

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

PHOTOCHEMICAL STRATEGIES FOR MACROMOLECULAR SYNTHESSES

Ph. D.THESIS

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Department of Chemistry

Chemistry Programme

DECEMBER 2015

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To my intention...

FOREWORD

First of all, I would like to thank, Prof. Yusuf Yagci, who has always been more than a supervisor to me, a father, a dependable friend, a life coach, someone who makes a difference in my life that probably will stay for the rest of it. I feel the honour to be the one and the only undergraduate, master and PhD student working with him. Still it makes it harder to be separated at least positionally, despite a separation can never be discoursed in such affiliations.

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Finally, I would like to thank (if only) my reason and my intention, that is the meaning of everything from the very beginning of my life. No words would ever mean to express my feelings about this reality, so it is best to keep it short...

Thank you all again!

NOVEMBER 2015

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ABBREVIATIONS

AAm	: Acrylamide
AgPF₆	: Silver Hexafluorophosphate
Alkyne-PCL	: α -Alkyne Functional Poly(ϵ -Caprolactone)
Anth	: Anthracene
ATRP	: Atom Transfer Radical Polymerization
BAAm	: Bisacrylamide
C₆₀	: Buckminster Fullerene
CDCl₃	: Deuterated Chloroform
CH₂Cl₂	: Dichloromethane
Conv	: Conversion
CuAAC	: Copper Catalyzed Azide-Alkyne Cycloaddition
CuCl	: Copper(I) Chloride
CuBr	: Copper(I) Bromide
DA	: Diels-Alder
DMF	: <i>N,N</i> -dimethylformamide
DMSO	: Dimethyl Sulphoxide
EO	: Ethylene Oxide
FT-IR	: Fourier Transform Infrared Spectrophotometer
GPC	: Gel Permeation Chromatography
HEMA	: Hydroxyethyl Methacrylate
¹H NMR	: Hydrogen Nuclear Magnetic Resonance Spectroscopy
IBVE	: Isobutyl Vinyl Ether
MMA	: Methyl methacrylate
NVC	: <i>N</i> -Vinyl Carbazole
NVP	: <i>N</i> -Vinyl Pyrolidone
M_n	: Number Average Molecular Weight
PCL	: Poly(ϵ -caprolactone)
PDI	: Polydispersity
PEO	: Poly(ethylene oxide)
Ph	: Phenothiazine
Ph₂I⁺PF₆⁻	: Diphenyliodonium Hexafluorophosphate
PMDETA	: <i>N, N, N', N'', N'''</i> - Pentamethyldiethylenetriamine
PMMA	: Poly(methyl methacrylate)
Pry	: Perylene
PS-Br	: ω -Bromo Functional Polystyrene
PS-C₆₀	: ω -Fullerene Functional Polystyrene
PS-N₃	: ω -Azido Functional Polystyrene
R-H	: Hydrogen Donor
ROP	: Ring-opening Polymerization
THF	: Tetrahydrofuran
TMPTA	: Trimethyloxypropane Triacrylate
TX	: Thioxanthone
UV	: Ultraviolet

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PHOTO-INDUCED STRATEGIES FOR MACROMOLECULAR SYNTHESSES

SUMMARY

Photo-induced reactions have been receiving a revitalized interest as it congregates a wide range of academical, commercial, economical and ecological anticipations. In the area of synthetic polymer chemistry, most of the research intensively focused on photopolymerizations, which is typically the process that transforms a monomer into a polymer by the help of the incident photon energy. Even when monomers are exposed to light of appropriate frequencies, polymers can be obtained. However such reactions are generally low-yielded reactions and almost always an additive is required to increase the efficiency. This additive is known as a photoinitiator which absorbs the light and decomposes to give the reactive species which are responsible for initiation of polymerization. Both free radical and cationic polymerizations are known and their mechanisms were investigated in detail. Both polymerization mechanisms have its own advantages and the researchers are generally interested in the development of new photoinitiating systems for both polymerizations. The reason behind the research for such developments lies on the fact that no photoinitiating system can be perfectly applied to all industrial applications.

There has been tremendous effort to develop photoinitiators with enhanced absorption characteristics, solubility, low odor, low migration, and non-yellowing properties. Specifically, the development of photoinitiators absorbing light in the near UV-visible light range of the electromagnetic spectra is a key challenge in the last decade due to the fulfillment of green chemistry demands.

Utilization of photochemistry to the synthetic polymer chemistry is not only based upon the photopolymerization methodologies, but also the use of photon energy for the triggering of various reactions. In such processes, the photo-inductions provide spatial and thermal control over the processes under mild conditions compare to the thermal modes. Recently, numbers of papers reported the use of photochemistry to induce the very well-known atom transfer radical polymerization and click chemistry reactions. Both processes require first oxidation state copper salts (CuCl or CuBr) and by photochemical reductions, it was demonstrated that one can generate Cu(I) starting from Cu(II) salts by using various photoinitiators. Thus, the necessity of preserving easily oxidizable Cu(I) species by cumbersome reaction conditions (i.e. inert atmosphere requirements, freeze-thaw pump cycles etc.) can be eliminated as a result of the stability of Cu(II) salts.

In this thesis, three different publications are presented, which are mainly based on the photo-induced processes for macromolecular syntheses. In the first part, the synthesis, characterization and initiation efficiency of a novel polymeric *Type II* photoinitiator, namely poly(ethylene oxide) dimethylammonium thioxanthone-methyl-carboxylate (PEO-NH⁺(CH₃)₂ TX-CH₂COO⁻) possessing both photochromophoric and hydrogen donating groups in the structure is demonstrated. In contrast to existing *Type II* photoinitiators, the present photoinitiator initiates free

radical polymerization by counter anion excitation even in the absence of added hydrogen donors. The photoinitiator can be applied to the polymerization of monomers soluble in organic solvents or water. Thus both hydrophobic and hydrophilic polymers can be easily obtained using this photoinitiator developed (Figure 1).

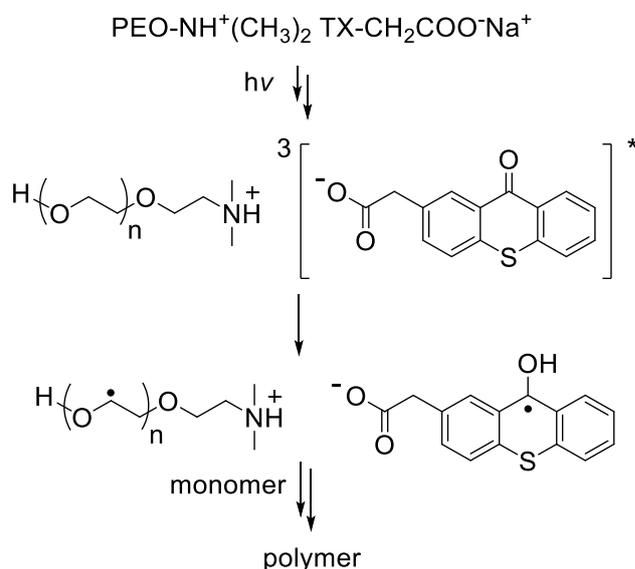


Figure 1 : Counter-anion sensitization approach to photo-initiated free radical polymerization.

In the second part of the thesis, a novel visible light sensitive photoinitiating system for the cationic polymerization of typical monomers, e.g. of oxiranes such as cyclohexene oxide, vinyl ethers such as iso-butyl vinyl ether, and other vinyl monomers such as *N*-vinylcarbazole, using fullerene derivatives is described. The cationic polymerization of these monomers was initiated at room temperature upon irradiation in the visible region ($\lambda_{inc} > 400$ nm) in bulk or chlorobenzene solutions with polystyrene-C₆₀ (PS-C₆₀) adduct or bare C₆₀, respectively in the presence of oxidizing salts such as silver hexafluorophosphate (AgPF₆) and diphenyliodonium hexafluorophosphate (Ph₂I⁺PF₆⁻). A feasible mechanism, as correlated with optical absorption measurements, free energy changes (ΔG), and proton scavenging studies, involves formation of exciplex by the absorption of light in the first step. Subsequent electron transfer from excited C₆₀ or PS-C₆₀ to oxidizing salt yields radical cations of the fullerene derivatives. Both radical cations and strong Bronsted acid derived by hydrogen abstraction initiate the cationic polymerization of variety of monomers.

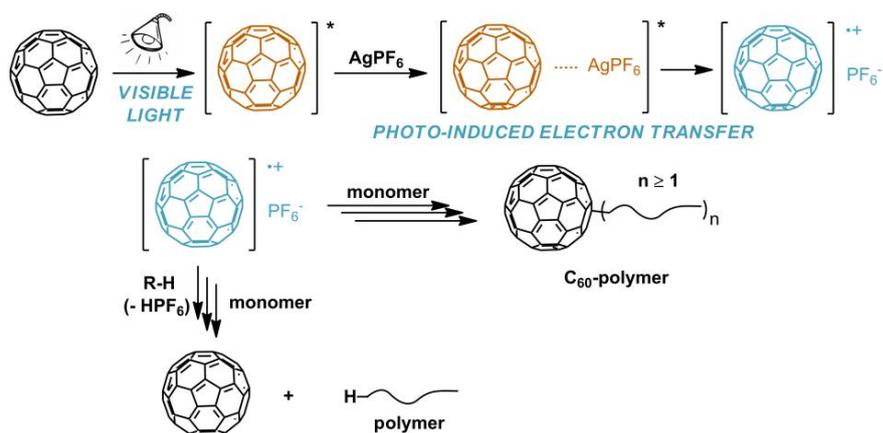


Figure 2 : Visible light-induced cationic polymerization using fullerenes.

Finally, development of a long wavelength photoinduced “Copper (I) Catalyzed Azide-Alkyne Cycloaddition (CuAAC)” click reaction based on the electron transfer reactions of excited states of polynuclear aromatic compounds such as anthracene, pyrene and phenothiazine and Cu(II), is presented. Although at different rates, all the sensitizers were shown to efficiently reduce Cu(II) to Cu(I) that catalyzes click reaction between model organic compounds. The applicability of the method for the construction of various macromolecular architectures including telechelic polymers and block copolymers was demonstrated. Spectroscopic and chromatographic investigations revealed that successful macromolecular syntheses were achieved.

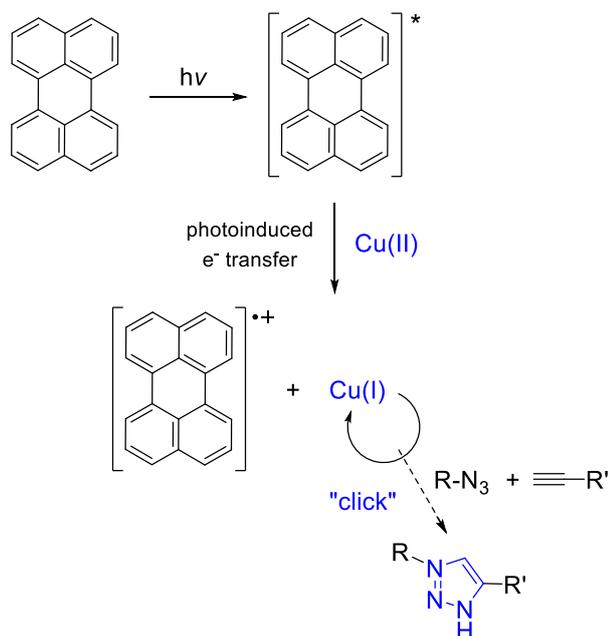


Figure 3 : Photoinduced copper(I)-catalyzed click chemistry by electron transfer process using polynuclear aromatic compounds.

MAKROMOLEKÜLER YAPILARIN FOTOKİMYASAL SENTEZİ

ÖZET

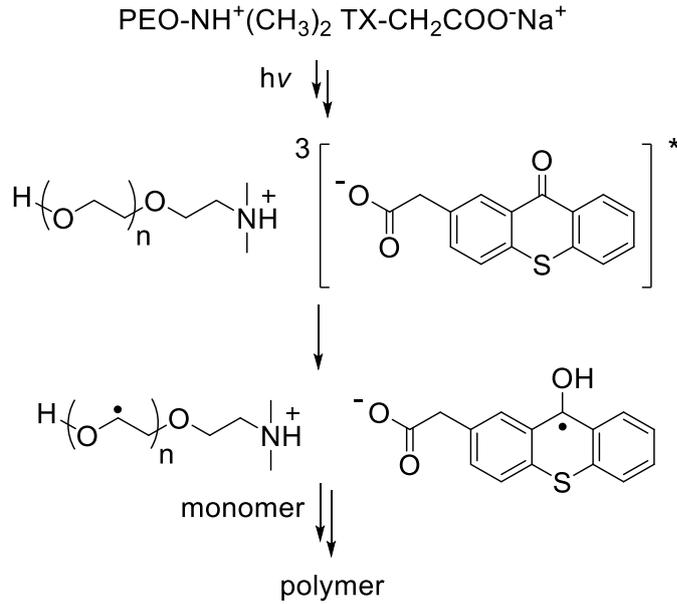
Işıkla başlatılmış tepkimeler akademik, ticari, finansal ve ekolojik bir çok beklentiyi karşıladığı için son dönemde yeniden ilgi odağı olmuştur. Polimer sentezi alanında, bu konu üzerinde yapılan çalışmalar daha çok fotopolimerizasyon üzerinde yoğunlaşmıştır. Fotopolimerizasyon, ışık enerjisi yardımı ile bir monomeri bir polimere dönüştüren sürecin adıdır. Monomerler tek başına uygun frekansa sahip ışığa maruz bırakıldıklarında dahi polimerlere dönüştürülebilir. Bununla birlikte bu süreç genellikle düşük verimle sonuçlanır ve etkinliği arttırmak için neredeyse her zaman bir katkı maddesi gereklidir. Bu katkı maddesi, ışığı absorbe ederek parçalan ve polimerizasyonun başlaması için gerekli olan reaktif türleri oluşturan fotobaşlatıcılardır. Hem serbest radikal hem de katyonik polimerizasyon türlerinin kendine özgü avantajları vardır. Araştırmacılar her iki polimerizasyon türüne yönelik fotobaşlatıcı sistenmlerin keşfi için çalışmalarını sürdürmektedir. Bu çalışmaların yapılıyor olmasının belki de en büyük sebebi, her endüstriyel uygulamaya uygun tek bir mükemmel fotobaşlatıcının var olmamasıdır.

Gelişmiş absorpsiyon karakterli, çözünebilir, kokusuz, film içerisinde göç etmeyen ve sarartma etkisine sahip olmayan özelliklere sahip fotobaşlatıcıların geliştirilmesine yönelik ciddi araştırmalar yapılmaktadır. Özellikle elektromanyetik spektrumun yakın UV-görünür bölgesinde absorbansa sahip fotobaşlatıcıların keşfi, çevre dostu beklentilerin karşılanabilmesi açısından büyük önem teşkil etmektedir.

Fotokimyanın polimer sentez bilimine olan uygulaması sadece yeni fotobaşlatıcıların keşfi ile sınırlı değildir. Özellikle ışık ile etkinleşen bazı tepkimelerin polimer bilimine olan uyarlamaları da oldukça hatırı sayılır bir önem arz etmektedir. Bu tepkime süreçleri, ısı ile gerçekleştirilen süreçlere göre üç boyutlu kontrol sağlaması ve ılımlı koşullarda gerçekleşebilmesi açısından avantaja sahiptir. Yakın zamanda yapılan çalışmalar, birinci yükseltgenme basamağındaki bakır tuzlarını (CuCl ya da CuBr) katalizör olarak kullanan “atom transfer radikal polimerizasyon” ve “çıt çıt” (click) kimyası tepkimelerinin, Cu(II) tuzu ve fotobaşlatıcılar yardımıyla gerçekleştirilebileceğini göstermiştir. Böylelikle hava varlığında kolaylıkla yükseltgenebilen Cu(I) tuzları yerine yüksek kararlılığa sahip Cu(II) tuzları kullanılabilmekte, ve Cu(I) tuzlarının etkilenmemesi için kullanılan ağır denetsel zorunlulukların önüne geçilerek deneylerin çok daha pratik koşullarda gerçekleştirilebildiği gösterilmiştir.

