperaturescan only be polymerized at low temperatures, otherwise depolymerization dominates over polymerization. Lowering the temperature helps to suppress side reactions likely to occur such as trans-esterification elimination, and thermal cross-linking and leads to a better control of the polymerization reaction. Additionally, biochemical applications, such as immobilization of enzymes by polymerization, also usually require low temperatures. Compared with the corresponding thermal processes, the light induced polymerization offers a number of advantages, including rapid polymerization rates at room temperature, and spatial and sequential control of the polymerization. Despite these advantages, photoinitiated polymerization processes lack the control of the final polymer properties and structurally well-defined polymers and block copolymers cannot be prepared by photochemical means. There currently exist only a few examples, photochemical initiation can be applied to the all conventional controlled/living radical polymerizations including iniferter, nitroxide mediated radical, atom transfer radical polymerization and reversible addition-fragmentation chain transfer polymerizations. The photochemical initiation not only enables the easy control of the polymerization under ambient temperature even for heat-sensitive monomers but also tends to minimize side reactions like chain transfer or depolymerization. The concentration of initiating species and finally growing polymer chains may be conveniently adjusted by choosing appropriate light intensities.

In this thesis, visible light-induced reverse and simultaneous reverse and normal initiation atom transfer radical polymerizations (SR&NI ATRP) of methyl methacrylate are examined by using various dyes (erythrosin B and eosin Y) and type I photoinitiators (bis (2,4,6-trimethyl benzoyl) phenyl phosphine oxide). The effect of the type of the photoinitiators on the control of molecular weight and distribution is described. The photoinduced SR&NI ATRP using type I photoinitiator proceed in a well-controlled manner under visible light at room temperature as evidenced by kinetic studies. There is a very good agreement between the experimental and theoretical molecular weights and molecular weight distributions compared to dye-sensitized SR&NI ATRP.

GÖRÜNÜR BÖLGE ATOM TRANSFER RADİKAL POLİMERİZASYONU

ÖZET

Son zamanlarda, fotobaşlatılmış polimerizasyon pek çok ekonomik ve ekolojik beklentiyi biraraya getirdiği için hayli ilgi çekmektedir. Fotobaşlatılmış polimerizasyon, sahip olduğu mükemmel avantajları dolayısı ile kaplama, mürekkep, baskı levhaları, optik frekans yönlendiricileri ve mikroelektronik gibi sayısız uygulamaların temelini oluşturmaktadır. Oda sıcaklığında yüksek polimerizasyon hızı, düşük enerji tüketimi, çözücüsüz ortamda polimerizasyon, uygulanacak yüzey alanı ve uygulama süresinin kontrol edilebilmesi gibi avantajlar sağlamaktadır.Fotopolimerizasyon radikalik, katyonik ve anyonik olarak başlatılabilse de çok sayıda fotobaşlatıcının ve yüksek reaktivitedeki monomerlerin bulunulabilirliği açısından radikalik sistemlere daha fazla ilgi duyulmaktadır.

Radikalik sistemlerin bir örneği olan ve yaşayan polimerizasyon reaksiyonları olarak da bilinen, kontrollü radikal polimerizasyonu mekanizmaları, polimer zinciri molekülünün kontrollü büyümesini sağlayan ve istenilen molekül ağırlığı elde etmeye yarayan farklı polimerizasyon mekanizmalarından oluşur. Bu reaksiyonlarda, sonlanma ve başlama basamakları kontrollü bir şekilde yapılır. Bu sayede polimerin molekül ağırlığı ve polimer zincirlerinin zincir sonu grupları kontrol edilir. Geleneksel serbest radikal polimerizasyonunda polimer zincirleri ilk adımlarda hızla büyüdükleri halde, kontrollü radikal polimerizasyonda polimer zincirlerinin büyümesi doğrusal bir yol izler.

Kontrollü radikal polimerizasyonların avantajları olarak molekül ağırlığının polimer dönüşümüyle doğrusal bağıntı içinde olması, dolayısıyla istenilen molekül ağırlığının elde edilmesi, monodisperse yakın dar bir molekül ağırlığı dağılımı elde edilmesi, zincir sonunda fonksiyonel gruplara sahip polimerler elde edilmesi (telekelik polimerler), polimer moleküler mimari yapısının kontrol edilmesi (blok kopolimerler), sayılabilir.

Sonlanma ve zincir transferi reaksiyonlarının olmadığı yaşayan polimerizasyon mekanizmalarında polimer zincirinin büyüme hızı hemen hemen sabittir ve reaksiyon sonunda elde edilen polimer moleküllerinin zincir büyüklükleri birbirine çok yakındır; yani monodisperse yakın molekül ağırlığı dağılımı vardır.

Günümüzde kullanılan kontrollü radikal polimerizasyon metodlarının çoğu termal olarak başlatılmaktadır. Fotopolimerizasyon yönteminde ise bu amaç için ısı yerine ışık kullanılmaktadır. Basitçe ışıkla başlatılmış polimerizasyon reaksiyonlarına fotopolimerizasyon denir. Genellikle mor ötesi veya görünür bölge ışık kaynakları kullanılır. Fotobaşlatıcının uygun bir dalga boyundaki ışık absorpsiyonu sonucunda oluşan primer radikaller tek fonksiyonlu monomerlerin polimerizasyonunu sağlarken çok fonksiyonlu monomerlerinde çapraz bağlı yapılara dönüştürülmesini sağlar.

Fotobaşlatıcılar, radikal oluşturma mekanizmalarına göre (birinci tip fotobaşlatıcılar) ve (ikinci tip fotobaşlatılar) fotobaşlatıcılar olmak üzere iki ayrı sınıfa ayrılır.

Birinci tip fotobaşlatıcılar, radikal vermek üzere doğrudan fotoparçalanmaya uğrayan çeşitli fonksiyonel gruplar içeren aromatik karbonil bileşiklerdir. Genellikle fotoparçalanma aromatik karbonil grubun yanındaki bağdan (α yarılması) gerçekleşir. İkinci tip fotobaşlatıcılar, (α yarılması) için gerekli olan yeterli enerjisine sahip olmadıkları için, ancak uygun hidrojen verici moleküllere enerji aktarımı veya bu moleküllerden hidrojen koparma sonucu radikalleri üretirler. En geniş kullanımı olan serbest radikal fotobaşlatıcılar, benzoin, benzil ketalleri, asetofenon türevleri, açilfosfin oksitler (birinci tip fotobaşlatıcılar) ve benzefenon, tiyokzanton, kinon /tersiyer amin kombinasyonlarıdır (ikinci tip fotobaşlatılar). UV ışığıyla fotopolimerizasyon için aktive edilen birinci tip fotobaşlatıcı bileşenleri, çok kullanışlı; fakat görünür ışık bölgesindeki kürleşmelerde yetersizlerdir. İkinci tip sistemlerde, polimerizasyonun başlaması hidrojen verici molekül üzerinde oluşan radikaller vasıtasıyla gerçekleşirken etkin olmayan ketil radikalleri birbirleriyle birleşerek ortamdan kaybolur. İkinci tip fotobaşlatıcılarda hidrojen verici moleküller olarak alkol, amin, eter ve tiyol molekülleri kullanılır. Bu moleküllerin arasında tersiyer aminler en çok tercih edilenlerdir. Ancak tersiyer aminlerin kötü kokulu, zehirli, kolay uçucu olması, göçme gibi olumsuz yönleri vardır.

Fotopolimerizasyon yönteminin kullanıldığı polimerizasyonlar daha düşük sıcaklıklarda gerçekleştirilebilmektedir. Polimerizasyonu düşük sıcaklıklarda gerçekleştirmek bir çok avantaj sağlamaktadır. Öncelikle maksimum çalışma sıcaklığı düşük olan monomerler sadece düşük sıcaklıklarda polimerleştirilebilirler, aksi halde oluşan polimerler depolimerizasyona uğrayarak tekrar monomer halini alırlar. Polimerizasyon sıcaklıklığının düşürülmesi esterleşme ve çarpaz bağlanma gibi yan reaksiyonların önlenmesini sağlarken, polimerizasyonun daha kontrollü bir şekilde yapılmasında sağlar. Bunlara ek olarak enzim ve protein gibi ısıya duyarlı biyoyapıların polimerizasyon işlemiyle polimerlere bağlanması gibi işlemlerde düşük sıcaklıklarda gerçekleştirilmelidir. Termal polimerizasyonla karşılaştırıldığında fotopolimerizasyon oda sıcaklığında hızlı, zamansal ve mekan kontrollü olmasından dolayı büyük avantajlara sahiptir. Fakat bu avantajların yanında fotopolimerizasyonla elde edilen polimerin molekül ağırlığı, molekül ağırlık dağılımı ve fonksiyonalitesi gibi özelliklerin kontrolü mümkün değildir. Bundan dolayıda blok ve aşı gibi kopolimerlerin sentezi fotopolimerizasyonla gerçekleşmesi kısıtlıdır. Günümüzde kullanılan iniferter, nitroksitle büyütülmüş radikal polimerizasyon, atom transfer radikal polymerizasyon (ATRP) ve tersinir katılma-ayrışma zincir transfer polimerizasyonu gibi kontrollü/yaşayan termal polimerizasyon tekniklerinin fotokimyasal başlatılmış birkaç örnekleri mevcuttur. Fotokimyasal olarak başlatılan kontrollü/yaşayan polimerizasyonlarda zincir transfer ve depolimerizasyon gibi yan reaksiyonların minimize edilmesinden dolayı daha düşük molekül ağırlık dağılımına sahip polimerler elde edilmektedir. Ayrıca uygun ışık şiddeti seçilerekte hem başlatıcı konsantrasyonu hemde polimer zincirlerinin boyu ayarlanabilir.

