ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

NEW APPROACHES FOR PHOTOINDUCED STEP-GROWTH POLYMERIZATIONS

Ph.D. THESIS

Hüseyin Cem KILIÇLAR

Department of Chemistry

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AUGUST 2023

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Thesis Advisor: Prof. Dr. Barış KIŞKAN

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

FOTOBAŞLATILMIŞ AŞAMALI POLYİMERİZASYONLAR İÇİN YENİ YAKLAŞIMLAR

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Hüseyin Cem Kılıçlar, a Ph.D. student of ITU Graduate School student ID 509192225, successfully defended the thesis/dissertation entitled "New Approaches for Photoinduced Step-Growth Polymerizations", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family and Prof. Dr. Yusuf Yağcı,

FOREWORD

I hope the research in this thesis will contribute to the development of science and inspire other scientists.

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May 2023 Hüseyin Cem KILIÇLAR

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ABBREVIATIONS

DBM	**:** Dibromomethane
DCM	**:** Dichloromethane
DBX	**:** Dibromoxylene
DMB	**:** Dimethoxybenzene
FTIR	**:** Fourrier-Transform Infrared
GMA	**:** Glycidyl Methacrylate
MB	**:** Methoxybenzene
MMA	**:** Methyl Methacrylate
NMR	**:** Nuclear Magnetic Resonance
PC	**:** Propylene Carbonate
PDPM	**:** Poly(Dimethoxyphenylene Methylene)
PMMA	**:** Poly(Methyl Methacrylate)
PPM	**:** Poly(Phenylene Methylene)
THF	**:** Tetrahydrofuran
UV	**:** Ultraviolet

SYMBOLS

λ	**:** Wavelength
ν	**:** Light
Đ	**:** Dispersity
$\boldsymbol{M}_{\mathbf{w}}$	**:** Weight Average Molecular Weight
$\boldsymbol{M}_{\mathbf{n}}$	**:** Number Average Molecular Weight
t	**:** Time

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NEW APPROACHES FOR PHOTOINDUCED STEP-GROWTH POLYMERIZATIONS

SUMMARY

Photoinduced reactions are receiving a tremendous interest recently due to the global need for renewable and more efficient procedures over conventional methods. Several photoinduced approaches were developed and applied over conventional techniques to increase the ecological and economical benefits of the industrial productions since it provides more efficient reaction conditions by involving lesser chemicals.

All of the polymerization mechanisms including radical, anionic and cationic polymerizations have benefited over the advancements in the photochemistry. Scientists across the globe have developed novel photoinitiators or sensitizing systems to create successful polymerization methods to be adapted over conventional techniques. Thus, enhanced the growing speed of industries including dentistry, additive manufacturing, coatings and electronics. However, most of the reactions that utilized photochemical methods were chain or ring opening polymerizations. Step-growth polymerizations on the other hand, were investigated scarcely compared to the previously mentioned alternatives. Step-growth polymerizations are mechanistically differ from the chain polymerizations. Photochemistry can be used to generate reactive species either in radical or cationic form to initiate the corresponding polymerizations using suitable monomers. However, for the step-growth polymerization, two different bifunctional monomers have to be used or generated in order to obtain polymers which limits the options for scientists. In the scope of the thesis, novel perspectives towards step-growth polymerizations involving substitution reactions have been presented and developed.

S_N1 type substitution reactions can occur in the presence of a good leaving group, heat, polar solvents and may be strong acid catalysts. Conditions tend to be very susceptible to humid and other nucleophilic impurities. Also applied heat catalyzes elimination reactions that is generating impurities. All the mentioned conditions brings up a challenge to obtain a pure product and safe conditions. However, this reactions can be conducted under ambient conditions by photochemical means using the harmony between dimanganese decacarbonyl chemistry and iodonium salts.

Dimanganesedecacarbonyl chemistry has been investigated thoroughly by Bamford *et al.* They have revealed its affinity towards halogens that is directly bonded to organic structures. With a quantum efficiency that is close to unity, dimanganese decacarbonyl absorbs light at visible region and disassociates from Mn–Mn bond to create manganese pentacarbonyl radical which can homolytically abstract halogens. Organoradicals generated by halogen abstraction can be oxidized to corresponding carbocations to initiate cationic polymerization or in this case, used as electrophiles to react with the nucleophiles present in the reaction media. Diols were used as nucleophiles initially to obtain polyethers derivatives. Later on, this approach was further extended to the aromatics to obtain Friedel-Crafts type electrophilic aromatic substitution reactions yielding poly(phenylene methylene) (PPM) derivatives.