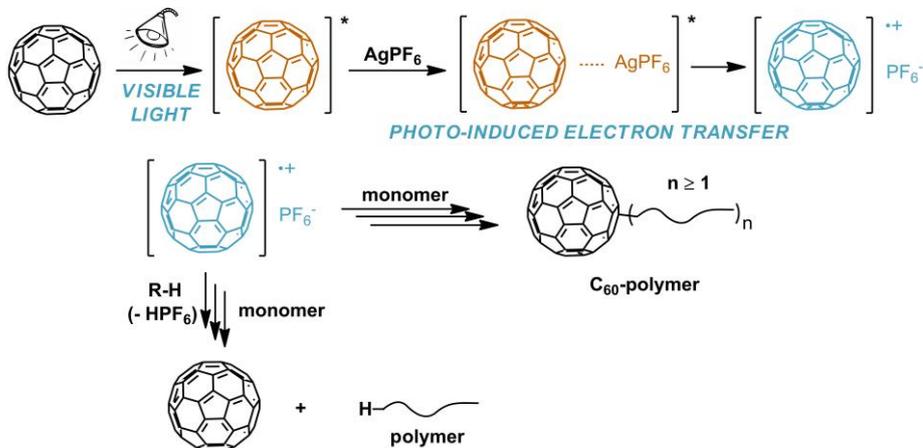
Bu tezde ışıkla başlatılmış süreçlerin makromoleküler sentezine olan uyarlamalarını konu alan üç farklı çalışma sunulmuştur. İlk kısımda, poli(etilen oksit) dietilamonyum tiyoksanton karboksilat (PEO-NH⁺(CH₃)₂ TX-CH₂COO⁻) isimli *II. Tip* polimöerik fotobaşlatıcının sentezi, karakterizasyonu ve başlatıcı etkinliği gösterilmiştir. Ticari olarak kullanılan fotobaşlatıcılardan farklı olarak, (PEO-NH⁺(CH₃)₂ TX-CH₂COO⁻) karşıt iyonun uyarılması ile ve herhangi bir ek yardımcı başlatıcıya ihtiyaç olmaksızın polimerizasyonu başlatabilmektedir. Başlatıcı hem suda hem de organik solventlerde çözünebilir bir çok monomere

uygulanabilmektedir. Dolayısı ile hem su-seven hem de sudan-korkan polimerlerin sentezine imkan vermektedir.



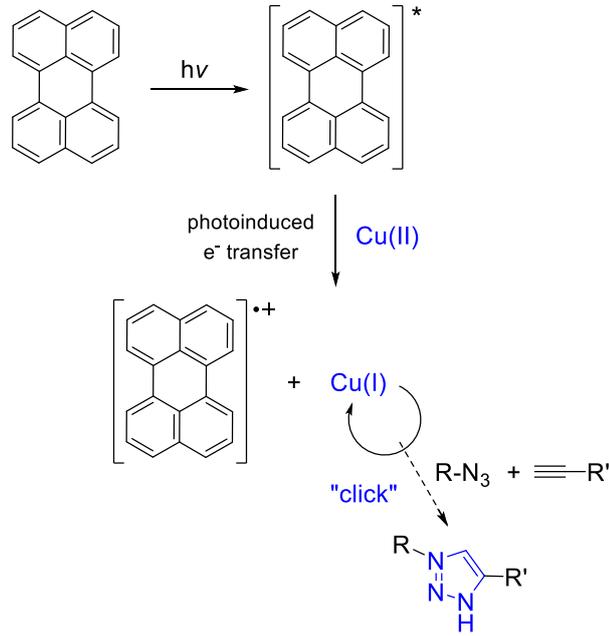
Şekil 1 : Karşıt anyon uyarılımı ile ışıkla başlatılmış serbest radikal polimerizasyonu.

İkinci kısımda sikloheksan oksit gibi oksiran monomerleri, izobutil vinil eter gibi vinil eter monomerlerini ve *N*-vinil karbazol gibi diğer vinil monomerlerini görünür bölgede katyonik yolla polimerleştirilen fulleren bazlı bir fotobaşlatıcı sisteminin kullanımı anlatılmıştır. Polimerizasyonlar oda sıcaklığında, görünür bölge ışığında ($\lambda_{inc} > 400 \text{ nm}$) solventsiz ortamda ya da klorobenzen solventi içerisinde ve polistiren- C_{60} (PS- C_{60}) ya da yalın C_{60} ile gümüş hekzaflorofosfat ya da difeniliyodonyum hekzaflorofosfat kullanılarak gerçekleştirilmiştir. Optik absorpsiyon ölçümleri, serbest enerji değişimi hesapları ve proton tutucu ortamında gerçekleştirilen deneylerin sonucu göstermektedir ki başlama mekanizması bir eksipleks oluşumu üzerinden gerçekleşmektedir. İkinci aşamada C_{60} ya da PS- C_{60} 'dan yükseltgeyici tuzlara bir elektron transferi gerçekleşmektedir ve sonuçta fulleren karbokatyonları oluşmaktadır. Hem radikal kation türlerinin hem de hidrojen koparma mekanizmaları sonucu oluşan protonların farklı türdeki monomerlerin polimerizasyonunu katyonik polimerizasyonu başlatabildiği gösterilmiştir.



Şekil 2 : Fullerenlerin kullanımıyla görünür bölge ışığında katyonik polimerizasyon.

Son bölümde, Cu(II) ile antrasen, piren fenotiyazin gibi aromatik bileşikler arasındaki elektron transferi mekanizmasına dayalı yüksek dalga boylu ışık ile başlatılmış “bakır katalizli azit-alkin halka katılması” (CuAAC) tepkimelerinin gerçekleştirilmesine ait çalışma sunulmuştur. Farklı hızlarla meydana geliyor olmalarına karşın, bahsi geçen üç aromatik bileşiğin de ışığa maruz bırakıldığı ortamlarda Cu(II) tuzlarını Cu(I) tuzlarına indirgeyerek “çıt çıt” tepkimelerini düşük molekül ağırlıklı organik bileşikler arasında başarıyla gerçekleştirebildiği gösterilmiştir. Kullanılan yöntemin yüksek molekül ağırlıklı polimerlerin sentezinde de kullanılabilir olduğunu göstermek için telekelik ve blok kopolimerler yine bu metotla sentezlenmiştir. Spektroskopik ve kromatografik incelemeler makromoleküler yapıların bu yöntemle başarı ile sentezlenebildiğini ortaya koymuştur (Şekil 3).



Şekil 3 : Çok merkezli aromatic bileşiklerin kullanımı ile ışıkla başlatılmış bakır(I) katalizli “çıt çıt” kimyası.

1. INTRODUCTION

Photo-induced processes is a well-known technique exploited in many technologically important areas. The application of photochemistry to the synthetic polymer science dates back to almost fifty years, although it recently gains higher priority as its advantages compare to other modes of syntheses has been noticed day by day. Most of the research on the utilization of photo-induced processes on polymer since is based on photopolymerization, which is the ideal process that transforms a monomer to a polymer by light assistance. photopolymerization has been the basis of numerous conventional applications in coatings, adhesives, inks, printing plates, optical waveguides, and microelectronics. Some other less traditional but interesting applications, including production of laser videodiscs, curing of acrylate dental fillings, and fabrication of 3D objects are also available. Many studies involving various photopolymerization processes have been continuously conducted in biomaterials for bones and tissue engineering, microchips, optical resins and recoding media, surface relief gratings, anisotropic materials, polymeric photo-optical control materials, clay and metal nanocomposites, photoresponsive polymers, liquid crystalline materials, interpenetrated networks, microlens, multilayers, surface modification, block and graft copolymerization, twophoton polymerization, spatially controlled polymerizations, topochemical polymerization, solid-state polymerization, living/ controlled polymerization, interfacial polymerization, mechanistically different concurrent polymerizations, pulsed laser polymerization, polymerizations in microheterogenous media, and so forth. Interest has also grown in identifying the reactive species involved in the polymerization process by laser flash photolysis, time-resolved fluorescence and phosphorescence, and electron spin resonance spectroscopy as well as monitoring the polymerization itself by different methods including real time IR spectroscopy, in-line NIR reflection spectroscopy, differential scanning calorimetry, in situ dielectric analysis, and recently developed optical pyrometry.

Both free radical and cationic photo-polymerization are known and their mechanisms were studied in detail. Both polymerization types have advantages and disadvantages over the other mode. For example, free-radical polymerizations are generally inhibited by air oxygen whereas cationic polymerizations are effected by moisture. Monomers polymerizable by radical mechanism include acrylates, methacrylates, substituted styrenes, unsaturated esters or urethanes and some vinyl monomers. Widely used cationically polymerizable monomers are oxiranes, vinyl ethers, some heterocyclic compounds and specific vinyl monomers.

There are numbers of photo-initiators available for free-radical polymerization. Generally, they are classified as *Type I* and *Type II* photoinitiators, which have different initiating mechanisms. *Type I* (or α -cleavage) initiators decompose upon irradiation at appropriate wavelengths and yield radicals responsible for initiation of polymerization. Examples of *Type I* initiators are benzoin and derivatives, benzil ketals, acetophenones and acylphosphine oxides. *Type II* photoinitiators are excited to their triplet states upon light exposure and abstract hydrogen from a co-initiator (or hydrogen donor) to produce the radicals, which initiate polymerization. Notably, ketyl radicals formed on the initiator skeleton do not initiate polymerization due to the steric hindrance and the delocalization of the single electron (Figure 1.1).

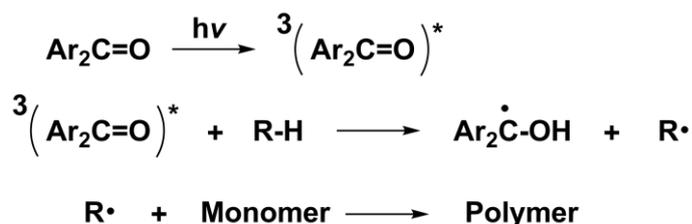
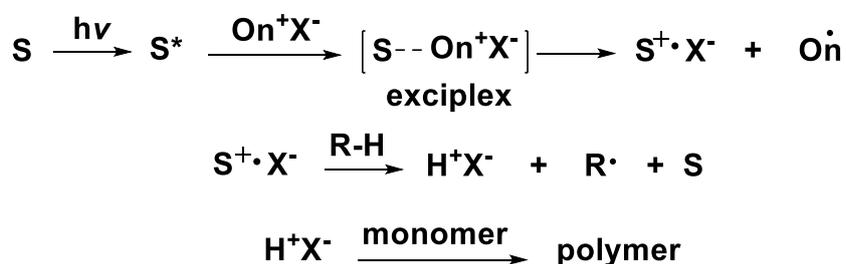


Figure 1.1 : Photoinitiated polymerization using *Type II* initiators.

The most widely used *Type II* initiators are camphorquinone, benzophenones and thioxanthone derivatives. Examples of co-initiators include amines, ethers, thiols and alcohols. Because of the bimolecular radical generation process, they are generally slower than *Type I* photoinitiators, which form radicals unimolecularly.

As cationic photo-polymerization is not affected by air, no complex precautions are need to be taken during industrial production processes. However, cationic polymerization suffers from the availability of limited number of photoinitiators especially in the low energy region of the spectrum. The well-known and most widely used examples of cationic photoinitiators, are diphenyliodonium and

triphenylsulfonium, *N*-alkoxy pyridinium salts and phosphonium salts with UV sensitivity. For the utilization of these photoinitiators in the long wavelength demanding applications, three modes of indirect activation are proposed. These include (a) oxidation of free radicals by oxidants (also called as free radical promoted cationic polymerization), (b) formation of charge transfer complexes, and (c) the use of photosensitizers in conjunction with onium salts. Among these, photosensitizers/onium salt combinations offer unique initiating systems involving an electron transfer from the excited state photosensitizer to the onium salts to yield Bronsted acid, which initiates cationic polymerization of appropriate monomers.^{4b} The suggested mechanism is shown in Figure 1.2.



S: Photosensitizer On⁺X⁻: onium salt R-H: Hydrogen donor

Figure 1.2 : Photosensitized electron transfer mechanism of cationic polymerization.

The contribution of photochemistry to the synthetic polymer science is not limited to the photopolymerization processes. There are various reactions induced by light, which are utilized to the polymer chemistry, recently. Atom transfer radical polymerization and copper catalyzed azide-alkyne cycloaddition reactions are the most-widely used techniques in synthetic polymer chemistry in the last decade. Both reactions need Cu(I) catalysis and require some experimental precautions to be taken due to the oxidizable nature of the catalyst. Thus, *in-situ* generation of Cu(I) species from the Cu(II) compounds became a popular approach to handle such reactions. Due to the chemical stability of the Cu(II) compounds, the reactions could be realized in much simple experimental conditions. In order to reduce Cu(II) in the reaction media, many approaches were proposed. Use of reducing agents such as hydrazine, phenol, ascorbic acid were all shown to operate successfully. Recently, use of photochemistry become another popular strategy to *in-situ* generate Cu(I) catalyst in the reaction media. Direct photochemical reduction of metal ions such as gold, silver and copper were all shown to be operative in appropriate wavelengths.

However, in the absence of an additional photo-initiator, such direct photolysis suffer from long irradiation times. If a photo-initiator is added into the system, radicals are formed upon light exposure, which reduce Cu(II) to generate the Cu(I) catalyst.

1.1 Purpose of the Thesis

The objective of the thesis is to demonstrate the application of induced photon energy for the synthesis of various macromolecular architecture. Different photo-initiating systems for both free-radical and cationic polymerizations are developed and presented in this thesis. In addition, another photo-initiated strategy for the induction of click chemistry between several clickable compounds are demonstrated. During this thesis, chromatographic (GPC) and spectroscopic ($^1\text{H-NMR}$, UV, FT-IR) analyses are performed. This thesis is organized in such that each chapter has its own introduction, experimental, results and discussion, and list of references.

Chapter 2 discusses overall background information about the development of a poly(ethylene oxide)-based free radical photo-initiator, which is operative in the UV-vis range of the spectrum and applicable to both hydrophilic and hydrophobic monomers.

Chapter 3 shows the utilization of fullerene derivatives as sensitizers on the visible light induced cationic polymerization of various monomers.

Chapter 4 demonstrates the use of polynuclear aromatic compounds for the photo-induced reduction of Cu(II) salts into Cu(I) species, which catalyses the CuAAC reactions between both small molecular weight organic compounds and macromolecular structures.

Finally, concluding remarks are summarized in Chapter 4 along with recommendations for further work.