Bu tez çalışmasında farklı boyar maddeler ve fotobaşlatıcılarla vinil monomerlerinin örneğin metil metakrilat, metil akrilat ve stiren'in görünür bölge ışığıyla tersinir ATRP, eş zamanlı tersinir ATRP ve klasik ATRP yöntemleriyle polimerizasyonları incelenmiştir. Bu anlamda ilk basamak, belirlenen dalga boyu aralığında absorbansı olan uygun boyar madde ve fotobaşlatıcıların seçilmesidir. Bunun için belirlenen

boyar madde ve fotobaşlatıcıların Uv-vis spektrumları alınmış ve çalışılacak boyar maddeler (eritrosin B and eosin Y) ve fotobaşlatıcı (bis (2,4,6-trimetil benzoil) fenil fosfin oksit) belirlenmiştir. Daha sonra tersinir ATRP, eş zamanlı tersinir ATRP ve klasik ATRP yöntemleriyle denemeler yapılmış ve fotobaşlatıcı tipi, alkil halojenür miktarı, bakır miktarı gibi birçok parametrenin polimerizasyon üzerine etkisi incelenmiştir. Elde edilen sonuçlar ışığında herbir sistem için monomer tüketimi/zaman ve molekül ağırlığı/dönüşüm grafikleri çizilip, sistemlerle ilgili kinetik çalışmalar yapılmış, böylelikle fotobaşlatıcı tipinin molekül ağırlığı ve dağılımı üzerindeki etkisi aydınlatılmıştır. Kinetik çalışmalar sonucu 1. tip fotobaşlatıcıların kullanıldığı eş zamanlı tersinir ATRP yöntemiyle daha iyi kontrollü polimerizasyonların gerçekleştirildiği ispatlanmıştır. Boyar madde kullanılarak gerçekleştirilen eş zamanlı tersinir ATRP sistemlerinde ise teorik ve deneysel molekül ağırlık ve dağılımları arasında iyi bir uyum gözlenmiştir. Tüm bu çalışmalar ışığında tersinir ATRP ve eş zamanlı tersinir ATRP sistemleri için uygun mekanizmalar önerilmiştir.
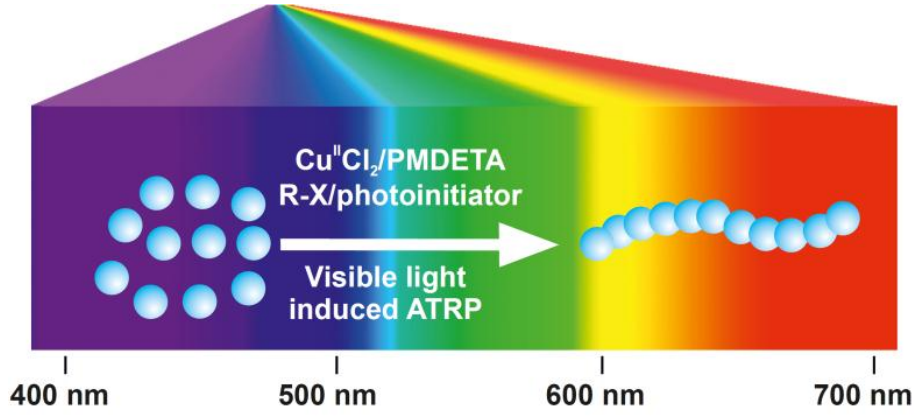
Şekil 1: Görünür bölge ışığıyla gerçekleştirilen ATRP

1. INTRODUCTION

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 [1]. 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 [2]. Among them, photoinitiated polymerization has many advantages over other polymerization processes including that 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 [3]. 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.

In recent years, the controlled/living radical polymerization (C/LRP) became an established synthetic method to prepare new complex architectures of polymers such as block, graft, star and functional polymers with well-defined structures. The most widely studied C/LRP methods are atom transfer radical polymerization (ATRP) [4, 5], reversible addition-fragmentation chain transfer polymerization (RAFT) [6], nitroxide-mediated radical polymerization (NMRP) [7]. Most of these techniques so far can be performed at fairly elevated temperatures, mostly between 90 and 120 $^\circ$C [8]. Although with limited success, there have been a number of attempts to extend such control to polymerization conducted photochemically. Recent approaches with regard to achieving polymerization control in both cationic [9-12] and radical systems [13-16] are based on the stabilization of unstable growing species by the reversible formation of the corresponding covalent and dormant species that rapidly exchange. In this thesis, visible-light induced atom transfer radical polymerizations and its mechanistic insights is discussed.

2. THEORETICAL PART

2.1 Photoiniferter-based Controlled Radical Polymerization

The first step in the development of C/LRP dates back to the early 1980s when it was found that the use of iniferter (namely, agents that initiate, transfer, and terminate) systems exhibited a degree of livingness. This polymerization can be initiated by both thermal and photochemical activation and polymerize most vinyl monomers under mild reaction conditions. Photoiniferter-based polymerizations utilize dithiocarbamate derivatives that can initiate, terminate, and act as transfer agents during the polymerization. A large number of monomers, such as styrene, methyl methacrylate, *n*-butyl acrylate, acrylamide, acrylonitrile, and methacrylonitrile, can be polymerized in a controlled manner with various photoiniferters (Figure 2.1).
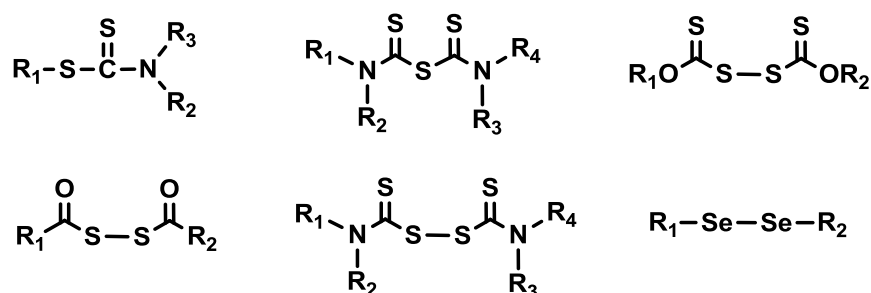
Figure 2.1 : Examples of photoiniferters.

UV irradiation of a dithiocarbamate yields a reactive carbon radical and a relatively unreactive dithiocarbamyl radical. The carbon radical, reacting with the monomer molecules, initiate the radical polymerization and propagates the process upon addition of monomer molecules. Whereas, the dithiocarbamyl radical does reversibly terminate growing polymer chains ("capping/decapping") and, depending on reaction conditions, enables controlled radical polymerization during photoirradiation (Figure 2.2). Simple evidence used to support this included the low polydispersities of the product (typically ranging from 1.2 to 2.0), a linear increasing trend of molecular weight with the conversion, and a formation of a related block copolymer.

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Figure 2.2 : C/LRP of methyl methacrylate using benzyl-*N, N*-diethyldithiocarbamate as photoiniferter.

A large number of monomers, such as styrene, methyl methacrylate, n-butyl acrylate, acrylamide, acrylonitrile, and methyl acrylonitrile, can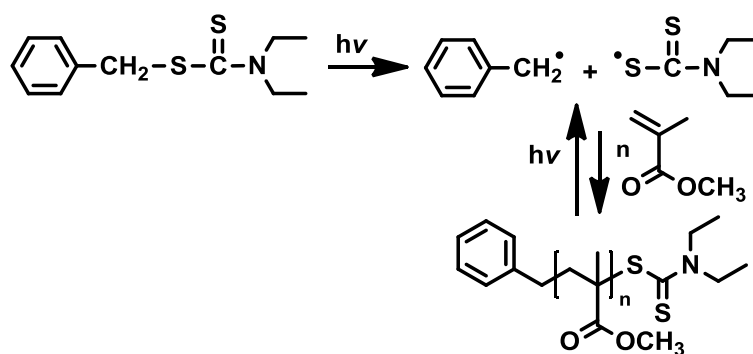 be polymerized in a controlled manner with photoiniferters. However, for other monomers such as vinyl acetate and methyl acrylate, dithiocarbamates served as a weak initiator or terminator, depending on the reactivities of the monomers. The living character of the polymerization decreases from styrene to methyl methacrylate, and to disappear in the case of acrylates. There are a number of other factors that affect the living character of the polymerization such as photoiniferter structures [17, 18], solvent [19], light intensity [20] and temperature. Steric effects contribute to the phoiniferter and monomer structures while solubility is affected by monomer, iniferter and solvent types. Since the photoiniferter itself is incorporated into the growing/propagating polymer chain during polymerization, a desirable end group functionality can be designed by careful choice of iniferter [21].

