ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PHOTO INITIATED METAL-FREE CONTROLLED/LIVING RADICAL POLYMERIZATION USING POLYNUCLEAR AROMATIC HYDROCARBONS

M.Sc. THESIS

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Department of Chemistry

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DECEMBER 2016

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POLİNÜKLEER AROMATİK BİLEŞİKLER KULLANARAK IŞIKLA BAŞLATILMIŞ METAL İÇERMEYEN ATOM TRANSFER RADİKAL POLİMERİZASYONU

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To my family,

FOREWORD

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ABBREVIATIONS

^{1}H NMR	**:** Hydrogen Nuclear Magnetic Resonance Spectroscopy
ATRP	**:** Atom transfer radical polymerization
C/LRP	**:** Controlled/living radical polymerization
Cu(II)CL_2	**:** Copper (II) chloride
EBP	**:** Ethyl-2-bromopropionate
GPC	**:** Gel Permeation Chromatography
MMA	**:** Methyl methacrylate
NMRP	**:** Nitroxide mediated radical polymerization
PI	**:** Photoinitiator
PMDETA	**:** N, N, N',N", N"-Pentamethyldiethylenetriamine
PMMA	**:** Poly(methyl methacrylate)
RAFT	**:** Reversible addition fragmentation chain transfer
TEMPO	**:** 2, 2, 6, 6-Tetramethyl-1-piperidinyloxy
THF	**:** Tetrahydrofuran
UV	**:** Ultraviolet
DMF	**:** N,N-Dimethylformamide

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SUMMARY

Recently, photoinitiated polymerization has received revitalized interest as it congregates a wide range of economic and ecological anticipations. Because of the excellent advantages, photoinduced polymerization has widely been applied in coatings, adhesives, inks, printing plates, optical waveguides and microelectronics. The advanteges of this method are high rate of polymerization at ambient temperatures, low energy consumption, solvent-free polymerization, spatial and temporal control over the processes. There currently exist a few methods, where photo induced polymerization can be applied including controlled/living radical polymerizations such as iniferter, nitroxide mediated radical polymerization(NMRP), reversible addition-fragmentation chain transfer polymerizations (RAFT) and atom transfer radical polymerization (ATRP). Among them, ATRP became the most commonly used method as it has higher range of tolerance not only to the initiators but also to various number of monomers. Traditional ATRP requires a low-oxidation state transition metal complex (commonly CuX/L, X = Cl or Br and L = ligand) in conjunction with an appropriate alkyl halide (R-X). The photochemical initiation both enables the easy control of the polymerization under ambient temperature even for heat-sensitive monomers and tends to minimize side reactions like chain transfer or depolymerization.

In this thesis, photo-initiated metal-free controlled living radical polymerization of (meth)acrylates, and vinyl monomers was investigated using the polynuclear aromatic compounds, pyrene and anthracene. Fluorescence spectral analyses along with nuclear magnetic resonance studies were performed to determine the rate constants of initiator radical formation and investigate the mechanisms of polymerization. The obtained polymers were analyzed by spectral and chromatographic methods. Results show that the excited state anthracene undergoes a faster electron transfer reaction with the alkyl halide initiator than the excited state of pyrene. Pyrene excimers, which are formed at higher concentrations, also react with alkyl halides to form initiator radicals. Although pyrene monomers and excimers are acting slower, polymers with higher control over the chain end functionalities and molecular weight characteristics are obtained in comparison to anthracene as sensitizer.

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ÖZET

Polimerler monomer denen basit yapıdaki organik moleküllerin uygun şartlarda kimyasal tepkimelerle birbirine bağlanmasıyla oluşan makromoleküllerdir. Monomerlerin polimerleri oluşturdukları bu tepkimelere ise polimerleşme (polimerizasyon) adı verilir. Polimerler, doğal ve yapay olmak üzere ikiye ayrılır. Selüloz, nişasta, proteinler, doğal kauçuk, polifosfatlar, ipek, ve yün doğal polimerlere örnek olarak gösterilebilir. Yapay (sentetik) polimerler ise, laboratuvar ortamında ve endüstride çeşitli tepkimeler ile elde edilebilirler. Poliester, poliamit, poliüretan gibi farklı isimlerle yapay polimerlerdir. Yapay polimerizayonu için kullanılan polimerizasyon tepkimeleri kondenzasyon (basamak) ve katılma (zincir) polimerizasyonu olarak iki gruba ayrılır. Kondenzasyon polimerleri, basit organik tepkimeler olup, bu tepkimeleri verebilecek birden çok fonksiyonel gruba sahip küçük moleküllerin birbirleriyle tepkime vermesi sonucu oluşur. Bu fonksiyonel gruplar genellikle karboksilik asit, ester, amin, alkol gibi kolaylıkla reaksiyona giren gruplardır. Sonuçta elde edilen polimerler ise ana zincirde tekrar eden fonksiyonel gruba göre poliester, poliamit, poliüretan gibi farklı isimlerle anılırlar. Katılma (zincir) polimerleri ise, katılma reaksiyonları ile monomerlerin doğrudan birbirine eklenmesi ile oluşur. Monomer çeşitlerine göre polimerler, homopolimer ve kopolimer olmak üzere ikiye ayrılırlar. Tek cins monomer içeren polimerler hompolimerdir.. Yapıda dallanma olsa da bu durum geçerlidir. Polietilen bu durum için uygun bir örnektir. Tekrarlayan ünitenin aynı olduğu bir durumda bu polimer şu şekilde gösterilebilir. Polimer zincirinde birden farklı çeşitte tekrarlayan birim varsa böyle polimerlere kopolimer denir. Kopolimerler, monomerlerinin diziliş durumlarına göre gelişigüzel, ardarda, aşı ve blok kopolimer olmak üzere dört kısma ayrılırlar. Birden fazla cins monomerin polimer zinciri boyunca düzensiz bir şekilde (rastgele) sıralandığı polimerlere gelişigüzel kopolimerdir. İki ayrı cins monomerin zincir boyunca birbiri ardına sırayla tekrarlanarak oluşturdukları polimerlere ardışık kopolimer denir. Ana zincirdeki tekrar eden ünitenin cinsinden farklı cinsteki birimlerin ana zincire bir veya birkaç yerinden bağlanarak oluşturuduğu kopolimerlere aşı kopolimerdir.Farklı cins monomerlerin oluşturduğu segmentlerin değişik şekillerde birbirine bağlanarak oluşturdukları polimerlere blok kopolimerdir. Blok sayısına göre diblok, triblok veya tetrablok kopolimerler biçiminde özel olarak adlandırılabilir.

Kontrollü/Yaşayan Radikal Polimerizasyon bir katılma (zincir) polimer türüdür. 1989 yılların sonunda Otsu tarafından ortaya konan ve "başlatıcı-transfer reaktifi-sonlandırıcı" ya da "iniferter" denen bileşiklerin kullanımıyla yapılan polimerizasyonlar radikal polimerizasyonlarına yeni bir bakış getirmiş ve bu polimerizasyonlar üzerindeki kontrolü kısmen de olsa ilk defa sağlamıştır. Bu sistem kontrollü polimerizasyon kinetiğinin karakteristik bir özelliği olan molekül ağırlığı/yüzde dönüşüm ve molekül ağırlığı/zaman değişimlerindeki lineer olma

trendini bir dereceye kadar göstermektedir. Kontrollü radikal polimerizasyonların avantajları olarak molekül ağırlığının polimer dönüşümüyle doğrusal bağıntı içinde olması, dolayısıyla hedeflenen molekül ağırlığının elde edilmesi, dar bir molekül ağırlığı dağılımına sahip, zincir sonunda fonksiyonel grupları olan polimerler elde edilmesi (telekelik polimerler), polimer moleküler mimari yapısının kontrol edilmesi (blok kopolimerler), sayılabilmektedir. Nitroksil ortamlı radikal polimerizasyon (NMRP), tersinir eklenme/ayrılma/transfer polimerizasyonu (RAFT), ve atom transfer radikal polimerizasyonu (ATRP) kontrol radikal polimerizayonun kullanılan yöntemlerdir.

Organik nitroksitler, havaya karşı hassas olmayan, belli sıcaklıklara kadar sterik etkisi ve daha çok elektronik yapısı nedeniyle inert davranabilen kararlı radikallerdir. Bu nedenle, çifte bağlara karşı reaktif özellik göstermezler, fakat diğer radikallerle genellikle kenetlenme tepkimesi verirler. Dolayısıyla çok iyi radikal tutucu oldukları söylenebilir. NMRP'de en yaygın olarak kullanılan organik nitrioksit 2,2,6,6-tetrametilpiperidinoksi (TEMPO)'dir.

RAFT kontrolü, transfer tepkimeleri ile aktif bölgenin yer değiştirmesi sayesinde sağlanır. En çok kullanılan RAFT reaktifleri disülfürler, ksantatlar, ditiyokarbonatlardır. RAFT metodun avantajların biri ise çok farklı solvent ortamlarında uygulanabilir. Ayni zamanda RAFT metodunun diger bir avantajı ise bir çok monomere uygulanabiliyor olmasıdır. Örneğin ATRP'de sonuç vermeyen akrilik asit, metakrilik asit gibi monomerleri RAFT yoluyla polimerleştirmek mümkündür. ATRP ve NMP'ye göre çok daha hızlı bir polimerizasyondur. RAFT yöntemin tek deazavantajı ise sülfür içeren bileşiklerin nahoş kokusudur.