Iodonium salts are known for their ability to initiate cationic polymerizations under irradiation with the suitable light. However, their oxidizing characteristic can be experienced even without light but under the presence of oxidizable organo radicals. Diphenyliodoniumhexafluorophosphate (DPI) was selected as the iodonium salt for this synthesis method since it contains a small chromophore group that is transparent in visible light region and bearing non nucleophilic counter anion. As the nucleophilic counteranions are known to terminate the living cations to halt the ongoing cationic reactions, counter anions like PF_6^-, BF_4^- or AsF_6^- are preferred since they are unable to make a covalent bond with the living cations.

Dibromoxylene and dimethoxybenzene were initially used as the electrophile and nucleophile respectively for the reaction. Fluorescent polymers have been obtained from the reactions. Even though no direct conjugation is present through the polymer chain, arising from the hyperconjugation, varying fluorescence properties occurred due to electron density of the benzene rings. By taking advantage of the benzylic bromines at the polymer chain ends, radical polymerizations have been done and block copolymers consisting of PPM and poly(methyl methacrylate) (PMMA) were synthesized and fibers of the blocks were prepared using electrospinning technique. Later on dibromomethane has been utilized in the synthesis of the PPM derivatives. Generated bromomethylenium cation after the abstraction of the bromine and oxidation to the corresponding cation, resulting electrophile is susceptible to be attacked by the dimethoxybenzene nucleophile. Subsequently generated dimethoxybromomethyl benzene is a more reactive species compared to dibromomethane which increases the rate of polymerization through the process. After the kinetic investigation with different concentrations, a shift to the novel chain-growth condensation (CCP) mechanism has been observed. Resulting in easier reactions to be conducted and higher molecular weights. The approach in this thesis is the first application of photochemistry in the CCP mechanism.

FOTOBAŞLATILMIŞ AŞAMALI POLİMERZASYONLAR İÇİN YENİ YAKLAŞIMLAR

ÖZET

Fotokimyasal reaksiyonlar son yıllarda bilimsel camianın büyük ölçüde ilgisini üzerine çekmeyi başarmıştır. Bunun altında yatan en büyük temeller ise fotokimyasal reaksiyonları kullanan teknolojilerin hızlıca gelişmesi ve çevreci olup yüksek etkinliğe sahip olan metotlara karşı artan küresel ilgidir. Geliştirilmiş olan bir çok fotokimyasal reaksiyon kendisine endüstrinin çeşitli dallarında kullanım alanı bulmuş olup, geleneksel metotların önüne geçmeyi başarmışlardır. Bu başarının altında ise ışık gibi verimli ve etkin bir şekilde enerji transferini gerçekleştirebilen kaynak ile reaksiyonların daha az kimyasallar kullanarak gerçekleştirilebilmesi yatmaktadır. Bu verimlilik ışığın kullanıldığı reaksiyonların çevreye olan zararını da azaltmakta olup, ekolojik ve ekonomik faydaları aynı anda kullanıcıya sunmaktadır.

Polimerleşme kimyası her alanda fotokimyasal gelişmelerden faydalanmaktadır. Organik olarak geliştirilen yeni metotların, radikal, katyonik, anyonik ve çeşitli çıtçıt kimyası reaksiyonlarında adaptasyonları görülmektedir. Küresel olarak, dünyanın dört bir yanında farklı çalışma gruplarının ürettiği yeni fotokimyasal başlatıcı sistemler veya tasarladıkları fotobaşlatıcı moleküller sayesinde foto kimyasal olarak gerçekleştilen reaksiyonların verimlilikleri arttırılmakta, uygulamada kullanılan ışığın dalga boyu yükseltilerek daha güvenli ortamlar ve daha ucuz enerji kaynakları kullanımının önü açılmaktadır. Bu gelişmeler de teknolojik ilerlemenin önünü açmakta olup, geleneksel metotların kullanımını azaltmakta, diş dolgusu, üç boyutlu yazıcı, kaplama ve elektronik endüstrilerinin de gelişme hızını arttırmaktadır.