2.2 Photoinduced NMRP

NMRP, based on the use of nitroxyl radicals (nitroxides) or alkoxyamines, is also extensively studied photoinduced controlled radical polymerization method. Scaiano et al [22]. first proposed that the homolysis of TEMPO-based alkoxyamines (where TEMPO is 2,2,6,6-tetramethylpiperidinyloxy-4-yl radical) can be photosensitized by a xanthone or a pyrene molecule at their triplet and singlet excited states (Figure 2.3). Although the photosensitization step was successful, only limited numbers of radicals were generated in these systems. On the other hand, they did not perform any polymerization study to see the relative contribution of these molecules in the polymerization.

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R¹ = H; R² = H, R¹ = H; R² = CH₃, R¹ = CH₃; R² = CH₃,
R¹ = H; R² = C₂H₅, R¹ = H; R² = C₆H₅
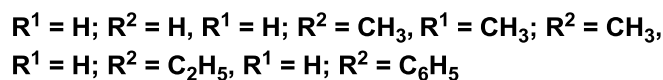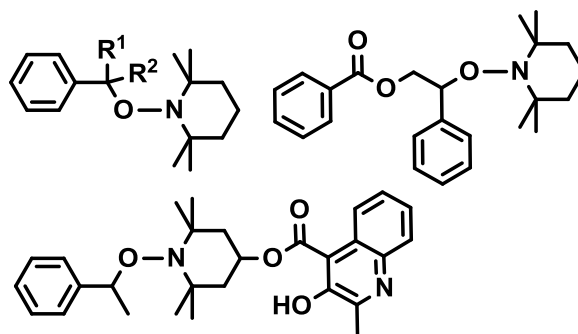
Figure 2.3 : Examples of photosensitive TEMPO-based alkoxyamines.

Later on, Yoshida et al. [23] attempted to activate the radical generation process by using photoacid generator iodonium salt in the presence of TEMPO derivatives or alkoxyamines. However, this system is still unclear as the function of the iodonium salt is also not known. Several attempts were also made to covalently attach different chromophoric groups to the TEMPO moiety [24, 25]. Although, some success was achieved, the conditions for true C/LRP were not attained, because the energy transfer from the sensitizer ("antenna") to the C-O bond was not found to be efficient enough to activate the process. More recently, Neckers and Lalevee groups [26] reported new alkoxyamines possessing a chromophore group with various positions to facilitate the homolysis of alkoxyamine (Figure 2.4). The effect of the type and position of chromophore groups (xanthone or benzophenone), distance between the chromophore and the nitroxide group, and the structure of the leaving nitroxide on the polymerization was studied [27-30].
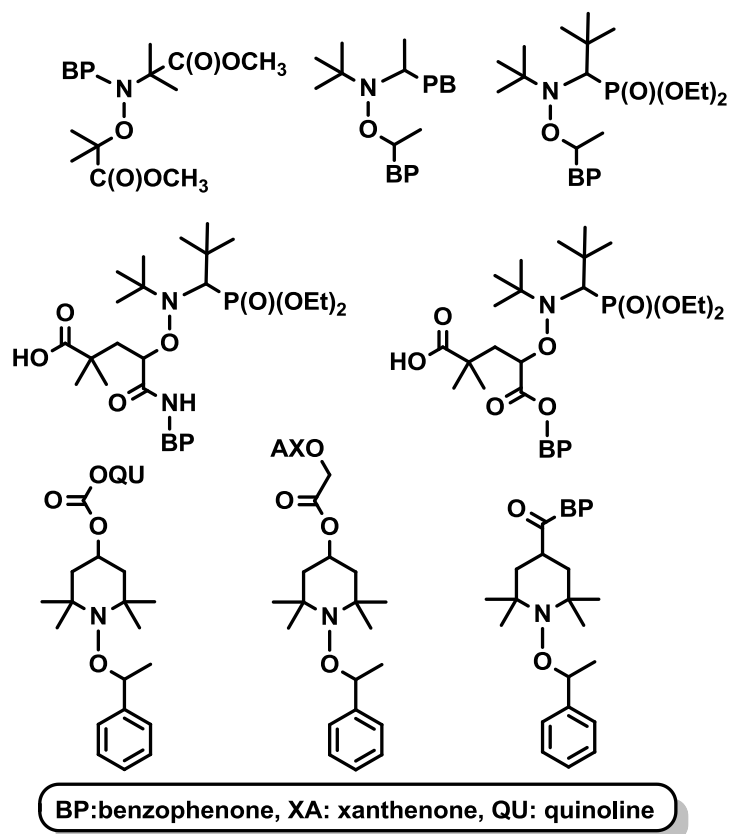
Figure 2.4 : Examples of photosensitive alkoxyamines possessing directly linked chromophore groups.

The first step in the process involves to the photodecomposition of the alkoxyamines with the concomitant formation of an initiating radical and a nitroxide (Figure 2.5). The reversible reaction between the polymeric radical and the nitroxide leads to a reduction in the contribution of irreversible bimolecular termination. Usually, the chromophore group must be located on the nitroxide group to ensure reversible cleavage of the macroalkoxyamine during the photopolymerization process. It was demonstrated that photoinitiated NMRP of *n*-butyl acrylate using these compounds indicated a linear growth of the polymer chain combined with a partial living character. However, the photoinitiated NMRP gives rise to polydispersities considerably higher than those obtained by thermally initiated NRMP process.
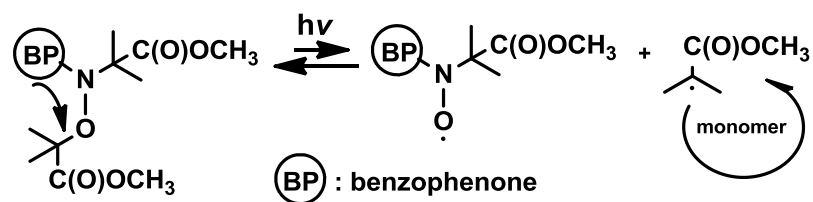
Figure 2.5 : Photoinitiated nitroxide-mediated radical polymerization of vinyl monomers with an alkoxyamine possessing a chromophoric benzophenone molecule.

2.3 Photoinduced RAFT Polymerization

Photoinduced controlled radical polymerization of vinyl monomers by RAFT process has been also studied under UV and solar irradiation. Among various RAFT agents, dithiobenzoate and trithiocarbonate derivatives were found to be particularly useful in establishing a dynamic equilibrium between propagating radicals and dormant chains via RAFT mechanism under UV irradiation (Figure 2.6).
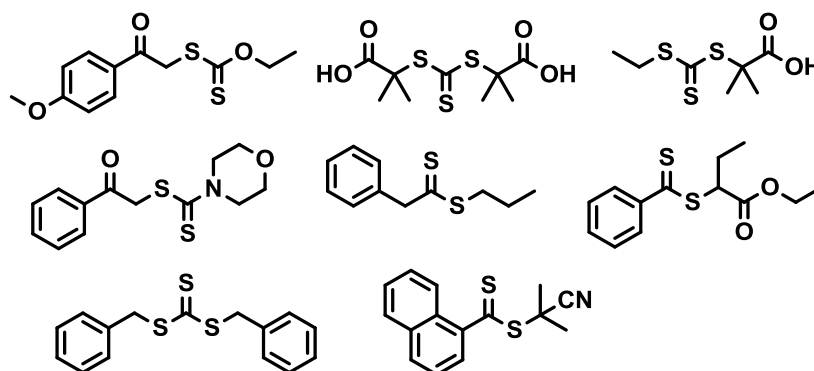
Figure 2.6 : Examples of photosensitive RAFT agents.

The first successful photoinduced RAFT polymerization at low temperature was reported by Pan et al. [31] who polymerized styrene, methyl acrylate and butyl acrylate with a dibenzyl trithiocarbonate under UV light between 254 and 366 nm. In another study, Quinn et al. [32] used different types of RAFT agents such as 1-phenylethyl phenyldithioacetate in the styrene polymerization. It produced well-defined polymers with controllable molecular weight up to monomer conversions of 30%. Later on, Barner-Kowollik et. al., have studied the photoinitiated RAFT polymerization of acrylic acid in aqueous solutions at ambient temperature using S, S'-bis(α, α'-dimethyl-α''-acetic acid) trithiocarbonate and reached 50% conversion without losing the control [33]. Cai and co-workers used S-ethyl-S'-(α, α'-dimethyl-

α''-acetic acid) trithiocarbonate as RAFT agent for water-soluble monomers in combination with acylphosphine oxide as the photoinitiator under visible light irradiation. Well defined polymers were obtained with narrow polydispersities at conversions over 75% [34-38].