İlk olarak Krzsytof Matyjaszewski tarafından, 1995 yılında keşfedilen ATRP bugün sentetik polimer kimyasında en çok kullanılan polimerizasyon yöntemlerinin başında gelmektedir. ATRP'nin bu kadar çok kullanılıyor olmasının nedenleri, molekül ağırlığı karakterlerindeki kontrolü sağlaması ve belirgin fonksiyonel gruplara olan toleransı, hem de deneysel basitliğidir. ATRP'de en sık kullanılan metal bakır (Cu) olmakla beraber demir (Fe), rutenyum (Ru), nikel (Ni), kobalt (Co) gibi farklı oksidasyon basamağında bulunabilen geçiş metalleri ile de bu polimerizasyonun gerçekleştirilebildiği gösterilmiştir. Bu geçiş metallerini organik fazda çözünür hale getirmek ve metali stabilize ederek reaktivitesini düşürmek için ligandlar kullanılır. Bunlar 2, 3 ya da daha çok dişli olabilen azot içeren organik moleküllerdir. ATRP'de kullanılan ligandlar halkasız yapıda olabildiği gibi (dipiridil, N,N,N',N',N''-pentametildietilentriamin (PMDETA). Normal ATRP ve Ters ATRP iki ayrı metod olarak uygulanmaktadır; normal ATRP'de uygun halojen grubu küçük bir organik molekül ya da bir makromolekül yukarıda bahsedildiği gibi bir geçiş metali ile dinamik ve tersinir bir dizi redoks tepkimesi gerçekleştirir. Bu sırada meydana gelen radikal türevleri de monomerleri üzerine katarak zincirler büyür. Süre uzatılarak, polimerin istenilen molekül ağırlığına kadar büyümesine izin verilebilir. Sonuç olarak, büyümekte olan zincir halojen atomunu yüksek oksaidasyon basamağındaki geçiş metalinden tekrar kopartır ve halojen uca sahip hedeflenen polimer elde edilmiş olur. Aşağıdaki şekilde bu mekanizma gösterilmiştir. Sistemin bir handikapı olarak ortamdaki moleküler haldeki oksijenin uzaklaştırılmasının gerekliliği söylenebilir. Bu olumsuzluk, serbest radikal polimerizasyonları için de geçerli olmakla birlikte, burada oksijen, polimerizasyonu klasik radikal katılmasıyla sonlandırmanın yanı sıra, geçiş metalini oksitleyerek tepkimeyi durdurabilir.Başlama aşamasındaki elektron transfer

ya da atom abstraksiyonu çok hızlı olduğundan polimerizasyonun başlaması çok hızlıdır ve bu da zincirlerin eş zamanlı olarak büyümesini sağlar. Ayrıca aktif ve uyuyan türler arasında hızlı ve dinamik bir denge vardır. Bu parametreler, ATRP'nin kontrollü bir polimerizasyon olmasını sağlayan etkenlerdir. Ters ATRP yöntemde, geleneksel radikal başlatıcılar (AIBN, DBPO vb.) ile seçilen bir Cu(II) tuzu tepkime ortamında organik halojenürü oluştururlar. Bozunan başlatıcılarının oluşturduğu radikaller Cu(II) halojenürden bir halojen atomu koparark organik halojenürü oluştururken eş zamanlı olarak Cu(I) tuzu da meydana gelir. Daha sonra sistem normal ATRP mekanizmasını takip eder ve polimerler oluşur. Bu sistem, Cu (II) tuzundan başladığı için, bakırın oksidasyonu söz konusu değildir ve dolayısıyla, normal ATRP'ye göre havaya olan hassasiyeti daha azdır. Bu da deneysel işlemlerde kolaylığı beraberinde getirir. Aşağıda ters ATRP mekanizması gösterilmiştir. Ters ATRP için söylenebilecek diğer bir avantaj ise bu metodun miniemülsiyon tepkimeleri için daha kullanışlı olmasıdır. Sistemde kontrolü düşüren etkenler belirli bir geleneksel başlatıcının başlamaya sebebiyet vermesi, sonuç olarak sentezlenen polimerin α-ucunun bu başlatıcıdan gelen radikal yapısında olabilmesidir. Ayrıca, başlangıçta eklenen Cu(II) tuzunun tamamen tepkimeye girdiği, böylelikle oluşan radikallerin kendisinin başlatıcı görevi görmemesi nedeniyle serbest radikal polimerizasyonu başlatamadığı kabul edilir. Yarışan bu tür bir tepkimede polimerlerin molekül ağırlığı karakteri daha zor kontrol edilebilmektedir.

ATRP'de kullanılan metal/ligand sistemlerinde en sık kullanılan metal bakır (Cu) olmakla beraber demir (Fe), rutenyum (Ru), nikel (Ni), kobalt (Co) gibi farklı oksidasyon basamağında bulunabilen geçiş metalleri ile de bu polimerizasyonun gerçekleştirilebildiği gösterilmiştir. Bu geçiş metallerini organik fazda çözünür hale getirmek ve metali stabilize ederek reaktivitesini düşürmek için ligandlar kullanılır. Bunlar 2, 3 ya da daha çok dişli olabilen azot içeren organik moleküllerdir. ATRP'de kullanılan ligandlar halkasız yapıda olabildiği gibi (dipiridil, N,N,N',N',N''-pentametildietilentriamin (PMDETA), Tris[2-(dimetilamino)etil]amin (Me6Tren)), siklik yapıdaki olanları (1,4,8,11-tetrametil-1,4,8,11-tetraazasiklotetradekan) da mevcuttur. Bu yapılar aşağıda örnek olarak gösterilmiştir. Son dönemde, daha az katalizör kullanılmasını hedefleyen (özellikle ppm mertebesinde) ve daha düşük sıcaklıklarda kontollü polimerizasyonu mümkün kılan sistemler üzerinde çalışmalar yapılmaktadır. ATRP'de kontrolü sağlayan can alıcı basamak, atom transfer adımında, düşük oksidasyon basamağındaki metal kompleksi ve alkil halojenür ile, oluşan radikal ve yüksek oksidasyon basamağındaki metal kompleksi arasındaki tersinir denge basamağıdır. Yukarıda bu denge kompleksin geometrik durumu ile birlikte verilmiştir. Kullanılan metalin redoks potansiyeli ve halojenfilitesi (halojen severliği) ve ligandların yapısı da katalizörün etkinliğini etkileyen parametrelerdir.

ATRP'de kullanılan başlatıcı sistemlerinde, genel olarak sekonder ve tersiyer alkil halojenürler, benzilik ve allilik halojenürler, α-haloesterler, α-haloketonlar, ile bu fonksiyonalitelere sahip makro yapılar başlatıcı olarak ATRP'de kullanılan monomerle en çok fonksiyonlandırılmış stirenler, akrilat ve metakrilatlar ile akrilonitril, vinilpiridin, metakrilamit gibi diğer monomerler kullanılır. Akrilik ve metakrilik asit katalizör ile tepkime verdiğinden ATRP'ye uygun monomerler değildirler. Bununla birlikte asit ucu basit bir esterifikasyon ile korunarak polimerleşme yapılabilir. Daha sonra ise esterin hidrolizi asit fonksiyonalitesine sahip polimeri verecektir. Bunun için tersiyer alkil grubu kolay hidroliz olabildiğinden uygun olabilir. Akrilamit de geçiş

metallerine koordine olabildikleri için yine uygun bir monomer değildir. Akrilonitril ise özel çözücüler gerektirmektedir.

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. Düşük enerji ile gercekleşen polimerizasyonu birçok gerçekleştirmek bir çok avantaj sağlamaktadır.Eğer çalışma sıcaklığı düşük olan monomerler yüksek sıcaklıkta polimerleştirirlerse depolimerizasyona uğrayarak tekrar monomer halini alırlar. Polimerizasyon sıcaklıklığının düşürülmesi esterleşme ve çarpaz bağlanma gibi yan reaksiyonların önlenmesini sağlarken, polimerizasyonun daha kontrollü bir şekilde yapılmasınıda sağlar. Bunlara ek olarak enzim ve protein gibi ısıya duyarlı biyoyapıların polimerizasyon işlemiyle polimerlere bağlanması gibi işlemlerde düşük sıcaklıklarda gerçekleştirilmelidir. Fotopolimerizasyon radikalik, katyonik ve anyonik olarak başlatılabilse de çok sayıda fotobaşlatıcının ve yüksek reaktivitedeki monomerlerin bulunulabilirliği açısından serbest radikal ve katyonik sistemlere daha fazla ilgi duyulmaktadır. Genellikle endüstriyel uygulamalarda serbest radikal fotopolimerizasyon sistemleri kullanılmaktadır. Ancak, bu tip polimerizasyonların oksijenin yavaşlatma etkisi ve son ürünün özelliklerini etkileyebilen kürleşme sonrasındaki kısıtlamalar gibi bazı dezavantajları bulunmaktadır. Bu nedenle, fotobaşlatılmış katyonik polimerizasyon özellikle bu dezavantajların giderilmesi açısından gelecekte daha fazla yer alacağı düşünülmektedir. Bilinen pek çok katyonik fotobaşlatıcı mevcuttur ve fotokimyaları detaylı bir şekilde incelenmiştir. Bunlar arasında, onyum tipi fotobaşlatıcılar, ısısal kararlılıkları, katyonik olarak polimerleşebilen pek çok monomer içindeki çözünürlükleri ve fotoliz sonucunda reaktif türler oluşturma kabiliyetleri bakımından önemli bir role sahiptirler. Brønsted asitlerinin yanı sıra radikal türlerinin de meydana getiriliyor olmasından dolayı bu tuzlar serbest radikal fotobaşlatıcısı olarak ve eşzamanlı serbest radikal ve katyonik polimerizasyonlarında da kullanılabilmektedir. 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. Fotobaşlatıcılar, radikal oluşturma mekanizmalarına göre (birinci tip fotobaşlatıcılar) ve (ikinci tip fotobaşlatılar) fotobaşlatıcılar olmak üzere iki ayrı sınıfa ayrılır. Fotopolimerizasyon yönteminin kullanıldığı polimerizasyonlar daha düşük sıcaklıklarda gerçekleştirilebilmektedir. Ayrica ışık şiddeti seçilerekte hem başlatıcı konsantrasyonu hemde polimer zincirlerinin boyu ayarlanabilir.

Biyo ve mikroelektronik uygulamalarda ppm seviyelerinde metal kontaminasyona bile dezavantaj olabilir. Bu açıdan metal içermeyen kontrollü/yaşayan radikal polimerizasyon, yeşil teknoloji kullanımlarına uygundur ve cevre dostu olarak tanımlanabilir. Metal içermeyen polimerizasyonla ilgili son zamanlarında bir çok araştırma yapılmaktadır. Örnek olarak, fenotiazin türevleri ve perilenin, alkil halojenürler ile birlikte Cu katalizörlerinin yokluğunda çeşitli monomerlerin ışıkla başlatılmış ATRP'sini gerçekleştirebildiği gösterilmiştir. Tez kapsamındaki çalışmada ise akrilatlar ve vinil monomerlerin ışıkla başlatılmış metal içermeyen kontrollü/yaşayan radikal polimerizasyonu piren ve antrasen gibi çok çekirdekli aromatik bileşikler kullanılarak incelenmiştir. Başlatıcı radikal oluşumunun hızı

sabitleri ve polimerizasyon mekanizmalarının araştırılması için floresan spektral analiz ve nükleer manyetik rezonans kullanılmıştır. Elde edilen polimerler spektral ve kromatografik yöntemler ile analiz edilmiştir. Sonuçlar, antrasenin uyarılmış halinin alkil halojenürler ile, pirenin uyarılmıs haline göre daha hızlı bir elektron transfer reaksiyonuna uğradığını göstermektedir. Ayrıca, yüksek konsantrasyonlarda oluşan pirin eksimeri, alkil halojenürlerle tapkimeye girerek başlatma radikaleri oluşturmaktadır. Piren monomerler ve eksimeri yavaş hareket ediyor olmasına rağmen, anteresene göre daha kontrol edilebilir zincir ucu fonksiyonlarına ve molekül ağırlığı özelliklerine sahip polimerlerin sentezine olanak vermektedir.