Daha hızlı gelişim kaydedilen reaksiyonlar genellikle zincir polimerizasyonları veya halka açılma polimerizasyonları olarak karşımıza çıkmaktadır. Aşamalı polimerizasyonlar diğer alternatiflerine göre fotokimyasal olarak daha az incelenmiş olup geliştirilme potansiyeline sahiptir. Mekanistik olarak farklılıklara sahip olan aşamalı polimerizasyonlar, doğrudan fotoaktif başlatıcıların kullanıldığı, ortamda reaktif türler oluşturulan polimerleşme yöntemlerine kıyasla daha itinalı ve fazla tepkime basamağının rol aldığı sistemlerin adaptasyonunu gerektirmektedirler. Işık etkisi ile radikal oluşturan başlatıcılar doğrudan kullanılarak yükseltgeyici tuzlar ile karbokatyona yükseltgenerek çeşitli radikal veya katyonik polimerleşme reaksiyonlarının başlatılmasını sağlayabilirler. Ancak aşamalı polimerizasyonlar için bu radikal veya katyonların doğrudan monomer üzerinde üretilmesi gerekmektedir. Bu durum olanakları kısıtladığı için aşamalı polimerizasyonların literatürdeki uygulamalarının daha kısıtlı olarak kalmasına neden olmuştur. Kullanılan monomerlerin de iki fonksiyonel grubu aynı anda molekül içerisinde taşıması gerekliliği de yapılan çalışmalarda safsızlığa neden olabilmekte ve istenmeyen yan ürünler oluşumuna neden olabilmektedir. Tezin kapsamında, yeni ve avantajlı foto başlatılmış aşamalı polimerizasyon metotları geliştirilmiş olup geleneksel metotlara göre kabiliyetleri kıyaslanmış ve sonuçlar raporlanmıştır. Bu kapsamda yer değiştirme reaksiyonları kullanılmış olup, yeni ve floresans moleküller elde edilmiştir.

S_N1 tipi yer değiştirme reaksiyonları iyi bir ayrılan grup varlığında polar solvent ve sıcaklık kullanılarak ısıl yollarla kolay bir şekilde gerçekleştirilebilmektedir. Ancak ayrılan grubun karakteristiğine göre kullanılan kimyasallar bozulmaya çok müsait olabilir veya çok kuvvetli asit katalizörü veya yüksek ısılara ihtiyaç duyabilir. Ayrıca bu reaksiyonlar bu zorlu ortamları nükleofilik bir kirlilik olarak addedilebilecek nemden veya arayapıların bozulmasını katalizleyebilecek oksijenden uzakta gerçekleştirmek durumunda kalabilirler. Ayrıca reaksiyonlar ısıl koşullarda gerçekleştirildiği için yüksek sıcaklıklarda eliminasyon reaksiyonlarının yer değiştirmeleri domine etmesi söz konusu olabilmektedir. Tüm bu bahsedilen durumlardan dolayı reaksiyonların sorunsuz bir şekilde devam etmesi ve saf ürün eldesi zorlaşmaktadır. Fotokimyasal koşullar ise bu durumun üstesinden gelerek, tek basamakta ısıl sorunları ortadan kaldırma, reaksiyona uzay-zamansal kontrol ve güvenilirlik kazandırma potansiyeline sahiptirler. Tez kapsamında dimanganez dekakarbonil kimyasalı ve difeniliyodonyum hegzaflorofosfat (DPI) tuzu arasındaki uyum kullanılarak oluşturulan karbokatyonların kullanılması hususuna dayanarak aşamalı bir polimerizasyon yöntemi geliştirilmiştir.

Dimanganez dekakarbonil kimyası Prof. Dr. Bamford'un araştırma grubu tarafından etraflıca araştırılmış ve sonuçları literatüre kazandırılmıştır. Bu sonuçlarından en kritik olanlarından bir tanesi ise, neredeyse tama yaklaşan, yüksek kuantum verimliliği ile gerçekleşen, iki mangan atom arasındaki kovalent bağın ışık ile homolitik olarak parçalanması ve ardından oluşan manganezpentakarbonil bileşiklerinin organoradikallere karşı duyduğu hassasiyetin tespitidir. Profesör Bamford, çeşitli moleküllerin bu yapıya karşı gösterdiği hassasiyeti incelemiş ve raporlamıştır. Ancak polimerizasyon alanında konuları derinleştirmemiştir. Belirtilen yolla oluşturulan organo radikal bileşikler radikal polimerizasayonlar başlatabilmekte ve dahası oksidatif tuzlar ile yükseltgenerek katyonik zincir polimerizasyonlarına öncülük edebilmektedir. Tez kapsamında ise iki fonksiyonlu, benzilik pozisyonda halojenlerin yer aldığı monomer kullanılması fikrine dayanan, manganezin ışık ile uyarıldığı, parçalandığı, halojen çıkartarak arkasında benzilik ve nispeten kararlı organik radikaller bırakan, ardından difeniliyodonyum tuzu ile benzilik katyonlara yükselen ve güçlü elektrofillere dönüşen bir sistem tasarlanmış ve aşamalı polimerizasyonlara uygulanmıştır.