Zhu[39] and Yagci [16] independently reported the tandem polymerization concept by combination of photoiniferter and photoinduced RAFT polymerization. In these systems, both (i) photoiniferter and (ii) RAFT mechanisms are operative in the photoinduced controlled radical polymerization (Figure 2.7). The results showed a good agreement between the theoretical molecular weight and experimental data with a PDI <1.3.
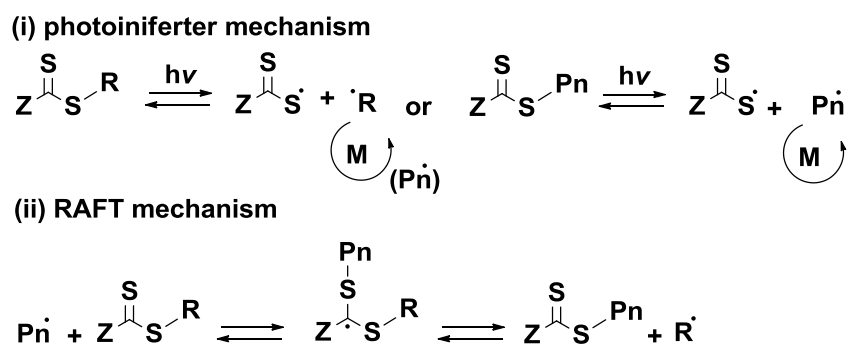
Figure 2.7 : Schematic representation of photoinitiated RAFT polymerization.

Several groups have also reported the synthesis of polystyrene [31, 40], poly(butyl acrylate) [31, 40-42], poly(methyl acrylate)[31], poly(methyl methacrylate) [43] and poly(styrene-*alt*-maleic anhydride) [44] via photoinduced RAFT polymerization. However, this method exhibits some limitations such as low conversions even at long polymerization times. The molecular weight distribution broadened significantly at long irradiation times due to the decomposition of the chain transfer agent moieties at the polymer ends. There have been a number of attempts to improve the photoinduced RAFT polymerization. For example, the degradation of chain transfer agent at the polymer ends can be minimized by cutting off the short-wave UV radiation using a filter or higher monomer conversion can be reached by addition of a commercially available photoinitiator to the polymerization media.

2.4 Photoinduced ATRP

The most versatile method of controlled radical polymerization is ATRP due to its simple polymerization procedure, functional group compatibility, and very good architectural and molecular weight control. A first attempt to integrate a photochemical activation in the ATRP is the use of a photoinitator in the reverse ATRP system. In this process, the initiating radicals originated from the decomposition of the photoinitiators (PI) can abstract the halogen atom (X) from the oxidized transition-metal species ($Cu^{II}X_2/L$) to form the reduced transition-metal species ($Cu^{I}X/L$) and the dormant species (I-X) or can react with the monomer to create a growing chain (I–P$^\bullet$) (Figure 2.8). The situation then becomes exactly the same as in a classical ATRP. Therefore, propagation step is also required additional heat energy to achieve a fast initiation and a rapid and reversible deactivation. Interestingly, there is one report on ATRP of methyl methacrylate in the presence of ferric tri(*N*,*N*-diethyldithio carbamate) as the catalyst with 2,2-dimethoxy-2-phenylacetophenone as photoinitiator under UV light irradiation, the exact mechanism of the system is still unclear. And GPC results showed that the obtained polymers have quite high molecular weight distribution.
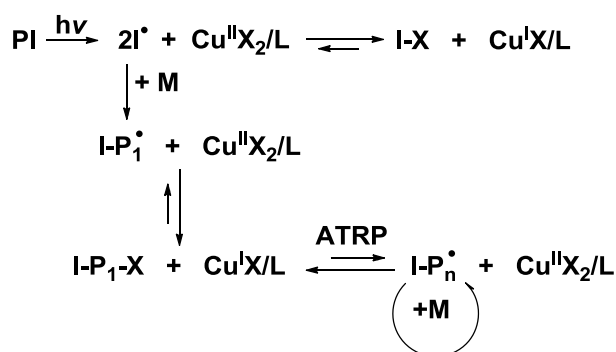
Figure 2.8 : Schematic representation of photoinitiated reverse ATRP process.

In another study, although authors claimed that light accelerates the rate of classical ATRP but also enhances the living character of the polymerization [45], k_{act} constants of ATRP system under UV and without UV irradiation were found quite similar, 0.10 and 0.092 M^{-1} s^{-1}[46]. Recently, Matyjaszewski and others reported the combination of ATRP and photoiniferter polymerization of methyl methacrylate using a dithiocarbamate photoiniferter [46-50]. Upon UV irradiation, dithiocarbamate molecules rapidly generate carbon-centered radicals that induce

radical propagation and are deactivated by copper complex. In this system, the copper complex mainly facilitates deactivation of propagating radicals rather than activation of initiator, particularly, at low temperature (Figure 2.9). Thus, inefficient chain transfer reactions in iniferter polymerization were eliminated by the fast deactivation of radicals by the copper complex.
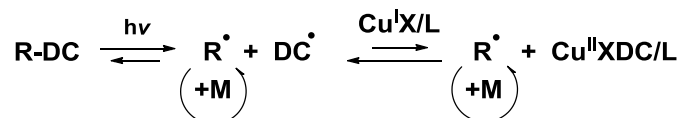
Figure 2.9 : General mechanism of ATRP with dithiocarbamate under UV irradiation.

Quite recently, our group presented a new photoinduced controlled radical polymerization, which is mainly based on photochemical generation of activator in the ATRP [14, 15]. The polymerization can be operated by *in situ* photogeneration of $Cu^{I}X/L$ as activator from the copper (II) species and the subsequent reaction of the activator with alkyl halide (Pn-X) resulting in the formation of active radical (Pn$^{\bullet}$) and $Cu^{II}X_2/L$. In the subsequent step, the radical adds to a monomer and rapidly deactivated by the $Cu^{II}X_2/L$ to form dormant species and $Cu^{I}X/L$ (Figure 2.10). The described photoredox process was also applied in copper-catalyzed azide-alkyne click reaction [51, 52].
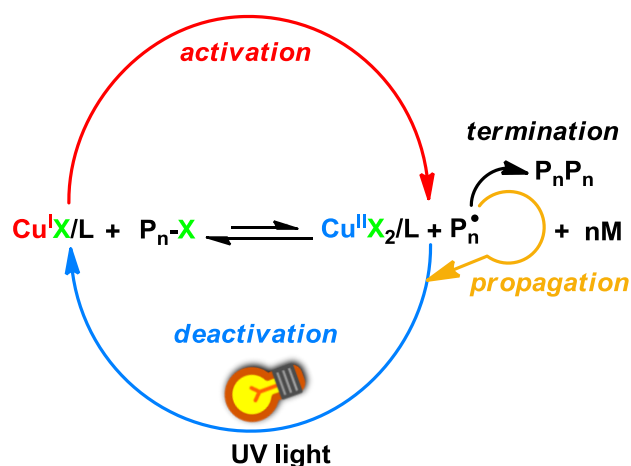
Figure 2.10 : Mechanistic scheme for photochemical generation of activator in the ATRP.