1. INTRODUCTION

Photochemical reactions occurring by the absorption of light to create an reactive species which undergoes a number of different reactions such as dissociation, isomerization, abstraction, electron or energy transfer, and bond formation [1]. These reactions have been studied widespread in different fields including, molecular biology, organic chemistry and electronics etc. Photoinduced chemical reactions are also used in the field of polymer chemistry. Photoinitiated polymerization has a lot of advantages over other polymerization processes such as rapidity, low energy consumption and mild medium requirements. For example usage of photoinitiated polymerization instead of thermal polymerization leads to reduce energy cost up to 30 %. [2]. That is why photoinitiated polymerization processes have been used in various applications such as surface coatings, printing inks, printing plates, microelectronics, adhesives, three dimensional imaging and micro-fabrication processes. Recently, introduction of the controlled/living radical polymerization (CLRP) concept to synthetic polymer chemistry made it possible to synthesize various polymeric architectures such as block, graft, star and functional polymers with narrow molecular weight distribution and controlled chain-end functionality [3]. The common methods include the atom transfer radical polymerization (ATRP) [4, 5], Nitroxide-mediated radical polymerization (NMRP) [6–8] and reversible addition-fragmentation chain transfer (RAFT) [9, 10] processes. Among them, ATRP became the most commonly used method due to the availability of a broad scale of initiators and adaptability of a higher number of monomers [11] Traditional ATRP requires a low-oxidation state transition metal complex (commonly CuX/L, X = Cl or Br and L = ligand) in conjunction with an appropriate alkyl halide (R-X) [12]. Recently, Guan and Smart performed ATRP with lower Cu(X) concentrations by applying photochemical approaches [13]. This study is followed by several other researchers for producing ATRP polymers using reduced amounts of inorganic catalyst. Removal of these metal complexes from the polymers is a cumbersome and a number of strategies have been proposed to obtain metal-free

ATRP polymers. In this thesis, photoinduced metal-free ATRP using polynuclear aromatic hydrocarbons is discussed.

2. THEORETICAL PART

The major concern of this thesis is to achieve controlled radical polymerization, metal free-ATRP; by photochemical means, it seemed appropriate to discuss existing controlled radical polymerization methods generally.

2.1 Polymerization

The word polymer consists of words poly and mer, which in old Greek means “many” and “part” respectively. Therefore, a polymer is a large molecule created by the replication of small monomer units. Polymers are divided into natural polymers such as proteins, DNA, silk and artificial polymers including polyvinylchloride, polyethylene glycol or poly(methyl methacrylate). Two common synthetic pathways for the production of artificial polymer consider step grow polymerization (poly condensation), which allows the preparation of polyesters. Polyurethanes, polyamides, etc. and chain growth polymerizatıon (addition polymerization). In the concept of addition polymerization, generally a reactive species is formed through a thermal, photochemical or redox steps, which in turn initiates the polymerization of convenient monomers present in the reaction media. Depending on the nature of the reactive species formed, the polymerization is named as anionic, cationic or radical polymerization. Due to the broad scale of initiating systems and monomer formulations preset, the radical polymerization is in advanced state in comparison to the other polymerization modes. The discovery of controlled/living radical polymerization (CLRP) concept, enabled researchers to synthesize a variety of macromolecular structures including homopolymers, telechelic polymers, block, graft and star copolymers with controlled chain-end functionalities and low-dispersity characteristics. The following sections will deal with the CLRP technique in general and its branches [14].

2.2 Controlled /Living Radical Polymerization Methods

It was the beginning of 1989 when it was found that radical polymerization can be controlled by using iniferter (agents that initiate, transfer, and terminate) [15]. Thermal and photochemical activation are the way used to polymerize most vinyl monomers under mild reaction conditions. The introduction of the controlled/living radical polymerization (CLRP) concept to synthetic polymer chemistry made it possible to synthesize various polymeric architectures with narrow molecular weight distribution and controlled chain-endfunctionality [14]. The most common methods include the atom transfer radical polymerization (ATRP) [4, 5], Nitroxide-mediated radical polymerization (NMRP) [6–8] and reversible addition-fragmentation chain transfer (RAFT) [9, 10] processes. Among them, ATRP became the most commonly used method due to the availability of a broad scale of initiators and adaptability of a higher number of monomers [11].

2.2.1 Nitroxide-mediated radical polymerization (NMRP)

Nitroxide-mediated radical polymerization (NMRP) is part of free radical polymerizations. Organic nitroxides are not sensitive to air. They are stable radicals up to different temperatures due to steric effect. For this reason, they do not show any reactive properties against double bonds; but they usually give rise to the coupling reactions with radicals. Therefore, it can be said that they are very good radical conservatives [16]. The most commonly used nitroxide is 2,2,6,6-Tetramethylpiperidinyloxyl (TEMPO). NMRP polymerization occurs in a medium containing a conventional radical initiator, TEMPO, and a monomer (usually styrene), which helps to produce a low-dispersity polymer. The general mechanism of the NMP is as follows :

The bimolecular initiation system consists of a conventional radical source such as (benzoylperoxyde) BPO and a nitroxide (i.e., TEMPO) [17]. The conventional radical initiator is decomposed at an appropriate temperature (around 90 ^{0}C for BPO) to add one styrene. This initiator-monomer adduct is trapped by the nitroxide leading to in-situ formation of the alkoxyamine. Upon raising the temperature to 130 ^{0}C, this adduct is decomposed into a nitroxide and an initiating radical. Thus formed radical

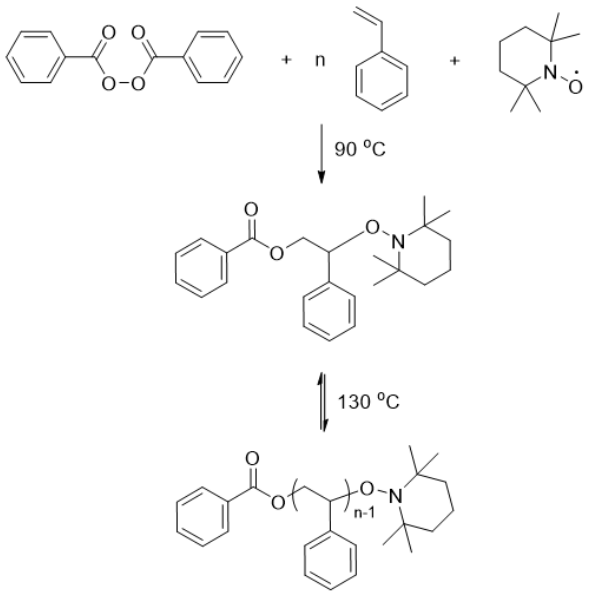


Figure 2.1: Mechanism of Nitroxide-mediated radical polymerization.

subsequently initiates the free-radical polymerization. NMRP technique supports a number of advanteges in synthesis of different monomer to acrylates diens and acrylamides. It also supresses the requirement of metal catalysts and smelly reactives (vide infra). However, this method holds the disadvantage of needing relatively high temperatures (>120 ^{0}C) [18, 19].

2.2.2 Reversible addition–fragmentation chain transfer process (RAFT)

Reversible addition-fragmentation chain transfer polymerization is one of the most frequently used method of controlled/living radical polymerization [20]. Due to the tolerance to a broad range of functional group such as -OH, -COOH, $CONR_2$, NR_2, SO_3Na, etc., in monomers and solvents, this method is more salutary compared to ATRP and NMRP methods [21, 22]. RAFT can be applied in very different solvent environments. It is a much faster polymer than ATRP and NMP. The disadvantage is the unpleasant smell of sulfur-containing compounds [20, 23]. The mechanism of RAFT polymerisation is shown below :

The mechanism of RAFT polymerization with the thiocarbonylthio-based RAFT agents involves a series of addition–fragmentation steps as depicted below. As for conventional free-radical polymerization, initiation by decomposition of an initiator leads to formation of propagating chains. In the early stages, addition of a propagating radical ($P_n \bullet$) to a RAFT agent [S=C(Z)SR] followed by fragmentation of the

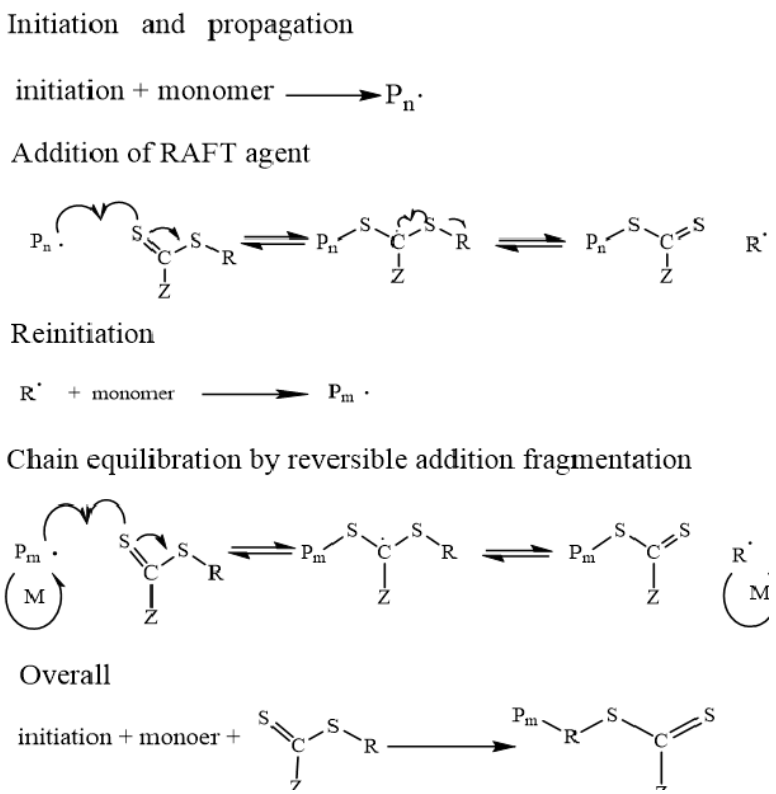


Figure 2.2: Mechanism for reversible addition-fragmentation chain transfer (RAFT).

intermediate radical gives rise to a polymeric RAFT agent and a new radical (R•). The radical R• reinitiates polymerization by reaction with monomer to form a new propagating radical (P_m•). In the presence of monomer, the equilibrium between the active propagating species (P_n• and P_m•) with the dormant polymeric RAFT compound provides an equal probability for all the chains to grow [22]. This feature of the RAFT process leads to the production of narrow polydispersity polymers. When the polymerization is complete, the great majority of the chains contain the thiocarbonylthio moiety as the end group [17].