Dioller öncelikle nükleofil olarak kullanılmış ve başarı ile polieter sentezleri gerçekleştirilmiştir. Sentezlenen polieterler lineer ve çapraz bağlı olarak sentezlenebilmiş, polimerlerin fiziksel özellikleri kullanılan diollerin yapısına göre ayarlanabilmiştir. Daha sonraki çalışmalarda ise nükleofilin gücü düşürülmüş ve aromatik yapılar nükleofil olarak kullanılmıştır. DPI tuzu parçalandığında da aromatik yapıları ortama saldığı için, elektronca zengin organik aromatik yapılar reaksiyon için tercih edilmiştir. Geliştirme sonucunda başarı ile Friedel-Crafts tipi elektrofilik aromatik sübstitüsyon reaksiyonlarını kullanarak yeni ve floresans polimer sentezi gerçekleştirilmiştir. Bu polimerler poli(fenilen metilen) türevleri olup polimer zinciri üzerindeki elektron yoğunlukları arttırılıp azaltılarak floresans özelliklerinde değişimler, çapraz bağlı yapılar, blok, graft ve fiber uygulamaları gerçekleştirilmiştir.

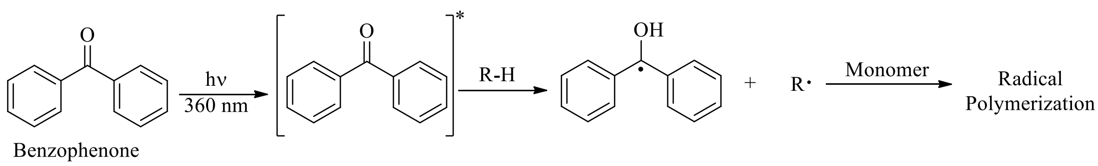
İyodonyum tuzlarının uygun ışık ile uyarıldıkları zaman parçalanarak aşırı oksidatif ara ürünler oluşturduğu bilinmektedir. Ortamda uygun hidrojen kaynağı bulunduğu zaman bu katyonik yapılar asitlere dönüşebilmekte, hidrojen kaynağı bulunmadığı ortamlarda ise monomerler ile elektron transferlerine giderek katyonik polimerizasyonlar başlatabilmektedirler. Ancak ortamda yükseltgenmeye çok açık başka bir deyişle karşıdakini indirgeme potansiyeline sahip kimyasal bulunduğu zaman iyodonyum tuzları herhangi bir uyarılmaya ihtiyaç duymaksızın parçalanarak karşıdakini yükseltgeyebilmektedir. Tez kapsamında dimanganezdekakarbonil ile üretilmiş organoradikaller bu işi gerçekleştirme kabiliyetine sahiptir. Bu özelliklerinden dolayı, dimanganez dekakarbonilin uyarıldığı görünür dalga boyunda herhangi bir absorpsiyon karakteri bulunmayan, tamamen transparan davranan küçük kromofor gruplu bir iyodonyum tuzu olarak difeniliyodonyum hegzaflorofosfat tercih edilmiştir. Ayrıca bu tuzun bulundurduğu hegzaflorofosfat grupları non nükleofilik olduğu için yukarıda bahsedildiği üzere katyonik polimerizasyona zarar vermemektedir.