In the process, the excess of $Cu^{II}X_2/L$ deactivator resulting from irreversibly unavoidable radical-radical termination reactions is also continuously regenerated to the $Cu^{I}X/L$ activator by light. However, it should be pointed out that, $Cu^{II}X_2/L$ complexes are usually less soluble in organic media than the corresponding $Cu^{I}X/L$ complexes, often resulting to heterogeneous polymerizations. The use of small amount of methanol as solvent in the polymerization facilitates to conduct the process in homogeneous system, as methanol exclusively penetrates the solubility of $Cu^{II}X_2/L$ complexes in the polymerization mixture. By applying homogenous polymerization of MMA could significantly increase the rate of polymerization in comparison with, and the control over molecular weights under homogenous system was also improved. Furthermore, one can note that the molecular weight distribution of polymers prepared by homogenous system is relatively narrower (1.06~1.13) than the heterogeneous one (Figure 2.11).
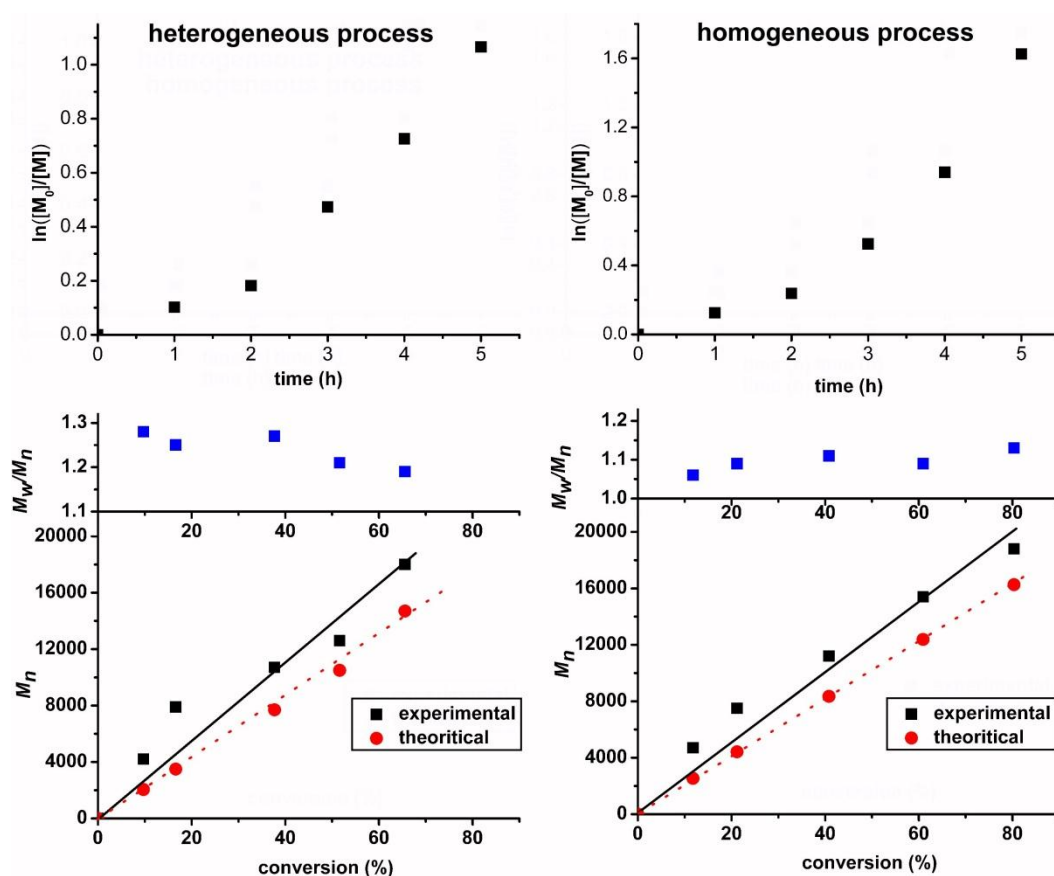
Figure 2.11 : Kinetic plots and molecular weights and distributions of resulting polymers as a function of degree of conversion for photoinduced controlled radical polymerization of methyl methacrylate in the absence or the presence of methanol indicated.

As a part of continuous efforts to develop the photoinduced ATRP, the use of reverse ATRP, and simultaneous reverse and normal initiation (SR&NI) ATRP as alternative initiating systems were also reported [13]. Photoinduced reverse ATRP was performed $Cu^{II}Cl_2$/PMDETA system in conjunction with several photoinitiators belonging to the *Type I a*nd *Type II* classes at room temperature. The polymerization of MMA could be initiated in the absence of alkyl halide; however, loss of control over the polymerization process was observed. Photoinduced SR&NI ATRP was successfully applied to MMA in the presence of alkyl halide. The molecular weights increased with conversion, and they were in good agreement with the theoretical values. Compared to the photoinduced reverse ATRP, it allowed better control over molecular weights with narrow molecular weight distributions (Figure 2.12). Notably, the chain extension reaction with the macroinitiator prepared by photoinduced SR&NI ATRP was more successful than photoinduced reverse ATRP.
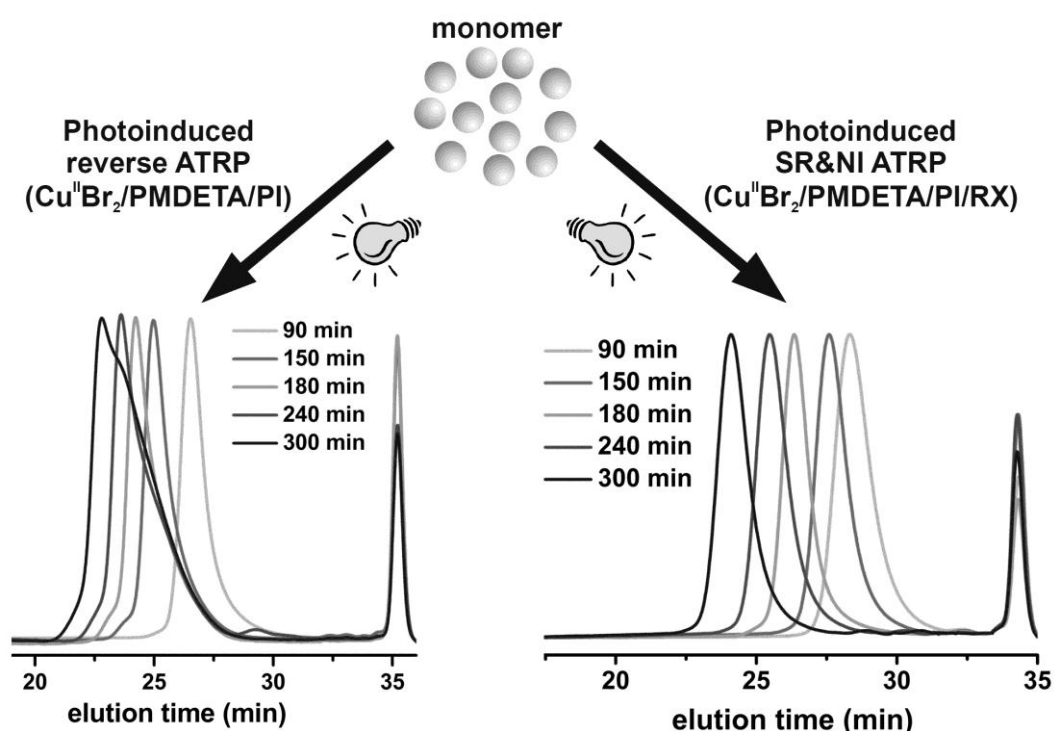
Figure 2.12 : GPC traces of PMMA prepared by photoinduced reverse ATRP, and simultaneous reverse and normal initiation (SR&NI) ATRP.

2.5 Photoinduced Degenerative-transfer Polymerization

Later on, Kamigaito et al. developed a visible light-induced controlled radical polymerization, based on degenerative iodine transfer processes, using a dinuclear manganese complex $[Mn_2(CO)_{10}]$ in conjunction with alkyl iodides [53-55]. Upon

absorption of light, [Mn$_2$(CO)$_{10}$] undergoes to photochemical homolysis of the metal-metal bond to form the highly reactive metal-centered radical [•Mn(CO)$_5$], which can even activate the less reactive C-I dormant species (Figure 2.13). This system was applicable to not only unconjugated monomer, vinyl acetate, but also conjugated monomers such as acrylates and styrene with the use of appropriate initiators.
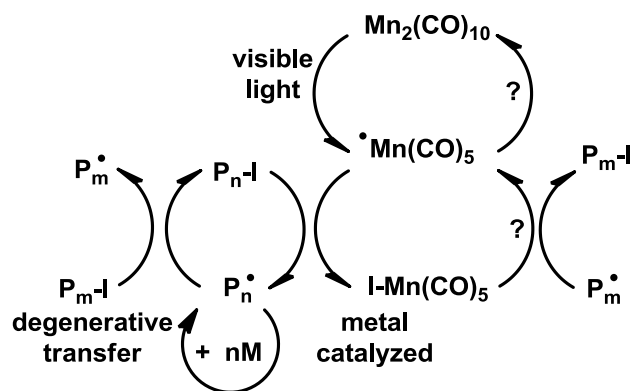
Figure 2.13 : Proposed mechanism of photoinduced controlled radical polymerization with manganese decacarbonyl/alkyl iodide system.

In another example, Yamago et al. reported a photoinduced organotellurium-mediated controlled radical polymerization of meth(acrylate)s by direct photolysis of the C−Te bond of the dormant species [56, 57]. The proposed mechanism for the polymerization involves that the activation process mainly occurred by degenerative (exchange) chain transfer with a small contribution of reversible termination (Figure 2.14). The main drawback of this technique is that organotellurium derivatives are sensitive to air and light, foul-smelling, and difficult to handle.
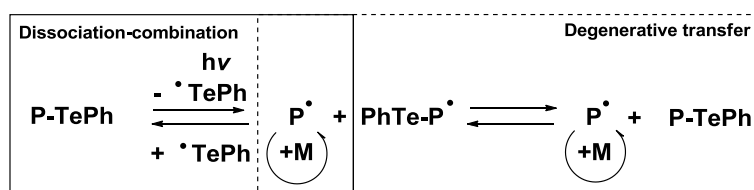
Figure 2.14 : General mechanism of photoinduced organotellurium-mediated controlled radical polymerization.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Reagents

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

*N, N, N', N'', N''-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%): N, N, N', N'', N''-*pentamethyldiethylenetriamine was distilled before use.

Ethyl 2-bromopropionate (EtBP, Aldrich, 98%): Ethyl 2-bromopropionate was used as received.

Copper (II) chloride ($Cu^{II}Cl_2$, Acros, 99%): Copper (II) chloride was used as received.

Bis (2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO, Ciba): Bis (2,4,6-trimethylbenzoyl)phenylphosphine oxide was used as received.