2.2.3 Atom transfer radical polymerization (ATRP)

Atom transfer radical polymerization (ATRP), discovered in 1995 by Krysyotof Matyjaszewski, is applied in large scale of polymer chemistry [11]. The reasons why ATRP is the most commonly utilized CLRP method are its tolerance to various functional groups, applicability to a wide-range of monomers and simplicity in experimentation [4]. Classical ATRP requires a low-oxidation state transition metal complex (i.e. CuX/L, L = Ligand, X=Br, Cl) in conjunction with an appropriate alkyl halide (R-X). Figure 2.3 shows the mechanism of ATRP.

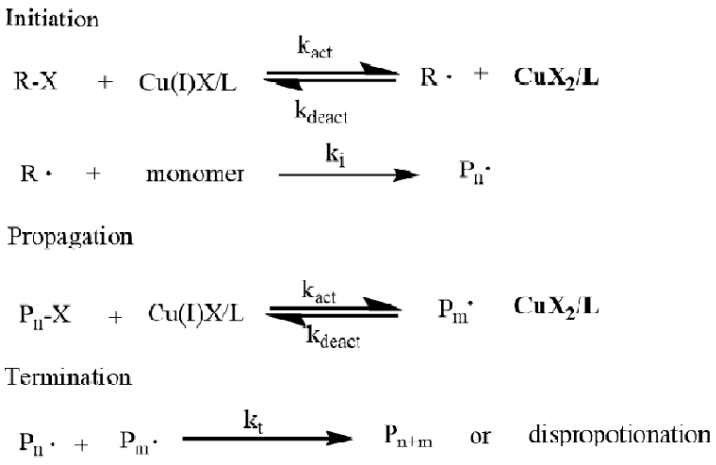


Figure 2.3: Mechanism of ATRP.

Initially, CuX abstracts a halogen atom from the alkyl halide to yield CuX_2 and alkl radical. These radicals, (P_n. As shown above), can act monomers and in the mean time it abstracts halogen atom back from CuX_2 and there is a fast equilibrium between this farward and backward halogen abstraction steps. This rate constants of these steps can be defined as k_a, and k_{da}, for activation and deactivation, respectively. Polymer chains grow by the addition of the monomers to the growing radicals in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Major drawbacks of this technique are the inhibition effect of molecular oxygen and incomatibility of monomers such as acrylic and metacrylic acid and amides.

2.2.3.1 Photo-induced ATRP

Due to the high susceptibility of the catalysts to undergo oxidation, conventionally, large amounts of catalyst is used. Different approaches have been proposed to reduce the catalyst concentration. One approach is grounded on the discovery of sophisticated catalysts, which can catalyze the process even in very low concentrations [24]. Other approach considers the use of reducing agents in the polymerization media, which continuously regenerates CuX to catalyze ATRP.

Guan and Smart performed photoinduced ATRP to reduce the amount of Cu catalysts. Photo-induced polymerization approaches were also shown to reduce the amount of

Cu catalysts required for ATRP. Firstly, the positive effect of light on ATRP systems was examined by Guan and Smart who performed the process by photochemical means in less Cu(X) concentrations [13]. Following this study, several other approaches were reported to produce ATRP polymers using reduced amounts of inorganic catalyst. Recent works from our laboratory showed that direct photo-irradiation of Cu(II) complexes results in the formation of Cu(I) catalysts in the reaction media, that could initiate ATRP of suitable monomers. The machanism is assumed to follow an electron transfer from π-electrons of the ligand to the guest metal to yield Cu(I) complexes. In this technique, the methanol is added to normalise the molecular weight distribution of the obtained polymers, as it enables farther reduction of Cu(II), that also supports polymerization to be initiated simultaneously. The general mechanism of photo-in ATRP by direct irradiation is shown in Figure 2.4 [25, 26] :

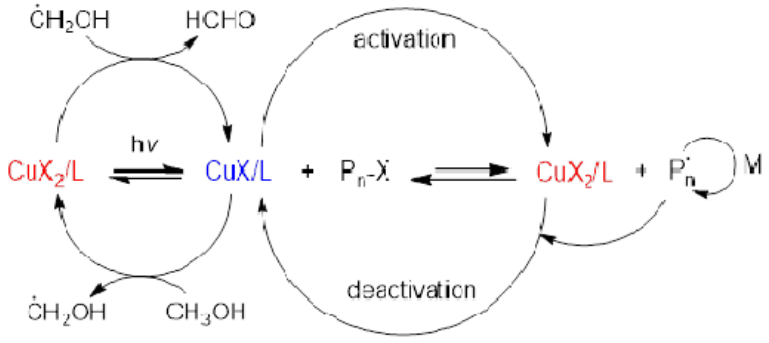


Figure 2.4: Mechanism of photo-initiated ATRP by direct irradiation using methanol.

If a free radical photoinitiator is applied and the reaction mixture is exposed to appropriate wavelength irradiation where the photoinitiator is activate, the rate of the generation of Cu(I) is much faster [27–29]. General mechanism of photo-initiated ATRP by using free radical photoinitiators is demonstrated in the scheme below :

Dimanganese decacarbonyl ($Mn_2(CO)_{10}$), which can abstract halides from numerous alkyl halide upon visible light irradiation can also be used in this method. Upon irradiation of the solution containing both $Mn_2(CO)_{10}$, RX, $CuBr_2$/L and monomer, Cu(II)/L was reduced to Cu(I) simultaneously by the formed $Mn(CO)_5$ species [30]. The general mechanism of using $Mn_2(CO)_{10}$ in light initiated ATRP is shown below.

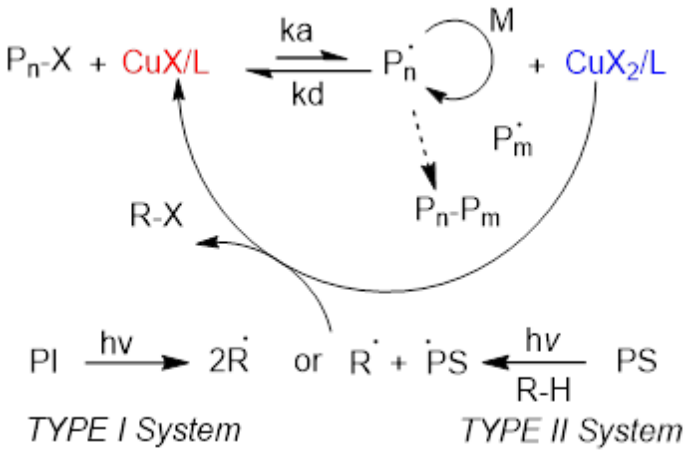


Figure 2.5: Mechanism of photo-initiated ATRP by using free radical photoinitiators.

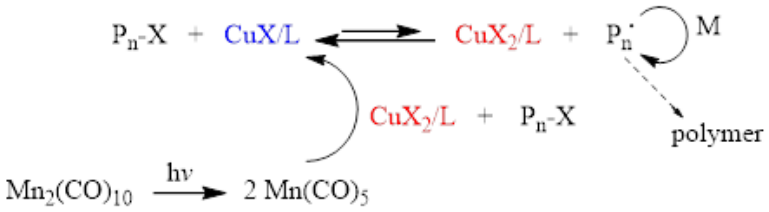


Figure 2.6: Mechanism of using $Mn_2(CO)_{10}$ in light initiated ATRP.

2.2.3.2 Photoinduced metal-free ATRP

For a varity of uses such as bioapplication and microelectronics even ppm levels of metal contamination could be a disadvantage [31, 32]. Metal-Free polymerization is concerned to be green technology and enviromental frendly [26, 33]. Recently, phenothiazine derivatives and perylene in conjunction with alkyl halides have been shown to realize photoinitiated ATRP of various monomers in the absence of Cu catalysts [29, 34]. Both sensitizers generated polymers with narrow molecular weight distribution and with controlled chain-end functionalities. In a more recent study, diaryl dihydrophenazines were also shown to display favorable thermodynamic characteristics to catalyze the syntheses of polymers with tunable molecular weights and low dispersities by metal-free photoATRP [35, 36]. Yagci and coworkers recently reported a new photoinitiating system involving electron acceptor dyes, namely, eosin Y and erythrosin B, in conjunction with alkyl halides and amines for photoinduced ATRP of (meth)acrylates and vinyl monomers in the absence of inorganic catalysts [1, 37]. Anthracene and pyrene are naturally occurring polynuclear

aromatic hydrocarbons with a wide range of photochemical and electrochemical applications. Both show excellent near-UV light absorption, a spectral region which is most commonly used for polymer curing applications. Pyrene derivatives are also used in various bio-applications such as fluorescence labeling [38]. This thesis demonstrates the use of anthracene and pyrene as photosensitizers for metal-free ATRP and shows detailed mechanistic studies.

3. EXPERIMENTAL

In this part of thesis, the detailed information regarding the chemicals used and synthesis and characterization methods were explained.

3.1 Materials and Chemicals

3.1.1 Chemicals

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

Styrene (St, 99%, Sigma-Aldrich) was was passed through a basic alumina column to remove the inhibitor.

2-hydroxyethyl methacrylate (HEMA, ($\geq$99.0%, Sigma-Aldrich) was used as received.

N,N,N',N",N"-Pentamethyldiethylenetriamine (PMDETA, $\geq$98.0%, Sigma-Aldrich) was distilled before use.

Ethyl α-bromoisobutyrate (EBI, 98%, Sigma-Aldrich) was used as received.

Ethyl 2-bromopropionate (EBP, 99%, Sigma-Aldrich) was used as received.

(1-bromoethyl)benzene (BEB, 97%, Sigma-Aldrich) was used as received.

(1-bromoethyl)benzene (Anth, 98%, Sigma-Aldrich) was crystallized from ethanol prior to use.

Pyrene (Py, 98%, Sigma-Aldrich) was crystallized from ethanol prior to use.

3.1.2 Solvents

N,N-Dimethyl formamide (DMF, 99.5 %, Aldrich) was stored over activated molecular sieves (4 Å).

Methanol (99.9 %, Merck) was used as received.

Toluene (99.5 %, Aldrich) was dried with calcium chloride and distilled over sodium wire.

Tetrahydrofuran (THF, 99.8%, J.T.Baker) was dried over KOH, distilled over sodium wire and finally distilled over sodium/benzophenone ketyl prior to use.

3.2 Equipments

3.2.1 Light Source

A Ker-Vis porple photoreactor equipped with 18 lamps (Philips TL-8W BLB) emitting light nominally at 350 nm was used in all polymerization experiments.

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 500 MHz on a Bruker DPX 250 spectrometer.