2. COUNTER-ANION SENSITIZATION APPROACH TO PHOTO-INITIATED FREE RADICAL POLYMERIZATION¹

Photopolymerization is a technique that finds practical applications in a wide range of diverse fields such as coatings, inks, adhesives high-tech domains, optoelectronics, laser imaging, stereolithography, and nanotechnology.[1-7] Photopolymerization processes present several important advantages compare to the corresponding thermal reactions. These advantages include low energy requirement, spatial and on and off control and fulfillment of green chemistry demands since polymerization processes may operate without solvent. Photopolymerizations are usually applied to all chain processes, namely free radical, cationic and anionic polymerizations, and also step-growth polycondensation.[8-13] However, most of the applications are based on the free radical mode due to the less purity demand, applicability to a wide range of formulations based on (meth)acrylates, unsaturated polyesters, and acrylated polyurethanes and the availability of photoinitiators having spectral sensitivity in a broad wavelength range.[13-28] Despite its superior status of free radical polymerization, there has been tremendous effort to develop free radical photoinitiators with enhanced absorption characteristics, solubility, low odor, low-migration and non-yellowing properties.[1-3] If the photon energy is absorbed by an added initiator, these photosensitive substances undergo homolytic bond rupture or hydrogen abstraction reactions forming radicals, which may initiate the polymerization.[4, 5] In addition, onium salts belonging iodonium,[6, 7] sulphonium,[8] ammonium,[9] alkoxy pyridium[10-12] and phosphonium[13] families also represent a class of free radical photoinitiators. Under favorable conditions, these salts can initiate the polymerization by the photoexcitation of the cationic part.[14] The selection of a photoinitiator is undoubtedly of great importance and depends on the chemical constitution of the particular formulation used.

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Depending on the absorption characteristics and specific application involved, either cleavage and hydrogen abstraction types of photoinitiators or their appropriate combinations can be used.[15-29] In some cases, these photoinitiators are incorporated into polymer structures. In this way, the macromolecules having covalently bonded photoinitiator groups overcome the problems associated with high volatility and high migration often observed with low-molar-mass photoinitiators.[30, 31] Previously, we reported that 1,3-dipolar azide-alkyne [3 + 2] “click chemistry”[32] and Diels–Alder [4 + 2] cycloaddition reactions[33, 34] could be used for obtaining macrophotoinitiators containing thioxanthone photoinitiator moieties as side chains and terminal groups. The resulting polymeric photoinitiators were shown to efficiently initiate the free-radical polymerization of mono and multifunctional monomers via hydrogen abstraction mechanism. We now report that structurally similar polymeric photoinitiators can be prepared by counter ion incorporation of the light sensitive group, namely thioxanthone (TX) into poly(ethylene oxide) (PEO) that it provides a novel means of photoinitiation of free radical polymerization by counter anion sensitization.

For the simple acid-base salt forming reaction to be applied, the thioxanthone group must be equipped with carboxylic acid functionality. The carboxylic group was attached to TX using 2-phenylacetic acid as the functional substrate in the synthesis of the photoinitiator. The other component of the salt forming process, α -amino functional PEO, was prepared by utilizing functional initiator approach in the ring opening anionic polymerization of ethylene oxide (EO). Starting with dimethylethanol amine and adding potassium naphthalene to initiate the EO polymerization readily afforded the mono aminofunctional PEO. Subsequent simple acid-base reaction of the amine chain-end with the thioxanthone carboxylic acid (TX-CH₂COOH) led to the formation of the polymeric salt with ionically attached thioxanthone moieties (Figure 2.1) in high yields (ca. 94%) as determined by NMR analysis.

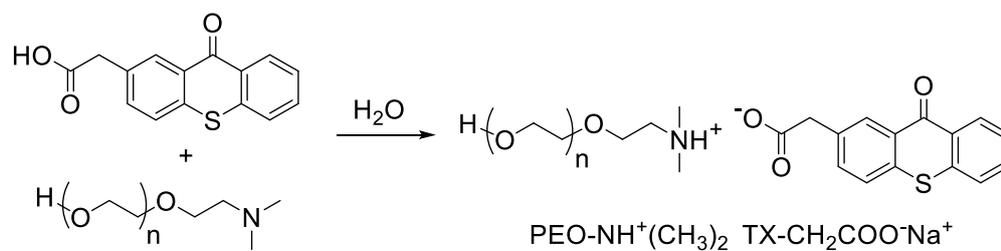


Figure 2.1 : Synthesis of PEO-NH⁺(Me)₂ TX-CH₂COO⁻.

The salt formation process was followed by ¹H-NMR analysis (Figure 2.2). The presence of the aromatic peaks between 7.09-8.60 ppm evidences the incorporation of the thioxanthone chromophore at the chain end. Moreover, after quaternization, the methyl protons of the amine functionality completely shift to lower frequencies (from 1.82 ppm to 2.60 ppm) indicating quantitative functionalization.

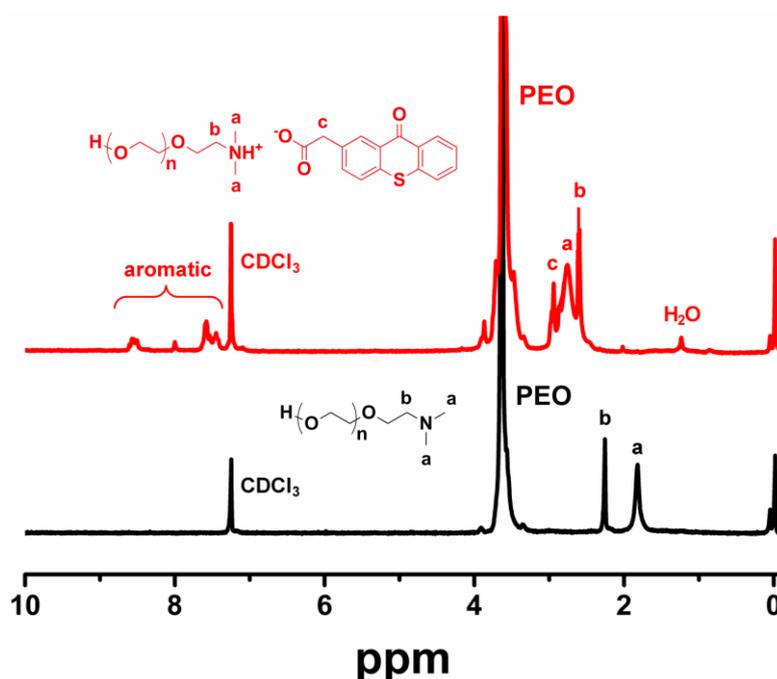


Figure 2.2 : ¹H NMR Spectra of α -dimethylamino functional PEO (black) and PEO-NH⁺(Me)₂ TX-CH₂COO⁻ (red) in CH₂Cl₂.

The GPC, ¹H-NMR and UV analyses revealed that molecular weight and molecular weight distribution of the polymer did not significantly change during the process (Table 2.1).

Table 2.1 : The molecular weight characteristics of the polymers at different stages.

Polymers	$M_{n,NMR}$ ($\text{g}\cdot\text{mol}^{-1}$)	$M_{n,UV}^a$ ($\text{g}\cdot\text{mol}^{-1}$)	$M_{n,GPC}^b$ ($\text{g}\cdot\text{mol}^{-1}$)	M_w/M_n^b
PEO-N(Me) ₂	1005	-	1025	1.07
PEO-NH ⁺ (Me) ₂ TX-CH ₂ COO ⁻	1150	1270	1280	1.03

^a Estimated by using $\lambda_{\text{max}}(\epsilon) = 380 (4925) \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ of TX-CH₂COOH

^b Determined by gel permeation chromatography using polystyrene standards.

Absorption characteristics of the polymeric photoinitiator were examined by UV spectroscopy. Figure 2.3 shows the UV spectra of PEO-NH⁺(Me)₂ TX-CH₂COO⁻ and the parent compound, TX-CH₂COOH. It can be seen that both of the compounds exhibit similar absorption characteristics in the UV-vis range (300–400 nm). Interestingly, an unexpected absorption between 470 and 630 nm is observed for TXCH₂COOH molecule.

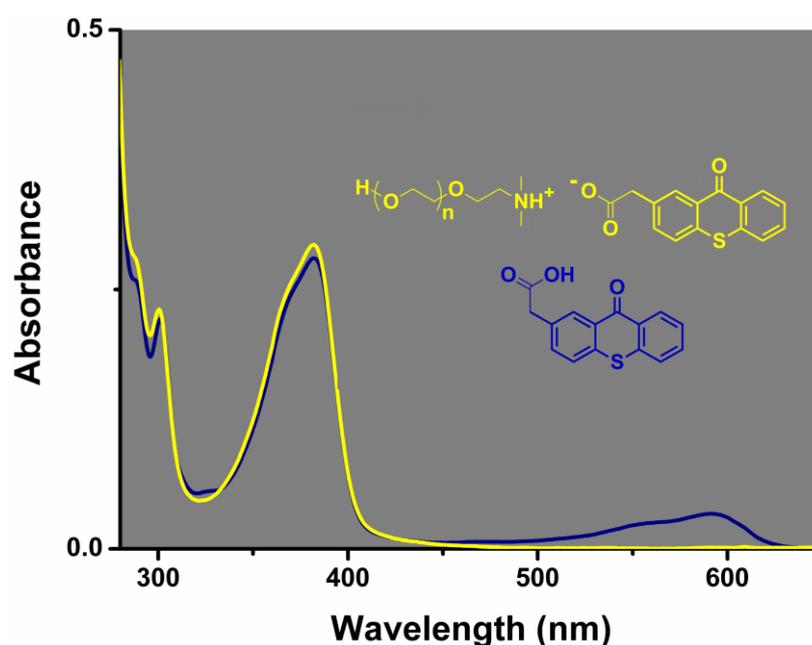


Figure 2.3 : Comparison of the UV-vis absorption spectra of PEO-NH⁺(Me)₂ TX-CH₂COO⁻ with TX-CH₂COOH in CH₂Cl₂ at equal concentrations ($6.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$)

On the other hand, TX-CH₂COO⁻Na⁺ has a very similar absorption signature with that of PEO-NH⁺(Me)₂ TX-CH₂COO⁻ (Figure 2.4). This observation demonstrates that the visible range absorption is clearly due to the hydrogen bonding. The sodium derivative is not susceptible to hydrogen bonding, eliminating the possibility of visible range absorption.

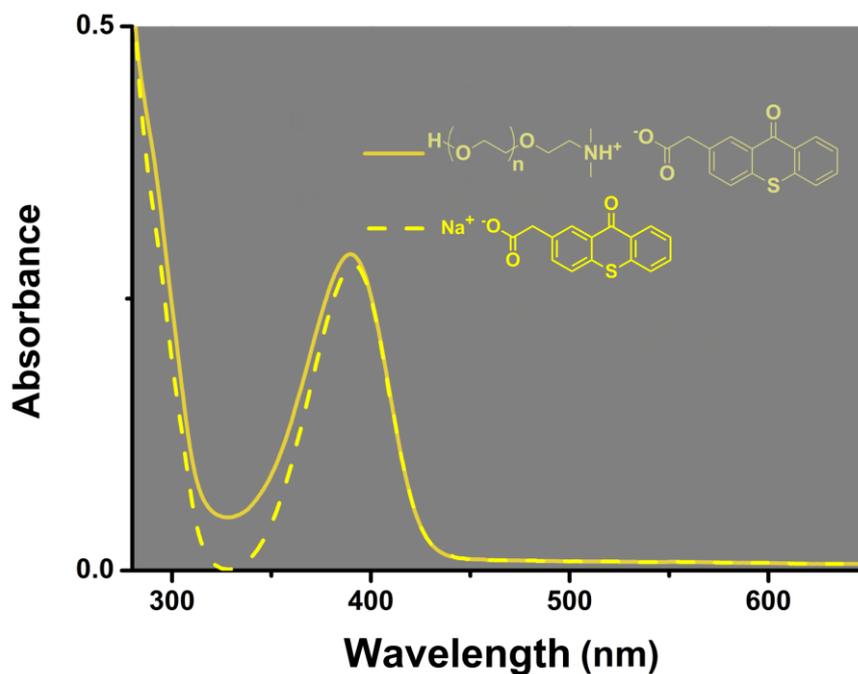


Figure 2.4 : Comparison of the UV-vis absorption spectra of PEO-NH⁺(Me)₂ TX-CH₂COO⁻ with TX-CH₂COO⁻ Na⁺ in water at equal concentrations ($6.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$).

To further confirm the contribution of hydrogen bonding to the absorption characteristics of TX-CH₂COOH, the visible absorption spectra in different solvents are taken (Figure 2.5b). As expected, increase in the dielectric constant of the solvents results in the destruction of hydrogen bonding, which eventually changes the absorption regime of the chromophore. The affect is known as solvatochromism, and images of the different solutions of TX-CH₂COOH are shown in Figure 2.5a.

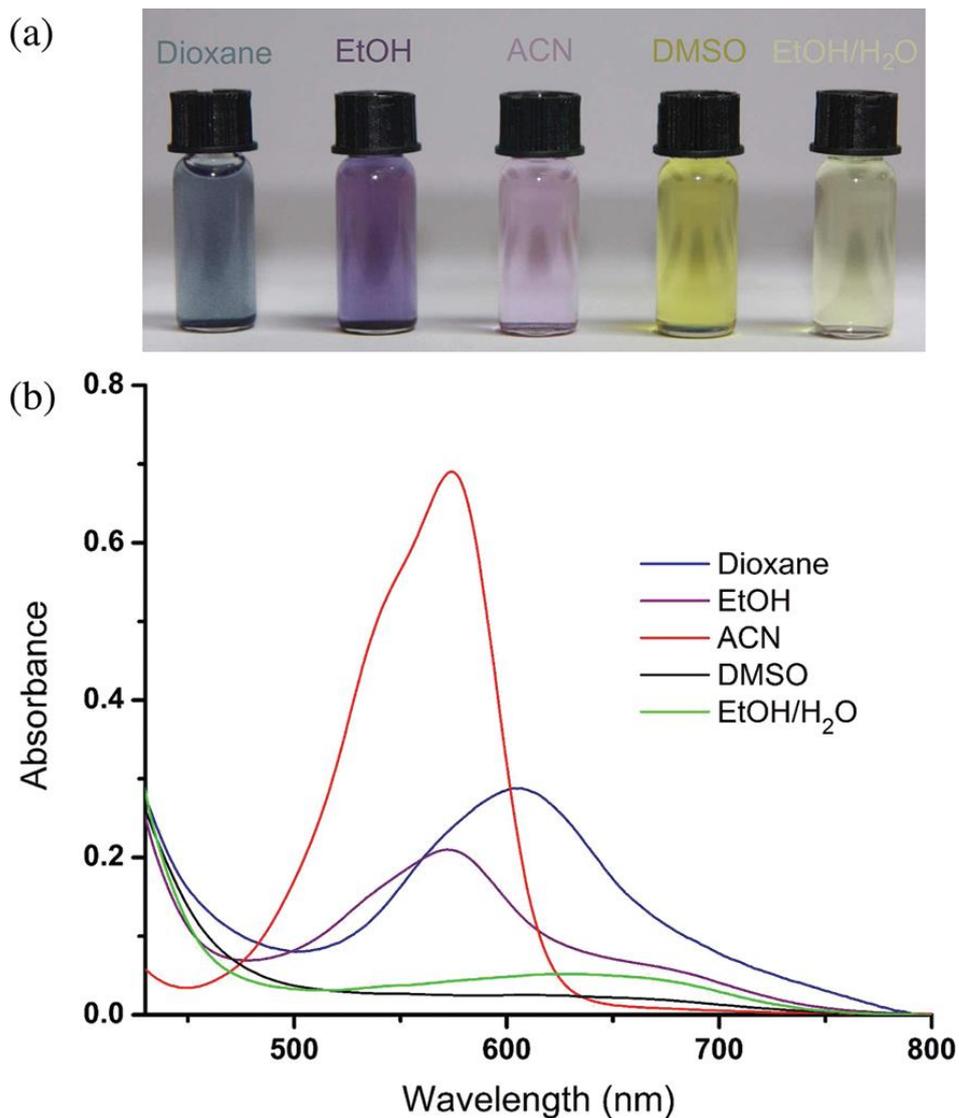


Figure 2.5 : Images of TX-CH₂COOH solutions (a) and their respective visible absorption spectra (b) in various solvents.