Friedel-Crafts tipi elektrofilik aromatik reaksiyonları gerçekleştirmek için dimetoksibenzen, hidrokinon ve metoksibenzen başlangıçta nükleofil olarak tercih edilmiş gelecek çalışmalarda da elektronca zenginleştirilmiş heteroaromatik yapılar kullanılmıştır. Elektrofil olarak ise dibromoksilen kimyasalı uygun görülmüştür. Dibromoksilenden elde edilen benzilik radikalle başarı ile benzilik katyonlara oksitlenmiş ve ortamda bulunan çevresine göre kuvvetli nükleofil olan dimetoksibenzenin nükleofilik atağı ile ilk yer değiştirme, bu reaksiyonun tekrarlanarak devam etmesi ile ise polimerleşme sağlanmıştır. Yapılan deneylerde elektrofil olarak dibromometan, diklorometan ve diiyodometan gibi kimyasalların da dimanganezdekakarbonil kimyası ile halojenlerini kaybedebileceği gözlemlenmiş ve elde edilen radikallerin DPI ile oksitlenebilirliği görülmüştür. Bahsedilen işlemler sonrasında oluşturulmuş olan halidometilenyum katyonları dimetoksibenzen tarafından saldırıya uğramaya açıktır. İlk yer değiştirme reaksiyonu sonrasında oluşan yapı ise artık benzilik bir halojen içermekte ve reaktivitesinin arttırılması gerçekleştirilmiş haldedir. Dolayısıyla bu reaktivite artışı reaksyion hızı artışını tetikler ve polimerizasyon mekanizması aşamalıdan zincir polimerizasyona evrilir. Yapılan çalışmalar sonucu gerçekten kimyasal oran bire birden başka oranlara çevirildiğinde zincir polimerizasyon karaktersitikleri gözlemlenmiştir. Aşamalı polimerizasyonun en büyük sorunlarından birisi olan “capping” olarak da adlandırılan, aktif zincir uçlarının molce dominant karşıt reaktif kısım tarafından kapatılarak zincirin erken kapatılması ve polimerizasyon gerçekleşmemesi sorunu, reaktiflerden diklorometan çözücü olarak kullanılsa dahi polimerizasyon gerçekleşmiştir. Bu daha kolay gerçekleştirilebilir reaksiyon metotlarının geliştirilmesini sağlamasına ek literatürdeki ilk fotobaşlatılmış “chain growth condensation” yani kondenzasyon zincir polimerizasyonu örneğidir.

1. INTRODUCTION

Photopolymerization is a unique tool that extends the grasp of chemistry by employing the efficient nature of light. Heat transfer has always been causing problems to conduct several reactions. To adjust the temperature and distribute the heat evenly, different stirring techniques or employing different solvents were the only options. After the initial advancements in photoinduced techniques, light has successfully decrease the dependence on heat in several methods.[1] In addition to this, it also provided spatiotemporal control over the reaction media. [2], [3], [4], [5], [6], [7], [8] This phenomenon makes the energy transfer occur efficiently over determined volumes to increase the yields and prohibit the formation of undesired byproducts[9] which emerged the development of 3D-VAT printing industry recently.[10]

Photopolymerization can occur when a suitable monomer and photoinitiator combination used in the correct molar ratios. Several different photoinitiators are available commercially to be used directly to conduct photopolymerization in cationic, anionic, or radical means. Mechanistic pathways that photoinitiators work can differentiate from one another. By the photochemical mechanism, photoinitiators are generally divided into two separate groups namely, Norrish Type I and Norrish Type II. (Figure 1.1)



Radical polymerization initiated by benzophenone.

Norrish Type I photoinitiators are photochemically active species that undergo homolytic cleavage under irradiation.[1] The resulting radical species can initiate radical reactions or can be further oxidized to their carbocations to promote cationic polymerizations. On the other hand, Norrish Type II photoinitiators involve a different mechanism. After irradiation, initiator became excited and there is a hydrogen transfer occurring between the photoinitiator and hydrogen donor. Aliphatic amines are generally utilized as the hydrogen donor in this cases.[11] The detailed mechanism has been depicted in Figure 1.2.

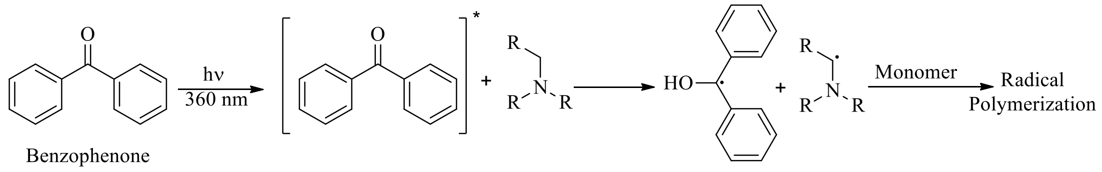


Figure 1.1 : Photoinitiated radical polymerization using benzophenone as Norrish Type II photoinitiator.