3.2.3 Gel-permeation chromatography

Molecular weights of the polymers soluble in organic solvents were determined by a gel permeation chromatography (GPC) instrument, Viscotek GPCmax Autosampler system, consisting of a pump, three ViscoGEL GPC columns (G2000HHR, G3000HHR, and G4000HHR), and a Viscotek differential refractive index (RI) detector with a THF flow rate of 1.0 mL min^{-1} at 30 ^{o}C. The RI detector was calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. GPC measurements with the water-soluble polymers were performed at room temperature with a setup consisting of a pump (HP 1050), a refractive index detector (HP 1047A), and three highresolution Waters columns (AQ3.0, AQ4.0, and AQ5.0). The effective molecular weight ranges were 1000-60000, 10000-400000, and 50000-4000000, respectively. Water was used as eluent at a flow rate of 0.5 mL/min at room temperature. Data analyses were performed with HP Chemstation Software. Calibration with linear poly (ethylene oxide) standards (Polymer Laboratories) was used to estimate the molecular weights.

3.3 Preparation Methods

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

In a typical experiment, MMA (1 mL, 100 eq), alkyl halide (1 eq), DMF (1 mL) and photosensitizer (pyrene or anthracene, 0.1 eq) were put into a Schlenk tube and the reaction mixture was degassed by a freeze-pump-thaw cycle and left in vacuum. The stirring solution was irradiated with a light source emitting light nominally at λ=350 nm for 2 h. At the end of the irradiation, the resulted polymers were precipitated in methanol and then dried under reduced pressure. Conversion was determined gravimetrically.

4. RESULTS AND DISCUSSION

To test the ability of anthracene and pyrene to mediate photoinduced CLRP, methyl methacrylate (MMA) was polymerized under reduced pressure using appropriate alkyl halide sources, such as, ethyl 2-bromoisobutyrate (EBI), (1-bromoethyl benzene) (BEB) and ethyl 2-bromopropionate (EBP). The results obtained with the Anth/EBP initiating system are tabulated in Table 4.1

Table 4.1: Photoinitiated Radical Polymerization of Methyl Methacrylate (MMA) in DMF Using Anthracene (Anth)/Ethyl 2-Bromopropionate (EBP) as the Initiating System Under Different Experimental Conditions [a].

Run	EBP/Anth/MMA	Conv. (%)[b]	$M^{c}_{n,GPC}$ ($g.mol^{-1}$)	PDI[c]
1	1/0.01/100	-	-	-
2	1/0.1/100	37.2	19100	1.44
3	1/1/100	16.8	4100	1.50
4	1/2/100	10.1	8700	1.41
5	1/3/100	2.8	-	-

[a] [EBP]=0.045 M, $\lambda = 350\ nm$, time=120 min,
[b] Determined gravimetrically,
[c]Determined by gel permeation chomatography using PS standards.

As can be seen, polymerizations occurred in a wide concentration range of Anth (Run 2-4). Though the observed polydispersities were below the desired limits (< 1.5 as a definition of controlled polymerization), the GPC traces displayed multimodal nature (Figure 4.1) which suggests that more than one initiation pathway is operative.

To understand the initiation mechanism a Anth/EBP solution in deuterated dimethyl sulfoxide (d_6-DMSO) was irradiated at 350 nm. ^{1}H NMR analyses showed that the characteristic peaks of anthracene completely disappeared and new aromatic signals at higher frequencies (6.8 and 6.9 ppm) were observed. In addition, new signals were detected in the region 4.5-3.1 ppm, which might be assigned to the protons, observed after probable radical coupling reactions (Figure 4.1). The ^{1}H NMR spectrum of PMMA (Run 3, Table 4.1) showed aromatic peaks around (6.8-6.9 ppm), which showed that the polymers are grafted through the anthracene rings (Figure 4.2).

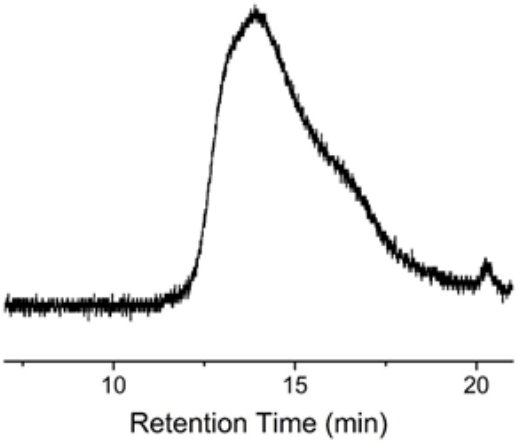


Figure 4.1: GPC trace of PMMA prepared by photo-induced radical polymerization using Anth/EBP.

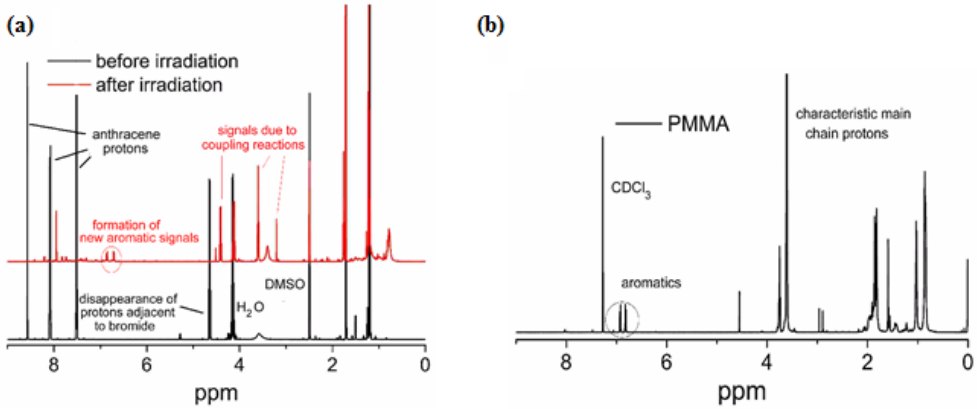


Figure 4.2: ^{1}H NMR spectra of a) d_6-DMSO solutions of Anth/EBP before and after irradiation and b) Purified PMMA prepared by using anthracene/EBP initiating system in $CDCl_3$.

Based on these spectral and chromatographic analyses results, the postulated mechanism for the radical polymerization using anthracene/EBP initiating system is shown below (Figure 4.3).

Photoexcitation of anthracene leads to singlet excited states which undergo electron transfer to alkyl halides and generate anthracene radical cations and alkyl radical. The rate constant of this first reaction step was determined by fluorescence lifetime measurements of anthracene at varying concentrations of alkyl halides (Figure 4.4) generation of initiator radicals.

Anthracene excited states are known to undergo [4+4]-cycloaddition with another anthracene molecule in the ground state to form dimers. This dimerization reaction is especially active at higher anthracene concentrations. The rate constant of

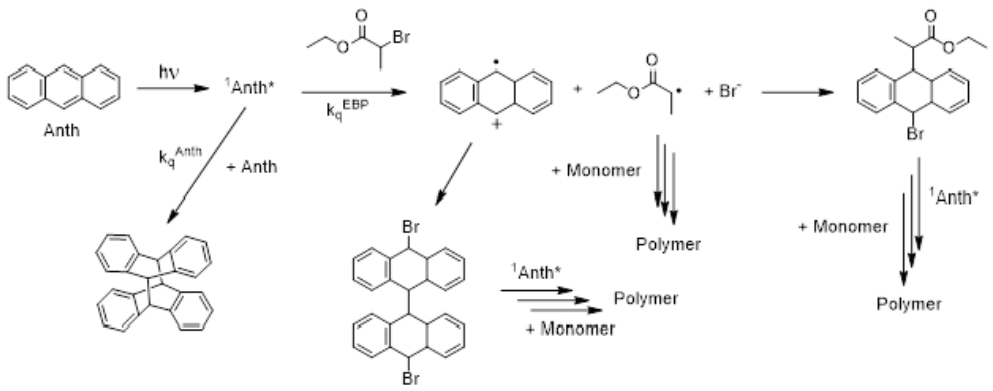


Figure 4.3: Proposed mechanism of photoinitiated radical polymerization using anthracene/alkyl halide system as initiator.

self-quenching of anthracene singlet excited states (k_q^{Anth}) was determined from fluorescence lifetimes at varying concentrations of Anth and found to be $7x10^9$ $M^{-1}s^{-1}$ (Figure 4.5).

This high self-quenching rate constant is most likely responsible for the reduced polymer yield at high Anth concentrations (Table 1, Run 5). To test the activity of pyrene in the controlled living radical polymerization, similar photoinduced polymerization procedures were also performed using structurally different alkyl halides and the results were compiled in Table 4.2.

As can be seen, increasing the alkyl halide concentration gave rise to an increase in the polymerization conversions (Runs 1, 2 and 4). When one equivalent of tetrabutylammonium bromide was added into the reaction media, polymerization conversion decreases dramatically without significantly effecting the molecular weight distribution (Run 3). The observed slow rate of the polymerization is due to the increased rate of termination by free bromide ions. The effect of alkyl halide sources on the polymerization conversion and molecular weight characteristics of the polymers obtained was also examined (Runs 2, 5, 6). Tertiary and benzylic alkyl halides (EBI and BEB) were found to exhibit higher initiator efficiency (I^*) in mediating the photoinduced controlled polymerization of MMA in the presence of pyrene (Runs 2 and 5). The unexpectedly high (I^*) value of EBI in Run 1 might be attributed to the molecular weight characterization with GPC calibrated according to polystyrene standards. However, using the secondary alkyl halide source (EBP) under typical experimental conditions did not yield any precipitable polymer, which might

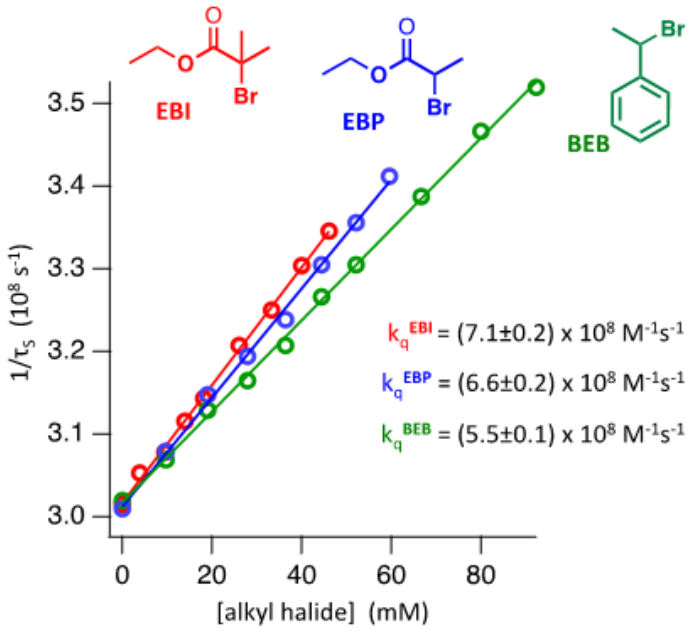


Figure 4.4: Determination of the bimolecular quenching rate constants (k_q) of quenching of anthracene singlet excited states by EBI (red), EBP (blue) and BEB (green).