The choice of PEO as the polymer support enables us to tailor readily the solubility properties of the photoinitiator, while providing hydrogen donating sites in the structure.[35] The one component nature of the photoinitiator was evidenced by photobleaching experiments (Figure 2.6a). PEO-NH⁺(Me)₂ TX-CH₂COO⁻ rapidly decomposes itself upon irradiation because it contains hydrogen donating ether groups in the structure. Interestingly, TX-CH₂COOH also undergoes similar photodecomposition (Figure 2.6b).[23] Expectedly, the absorption band in the visible range also decreases by irradiation as a result of loss of hydrogen bonding by the abstraction of acidic hydrogen.

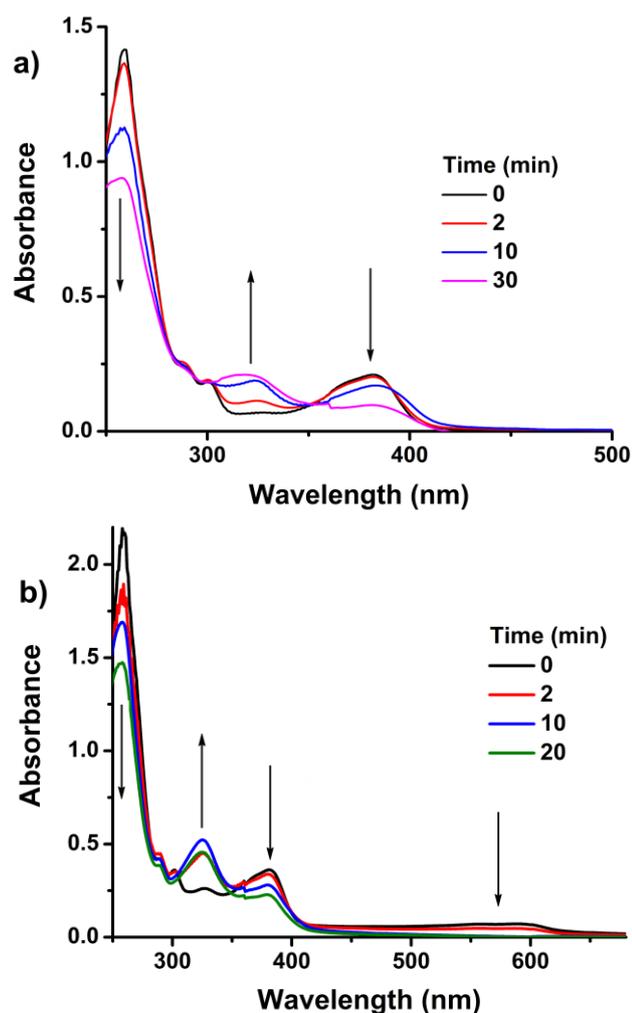


Figure 2.6 : Photobleaching studies of PEO-NH⁺(Me)₂ TX-CH₂COO⁻ and TX-CH₂COOH in CH₂Cl₂ with identical initial concentrations (4.0×10^{-5} mol·L⁻¹) at 350 nm.

In order to show the potential value of the initiating system in visible light applications, similar photobleaching (Figure 2.7) and polymerization experiments have been conducted at 430-490 nm. Although at lower rate, upon irradiation PEO-NH⁺(Me)₂ TX-CH₂COO⁻ efficiently yields radicals and initiates the polymerization. In this case, the salt is excited through its tail absorption at visible range.

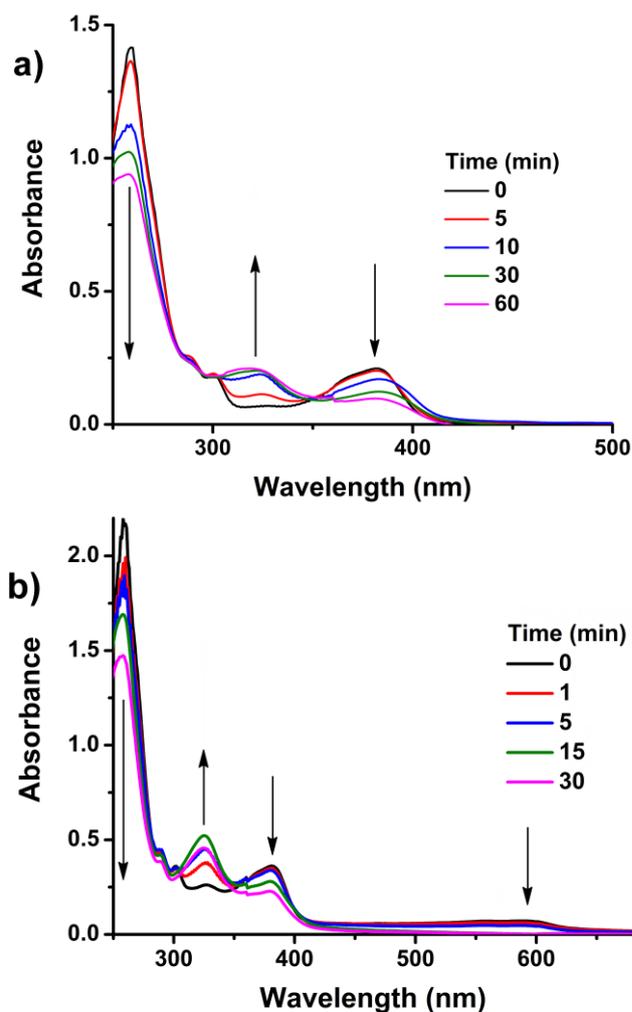


Figure 2.7 : Photobleaching studies of PEO-NH⁺(Me)₂ TXCH₂COO⁻ and TX-CH₂COOH with identical initial concentrations ($4.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) at 430-490 nm.

Polymerization experiments confirm the crucial role of PEO segment (Table 2.2 and 2.3). Thus, comparative photopolymerization studies of methyl methacrylate (MMA) using PEO-NH⁺(Me)₂ TX-CH₂COO⁻ itself and combination of bare TX or camphorquinone (CQ) with PEO with the same molecular weight as initiators were performed (Table 2.2). The conversion of the polymerization initiated with the salt was higher than that with the combined initiating system involving TX or CQ. Furthermore, irradiations using styrene failed to produce any precipitable polymer because of quenching of excited triplet TX moiety with the monomer.

Table 2.2 : Photoinitiated free radical polymerization of monomers^a soluble in organic solvents.

Monomer	Initiator	λ (nm)	Conv. (%) ^b	M_n^c (g·mol ⁻¹)	PDI ^c
MMA ^d	PEO-NH ⁺ (Me) ₂ TX-CH ₂ COO ⁻	350	12.1	19660	2.01
MMA ^d	PEO-NH ⁺ (Me) ₂ TX-CH ₂ COO ⁻	430-490	8.3	9500	4.75
MMA ^d	CQ / PEO	350	9.9	46980	1.49
MMA ^d	CQ / PEO	430-490	7.0	9500	4.25
MMA ^d	TX / PEO	350	7.3	15640	2.16
MMA ^d	TX / PEO	430-490	< 1	-	-
MMA ^e	PEO-NH ⁺ (Me) ₂ TX-CH ₂ COO ⁻	350	28.8	23290	2.32
MMA ^e	PEO-NH ⁺ (Me) ₂ TX-CH ₂ COO ⁻	430-490	13.4	17000	1.18
St ^d	PEO-NH ⁺ (Me) ₂ TX-CH ₂ COO ⁻	350	0	-	-
St ^d	PEO-NH ⁺ (Me) ₂ TX-CH ₂ COO ⁻	430-490	0	-	-

^a [Monomer]/[PEO-NH⁺(Me)₂ TX-CH₂COO⁻] = 200/1, Irradiation time = 2h.

^b Determined gravimetrically

^c Determined by gel permeation chromatography using polystyrene standards where THF is the eluent.

^d In CH₂Cl₂, ^e In bulk

The hydrophilic nature of cationic part of the photoinitiator facilitates solubility in water and aqueous polymerizations can be performed (Table 3). Indeed, water soluble monomers such as acrylamide (AAm), N-vinyl pyrrolidone (NVP) and hydroxyethyl methacrylate (HEMA) were efficiently polymerized by PEO-NH⁺(Me)₂ TX-CH₂COO⁻ with high conversion. Notably, insoluble polymers were obtained with HEMA. This behavior may be explained by the possibility of generation of the additional initiating radicals through hydrogen abstraction reaction from the hydroxymethylene group present in the monomer since alcohols are known to be good hydrogen donors for triplet aromatic carbonyl compounds.

Table 2.3 : Photoinitiated free radical polymerization of water soluble monomers in water using PEO-NH⁺(Me)₂ TX-CH₂COO^{-a} is initiator at different irradiation wavelengths.

Monomer	λ (nm)	Conv. (%) ^b	M_n^c (g·mol ⁻¹)	PDI ^c
AAm	350	93.4	32790	4.80
AAm	430-490	85.7	ND ^d	ND ^d
NVP	350	26.1	ND ^d	ND ^d
NVP	430-490	14	ND ^d	ND ^d
HEMA	350	48	∞^d	-
HEMA	430-490	27.7	∞^d	-

^a [Monomer]/[PEO-NH⁺(Me)₂ TX-CH₂COO⁻] = 200/1, Irradiation time = 2h.

^b Determined gravimetrically

^c Determined by gel permeation chromatography using PEO standards with water as eluent

^d The total exclusion limit of the GPC column was exceeded

The proposed polymerization mechanism is demonstrated in Figure 2.8.

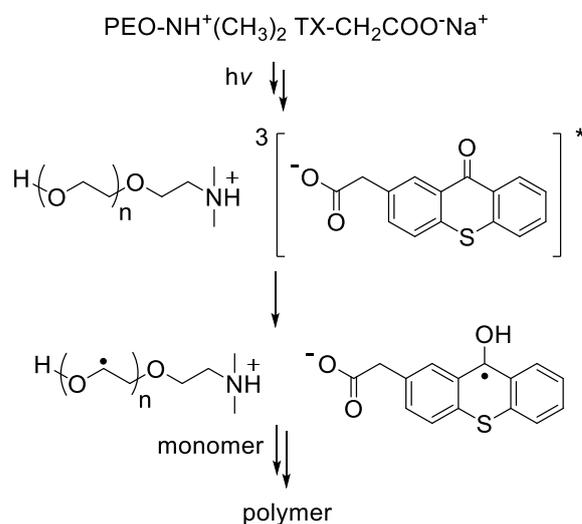


Figure 2.8 : Photoinitiated free radical polymerization using PEO-NH⁺(Me)₂ TX-CH₂COO⁻ as initiator.

As a very simple demonstration of the possible value of PEO-NH⁺(Me)₂ TX-CH₂COO⁻ in UV curing applications, several experiments were performed using

multifunctional monomers. All the formulations tested underwent rapid cross-linking upon irradiations for few minutes (Table 2.4).

Table 2.4 : The photoinduced gelation time and gel contents of several formulations^a consisting of PEO-NH⁺(Me)₂ TX-CH₂COO⁻ and multifunctional monomers.

Monomers	λ (nm)	Gelation Time (s)	Gel Content (%)
TMPTA ^b	350	35	97
TMPTA ^b	430-490	50	91
PEG-diacrylate ^c	350	40	92
PEG-diacrylate ^c	430-490	60	81
AAM+BAAM ^c	350	90	97
AAM+BAAM ^c	430-490	145	97

^a [Monomer]/[PEO-NH⁺(CH₃)₂ TX-CH₂COO⁻] = 200/1, ^b In CH₂Cl₂, ^c In water, [AAM]/[BisAAM] = 100/1. ^d Determined gravimetrically after the gels are washed with the reaction solvents and dried.

The efficiency of the in the photocuring of formulations containing multifunctional monomers was also studied. In Figure 2.9, photo-DSC exotherm referring to the polymerization of Trimethylolpropane triacrylate (TMPTA) initiated by PEO-NH⁺(Me)₂ TX-CH₂COO⁻ under polychromatic light is shown. Inset, the plot of the conversion vs irradiation time derived from the same polymerization system is given. The shape of this “conversion time” kinetics curve indicates two stages: a rapid first stage followed by a slow stage. At the second stage, gelation and vitrification of the polymerizing trifunctional acrylate most likely render the diffusion of the components more difficult.

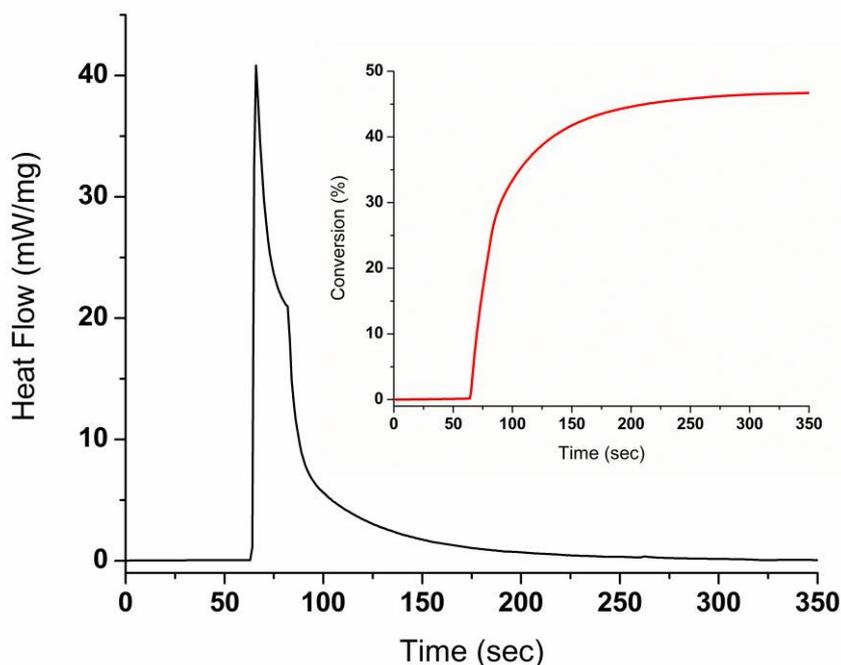


Figure 2.9 : Photo-DSC profile for polymerization of TMPTA in the presence of PEO-NH⁺(Me)₂TX-CH₂ (27%) macrophotoinitiator, cured at 30°C by UV light ($\lambda=320\text{-}500\text{ nm}$) with an intensity of 180 mW/cm². Inset: Conversion vs. time curves derived from the heat flow data.

In summary, we established an easy and efficient method to form a polymeric *Type II* photoinitiator possessing both chromophoric and hydrogen donating sites in the structure. This novel photoinitiator initiates the free radical polymerization by hydrogen abstraction of excited triplet TX moiety from PEO segment. Best to our knowledge, this is the first description of a method that initiates free radical polymerization by counter anion excitation. The concept described here will further be expanded to the newly emerging polymeric materials such as polymeric ionic liquids.[36-38] We anticipate that photolysis of such polyelectrolytes equipped with photosensitive anions will provide possibility to regulate ionic liquid properties and design photoinitiating systems for environmental friendly UV curing applications due its polymeric nature eliminating problems associated with volatility and migration.