Eosin Y ($C_{20}H_6Br_4Na_2O_5$, Merck, 99%): Eosin Y was used as received.

Erythrosin B ($C_{20}H_6I_4Na_2O_5$, Merck, 99%): Erythrosin B was used as received.

3.1.2 Solvents

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

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

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

3.2 Equipments

3.2.1 Light Source

A Ker-Vis blue photoreactor equipped with 6 lamps (Philips TL-D 18 W) emitting light nominally at 400–500 nm was used in all polymerization experiments. The light intensity was 45 mW.cm-2 as measured by Delta Ohm model HD-9021 radiometer.

3.2.2 ^{1}H-Nuclear magnetic resonance spectroscopy (^{1}H-NMR)

^{1}H-NMR spectra of 5–10 % (w/w) solutions in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer.

3.2.3 Gel permeation chromatography (GPC)

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

3.3 Preparation Methods

3.3.1 General procedure for visible-light induced atom transfer radical polymerization

General procedure for visible light induced ATRP of MMA, targeted number-average degree of polymerization (DP_n)= 200: MMA (2mL, 18.6 mmol), PMDETA (22 μL, 0.1 mmol), $Cu^{II}Cl_2$ (1.3 mg, 9.4×10^{-3} mmol), EtBP (12.2 μL, 9.4×10^{-2} mmol), toluene (1 mL, 9.4 mmol), dye (eosin Y, 6.5 mg, 9.4×10^{-3} mmol) and methanol (0.5 mL, 12 mmol) were put into a Schlenk tube (i.d = 9mm), 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 6 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. After given time (from 1 to 4 h), the resulted polymers were precipitated in the n-hexane and then dried under reduced pressure. Conversion of the monomer was determined gravimetrically.

4. RESULTS AND DISCUSSION

Controlled/living radical polymerization (C/LRP) techniques have received widespread interest in recent years due to their ability to produce vinyl polymers with predetermined molecular weight, narrow molecular weight distribution, various architectures, and useful end-functionalities. The most important methods of such controlled processes are atom transfer radical polymerization (ATRP) [4, 5], reversible addition-fragmentation chain transfer polymerization (RAFT) [6], nitroxide-mediated radical polymerization (NMRP) [7]. Although ATRP is chemically versatile, compatible with various monomers and functional groups, the metal catalyst, it has some limitations such as large metal requirement and easy oxidation of metal catalyst [58, 59]. Recently, various strategies have been developed to overcome those problems, the activators generated or regenerated by electron transfer (AGET or ARGET) ATRP provides an excellent way to overcome the drawbacks of conventional ATRP[60]. The required copper (I) catalyst for the ATRP can be generated by several approaches involving the *in situ* reduction of Cu(II) to Cu(I) by (i) various reducing agents [61], (ii) photochemical and (iii) electrochemical [62] redox processes, and (iv) copper-containing nanoparticles [63, 64]. Quite recently, our group presented a new photoinduced ATRP [14, 15], which is mainly based on *in situ* generation of $Cu^{I}X/L$ from $Cu^{II}X_2/L$ by light directly or indirectly. In the direct system, the polymerization activators, $Cu^{I}X/L$ was generated from $Cu^{II}X_2/L$ under UV light without any photoinitiator and the polymerization was initiated by reaction of the $Cu^{I}X/L$ with alkyl halide (Pn-X) resulting in the formation of active radical (Pn$^{\bullet}$) and $Cu^{II}X_2/L$. In the subsequent step, the radical adds to a monomer and rapidly deactivated by the $Cu^{II}X_2/L$ to form dormant species and $Cu^{I}X/L$. In the inderect system involving photoinduced reverse ATRP and simultaneous reverse and normal initiation (SR&NI) ATRP processes, the polymerization activators, $Cu^{I}X/L$ can be generated from $Cu^{II}X_2/L$ under UV light through the help of photoinitiators (Figure 4.1) [13]. The described photoredox process was also applied in copper-catalyzed azide-alkyne click reaction [51, 65, 66].
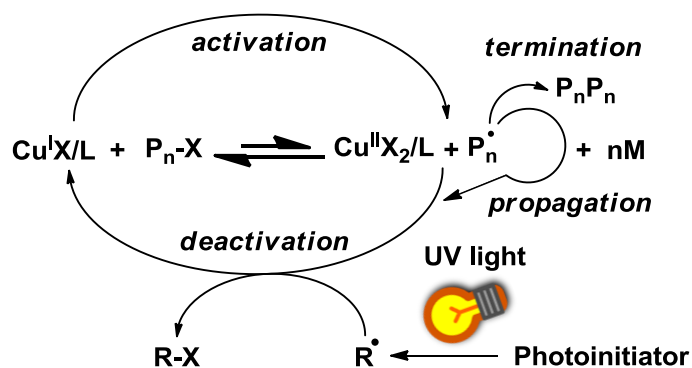
Figure 4.1 : Mechanistic scheme for photoinduced simultaneous reverse and normal initiation (SR&NI) ATRP.

The present study aimed to develop the photoinduced (SR&NI) ATRP to extend its spectral sensitivity to the visible range by either adding a dye or a visible light photoinitiator. Control experiments with various conditions were performed to support the proposed polymerization mechanism.

It is well established that the combination of many dyes with a co-initiator provides an excellent visible light photoinitiators for the vinyl monomers [67]. Depending on the nature of the dye involved, namely photoreducible or photooxidizable dyes, two distinct mechanisms need to be considered. These are electron transfer from the co-initiator to the excited, photoreducible dye and electron transfer from the excited, photooxidizable dye to the co-initiator. Although, both reactions have been included in the literature, photoreduction of dyes is by far the more common process. Photoreducible dyes including rose bengal, erythrosin B, eosin Y, fluorescein, acriflavine, thionin, and methylene blue can act as electron acceptors from donors such as tertiary amines, *N*-phenylglycine, thiols, borate salts, etc. to generate the reduced dye and a primary radical, which initiates the vinyl polymerization [68].

Recently much attention has been paid to the use of visible light to initiate controlled/living radical polymerization of vinyl monomers [1]. In our continued efforts to develop the photoinduced ATRP, various initiating systems including conventional ATRP, reverse ATRP, and simultaneous reverse and normal initiation (SR&NI) ATRP were extensively studied. Compared to the conventional and reverse photoinduced ATRP (Table 1, entry 3), photoinduced SR&NI ATRP has allowed better control over molecular weights with narrow molecular weight distributions. Therefore, from this point of view, the focus of the research was shifted towards to

the photoinduced SR&NI ATRP by using visible light and the corresponding photoinitiators with the following structures (Figure 4.2).
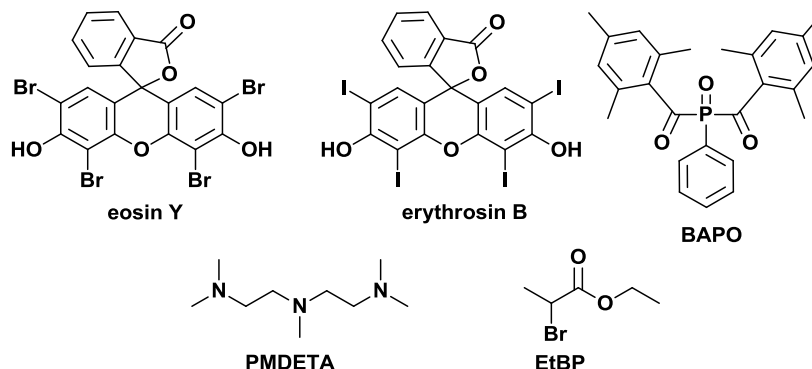
Figure 4.2 : Structures of visible light photoinitiators and ATRP catalysts.

First, optical properties of reaction mixture (MMA/Cu^{II}Cl$_2$/PMDETA), bis (2,4,6-trimethylbenzoyl) phenylphosphine oxide (BAPO), eosin Y and erythrosin B in the visible range have been examined by UV-vis spectroscopy. As shown in Figure 4.3, all photoinitiators strongly absorbs visible light where the reaction mixture is completely transparent.
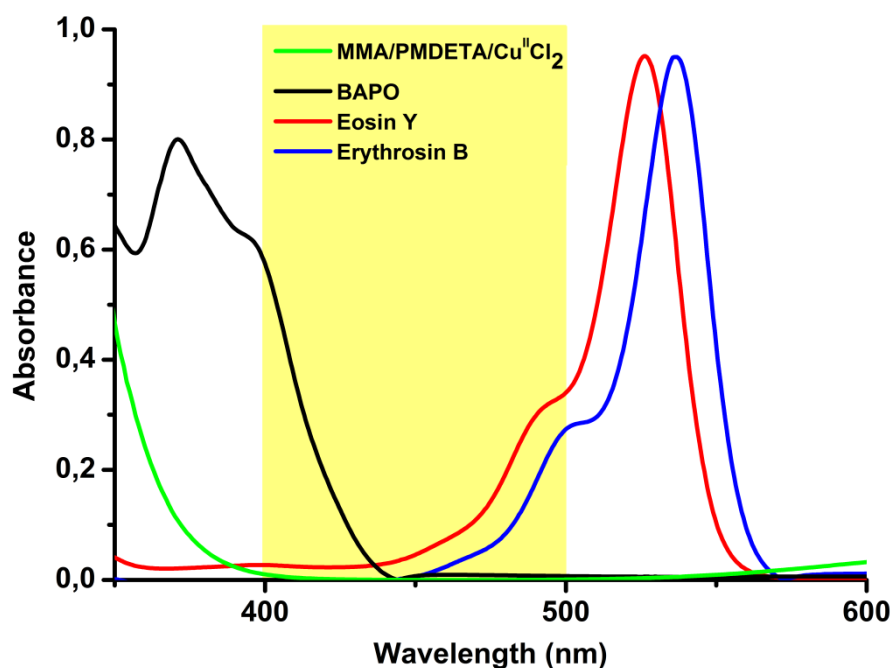
Figure 4.3 : UV-vis spectra of various visible light photoinitiators and reaction mixture in methanol. The concentration of BAPO was 9, 6 x 10^{-4} M; others were 1, 2 x 10^{-5} M.