be explained by the instability of the generated secondary radicals compare to the tertiary and benzylic analogs (Run 6). The effect of photocatalyst concentration on the polymerization was examined (Runs 7-11). At very low pyrene concentrations (0.45 mM) no polymerization was observed (Run 7) which is probably due to poor light absorption. However, at moderate (4.5 mM; Run 8) and high (45 – 135 mM; Runs 9-11) pyrene concentrations polymerization was achieved. Pyrene is known to form excimers (excited state dimers) in the quenching reaction of singlet excited states by another pyrene molecule in the ground state. The rate constant for this process was estimated by fluorescence lifetime measurements (k_q^{Py} $2x10^9$ $M^{-1}s^{-1}$; Figure 4.6)

This reaction is expected to be the dominant process at high pyrene concentrations. Because the polymer yield did not decline significantly with increasing pyrene concentrations (Table 2, Runs 8-11), both pyrene singlet excited states and pyrene excimers are involved in initiator radical formation. The rate constants of the reaction of pyrene singlet excited states and excimers with alkyl halides were determined by fluorescence lifetime measurements at varying concentrations of alkyl halides (Figure 4.4). For the reaction of pyrene singlet excited states with EBI, EBP and BEB, rate constants of 10-4x$10^{-7}M^{-1}s^{-1}$ were observed. The rate constants of pyrene excimers with alkyl halides were about half compared to the monomeric form. In general, these

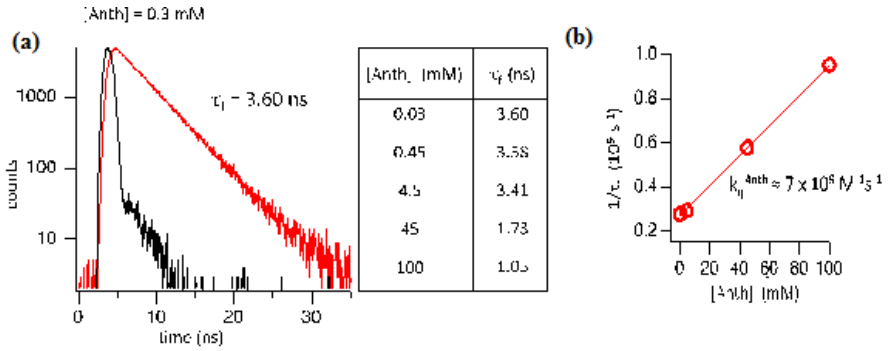


Figure 4.5: a) Fluorescence decay of anthracene in DMF (red) at 404 nm. b) Determination of the bimolecular quenching rate constants k_q^{Anth} of anthracene singlet excited states by ground state anthracene.

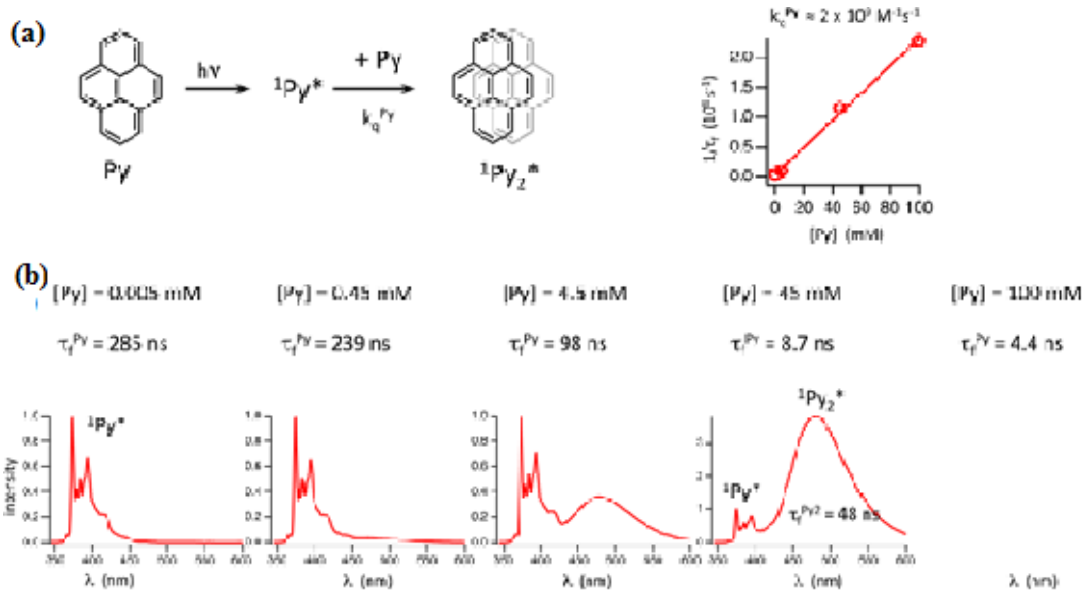
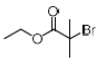
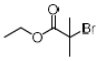
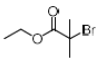
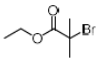
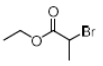
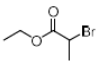
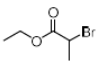
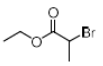
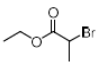
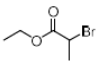


Figure 4.6: a) Determination of the bimolecular quenching rate constants k_q^{Py} of pyrene singlet excited states by ground state pyrene. b) Fluorescence spectra of pyrene at different concentrations in DMF.

rate constants are lower than for anthracene singlet excited state quenching. However, the singlet excited state lifetime for pyrene (285 ns in highly dilute DMF, (Figure 4.5) and pyrene excimers (48 ns in DMF, Figure 4.5) are significantly longer than for anthracene (3.6 ns in DMF, (Figure 4.4). Because of the longer excited state lifetimes of pyrene and pyrene excimers, initiating radical formation is efficient if sufficient amounts of alkyl halides are present.

To compare the efficiency of pyrene in mediating the controlled radical photopolymerization of structurally different monomers, acrylic and vinyl monomers namely, tert-butyl acrylate (t-BA) and styrene (St) were also polymerized and the results were

Table 4.2: Photoinitiated Metal Free Living Radical Polymerization of Methyl Methacrylate in DMF Using Pyrene (Py) as Photosensitizer Under Different Experimental Conditions[a].

Run	R-Br/Br/Py/MMA	R-Br	Conv. (%)[c]	$M^{d}_{n,GPC}$ (g. mol^{-1})	PDI[d]	I*(R-Br) (%)[e]
1	0.10/1/100 (4.5 mM/45 mM/4.5 M)		18.3	16400	1.50	111.6
2	0.25/1/100 (11 mM/45 mM/4.5 M)		21.1	13100	1.38	64.4
3	0.25/1/100[b] (11 mM/45 mM/4.5 M)		6.9	17000	1.41	16.2
4	1/1/100 (45 mM/45 mM/4.5 M)		38.4	11000	1.96	34.9
5	0.25/1/100 (11 mM/45 mM/4.5 M)		26.6	20500	1.37	51.9
6	0.25/1/100 (11 mM/45 mM/4.5 M)		<1	-	-	-
7	1/0.01/100 (45 mM/0.45 mM/4.5 M)		-	-	-	-
8	1/0.1/100 (45 mM/4.5 mM/4.5 M)		29.4	36000	2.08	8.2
9	1/1/100 (45 mM/45 mM/4.5 M)		27.8	15300	1.96	18.2
10	1/2/100 (4.5 mM/90 mM/4.5 M)		26.1	18200	1.44	14.3
11	1/3/100 (45 mM/135 mM/4.5 M)		25.4	21200	1.44	12.0

[a] $\lambda = 350\ nm$, time=120 min, [b] Using tetrabutylammonium bromide (1 eq, 45 mM)
[c] Determined gravimetrically,
[d]Determined by gel permeation chomatography using PS standards.

collected in Table 3. Clearly, both monomers yield polymers with relatively low polydispersities.

Notably, the differences in polymerization conversions can be attributed to the variations in the propagating rate constants of the monomers.

In order to examine the chain-end fidelity of the polymers obtained, chain extension and block copolymerization experiments were performed. For this purpose, PMMA-Br obtained by aforementioned process, was used as the halide source and identical

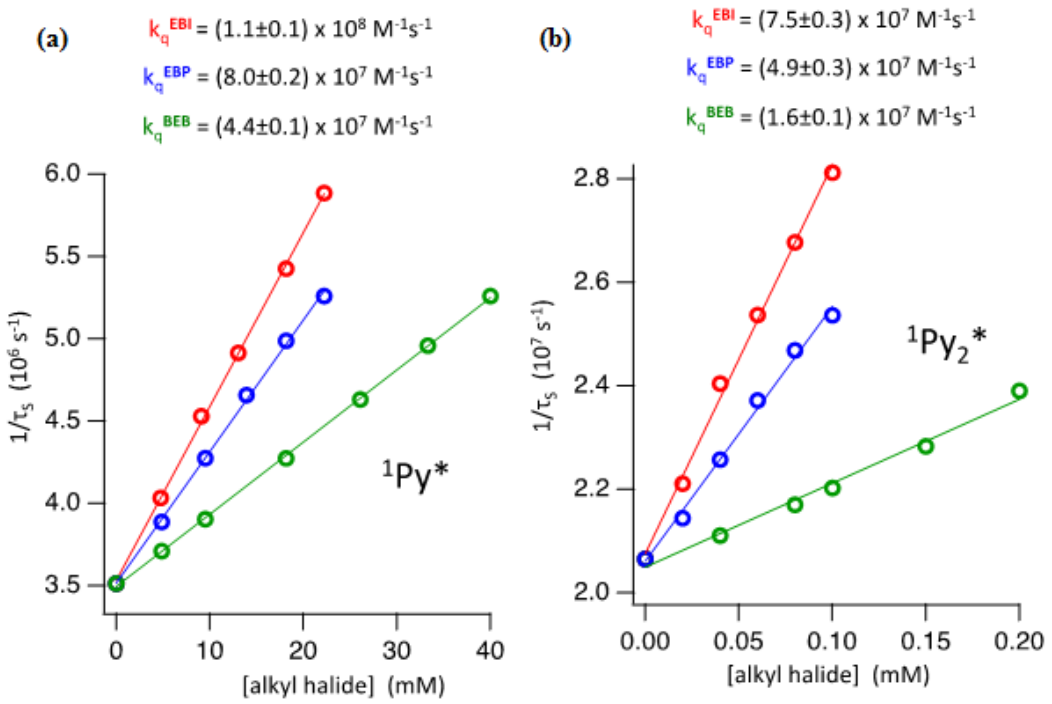


Figure 4.7: Determination of the bimolecular quenching rate constants k_q of a) quenching of pyrene singlet excited states and b) excimers by EBI (red), EBP (blue) and BEB (green).

Table 4.3: Photoinitiated Metal Free Living Radical Polymerization of Various Monomers Using Pyrene (Py) as Photosensitizer[a].