2.1 Experimental

2.1.1 Materials

Thiosalicylic acid (97%, Sigma-Aldrich), 2-phenylacetic acid (99%, Merck) and sodium hydroxide (NaOH, Carlos Erba) were used without further purification. Methyl methacrylate (MMA, $\geq 99\%$, Aldrich) and styrene (St, $\geq 99\%$, Merck) were passed through basic alumina column before use to remove the inhibitor. 2-Dimethylaminoethanol (99.5%, Aldrich), *N*-vinyl pyrrolidone (NVP, 99%, Aldrich) and hydroxyethyl methacrylate (HEMA, 98%, Aldrich), were distilled under vacuum before use. Acrylamide (AAm, 97%, Aldrich) and *N, N'*-methylenebisacrylamide (BAAm, 99%, Aldrich) were crystallized from methanol prior to use. Dichloromethane (CH_2Cl_2 , 98%, Sigma-Aldrich) was distilled over P_2O_5 and collected in molecular sieves prior to use. Trimethylolpropane triacrylate (TMPTA, 95%, Aldrich) were passed through short column of basic alumina prior to use. Poly(ethylene glycol) dimethyl ether (PEG, $M_n \sim 1000$, Aldrich) were used as received. All solvents were used as received without further purification.

2.1.2 Instrumentation

$^1\text{H-NMR}$ measurements were recorded in CDCl_3 with $\text{Si}(\text{CH}_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One-B spectrometer. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Molecular weights were determined by gel permeation chromatography (GPC) instrument, Viscotek GPCmax Autosampler system, consisting of a pump, three ViscoGEL GPC columns (G2000HHR, G3000HHR and G4000HHR), a Viscotek differential refractive index (RI) detector with a THF flow rate of 1.0 mL min^{-1} at 30°C . The detector was calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software.

2.1.3 Photopolymerizations

Appropriate solutions of the monomer and initiator were irradiated with a light source emitting light nominally at 350 nm with a light intensity of 3.0 mWcm^{-2} and a dental LED lamp (Bluephase, supplied by Ivoclar Vivadent company) with a wavelength range of 430–490 nm and maximum light performance of 1110 mWcm^{-2}

±10%. Polymers were obtained after precipitation in convenient non-solvents and drying under vacuum. Conversions were calculated for all samples gravimetrically.

2.1.4 Photocalorimetry (Photo-DSC)

The photo-differential scanning calorimetry (photo-DSC) measurements were carried out by means of a modified Perkin-Elmer Diamond DSC equipped with a high pressure mercury arc lamp (320–500 nm). A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 53 mW cm⁻² by a UV radiometer capable of broad UV range coverage. The mass of the sample was 3 mg, and the measurements were carried out in an isothermal mode at 30 °C under a nitrogen flow of 20 mL min⁻¹. The reaction heat liberated in the polymerization was directly proportional to the number of acrylate groups reacted in the system. By integrating the area under the exothermic peak, the conversion of the acrylate groups (C) or the extent of the reaction was determined according to eqn (1):

$$C = \Delta H_t / \Delta H_{0\text{theory}} \quad (2.1)$$

where ΔH_t is the reaction heat evolved at time t and $\Delta H_{0\text{theory}}$ is the theoretical heat for complete conversion. $\Delta H_{0\text{theory}} = 86 \text{ kJ mol}^{-1}$ for an acrylic double bond.

The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by eqn (2):

$$R_p = dC/dt = (dH/dt) / \Delta H_{0\text{theory}} \quad (2.2)$$

Synthesis of α -dimethylamino functionalized polyethylene oxide (PEO-N(CH₃)₂)

Synthesis of α -(dimethylamino)polyethylene oxide have been performed as described previously.[39]

2.1.5 Synthesis of thioxanthone-carboxylic acid (TX-CH₂COOH)

Thiosalicylic acid (0.2 g, 1.3 mmol) was slowly added to concentrated sulfuric acid (10 mL), and the mixture was stirred for 5 min to ensure through mixing. 2-phenylacetic acid (0.85 g, 3.9 mmol) was added slowly to the stirred mixture over a period of 30 min. After the addition, the reaction mixture was stirred at 75 °C for 2 hours and later it was left to stand at room temperature overnight. Afterwards, the resulting mixture was poured carefully with stirring into a 10-fold excess of boiling water, and it was then boiled further for 5 min. The solution was cooled and filtered. The residue was recrystallized from dioxane/water mixture to give the pure blue

solid. Yield: 83%; $^1\text{H-NMR}$ (250 MHz, CDCl_3 , 25 °C, TMS): δ = 8.59–7.50 (m, 7H, aromatic), 3.97 (s, 2H, $-\text{CH}_2\text{-COO}$).

2.1.6 Synthesis of $\text{PEO-NH}^+(\text{Me})_2 \text{TX-CH}_2\text{COO}^-$

$\text{PEO-N}(\text{Me})_2$ (1.0 g, 1.0 mmol) was dissolved in 20 mL water and heated to 60 °C. Next, $\text{TX-CH}_2\text{COOH}$ (0.41 g, 1.5 mmol) was slowly added to the solution and the reaction mixture was allowed to stir for overnight. In the following step, the reaction mixture was cooled and filtrated to remove the unreacted TX-COOH . Then, water was evaporated using a rotary evaporator. The polymer was further dissolved in THF and precipitated into diethyl ether to give pale yellow $\text{PEO-NH}(\text{Me})_2^+ \text{TX-COO}^-$. Yield: 94 %; $^1\text{H-NMR}$ (250 MHz, CDCl_3 , 25°C, TMS): δ = 8.60–7.44 (m, 7H, aromatic), 3.62 (s, PEO chain), 2.86 (s, 2H, $-\text{CH}_2\text{-COO-}$), 2.76 (s, 6H, $-\text{N}(\text{CH}_3)_2$), 2.60 (s, 2H, $-\text{CH}_2\text{-N}$).

2.1.7 Synthesis of sodium thioxanthone-carboxylate ($\text{TX-CH}_2\text{COO}^- \text{Na}^+$)

$\text{TX-CH}_2\text{COOH}$ (0.5 g, 1.8 mmol) was added into 25 mL of distilled water. Aqueous solution containing NaOH (0.06 g, 1.5 mmol) was added to the suspension which was refluxed for overnight through mixing. The reaction mixture is cooled and filtrated to remove the unreacted $\text{TX-CH}_2\text{COOH}$. The water is evaporated to yield the yellow $\text{TX-CH}_2\text{COO}^- \text{Na}^+$ crystals. Yield: 96 %; $^1\text{H-NMR}$ (250 MHz, D_2O , 25°C, TMS): δ = 7.96–7.03 (m, 7H, aromatic), 3.45 (s, 2H, $-\text{CH}_2\text{-COO}^- \text{Na}^+$).

3. VISIBLE LIGHT-INDUCED CATIONIC POLYMERIZATION USING FULLERENES¹

Solar energy is the basis of all natural chemistry. In nature, a variety of electron transfer reactions such as photosynthesis are promoted by visible light.[40, 41] Artificially, many organic reactions are also driven by solar energy affording important advantages meeting the actual objectives of green chemistry.[42-46] The most common organic and polymeric compounds are transparent in the visible region (400–800 nm), which accounts for about 43% of the incoming solar spectrum. As a result, there has been great interest in developing soluble and processable organic and polymer based catalysts absorbing efficiently in the visible region of the spectrum.[47-52]

Photoinitiated polymerization is a well-known technique exploited in many industrially important areas.[1] Both free radical and cationic polymerizations have been used, and the mechanisms of initiation have been studied in detail.[7, 23, 53-60] The free radical mode is in more advanced state due to not only its applicability to a wide range of monomers but also availability of photoinitiators with broad spectral sensitivity including visible range.[23, 61] Such photoinitiators are widely used in many targeted applications such as dental filling materials, photoresists, printing plates, integrated circuits, laser-induced 3D curing, holographic recordings, and nanoscale micromechanics. The most prominent cationic photoinitiators are iodonium[6] and sulphonium salts,[8] which absorb the light in far and mid-UV region. Extension of the spectral sensitivity of cationic polymerization to near UV and visible range is realized by the activation with light sensitive additives, which do not directly initiate the polymerization.[5, 62] Three different modes can be distinguished to externally stimulate the activity of the onium salts in the visible range: (i) oxidation of free radicals by onium salts (also called free radical promoted cationic polymerization),[63-65] (ii) electron transfer between photoexcited

¹This chapter published as “Yilmaz G., Iskin B., Yilmaz F., and Yagci Y., Visible Light-Induced Cationic Polymerization Using Fullerenes. ACS Macro Letters, 1, 1212-1215, 2012.”

sensitizer and onium salt,[66, 67] and (iii) electron transfer in photoexcited charge transfer complexes of certain onium salts.[68] Among them, photosensitizer and onium salt combinations give rise to the unique initiating systems through electron transfer within the exciplex formed, consequently becoming useful tool to adjust the absorption characteristics and initiation efficiency. The excellent photosensitizers of aromatic compounds include several requirements, such as suitable solubility in monomers, excitation and oxidation energy levels well-matched with the acceptors, and absorption bands in the near UV and visible range. Electron-rich polynuclear aromatic compounds such as anthracene, perylene, pyrene, and phenothiazine appear to be efficient photosensitizers fulfilling these requirements. In our previous studies, we reported that several conjugated thiophene derivatives with extended conjugation can also act as electron-transfer photosensitizers in the near UV and visible region for the photoinitiated cationic and free radical polymerization using onium salts.[69]

Buckminster fullerene (C_{60}) exhibits excellent photochemical, superconducting, electrical and magnetic properties due its aromatic-like character.[70-72] Each carbon atom of its skeleton is connected to the others by 3 σ -bonds and carries a single electron at the outer shell to yield highly conjugated π -bonds at the surface. However, due to the s character in the π system induced by the curvature, the oxidation potential of C_{60} is high (~ 1.7 V versus saturated calomel electrode). Generally, C_{60} has strong tendency to be reduced in multiple single-electron transfer steps (from 0 to maximum -6), and to react with nucleophiles as it is said to be “electrophile par excellence”. [73-76] However, recent studies showed that C_{60} can be oxidized to its respective cations. Reed *et al.* described the synthesis and tame of C_{60}^{+} and HC_{60}^{+} in solution by treating C_{60} with superacids.[77]

In virtue of all these points, we decided to focus our attention on the possibility of the oxidation of fullerenes by photoinduced electron transfer reactions and its use in synthetic polymer chemistry. Herein we introduce a novel visible light method for the initiation of cationic polymerization of oxirane and vinyl monomers such as cyclohexene oxide (CHO), and *n*-isobutyl vinyl ether (IBVE) and *N*-vinyl carbazole (NVC), respectively. The components used for the initiation consist of a fullerene derivative (bare C_{60} or polystyrene- C_{60}) as the light absorbing molecule and an oxidizing agent, namely silver hexafluorophosphate ($AgPF_6$) or diphenyl iodonium hexafluorophosphate ($PhI^+PF_6^-$). Experimentally, the photopolymerization of these

representative monomers was conducted by exposing bulk or chlorobenzene solutions in visible light at different experimental conditions. At the irradiation wavelength, $\lambda > 400$ nm, the light emission is well matched with the absorption of C_{60} (Figure 1) and oxidants are transparent.

In the polymerizations, chlorobenzene was used as the aromatic reaction solvent since C_{60} is not soluble in monomers. Compare to the other possible C_{60} dissolving solvents (benzene, toluene, etc.), chlorobenzene has a lower nucleophilicity due to the negative inductive effect of chloro-substituent. Thus, its interference with the cationic species is restricted. Typical results are collected in Table 3.1. It should be pointed out that no polymerization took place in the control experiments in which either of the components was missing.

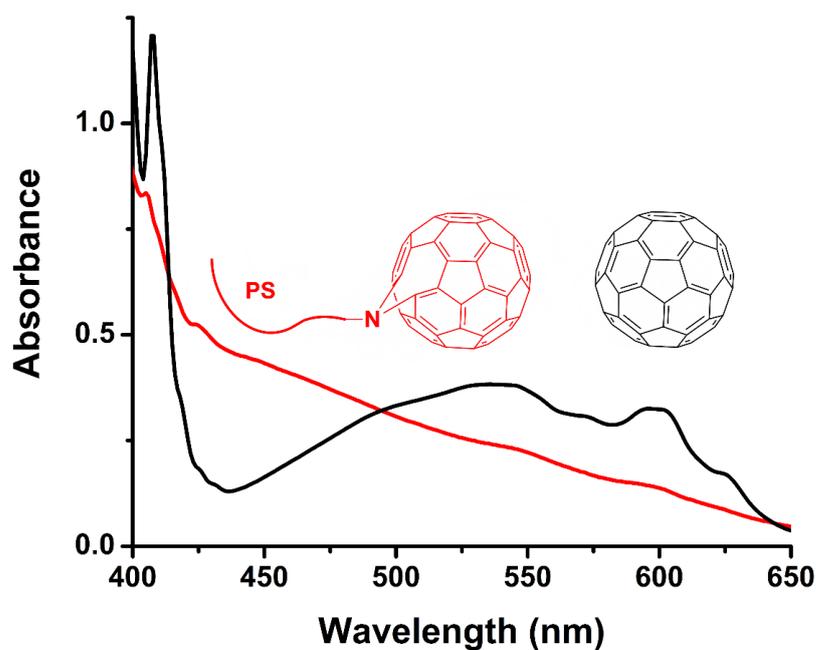


Figure 3.1 : Visible absorption spectra of C_{60} and $PS-C_{60}$.

Table 3.1 : Visible Light Induced Cationic Polymerization of Various Monomers Using C₆₀ in the Presence of Oxidants in Chlorobenzene.

Oxidant	Monomer ^b	Conv. (%) ^c	M_n^d (g mol ⁻¹)	M_w/M_n^d
AgPF ₆	CHO	4.2	3020	1.6
AgPF ₆	IBVE	4.7	9480	1.1
Ph ₂ I ⁺ PF ₆ ⁻	CHO	<1	3200	1.2
Ph ₂ I ⁺ PF ₆ ⁻	IBVE	<1	9700	1.8

^a [Monomer]/ [oxidant]/ [C₆₀] = 200/3/1, [C₆₀] = 1.7 × 10⁻³ M, λ > 400 nm, light intensity = 45 × 10⁻³ W m⁻², irradiation time = 2h

^b CHO: cyclohexene oxide, IBVE: isobutyl vinyl ether ^c Determined gravimetrically

^d Determined by gel permeation chromatography using polystyrene standards

With all the monomers tested, rather low conversions were attained which may be due to poor solubility, the employment of a solvent and relatively less favorable thermodynamic conditions (vide infra). To increase the efficiency of the fullerene based photosensitizing system by improving solubility and electrochemical properties, C₆₀ was modified by a simple conjugation process. Previously, several click strategies involving Cu(I)-mediated 1,3-dipolar Huisgen,[79] Diels–Alder-coupling[80] and thiol-ene reactions[81] were successfully used to modify C₆₀. In the present work, the reaction of an azide terminal polystyrene with bare C₆₀ readily afforded a mono-addition polymeric derivative of fullerene (PS-C₆₀) using a previously reported procedure.[82]

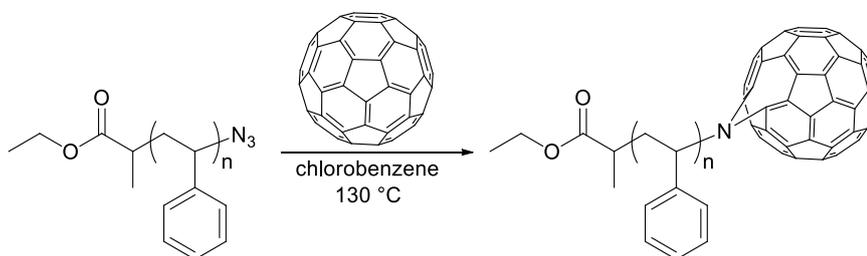


Figure 3.2 : Synthesis of polystyrene derivative of fullerene (PS-C₆₀).