Further approaches involve the heterolytic cleavage of the covalent bonds to generate reactive species to yield in either cationic or anionic polymerization. This disassociation may not yield directly electrophilic or cationic species but further transformations occurring inside the molecule can yield the mentioned species. These kinds of photoinitiators were also examined as photoacid generators and photobase generators.[12], [13], [14], [15], [16], [17] They had a huge impact on both organic chemistry and polymer chemistry.[6], [7], [8], [18], [19], [20], [21] Detailed mechanisms are depicted in Figure 1.3.

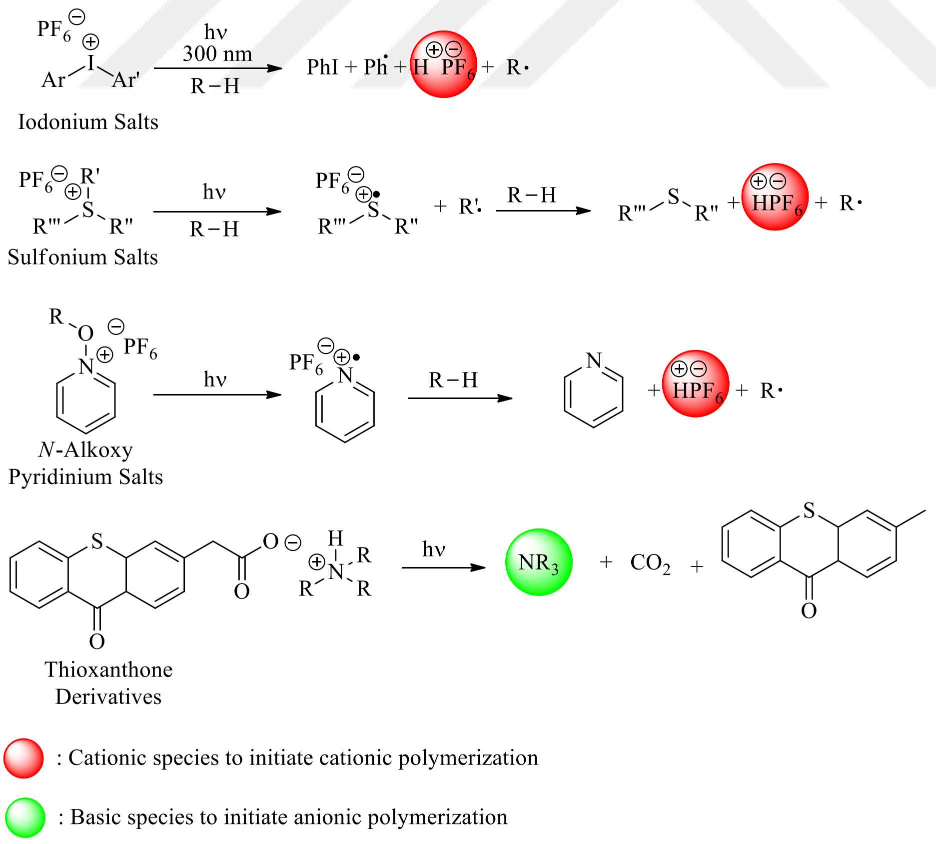


Figure 1.2 : Generations of acids and bases using photoacid generators and photobase generators

Some of them involve in situ generation of reactive species that can reduce or oxidize metals to initiate the reactions that have recieved great attention.

1.1 Photoinduced Radical Polymerizations

Conventional radical polymerization methods are well established and several applications of them produce the majority of the commodity plastics. A wide range of applications made the polymer derivatives namely polystyrenes and polyacrylates the fundamental monomer derivatives that can be polymerized by radical means efficiently. However, some drawbacks can be taken care of when dealing with large scales including the gel effect. These kinds of drawbacks of conventional methods can be neutralized by applying photoinduced techniques in the reaction media.

The most commonly used commercial photoinitiators for photoinduced radical polymerizations can be divided into three by the light absorption characteristics which use UV light, visible light and near IR light.