Monomers	Time (min)	Conv. (%)[b]	$M_{n,GPC}^{d}$ ($g.mol^{-1}$)	PDI[d]	I*(R-Br) (%)[d]
MMA	120	21.1	13100	1.38	111.6
t-BA	40	52.2	107000	1.32	25.0
St	120	18.4	2000	1.32	382.7

[a] [EBP]=0.045 M, [EBP]/[Pyr]/[Monomer]=0.25/1/100, $\lambda = 350\ nm$.
[b] Determined gravimetrically.
[c] Determined by gel permeation chomatography using PS standards.
[d] Initiator efficiency (I*) calculated according to equation

polymerization conditions were applied as described in Table 2, except using styrene (St) in place of MMA for block copolymerization (Figure 4.7). Chromatographic results demonstrated that there are clear shifts to higher molecular weight regions in both cases, which reveal the efficiency of initiation of polymerization from the ω-chain end of the precursor PMMA. Thus, one can undoubtedly judge the presence of bromide functionalities at the chain ends of polymers obtained by this strategy. The absence of any tail regime in higher retention times showed the high efficiency of

pyrene to activate the initiation. In addition, both polymerizations afforded polymers with narrow molecular weight distributions (Figure 4.10).

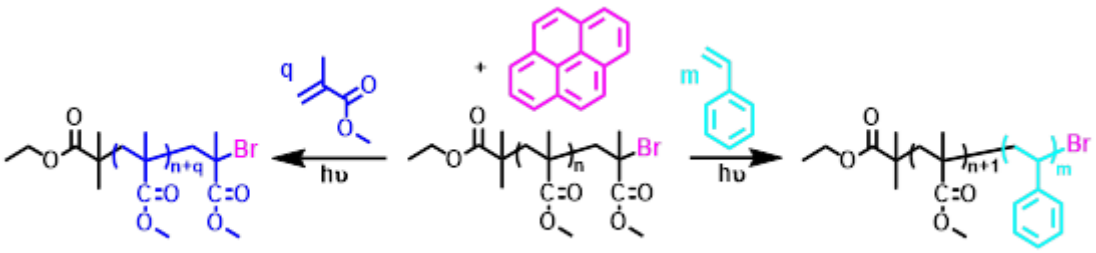


Figure 4.8: Photoinduced ATRP for chain extension and block copolymerization starting from precursor PMMA using pyrene.

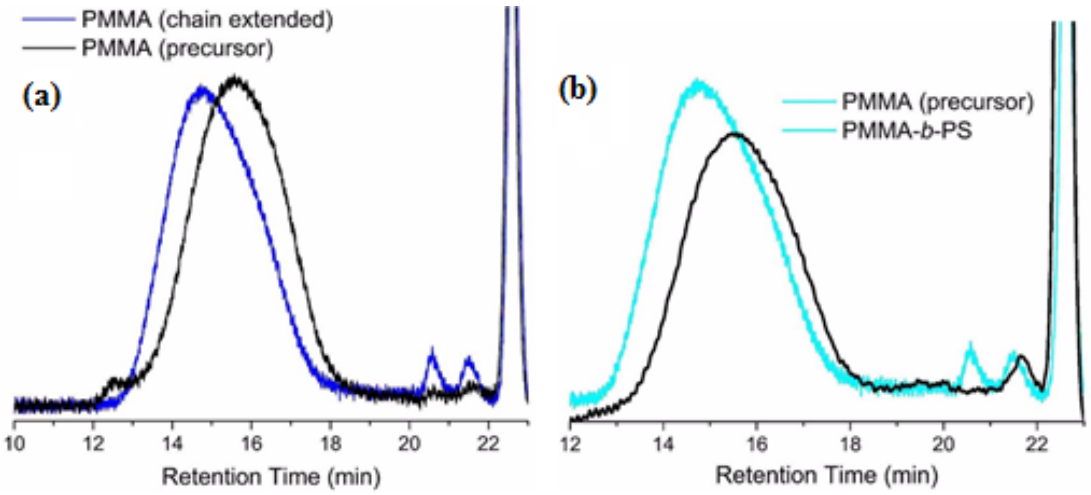


Figure 4.9: Comparison of the GPC traces of precursor PMMA with a) chain extended PMMA b) PMMA-b-PSt.

To show the temporal control over polymerization, typical polymerization experiments were conducted under nitrogen atmosphere, where the reaction tube was exposed to repeated cycles of UV light (λ = 350 nm) for 60 minutes and kept in dark for 30 minutes. In these subsequent intervals, certain volumes of reaction mixture were syringed out from the polymerization media and precipitated in methanol. Next, the polymers were analyzed gravimetrically to determine the conversions. Results demonstrate the polymerization is ultimately irradiation dependent and almost no polymerization occurred when the light is switched off (Figure 4.10 A). Similar experimentation was also performed without switching of the light and the polymers obtained at each time intervals were analyzed by GPC for molecular weight characterization. GPC measurements reveal the molecular weight increases upon irradiation, but shows a decrease after two hours with an increase in polydispersity.

After continuation of irradiation, the molecular weights increased and polydispersites decreased to desired limits (Figure 4.10 B). This behavior might be attributed to the activation of initiation on unreacted halide terminated chains, which might still be present in the media [39].

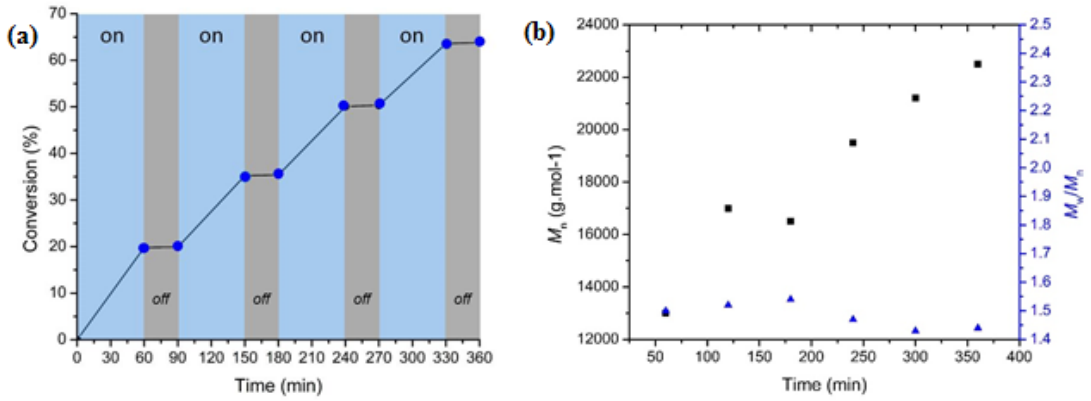


Figure 4.10: a) Monomer conversion (%) vs time concluding the dependency of propagation on irradiation: light on (blue regions) light off (grey regions) b) Molecular weight characteristics of PMMA vs irradiation time.

To give further insight to the polymerization kinetics, the course of polymerization was followed by NMR spectroscopy. For this purpose, MMA (100 eq), EBI (0.25 eq) and pyrene (1 eq) were dissolved in d_6-DMSO (V_{MMA}/V_{DMSO}: 1/1) and taken to an NMR tube under nitrogen flow. Then, NMR spectra of the samples were recorded starting from 0 to 180 minutes of irradiation at certain time intervals. As can be seen from (Figure 4.11 a), the double bond protons of MMA decreased upon irradiation (at 6.01 and 5.65 ppm) and a new broad peak around 3.63 ppm appeared, which shows the polymerization was operative. By comparing the integrated ratios of methylene protons to polymeric $-OCH_3$ protons while taking the integrated area of pyrene protons as internal standard in each spectra, monomer consumptions were calculated and plotted as demonstrated in (Figure 4.11 b). Clearly, the rate of monomer consumption was almost constant during irradiation, which proved this system provides control over polymerization.

In the light of these studies, the following mechanism can be proposed for polymerizations using pyrene as photoactivator (Figure 4.11). The ground state pyrene is excited upon irradiation, followed by an electron transfer to the alkyl bromide to generate radicals responsible for initiation. The concomitantly formed bromide ion

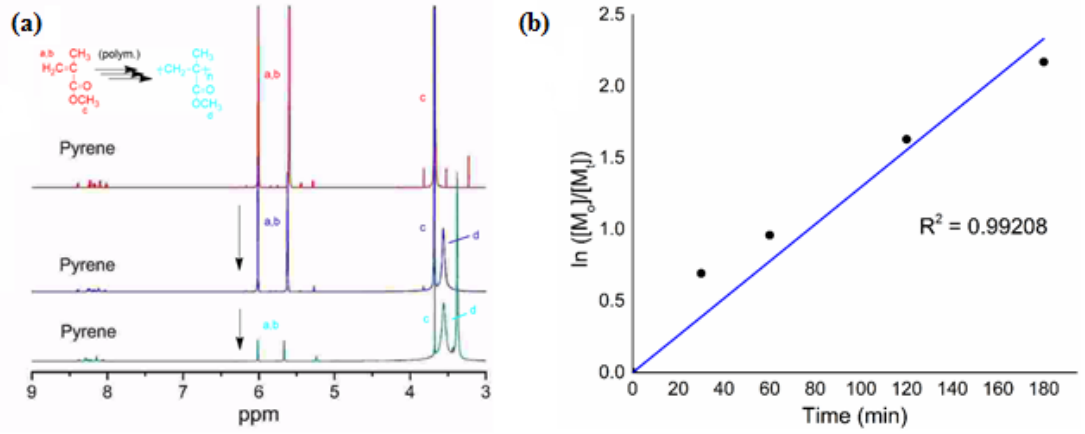


Figure 4.11: a) ^{1}H NMR spectra of polymerization media in 0 (red), 120 (blue) and 180 minutes of irradiation (green) showing the consumption of MMA upon irradiation b) Kinetic plot of polymerization.

gives an electron back to the pyrene radical cations to produce ground state pyrene, that takes part in later steps of activation while yielding the dormant halide end-functional polymer. At high pyrene concentrations, such as 45 mM, pyrene singlet excited states predominantly form excimers ($^1Py_2^*$), which are also able to undergo electron transfer reactions with alkyl halides to generate the initiating radicals.

5. CONCLUSION

In conclusion, we have studied the use of polynuclear aromatic hydrocarbons as photosensitizers for metal free atom transfer radical polymerization of various vinyl monomers on the example of anthracene and pyrene. Fluorescence studies reveal that the excited states of these compounds undergo a photoinduced electron transfer reaction with appropriate alkyl halides through an oxidative quenching mechanism. Although anthracene was found to be more efficient in radical generation step, the detailed experiments show that anthracene/alkyl halide initiating system produces polymers via a free radical mechanism due to the transfer of the propagating sites to the labile positions on the anthracene ring. However, polymerizations using pyrene/alkyl halide system yielded polymers with narrow molecular weight distribution and controlled chain-end functionality as confirmed by the spectroscopic analyses, and chain extension and block copolymerization experiments. In such controlled process, possible chain transfer reactions can be excluded due to the delocalization of the radical cation on the pyrene structure. Light on/off experiments clearly presents the dependency of polymerizations on light exposure. Based on the spectral studies and polymerization experiments free radical and metal free atom transfer radical polymerization mechanisms using anthracene and pyrene respectively, are proposed. The success of the pyrene based photo redox system may lead to new possibilities for not only control over the polymerization but also surface modification and spatiotemporal control under metal free conditions.