The visible light initiated polymerizations were conducted with the PS-C₆₀ under similar experimental conditions to that of bare fullerene. The results are collected in Table 3.2.

Table 3.2 : Visible Light Induced Cationic Polymerization^a of Various Monomers Using PS-C₆₀ in the Presence of Oxidants in Chlorobenzene.

Oxidant	Monomer ^b	Conv. (%) ^d	M_n^e (gmol ⁻¹)	M_w/M_n^e
AgPF ₆	CHO	78.0	4160	2.2
AgPF ₆	CHO ^c	11.1	2720	1.3
AgPF ₆	IBVE	46.6	10140	3.4
AgPF ₆	NVC	70.1	3300	15.6
Ph ₂ I ⁺ PF ₆ ⁻	CHO	15.4	4010	3.1
Ph ₂ I ⁺ PF ₆ ⁻	IBVE	24.1	7200	4.2

^a [Monomer]/ [oxidant]/ [C₆₀] = 200/3/1, [C₆₀] = 1.7 × 10⁻³ M, λ > 400 nm, light intensity = 45 × 10⁻³ W m⁻², irradiation time = 2h

^b CHO: cyclohexene oxide, IBVE: isobutyl vinyl ether, NVC: *N*-vinylcarbazole

^c In the presence of 2,6-di-*tert*-butylpyridine (5.0 × 10⁻³ M)

^d Determined gravimetrically

^e Determined by gel permeation chromatography using polystyrene standards

Although much higher conversions were obtained with all monomers, IBVE and NVC were polymerized more effectively due to their strong electron donating nature. Silver salt exhibited better activation efficiency than iodonium salt, which correlates well with their reduction potentials. It is also noted that although at much reduced rate, polymerization also proceeds in the presence of a proton scavenger, 2, 6-di-*tert*-butylpyridine indicating reactive species other than Brønsted acid are involved in the initiation process.

As for the all polynuclear aromatic compounds, electron transfer from the excited fullerene derivative to oxidant is feasible if the change in free energy (ΔG) is negative. On the basis of the oxidation potential (E_{ox}) and active excitation energy (E^*) of fullerene (C₆₀) and the reduction potential (E_{red}) of the oxidant (Ox), the free energy change (ΔG) for the photoinduced electron transfer process was estimated by Rehm-Weller equation constant according to eq 1 where f_c is the Faraday constant.

$$\Delta G = f_c [E_{\text{ox}}(\text{C}_{60}) - E_{\text{red}}(\text{Ox})] - E^*(\text{C}_{60}) \quad (3.1)$$

Table 3.3 summarizes the ΔG values of the free energy changes for the electron transfer from the singlet states of the fullerene to the ground-state oxidant. Eox and ES^* for C_{60} and PS- C_{60} were determined by cyclic voltammetry and fluorescence measurements, respectively.

Table 3.3 : Free energy changes for the electron transfer from singlet excited states of fullerenes to cationic salts.

Fullerene (E_{ox})	Oxidant	ΔG (kcal/mol)
C_{60}	AgPF_6	- 50.2
(1.7 V)	$\text{Ph}_2\text{I}^+ \text{PF}_6^-$	- 27.3
PS- C_{60}	AgPF_6	- 62.1
(1.2 V) ^b	$\text{Ph}_2\text{I}^+ \text{PF}_6^-$	- 38.8

^b As found by cyclic voltammetry measurements

As can be seen from Table 3, electron transfer in singlet excited state of both fullerene compounds is thermodynamically favorable. A mechanism based on electron transfer concerning the reaction of excited C_{60} with oxidant is described in Figure 3.3. The same mechanism may also be postulated for the PS- C_{60} .

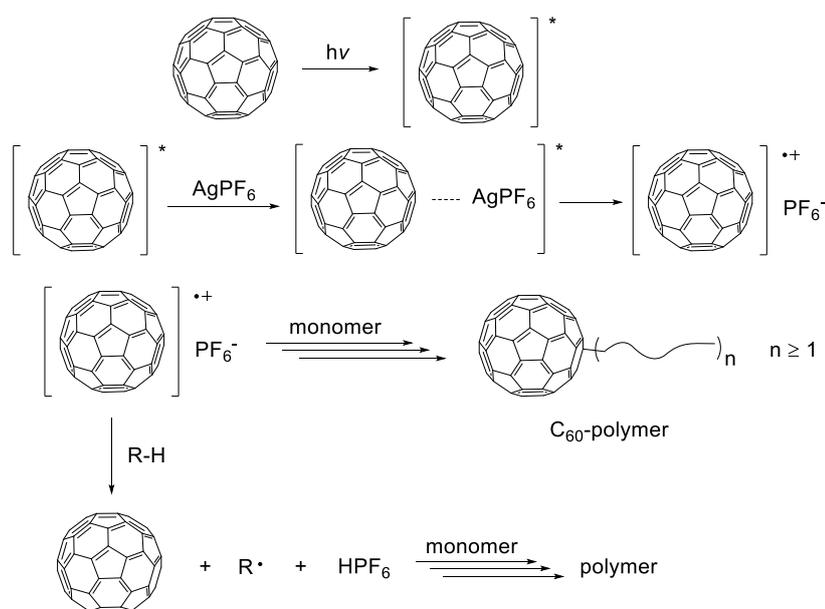


Figure 3.3 : Visible light induced cationic polymerization by fullerene sensitization.

The radical cations of C_{60} formed would be capable of initiating cationic polymerization since direct initiation by the species formed from polynuclear aromatic compounds is a well-known process, and because of the non-nucleophilicity of PF_6^- ions, cationic chain propagation would not be prevented. Principally, polymerization could also be initiated by the Brønsted acids formed via hydrogen abstraction. The polymerization proceeded even in the presence of a proton scavenger (see Table 3.2) indicates that both radical cations and Brønsted acids play an important role regarding the initiation of cationic polymerization.

In conclusion, a new visible light sensitive cationic photoinitiator system consisting of fullerenes and oxidizing salt has been designed. Key features of this initiating system are (i) the use of visible light, e.g., $\lambda > 400$ nm, to excite fullerenes which undergo electron transfer reactions with the oxidizing salt, and (ii) the resulting radical cations and/or Brønsted acid formed from the hydrogen abstraction reaction initiate the polymerization. New initiating systems for cationic polymerization acting at visible range such as this will play an important role in emerging fields such as highly pigmented coatings, rapid setting inject inks, coatings for wood preservation, and three-dimensional imaging processes that require visible light sensitization. The initiation through the radical cations by preventing Brønsted acid initiation using proton scavenger may open a new pathway for the preparation of polymer-fullerene conjugates. Further studies in this line are now in progress.

3.1 Experimental

3.1.1 Materials

Fullerene (98%, Sigma-Aldrich), silver hexafluorophosphate (97%, Sigma-Aldrich), diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$, $\geq 99\%$, Sigma-Aldrich), ethyl 2-bromopropionate (99%, Sigma-Aldrich), sodium azide ($\geq 99.5\%$, Sigma-Aldrich) and *N*-vinylcarbazole (NVC, 98%, Sigma-Aldrich) were used as received. Styrene ($\geq 99\%$, SigmaAldrich), cyclohexene oxide (CHO, 98%, Sigma-Aldrich) and isobutyl vinyl ether (IBVE, 99%, Sigma-Aldrich) were vacuum distilled prior to use. Chlorobenzene was distilled under reduced pressure for purification. Dichloromethane (CH_2Cl_2 , 98%, Sigma-Aldrich) was distilled over P_2O_5 and collected in molecular sieves. All other solvents were used as received without further purification.

3.1.2 Instrumentation

¹H NMR measurements were recorded in CDCl₃ with Si(CH₃)₄ as internal standard, using a Bruker AC250 (250.133 MHz) instrument. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Molecular weights were determined by gel permeation chromatography (GPC) instrument, Viscotek GPCmax Autosampler system, consisting of a pump, three ViscoGEL GPC columns (G2000HHR, G3000HHR and G4000HHR), a Viscotek differential refractive index (RI) detector with a THF flow rate of 1.0 mL min⁻¹ at 30°C. The detector was calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. FTIR spectra were recorded on a Perkin-Elmer FTIR Spectrum One-B spectrometer.

3.1.3 Synthesis of ω-Azido Terminated Polystyrene (PS-N₃)

PS-N₃ was synthesized by following a reported procedure,¹ starting from ω-bromo terminated polystyrene which was prepared by atom transfer radical polymerization.²

$$(M_{n,NMR}(PS-N_3) = 1910 \text{ gmol}^{-1}, M_{n,GPC}(PS-N_3) = 1970 \text{ gmol}^{-1}, M_w/M_n = 1.1)$$

3.1.4 Synthesis of ω-Fullerene Terminated Polystyrene (PS-C₆₀)

PS-C₆₀ was synthesized according to a previously reported procedure.³ $M_{n,GPC}(PS-C_{60}) = 2800 \text{ gmol}^{-1}$, $M_w/M_n = 1.3$)

3.1.5 Photopolymerizations

A typical photopolymerization procedure of IBVE was as follows. A Pyrex tube was heated in vacuo with a heat gun and flushed with dry nitrogen. Then C₆₀ (or its polymeric form, PS-C₆₀), solvent (if any), the monomer and the oxidant were introduced to the tube. The resulting mixture was further bubbled with dry nitrogen and the tube was properly sealed. The stirring solution was irradiated with a light source emitting light at $\lambda > 400 \text{ nm}$ for 2h and precipitated into methanol. The obtained polymers were dried under reduced pressure. Conversions were calculated for all samples gravimetrically.

4. PHOTOINDUCED COPPER(I)-CATALYZED CLICK CHEMISTRY BY ELECTRON TRANSFER PROCESS USING POLYNUCLEAR AROMATIC COMPOUNDS¹

The introduction of the click chemistry concept gave rise to a great advancement in synthetic chemistry as it served as an inspiration for chemists from various research areas including organic chemistry,[83, 84] supramolecular chemistry,[85] drug discovery,[86, 87] bio-conjugation[88] and materials science.[89] Click reactions exhibit chemoselective and single reaction path characteristics, which are of great importance for the synthetic community. Indeed, chemists are increasingly focusing on the high yields, which can be achieved on a fast-time scale under mild conditions even if equimolar amounts of components are reacted. In these processes only negligible concentration of easily removable by-products may be formed. Another feature of the concept concerns orthogonality, since they are generally insensitive to moisture, oxygen or any other contamination in the reaction media.[90]

In the context of click reactions, “Copper (I) Catalyzed Azide-Alkyne Cycloaddition (CuAAC)” and “Diels-Alder cycloaddition (DA)” reactions have been most extensively employed.[32, 91-95] Although they do not possess all the typical characteristics, thiol-ene reactions are also acknowledged as a click route due to its efficiency, rapidity and easy handling features.[96-102] Despite being at an earlier stage, ketene chemistry has recently been proposed as an alternative click reaction, since most of the click reaction prerequisites such as simplicity, selectivity and efficiency are observed.[103-109]

Although acknowledged as being the most efficient strategy for synthesis and functionalization applications, established click reactions have some drawbacks, which need to be overcome. To exemplify, CuAAC reactions suffer from the necessity of using Cu(I) species as catalysts which are prone to oxidation in the

¹This chapter published as “Yilmaz G., Iskin B., and Yagci Y., Photoinduced copper(I)-catalyzed click chemistry by the electron transfer process using polynuclear aromatic compounds. *Macromolecular Chemistry and Physics*, 215, 662-668, 2014.”

presence of air. For the industrial scale utilization of such technology, various solutions have been proposed, such as using reducing agents for the in situ formation of Cu(I) species, starting from the respective Cu(II) salts. These reducing agents include ascorbic acid, hydrazine, and phenol derivatives which not only take part in the reduction of Cu(II) salts, but also prevent the inhibition effect of molecular oxygen.[110-113] Similar reduction process can also be achieved by electrochemical techniques.[114, 115] Notably, these methods have also been utilized for atom transfer radical polymerization (ATRP) reactions, which also require Cu(I) salts as catalyst for the synthesis of mono-disperse polymers. The use of reducing agent for the in situ generation of Cu(I) has also displayed problems, particularly in bio-conjugation applications, as it may react with protein chains and causes degradation of DNA molecules.[116]

Photoinitiated cationic polymerization of epoxy and vinyl ether based monomers is an industrially important technological process which finds applications in coatings, adhesives, inks, printing plates, optical waveguides, and microelectronics.[1] Although the most prominent onium salt cationic photoinitiators are sensitive to light at around 300 nm,[7] many targeted applications require activation in the near UV and visible range. The generally applied method for shifting spectral sensitivity to longer wavelengths, are (i) oxidation of free radicals by using onium salts such as triarylsulfonium[8] or diaryliodonium salts[6] or alkoxy pyridinium salts.[117], (ii) charge transfer complexes,[118] and (iii) using photosensitizers.[67] In the case of photosensitizers, polynuclear aromatic compounds (PACs) such as anthracene (Anth), perylene (Pry), phenothiazine (Pht) and highly conjugated thiophene derivatives[119] form exciplexes with onium salts as a consequence of light absorption at long wavelengths by the sensitizers (S). In the complexation state, electron transfer to the onium salt is observed, giving rise to positively charged sensitizer species capable of initiating cationic polymerization of appropriate monomers.

We have recently developed a new photochemical protocol to catalyze the CuAAC reaction between azides and alkynes, by in situ generation of Cu(I) from Cu(II) complexes directly or indirectly with UV or visible light irradiation, respectively.[120-122] In direct photolysis, the absorption of light by copper ligand promotes the intramolecular electron transfer from the π -system of the ligand to the

central ion resulting in the transformation of Cu(II) ion into Cu(I) and the ligand into the radical complex.[123] However, the direct method involving UV exposure, suffers from the need for long irradiation times. In the indirect approach, photoinitiator absorbs light in the UV–visible region, where the copper complex is transparent, and forms reactive intermediates such as free radicals capable of promoting the photoreduction of the Cu(II) into Cu(I).

This approach was elegantly exploited by Bowman and coworkers for comprehensive spatial and temporal control in click reactions using standard photolithographic systems.[124] More recently, these authors have also demonstrated the selectivity and versatility of the approach via a sequential and orthogonal photo-CuAAC step growth reaction.[125] The described redox process between photochemically generated radicals and metal ions can also be used for the initiation of atom transfer radical polymerization.[126-128]

As part of our current research program on the design and development of photochemical systems for macromolecular syntheses, we herein report the first successful use of PACs as a long wavelength absorbing sensitizers in click reactions. The photosensitizer in the exciplex form works to provide an electron to reduce Cu(II) upon irradiation. We demonstrate the versatility of this long wavelength approach on the example of a model click reaction of small organic molecules and also for macromolecular synthesis.

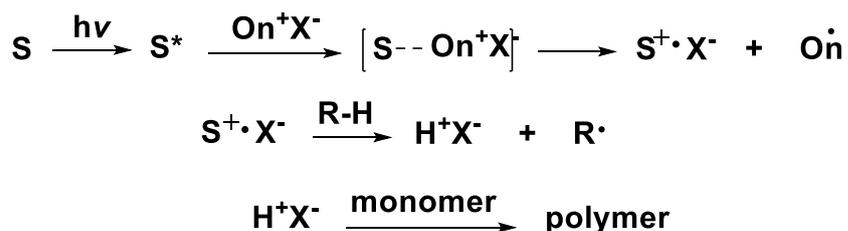


Figure 4.1 : Photosensitized electron transfer process for the initiation of cationic polymerization.