In order to extend the spectral sensitivity of the photoinduced ATRP into the visible-light region, various control experiments including in the absence of dye, alkyl halide or metal complexes were conducted to reveal the role of each component on the polymerization. When the polymerization was performed without dye (Table 1, entry 1) or CuIICl$_2$/PMDETA complex (Table 1, entry 2) or without alkyl halide (Table 1, entry 3), either no polymer or a small amount of polymer with uncontrolled molecular weight was formed after the same polymerization time. The use of bisacylphosphine oxide (BAPO), eosin Y or erythrosin B with alkyl halide in the presence of CuIICl$_2$/PMDETA complex was surely responsible for the initiation of the C/LRP. Photoinduced electron transfer from the either exited dyes or benzyl and phosphinoyl radicals of BAPO to the CuIICl$_2$ leads to formation of CuICl which reacts with alkyl halide to generate active radicals. The results showed that the visible light-induced ATRP of MMA initiated by eosin Y (Table 1, entry 4) or (Table 1, entry 5) or BAPO (Table 1, entry 6) displayed narrow and monomodal molecular weight distribution (Mw/Mn < 1.38). The effect of the catalyst concentration on the polymerization was further examined by lowering the catalyst concentration from 0.1/1.1 to 0.01/0.11 (Table 1, entry 7). The decrease in catalyst concentration not only slowed the rate of the polymerization but also led to the polymer with high molecular weight distribution (Mw/Mn =1.45). This result suggested that at the lower concentration of [CuIICl$_2$/PMDETA] the amount of catalyst is not sufficient to initiate and maintain the required equilibrium needed for the polymerization. The applicability of this method was extended to other vinyl monomers such as methyl acrylate and styrene. Although visible light induced ATRP represented well-controlled system for the polymerization of methyl acrylate (Table 1, entry 8), the system was less controlled toward styrene monomer (Table 1, entry 9) due to the high quenching rate of the monomer [69].

Entry [a]	[Mon]$_0$/[RX]$_0$/[MtX]$_0$/ [PMDETA]$_0$/[PI]$_0$	Conv. (%)	$M_{n,theo}$ [b] (g mol^{-1})	$M_{n,GPC}$ [c] (g mol^{-1})	M_w/M_n [c]
1	200/1/0.1/1.1/0	-	-	-	-
2 [d]	200/1/0/0/0.1	-	-	-	-
3 [d]	200/0/0.1/1.1/0.1	5	-	54500	3.60
4 [d]	200/1/0.1/1.1/0.1	34	6800	11000	1.23
5 [e]	200/1/0.1/1.1/0.1	28	5600	16800	1.38
6 [f]	200/1/0.1/1.1/0.1	45	9000	8800	1.13
7 [d]	200/1/0.01/0.11/0.01	MMA	18	3600	25000
8 [f]	200/1/0.1/1.1/0.1	MA	25	5000	5500
9 [f]	200/1/0.1/1.1/0.1	St	11	2200	4200

[a] polymerization experiments were performed at 400-500 nm, time = 120 min, light intensity = 45 mW cm^{-2}; [b] $M_{n,th}$ = [MMA]$_0$/([RX]$_0$ + (Φ_R x [dye]$_0$) x M_{WMMA} x conv. for dye systems; $M_{n,th}$ = [MMA]$_0$/([RX]$_0$ + (2 x Φ_R x [BAPO]$_0$) x M_{WMMA} x conv. for BAPO system; [c] Molecular weight ($M_{n,GPC}$) and distribution (M_w/M_n) were determined by gel permeation chromatography; [d] with eosin Y; [e] with erythrosin B and [f] with BAPO.

On the basis of the above results, the kinetic plot and the evolution of molecular weight and distribution with conversion for the visible light-induced ATRP targeting DP = 200 were investigated. All ln([M]$_0$/[M]) versus the polymerization time plots were linear, which indicated that the propagating radical concentrations were almost constant during the processes of the polymerization (Figure 2-4). In the case of eosin Y or erythrosin B dyes, the molecular weights increased linearly with conversions, which were consistent with the polymerizations proceeding in a controlled fashion. However, the experimental molecular weights were slightly higher than the theoretical values, indicating low initiation efficiency. In dye/amine system, back electron transfer generally limited the efficient generation of free radicals which directly reduce the Cu^{II} to Cu^{I} [70]. The theoretical molecular weights of obtained polymers from visible light-induced SR&NI ATRP were calculated by modified equation (equation 1). The quantum yields (Φ_R·) of eosin Y and erythrosin B as obtained from literature were 0.28 and 0.62, respectively [71].

$$M_{n,th} = [MMA]_0/([RX]_0 + (\Phi_R \text{ x } [dye]_0) \text{ x } M_{WMMA} \text{ x conv.} \tag{1}$$

Figure 4.4 : Visible light-induced SR&NI ATRP of methyl methacrylate ([MMA]$_0$/[RX]$_0$/[Cu^{II}Cl$_2$]$_0$/[PMDETA]$_0$/[eosin Y]$_0$ = 200/1/0.1/1.1/0.1), a) kinetic plot and b) molecular weights and distributions of resulting polymers as a function of degree of conversion.

The molecular weight distributions of the resulting polymers were also increased from 1.28 to 1.60 in the course of conversion from 10% to 60% in both eosin Y or erythrosin B cases. In the later stage of polymerizations, the concentrations of the propagating radicals were decreased and normal bimolecular termination became significant, which resulted in a loss of control. The loss of initiator efficiency in the system was much higher compared the eosin Y system (Figure 4.5). This may be due to its apparently high quantum yield.
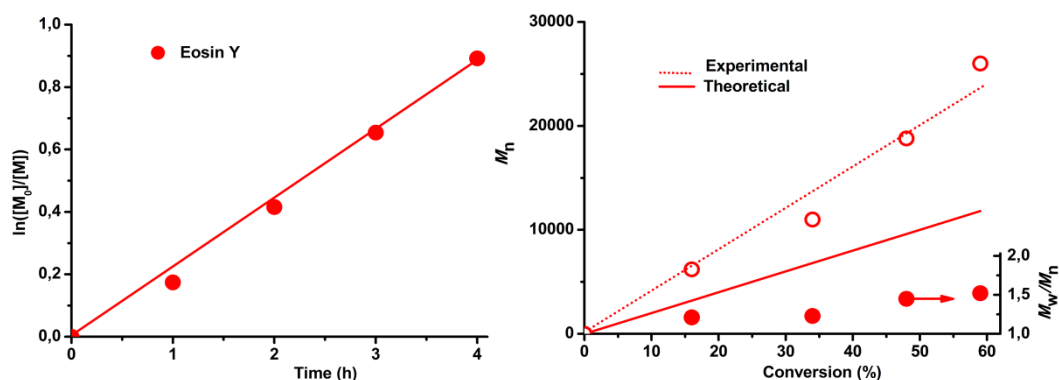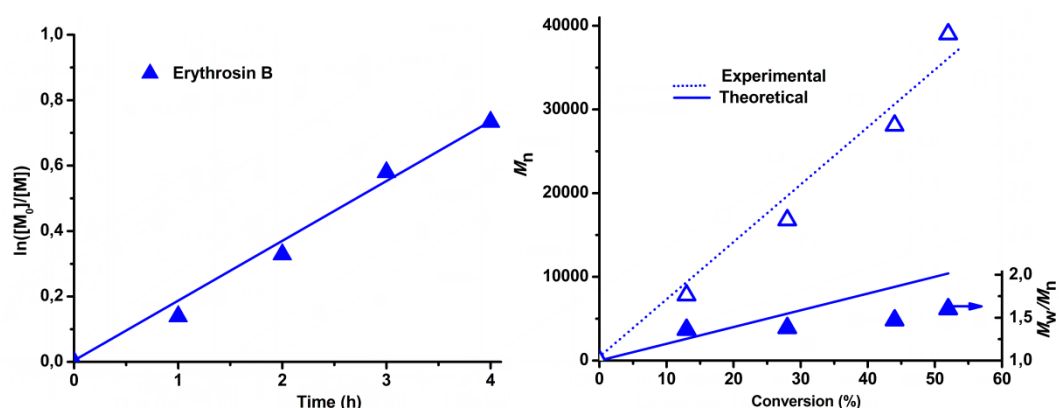

Figure 4.5 : Visible light-induced SR&NI ATRP of methyl methacrylate ([MMA]$_0$/[RX]$_0$/[Cu^{II}Cl$_2$]$_0$/[PMDETA]$_0$/[erythrosin B]$_0$ = 200/1/0.1/1.1/0.1), a) kinetic plot and b) molecular weights and distributions of resulting polymers as a function of degree of conversion.