1.1.1 Radical photoinitiation systems using UV light

Both Norrish Type I and Norrish Type II alternatives of photoinitiators using UV light as an energy source to initiate polymerization can be easily purchasable commercially. Benzophenone can be given as an example for Norrish Type II photoinitiator in this section the as it is the most known and oldest chemical to perform such a task. Benzophenone is a simple and stable chemical that undergoes light induced radical polymerization using UV light. After irradiation, subsequently formed excited state abstracts a hydrogen from a hydrogen donor inside the reaction media such as isopropyl alcohol or aliphatic amines. Generated radicals either start polymerization or result in coupling with each other to create dimerization also known as the Pinacol reaction. Pinacol reaction occurs only if there is no suitable, polymerizable monomer present inside the reaction media. The mechanism is depicted in Figure 1.1.1.1.

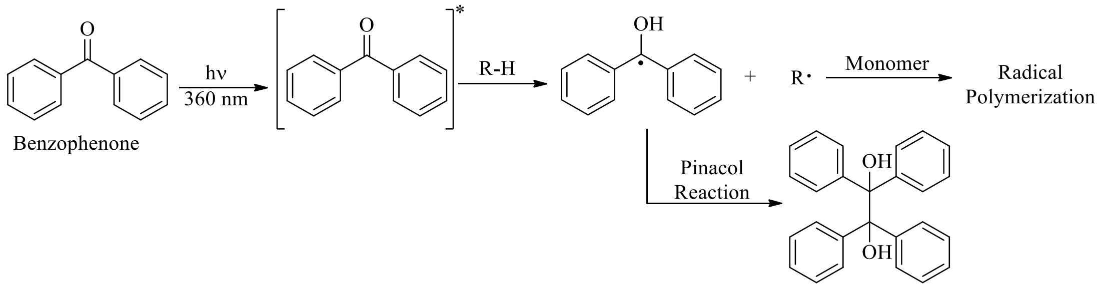


Figure 1.3 : Radical polymerization initiated by benzophenone and coupling of two benzophenone molecules to result in Pinacol Reaction.

1.1.2 Radical photoinitiation systems using visible light

Visible light initiation systems bring operational safety and ease in addition to higher energy-conversion efficiency. It eliminates the need to use expensive quartz glassware for conducting polymerization since regular glass has almost perfect transparency in the visible light region. Furthermore, the energy of visible light itself and the costs of visible light emitting lamps are lower than the UV alternatives, it has a direct effect to reduce the production costs of the methods. Scientists across the globe have been racing to develop efficient visible light photoinitiators in order to leverage the previously mentioned advantages. The commercialized alternatives of some Norrish Type I photoinitiators can be found under different brand names like IRGACURE. The disassociation mechanism of bisacylphosphineoxide (BAPO - IRGACURE 819) and initiation of the polymerization have been depicted in Figure 1.1.2.1.

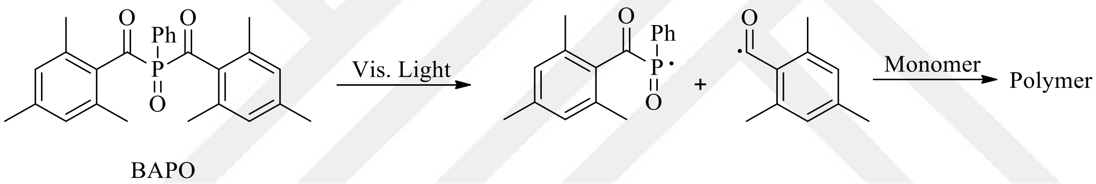
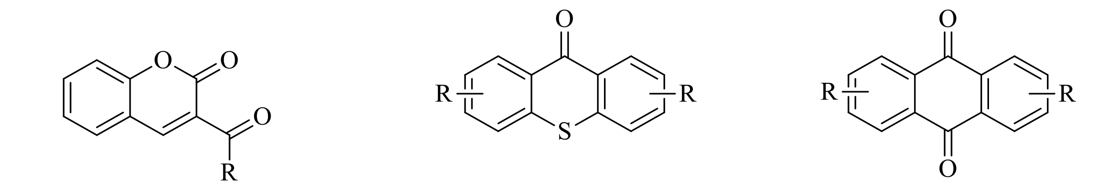


Figure 1.4 : Radical polymerization initiated by Norrish Type I photoinitiator bisacylphosphineoxide (BAPO)