We have recently developed a new photochemical protocol to catalyze the CuAAC reaction between azides and alkynes, by *in situ* generation of Cu(I) from Cu(II) complexes directly or indirectly with UV or visible light irradiation, respectively.[78-80] In direct photolysis, the absorption of light by copper ligand promotes the intramolecular electron transfer from the π -system of the ligand to the central ion

resulting in the transformation of Cu(II) ion into Cu(I) and the ligand into the radical complex.[81] However, the direct method involving UV exposure, suffers from the need for long irradiation times. In the indirect approach, photoinitiator absorbs light in the UV–visible region, where the copper complex is transparent, and forms reactive intermediates such as free radicals capable of promoting the photoreduction of the Cu(II) into Cu(I) as presented in Figure 4.2 on the example using 2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMDPO) as the oxidizable free radical source.

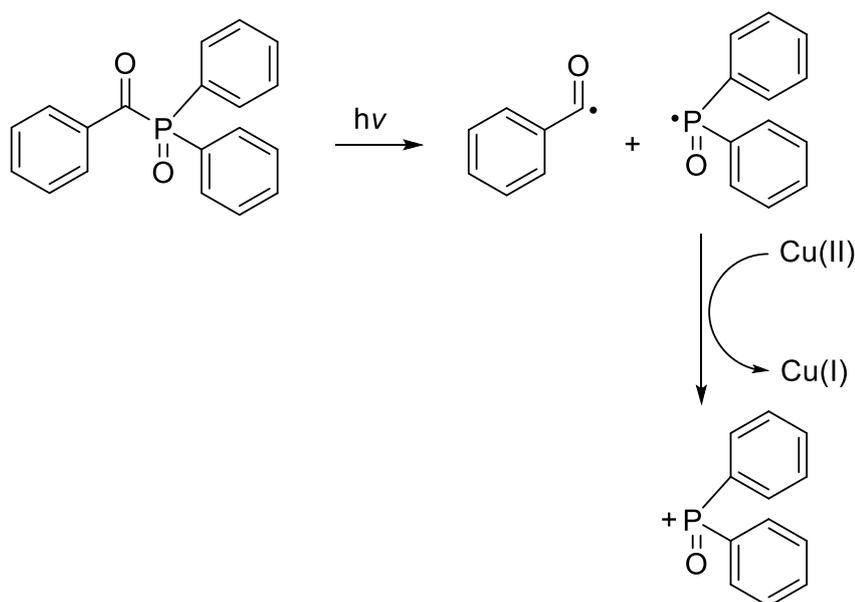


Figure 4.2 : Photochemical generation of Cu(I) by TMDPO.

This approach was elegantly exploited by Bowman and coworkers for comprehensive spatial and temporal control in click reactions using standard photolithographic systems.[82] More recently, these authors have also demonstrated the selectivity and versatility of the approach via a sequential and orthogonal photo-CuAAC step growth reaction.[83] The described redox process between photochemically generated radicals and metal ions can also be used for the initiation of atom transfer radical polymerization.[84-86]

As part of our current research program on the design and development of photochemical systems for macromolecular syntheses, we herein report the first successful use of PACs as a long wavelength absorbing sensitizers in click reactions. The photosensitizer in the exciplex form works to provide an electron to reduce Cu(II) upon irradiation. We demonstrate the versatility of this long wavelength

approach on the example of a model click reaction of small organic molecules and also for macromolecular synthesis.

4.1 Results and Discussion

Successful application of the photoinduced electron transfer reactions of PACs and onium salts¹⁵ for the initiation of cationic polymerization prompted us to employ similar photoredox system in click chemistry. Thus, the photoinduced model click reaction of benzyl azide ($\text{PhCH}_2\text{-N}_3$) with phenyl acetylene (Ph-ac) was conducted by exposing a solution containing CuCl_2 -PMDETA ligand and one of the following compounds; Pry, Anth and Pht in near UV light. $\text{PhCH}_2\text{-N}_3$ and Ph-ac were deliberately selected as simple model click components, so as to eliminate the substituent effect on the click reaction. At the irradiation wavelength, Cu(II) /ligand has no absorption and all the light is absorbed by the sensitizers since these compounds are highly conjugated, planar molecules, with photoactivity in the near UV and visible range of the electromagnetic spectra (Figure 4.3).

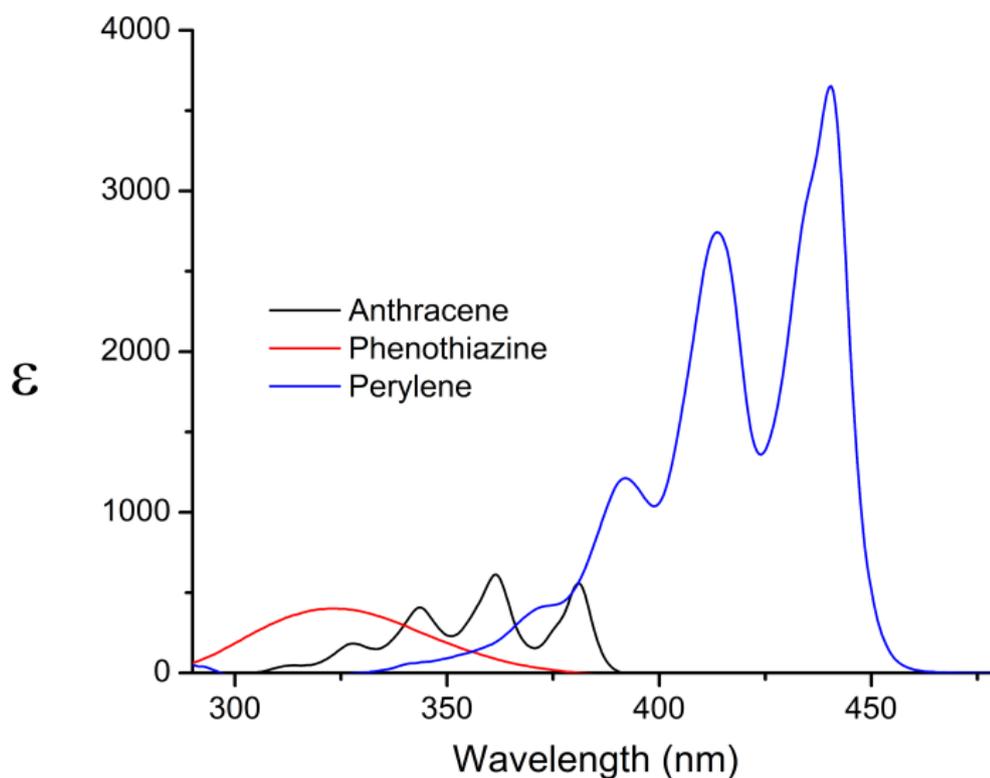


Figure 4.3 : UV-vis spectra of anthracene, phenothiazine and perylene.

Typical results are collected in Table 4.1.

Table 4.1 : Photoinduced click reaction of benzyl azide ($\text{PhCH}_2\text{-N}_3$) with phenyl acetylene (Ph-ac) using polynuclear aromatic compounds (PACs)^a

PAC	E_{ox} (V)	E^* ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔG ($\text{kJ}\cdot\text{mol}^{-1}$) ^b	Time (min)	Yield ^c
Pry	0.90	277	-205.2	100	99
Anth	1.10	319	-227.8	120	99
Pht	0.60	239	-196.3	180	94

^a $[\text{PhCH}_2\text{-N}_3]:[\text{Ph-ac}]:[\text{PAC}]:[\text{CuCl}_2]:[\text{PMDETA}] = 1/1/0.2/0.1/0.1/0.1$, $\lambda \geq 350$ nm

^b Calculated by the Rehm-Weller equation

^c Calculated by $^1\text{H-NMR}$ data

The reactions were monitored by means of $^1\text{H-NMR}$ spectroscopy. Figure 4.4 demonstrates the change of the NMR spectra during the click reaction, where Pry is used as the sensitizer molecule. Conversions were determined by the integration of a particular signal from a proton in one of the starting molecules and the corresponding proton in the product (e.g., protons a and a', Figure 4.4). Similar spectral changes were also observed for the click products obtained with Anth and Pht (Figure 4.5 and 4.6).

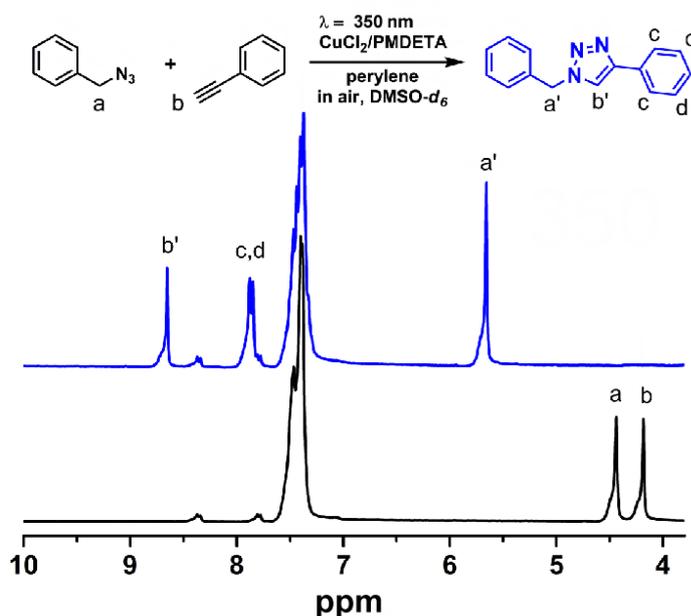


Figure 4.4 : $^1\text{H-NMR}$ spectra of the reaction media before and after the photoinduced click reaction.

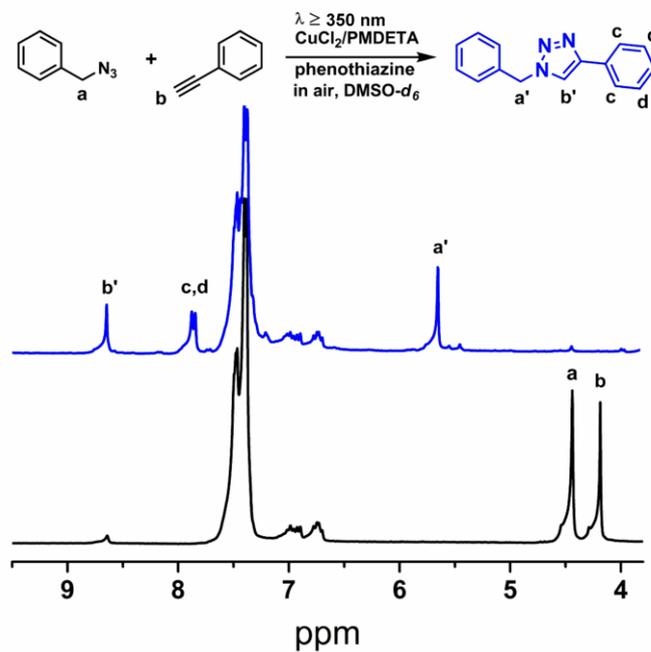


Figure 4.5 : $^1\text{H-NMR}$ spectra of the reaction media before and after the photoinduced click reaction using phenothiazine as photosensitizer.

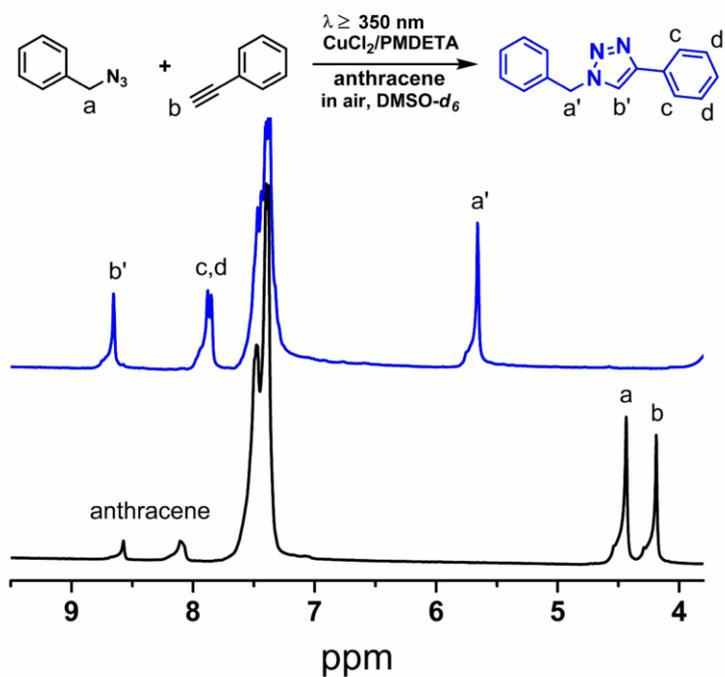


Figure 4.6 : $^1\text{H-NMR}$ spectra of the reaction media before and after the photoinduced click reaction using anthracene as photosensitizer.

The strategy implemented in this study is outlined on the example of Pry in Figure 4.7.

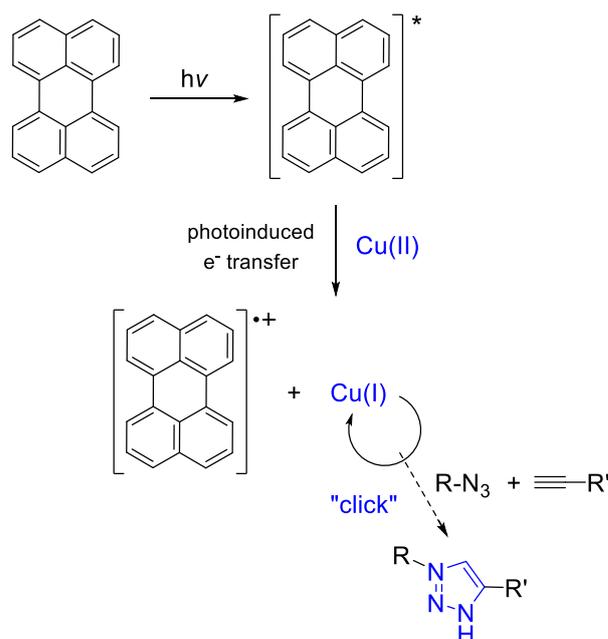


Figure 4.7 : Mechanism of the photoinduced click reaction using perylene and high oxidation state copper.

On the basis of the previous photopolymerization studies, the sensitization action is based on the electron transfer resulting in the formation of the radical cation of the sensitizer. According to the Rehm-Weller equation, electron transfer from the excited sensitizer to Cu(II) ion is feasible, if the change in free energy is negative:

$$\Delta G = f_c (E_{\text{ox}}(\text{PS}) - E_{\text{red}}(\text{ox})) - E^*(\text{PS}) \quad (4.1)$$

where $E_{\text{ox}}(\text{PS})$ and $E_{\text{red}}(\text{ox})$ are the half wave oxidation and reduction potentials of sensitizer and Cu(II) (in V), respectively; conversion factor $f_c = 97 \text{ kJ mol}^{-1} \text{ V}^{-1}$; and $E^*(\text{PS})$ is the excitation energy of the sensitizer. The ΔG values listed in Table 1 suggest that electron transfer from singlet excited states of the sensitizers to Cu(II) ions is favorable in all cases. Copper is known to be a semi-noble metal, which takes part in the so-called inert zone of the galvanic series. These noble metals are, in general, resistant to oxidation under moist air, unlike other active metals. In other words, their oxidized forms have higher tendencies to be reduced to their lower oxidation states. The reduction potential of Cu(II) to Cu(I) is equal to 0.16 V as measured by the saturated calomel electrode (SCE). Apparently, this value is more favorable for the redox reaction with the photoexcited sensitizers than all onium salts successfully used in photoinitiated cationic polymerization. Although at present the

fate of the photosensitizer radical cation is not known, it is very likely that they abstract hydrogen from the solvent and/or a hydrogen donating compound present in the media. This claim was further supported by the $^1\text{H-NMR}$ analysis as the photosensitizer aromatic protons remain in the spectra even after the click reaction. Kinetic profiles referring to the click reaction between $\text{PhCH}_2\text{-N}_3$ and Ph-ac under near UV light irradiation are also investigated. Almost quantitative conversions are attained in shorter irradiation times with Pry and Anth photosensitizers, which is in accordance with their oxidation potentials. Relatively longer reaction times required with Pht photosensitizer may be attributed to its lower absorption in the near UV range (Figure 4.8). To test the efficiency of this system in macromolecular scale, several experiments were performed using alkyne and azide end functionalized polymers in conjunction with low molecular weight compounds with antagonist functionalities. For this purpose, alkyne functionalized poly(ϵ -caprolactone) (Alkyne-PCL) and azide functionalized polystyrene (PS-N_3) were used together with benzyl azide and propargyl alcohol and propargyl amine, respectively.