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The key steps of the initiation mechanism in the case of dye systems, the dye molecule acted as a light absorber, while an amine co-initiator was a reducing agent for the excited dye (Figure 4.6). The primary photochemical reaction involves the excited dye molecules abstract an electron from the amine molecules to form radical-cation/radical-anion pairs. After the proton transfer, some of the radicals were in the system. These radicals were not only able to add to monomer molecules to initiate growth of polymer chains but also reduced the $Cu^{II}Cl_2$ to $Cu^{I}Cl$, which was used as activator in the ATRP. Generally, only the radicals generated from the amine component were reactive enough to activate the polymerization. The radicals generated from the dye molecules were believed to act mostly as radical chain terminators or they undergo other reactions leading to bleaching of the dye.
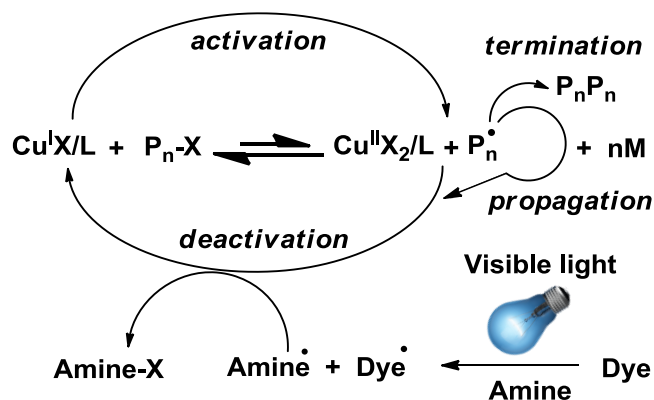
Figure 4.6 : Proposed mechanism for dye-sensitized SR&NI ATRP.

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 4.7). The photoreduction of eosin Y with PMDETA was confirmed experimentally by UV/Vis-spectroscopy as the absorption spectra of eosin Y significantly decreased. Although, the maximum absorption spectrum at 535 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.
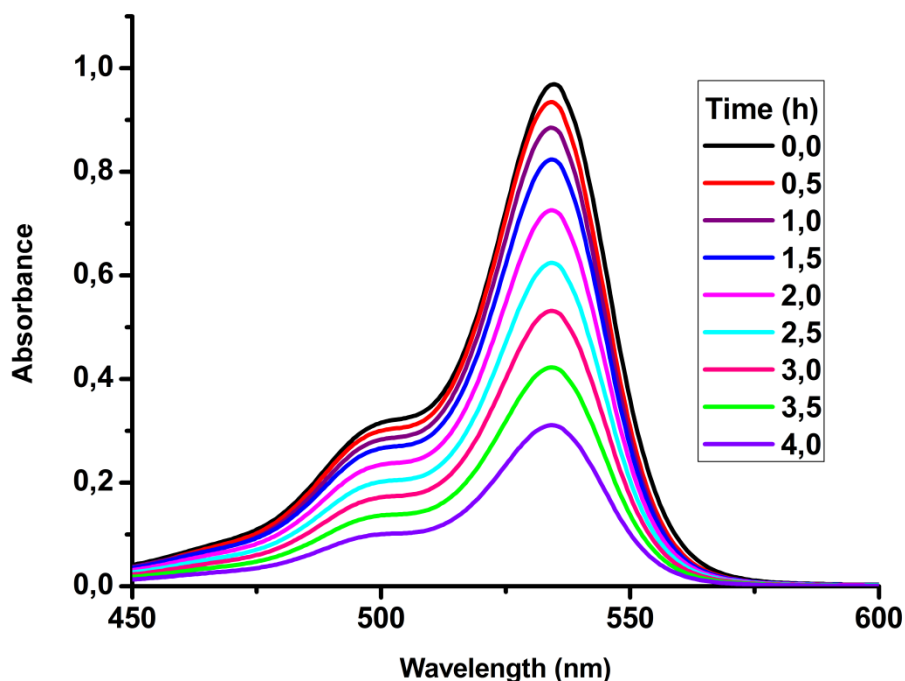
Figure 4.7 : Photobleaching behavior of the photoinitiating system in a formulation consisting of 1,2 x 10^{-5} M, eosin Y in toluene during irradiation at 400-500 nm in a quartz cell with 0.5 mm thickness at room temperature.

When the polymerization was performed with BAPO, two reactive radicals including benzoyl and phosphinoyl radicals were generated according to following reaction. These radicals induce chain-growth propagation and deactivated by Cu^{II}Cl$_2$/PMDETA species to form dormant species and Cu^{I}Cl/PMDETA. In this case the polymerization proceeds by a mechanism analogous to that described for the UV photoinitiators (see Figure 4.1). The experimental molecular weights of polymers were in good agreement with the theoretical values, indicating high initiation efficiency. The molecular weight distribution remained narrow (1.11~1.18) and unimodal during the polymerization (Figure 4.8). The theoretical molecular weights of obtained polymer were calculated by modified equation using 0.60 as the quantum yield of BAPO (equation 2).

$$M_{n,th} = [MMA]_0/([RX]_0 + (2 \times \Phi_R \times [BAPO]_0) \times M_{WMMA} \times conv. \tag{2}$$
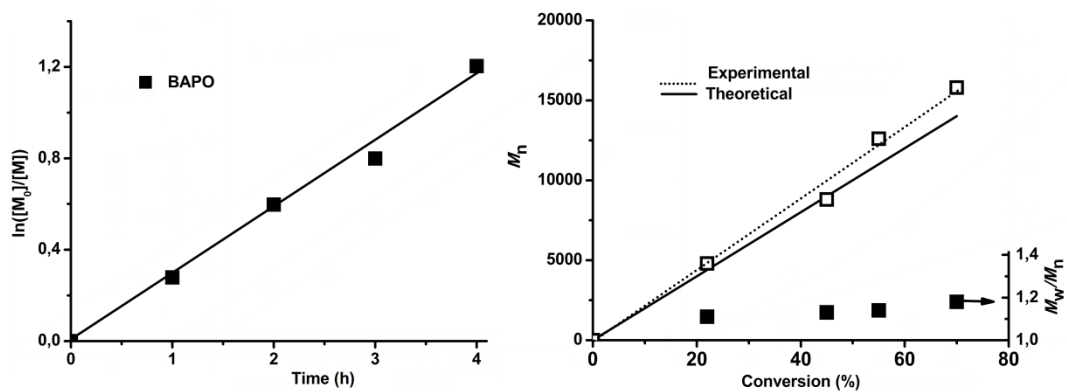
Figure 4.8 : Visible light-induced SR&NI ATRP of methyl methacrylate ($[MMA]_0/[RX]_0/[Cu^{II}Cl_2]_0/[PMDETA]_0/[BAPO]_0 = 200/1/0.1/1.1/0.1$), a) kinetic plot and b) molecular weights and distributions of resulting polymers as a function of degree of conversion.

5. CONCLUSIONS AND RECOMMENDATIONS

In this thesis, visible light induced SR&NI ATRP of methyl methacrylate were investigated by $Cu^{II}Cl_2$/PMDETA in conjunction with several photoinitiators including bis (2,4,6-trimethylbenzoyl)phenylphosphine oxide, eosin Y and erythrosin B. Although, the molecular weights increased with conversion linearly, the experimental molecular weights were considerably higher than theoretical values in the dye-sensitized systems. In addition, the molecular weight distributions were relatively high, ranging from 1.28-1.60 and reasonable control were observed under visible light irradiation. The polymers obtained by BAPO system had molecular weight values close to the theoretical ones and very narrow molecular weight distributions, ranging from 1.11-1.18 were obtained. Compared to the dye-sensitized SR&NI ATRP, it showed better control of molecular weight and its distribution under the same experimental conditions.

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▪ M. A. Tasdelen, M. A., **Ciftci, M.,** Uygun, M., Y. Yagci, Possibilities for Photoinduced Controlled Radical Polymerizations, ACS Symposium Series, Vol. 1100, Chapter 5, 59-72, **(2012)**

▪ M. A. Tasdelen, **Ciftci, M.,** Y. Yagci, Visible Light-Induced Atom Transfer Radical Polymerization, Macromol. Chem Phys., DOI: 10.1002/macp.201200204, **(2012)**