REFERENCES

[1] **Kutahya, C.**, **Aykac, F.S.**, **Yilmaz, G. and Yagci, Y.** (2016). LED and visible light-induced metal free ATRP using reducible dyes in the presence of amines, *Polymer Chemistry*, 7(39), 6094–6098.

[2] **Yagci, Y.**, **Jockusch, S. and Turro, N.J.** (2010). Photoinitiated polymerization: advances, challenges, and opportunities, *Macromolecules*, *43*(15), 6245–6260.

[3] **Dadashi-Silab, S.**, **Atilla Tasdelen, M. and Yagci, Y.** (2014). Photoinitiated atom transfer radical polymerization: Current status and future perspectives, *Journal of Polymer Science Part A: Polymer Chemistry*, *52*(20), 2878–2888.

[4] **Matyjaszewski, K. and Xia, J.** (2001). Atom transfer radical polymerization, *Chemical reviews*, *101*(9), 2921–2990.

[5] **Wang, J.S. and Matyjaszewski, K.** (1995). Controlled/" living" radical polymerization. Atom transfer radical polymerization in the presence of transition-metal complexes, *Journal of the American Chemical Society*, *117*(20), 5614–5615.

[6] **Hawker, C.J.**, **Bosman, A.W. and Harth, E.** (2001). New polymer synthesis by nitroxide mediated living radical polymerizations, *Chemical Reviews*, *101*(12), 3661–3688.

[7] **Benoit, D.**, **Chaplinski, V.**, **Braslau, R. and Hawker, C.J.** (1999). Development of a universal alkoxyamine for “living” free radical polymerizations, *Journal of the American Chemical Society*, *121*(16), 3904–3920.

[8] **Audran, G.**, **Brémond, P. and Marque, S.R.** (2014). Labile alkoxyamines: past, present, and future, *Chemical Communications*, *50*(59), 7921–7928.

[9] **Chiefari, J.**, **Chong, Y.**, **Ercole, F.**, **Krstina, J.**, **Jeffery, J.**, **Le, T.P.**, **Mayadunne, R.T.**, **Meijs, G.F.**, **Moad, C.L.**, **Moad, G.** *et al.* (1998). Living free-radical polymerization by reversible addition-fragmentation chain transfer: the RAFT process, *Macromolecules*, *31*(16), 5559–5562.

[10] **Moad, G.**, **Rizzardo, E. and Thang, S.H.** (2005). Living radical polymerization by the RAFT process, *Australian journal of chemistry*, *58*(6), 379–410.

[11] **Matyjaszewski, K.** (2012). Atom transfer radical polymerization (ATRP): current status and future perspectives, *Macromolecules*, *45*(10), 4015–4039.

[12] **Kamigaito, M.**, **Ando, T. and Sawamoto, M.** (2001). Metal-catalyzed living radical polymerization, *Chemical Reviews*, *101*(12), 3689–3746.

[13] **Guan, Z. and Smart, B.** (2000). A remarkable visible light effect on atom-transfer radical polymerization, *Macromolecules*, *33*(18), 6904–6906.

[14] **Braunecker, W.A. and Matyjaszewski, K.** (2007). Controlled/living radical polymerization: features, developments, and perspectives, *Progress in Polymer Science*, *32*(1), 93–146.

[15] **Yamada, B. and Otsu, T.** (1989). Preparation of monomers functioning as initiators and use of their polymers for graft copolymerization, *Die Makromolekulare Chemie*, *190*(5), 915–927.

[16] **Scaiano, J.C.**, **Connolly, T.J.**, **Mohtat, N. and Pliva, C.N.** (1997). Exploratory study of the quenching of photosensitizers by initiators of free radical" living" polymerization, *Canadian journal of chemistry*, *75*(1), 92–97.

[17] **Versace, D.L.**, **Lalevée, J.**, **Fouassier, J.P.**, **Gigmes, D.**, **Guillaneuf, Y. and Bertin, D.** (2010). Photosensitized alkoxyamines as bicomponent radical photoinitiators, *Journal of Polymer Science Part A: Polymer Chemistry*, *48*(13), 2910–2915.

[18] **Guillaneuf, Y.**, **Bertin, D.**, **Gigmes, D.**, **Versace, D.L.**, **Lalevée, J. and Fouassier, J.P.** (2010). Toward nitroxide-mediated photopolymerization, *Macromolecules*, *43*(5), 2204–2212.

[19] **Hu, S.**, **Malpert, J.**, **Yang, X. and Neckers, D.** (2000). Exploring chromophore tethered aminoethers as potential photoinitiators for controlled radical polymerization, *Polymer*, *41*(2), 445–452.

[20] **Jiang, W.**, **Lu, L. and Cai, Y.** (2007). Highly Efficient and Well-Controlled Ambient Temperature RAFT Polymerization under Solar Radiation, *Macromolecular rapid communications*, *28*(6), 725–728.

[21] **Lu, L.**, **Zhang, H.**, **Yang, N. and Cai, Y.** (2006). Toward rapid and well-controlled ambient temperature RAFT polymerization under UV-Vis radiation: effect of radiation wave range, *Macromolecules*, *39*(11), 3770–3776.

[22] **Quinn, J.F.**, **Barner, L.**, **Barner-Kowollik, C.**, **Rizzardo, E. and Davis, T.P.** (2002). Reversible addition-fragmentation chain transfer polymerization initiated with ultraviolet radiation, *Macromolecules*, *35*(20), 7620–7627.

[23] **Lu, L.**, **Yang, N. and Cai, Y.** (2005). Well-controlled reversible addition–fragmentation chain transfer radical polymerisation under ultraviolet radiation at ambient temperature, *Chemical communications*, (42), 5287–5288.

[24] **Wang, Y.**, **Zhang, Y.**, **Parker, B. and Matyjaszewski, K.** (2011). ATRP of MMA with ppm levels of iron catalyst, *Macromolecules*, *44*(11), 4022–4025.

[25] **Tasdelen, M.A.**, **Uygun, M. and Yagci, Y.** (2010). Photoinduced controlled radical polymerization in methanol, *Macromolecular Chemistry and Physics*, *211*(21), 2271–2275.

[26] **Tasdelen, M.A.**, **Uygun, M. and Yagci, Y.** (2011). Photoinduced controlled radical polymerization, *Macromolecular rapid communications*, *32*(1), 58–62.

[27] **Tasdelen, M.A.**, **Ciftci, M. and Yagci, Y.** (2012). Visible Light-Induced Atom Transfer Radical Polymerization, *Macromolecular Chemistry and Physics*, *213*(13), 1391–1396.

[28] **Tasdelen, M.A.**, **Yilmaz, G.**, **Iskin, B. and Yagci, Y.** (2011). Photoinduced free radical promoted copper (I)-catalyzed click chemistry for macromolecular syntheses, *Macromolecules*, *45*(1), 56–61.

[29] **Taskin, O.S.**, **Yilmaz, G.**, **Tasdelen, M.A. and Yagci, Y.** (2014). Photoinduced reverse atom transfer radical polymerization of methyl methacrylate using camphorquinone/benzhydrol system, *Polymer International*, *63*(5), 902–907.

[30] **Tasdelen, M.A.**, **Yilmaz, G.**, **Iskin, B. and Yagci, Y.** (2011). Photoinduced free radical promoted copper (I)-catalyzed click chemistry for macromolecular syntheses, *Macromolecules*, *45*(1), 56–61.

[31] **Lutz, J.F.** (2008). Copper-Free Azide–Alkyne Cycloadditions: New Insights and Perspectives, *Angewandte Chemie International Edition*, *47*(12), 2182–2184.

[32] **Becer, C.R.**, **Hoogenboom, R. and Schubert, U.S.** (2009). Click Chemistry beyond Metal-Catalyzed Cycloaddition, *Angewandte Chemie International Edition*, *48*(27), 4900–4908.

[33] **Treat, N.J.**, **Sprafke, H.**, **Kramer, J.W.**, **Clark, P.G.**, **Barton, B.E.**, **Read de Alaniz, J.**, **Fors, B.P. and Hawker, C.J.** (2014). Metal-free atom transfer radical polymerization, *Journal of the American Chemical Society*, *136*(45), 16096–16101.

[34] **Pan, X.**, **Fang, C.**, **Fantin, M.**, **Malhotra, N.**, **So, W.Y.**, **Peteanu, L.A.**, **Isse, A.A.**, **Gennaro, A.**, **Liu, P. and Matyjaszewski, K.** (2016). Mechanism of Photoinduced Metal-Free Atom Transfer Radical Polymerization: Experimental and Computational Studies, *Journal of the American Chemical Society*, *138*(7), 2411–2425.

[35] **Theriot, J.C.**, **Lim, C.H.**, **Yang, H.**, **Ryan, M.D.**, **Musgrave, C.B. and Miyake, G.M.** (2016). Organocatalyzed atom transfer radical polymerization driven by visible light, *Science*, *352*(6289), 1082–1086.

[36] **Shanmugam, S. and Boyer, C.** (2016). Organic photocatalysts for cleaner polymer synthesis, *Science*, *352*(6289), 1053–1054.

[37] **Yagci, Y.**, **Jockusch, S. and Turro, N.J.** (2007). Mechanism of photoinduced step polymerization of thiophene by onium salts: Reactions of phenyliodinium and diphenylsulfinium radical cations with thiophene, *Macromolecules*, *40*(13), 4481–4485.

[38] **Karadag, M.**, **Yilmaz, G.**, **Toiserkani, H.**, **Demirkol, D.O.**, **Sakarya, S.**, **Torun, L.**, **Timur, S. and Yagci, Y.** (2011). Polysulfone/pyrene membranes: a new microwell assay platform for bioapplications, *Macromolecular bioscience*, *11*(9), 1235–1243.

[39] **Miyake, G.M. and Theriot, J.C.** (2014). Perylene as an organic photocatalyst for the radical polymerization of functionalized vinyl monomers through oxidative quenching with alkyl bromides and visible light, *Macromolecules*, *47*(23), 8255–8261.

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- **Allushi A., Jockusch S., Yilmaz G., Yagci Y.**, Photoinitiated Metal-Free Controlled/Living Radical Polymerization Using Polynuclear Aromatic Hydrocarbons, World Polymer Congress, 2016, Istanbul, Turkey