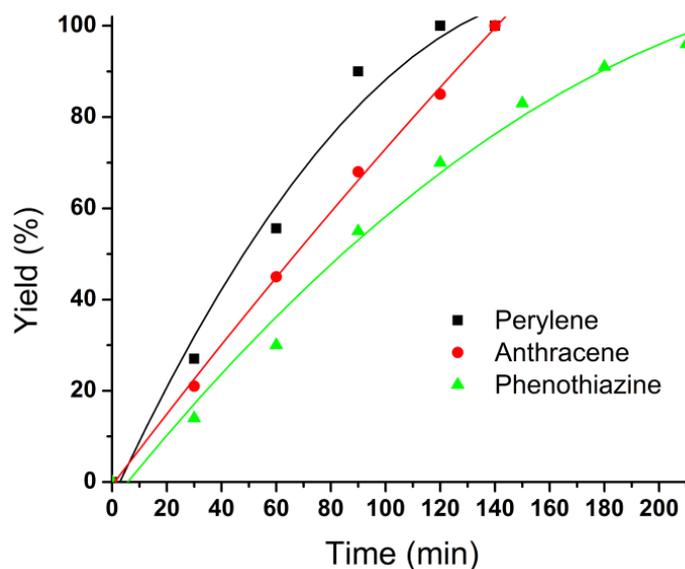
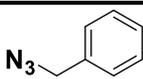
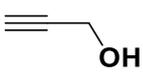
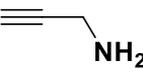


Figure 4.8 : Photoinduced click reaction of benzyl azide and phenyl acetylene using Cu(II) in conjunction with different photosensitizers. Yields were determined by $^1\text{H-NMR}$ spectroscopy.

Syntheses of functional polymers were achieved by using corresponding controlled polymerization methods, namely ROP and ATRP for PCL and PS, respectively (see experimental section). Since the model reactions revealed that Pry was the most efficient photosensitizer, all experiments at macromolecular scale were performed in

the presence of Pry. Amine and alcohol functional telechelic polymers are obtained almost with quantitative yields regardless of their click components (Table 4.2).

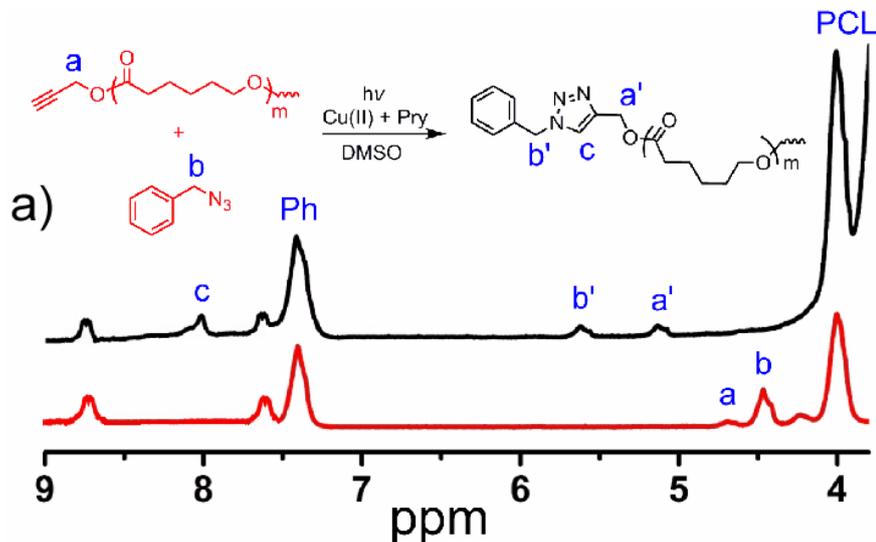
Table 4.2 : Telechelic Polymers by Photoinduced CuAAC using Perylene (Pry)^a

Entry	Clickable Polymer	Antagonist Molecule	Yield (%) ^b
1	Alkyne-PCL		94
2	PS-N ₃		90
3	PS-N ₃		90

^a [azide]:[alkyne]:[Pry]:[CuCl₂]:[PMDETA] = 1/1/0.2/0.1/0.1, $\lambda \geq 350$ nm, t = 10h

^b Calculated by ¹H-NMR results

In the ¹H-NMR spectrum of the CuAAC reaction product with Alkyne-PCL, appearance of new signals at the aromatic region (~7.6 ppm) gives a clear indication for the successful functionalization (Figure 4.9a). The peak of triazole was not distinguishable as it is masked by the aromatic peaks of Pry in the reaction media. Similar spectral evidences were also obtained for the functionalization of PS-N₃.



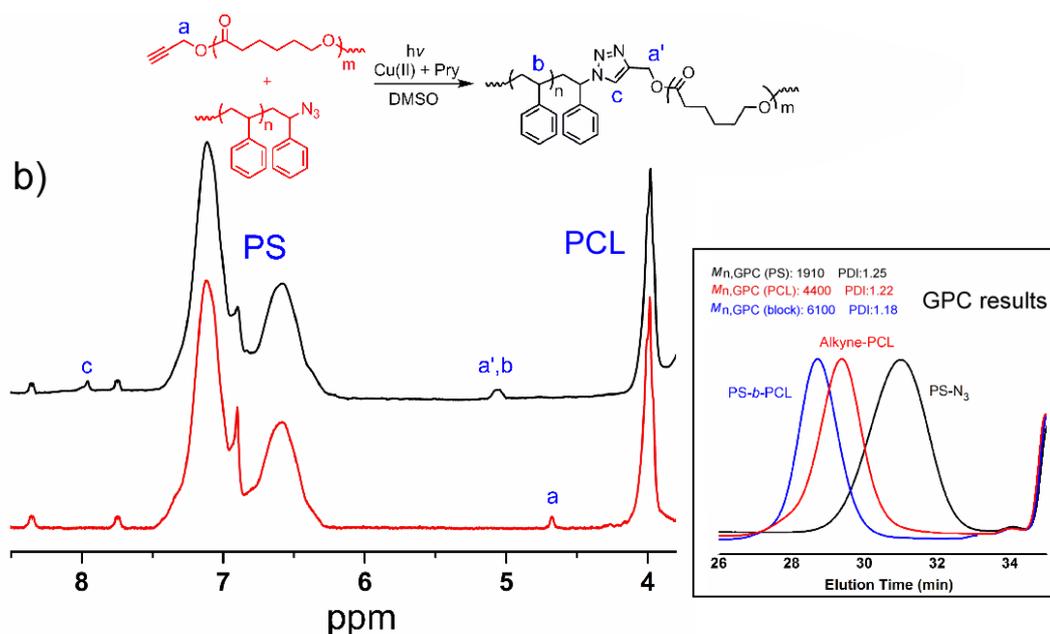


Figure 4.9 : a) ¹H NMR spectra of the mixture of Alkyne-PCL and benzyl azide (red), and benzyl end-capped PCL (black) b). ¹H NMR spectra of the mixture of Alkyne-PCL and PS-N₃ (red), and PS-*b*-PCL (black). Inset: GPC traces of the precursors and the resulting PS-*b*-PCL.

To further expand the scope of this methodology, Alkyne-PCL was reacted with PS-N₃ under the same experimental conditions to afford PCL-*b*-PS. In the ¹H-NMR spectrum of the resulting block copolymer (Figure 4.9b), the signals which belong to the methylene protons at the propargyl group of PCL had completely disappeared, while new peaks around 5.1 ppm, corresponding to the methylene protons adjacent to the triazole ring were observed. These results clearly show the successful application of this photoredox system for block copolymer formation by CuAAC reaction.

The block copolymer formation is also analyzed by chromatographic techniques. GPC curves of the precursor Alkyne-PCL and PS-N₃ polymers together with the resulting PS-*b*-PCL block copolymer are depicted in Figure 9b. As can be seen all polymers display mono-disperse molecular weight characteristics and the GPC trace of PS-*b*-PCL is observed at lower elution times, which corresponds to higher molecular weight of the polymer. In this context, it should also be pointed out that the long wavelength sensitivity of the system prevents absorption and consequently photodegradation of the polymer click components at high-energy irradiation. These GPC results further confirm the success of the click strategy described.

In conclusion, a conceptually new photo CuAAC approach based on electron transfer reactions of PACs with Cu(II) complex has been developed. The near UV activation facilitates application of the system for macromolecular structures without chain

degradation as demonstrated for the synthesis of telechelic polymers and block copolymers. The method has capability for expanding further implementations in the preparation of complex macromolecular structures such as graft and star copolymers, and surface modifications. Further studies in this line are now in progress.

4.2. Experimental

4.2.1 Materials

Phenylacetylene (98%, Aldrich), benzyl bromide (98%, Aldrich), sodium azide (99%, Aldrich), dimethyl-*d*₆ sulfoxide (Aldrich), benzyl alcohol (99%, Aldrich) and copper(II) chloride (98%, Aldrich) were used as received. *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (99%, Aldrich) was distilled before use. Benzyl azide was synthesized according to literature procedure. ¹H-NMR (250 MHz, CDCl₃): δ (ppm) = 4.4 (Ph-CH₂-N₃), 7.4–7.5 (aromatic protons). Anthracene (Aldrich, ≥99%), perylene (Aldrich, ≥99%), phenothiazine (Aldrich, ≥98%) were used as received.

4.2.2 Characterization

UV spectra were recorded on a Shimadzu UV- 1601 spectrometer. ¹H NMR spectra in DMSO-*d*₆ with Si(CH₃)₄ as an internal standard were recorded at room temperature at 250 MHz using a Bruker DPX 250 spectrometer.

4.2.3 Synthesis of intermediates and precursor polymers

ω-Bromo functional polystyrene (PS-Br)[129] (*M*_{n,NMR}= 1910, *M*_{n,GPC} = 2030 g/mol, *M*_w/*M*_n = 1.23) and α-alkyne functional poly(ε-caprolactone) (Alkyne-PCL)[130, 131] *M*_{n,NMR}= 2910; *M*_{n,GPC}= 4400 (relative to linear PS); *M*_w/*M*_n= 1.22 were prepared according to modified literature procedures.

4.2.4 General Experimental Procedure for the Spectroscopic Investigations of Click Reactions

General experimental procedure for the light-induced copper(I)-catalyzed click reaction: DMSO-*d*₆ (0.5 mL) and benzyl azide (11 μL, 0.2 mM) were added to an NMR tube containing CuCl₂ (1.4 mg, 0.02 mM), PMDETA (2.2 μL, 0.02 mM) and a photosensitizer (0.04 mM). After 1–2 min, the phenylacetylene (13 μL, 0.2 mM) was added via syringe. The reaction tube was irradiated by a Ker-Vis blue photoreactor equipped with a circle of 6 lamps (Philips TL-D 18W) emitting light nominally at

350 nm. ^1H -NMR spectra were periodically recorded, with each measurement involving 16 scans. Conversions were determined by integration of the signal from a proton in one of the starting molecules and the corresponding proton in the product (e.g., protons a' and b' in Figure 2, main text).

4.2.5 Spectroscopic Investigations of Click Reactions on the Synthesis of Telechelic Polymers

Experimental procedure for the light-induced copper(I)-catalyzed click reaction: DMSO- d_6 (0.5 mL) and benzyl azide (1 eq) were added to an NMR tube containing CuCl_2 (1 eq), PMDETA (1 eq) and a photosensitizer (2 eq). After 1–2 min, the Alkyne-PCL (1 eq) was added. The reaction tube was irradiated by a Ker-Vis blue photoreactor equipped with a circle of 6 lamps (Philips TL-D 18W) emitting light nominally at 350 nm. ^1H NMR spectra were periodically recorded, with each measurement involving 16 scans. Conversions were determined by integration of the signal from a proton in one of the starting molecules and the corresponding proton in the product. Similar procedure was also applied for the syntheses of polystyrene telechelics with propargyl alcohol and propargyl amine.

4.1.6 Spectroscopic Investigations of Click Reactions on the Synthesis of Block Polymers

Experimental procedure for the light-induced copper(I)-catalyzed click reaction: DMSO- d_6 (0.5 mL) and PS- N_3 (1 eq) were added to an NMR tube containing CuCl_2 (1 eq), PMDETA (1 eq) and a photosensitizer (2 eq). After 1–2 min, the Alkyne-PCL (1 eq) was added. The reaction tube was irradiated by a Ker-Vis blue photoreactor equipped with a circle of 6 lamps (Philips TL-D 18W) emitting light nominally at 350 nm. ^1H -NMR spectra were periodically recorded, with each measurement involving 16 scans. Conversions were determined by integration of the signal from a proton in one of the starting molecules and the corresponding proton in the product.

5. CONCLUSIONS

Photo-induced processes hold increasing priority in polymer syntheses. There has been significant efforts to discover new initiating species with enhanced spectral sensitivity and solubility properties. In addition photochemical methods have been employed for the induction of various reactions in the construction of macromolecular architectures. Specifically, atom transfer radical polymerization and copper catalyzed azide-alkyne cycloaddition reactions were recently shown to be promote under light irradiation in simple experimentation procedures. Here in this thesis, three distinct applications of photo-induced strategies were deliberately selected in order to reflect their versatility and efficiency in macromolecular syntheses.

In the first part of the thesis, synthesis and characterization of a polyethylene oxide (PEO) based macrophoto-initiator is presented. Dimethyl aminofunctional PEO was synthesized by controlled anionic polymerization. In a parallel step, thioxanthone chromophore with carboxylic acid functionality was prepared. Mixing these two components in aqueous media readily afforded the desired initiator with thioxanthone carboxylate anion as the light absorbing group, which is soluble both in aqueous media and most of the common organic solvents. Photopolymerization experiments in both solvent phases showed that the photoinitiator efficiently initiates the polymerization of various monomers by radical mechanism, even in the absence of a co-initiator needed.

In the second part, a new photo-initiating system for cationic polymerization was described. In this study, bare fullerene and polystyrene end-capped fullerene were used as photosensitizer in combination with oxidant salts for the initiation of cationic polymerization of appropriate monomers. Upon irradiation at visible light, oxirane and vinyl ether type monomers were shown to readily polymerize. When a proton scavenger was used in the system, polymerization still took place, which proves that fullerene radical cations played role in the initiating system.

In the last part of the thesis, employment of polyaromatic compounds such as perylene, anthracene and phenothiazine were used as photo-reducing agents for the generation of Cu(I), which catalyzed click reactions between clickable compounds. The strategy was successfully used both for low molecular mass organic compounds and polymeric structures.

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