Since the efficient nature of light brings spatiotemporal control to the reaction media, high spatiotemporal control over the reaction makes the energy transfer occur efficiently on the exactly determined volumes. Additionally, it is possible to excite chemicals selectively to initiate selective reactions in a mixture of chemicals which can result in tuneable printouts using the 3D-VAT method. The demand of industry for such photoinitiators are gradually increasing since the 3D printing devices are becoming easily reachable by small scale businesses and even the homes of the individuals. Technological advancements in this particular area push the scientist to develop systems that can yield printouts with higher resolution. In the systems of Norrish Type II photoinitiators on the other hand, bigger chromophore selection has been observed due to alter the absorption characteristics of the photoinitiator. Keto-coumarines, thioxanthones and anthraquinone derivatives are generally used to create a photoinitiation mechanism using a hydrogen transfer technique. (Figure 1.1.2.2)



Keto-coumarin Derivatives Thioxanthone Derivatives Anthraquinone Derivatives

Figure 1.5 : Most common Norrish Type II photoinitiators.

A similar reaction mechanism is observed as the benzophenone but the kinetics of the reaction may differ due to the stability of the generated radical, rigidity of the molecular structure, quantum efficiency, and the absorption coefficient of the molecule itself. One different approach can be given as an example in this section which utilizes the halogen abstraction capabilities of the metal carbonyl compounds. Ruthenium and manganese decacarbonyls are especially well-established by the research made by Bamford et al. They have expressed the possibilities of employing such chemistry in the photopolymer science. Halogen abstraction and subsequent initiation of the radical polymerization have been depicted in Figure 1.1.2.3.

$$Mn_2(CO)_{10} \xrightarrow{\text{Vis. Light}} 2\cdot Mn(CO)_5 \xrightarrow[\text{-BrMn(CO)}_5]{\text{R-Br}} R\cdot \xrightarrow{\text{Monomer}} \text{Polymer}$$

Figure 1.6 : Visible light induced radical polymerization initiated by halogen transfer using dimanganesedecacarbonyl.

Norrish Type II initiation mechanism has been observed using a halogen donor instead of a hydrogen donor in the mentioned system. In the scope of this thesis, this chemistry is further developed into the step-growth polymerization reactions by oxidizing the resulting organo radicals.

One last approach by Fors and Hawker further develops that idea to the organic molecules that can be excited around 400 nm and abstract halogens. Phenothiazines, especially 10-phenylphenothiazine were found to be the best photoinitiator for such task. The initiation mechanism has been shown in Figure 1.1.2.4.

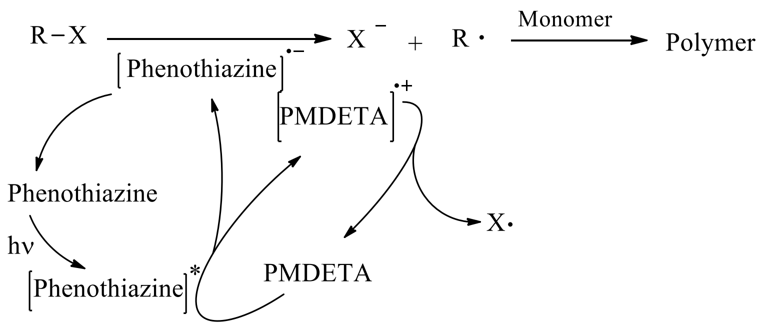


Figure 1.1 : Visible light induced radical polymerization initiated by halogen transfer using phenothiazines.

1.1.3 Radical photoinitiation systems using NIR light

Polymerization reactions utilizing NIR light has been gained tremendous attention in the recent years. Since it is the most abundant type of light emitted from the sun and has the highest operational safety, the race amongst the scientists to develop photoinitiating systems using NIR light is resuming rapidly. Larger chromophore groups are selected to extend the absorption range of the photoinitiators. Since the NIR light is the most abundant type of light in the environment, direct photoinitiators can be decomposed before use which is a challenging task to overcome. Therefore developments in that particular area focus more on developing Norrish Type II photoinitiating systems that take benefit from the photosensitizer and a hydrogen donor. Strehmel's group focuses on the development of NIR absorbing photosensitizers for such polymerizations. They mainly functionalize and develop cyanine dye derivatives to adjust the characteristics of the polymerization that is being used. By our research group, halogen abstraction capabilities of the organodyes have been investigated as an atom transfer radical polymerization mechanism and the results were reported. Organodyes that absorb light at visible to NIR namely, eosin Y and erythrosine B have been used to abstract halogens of the coinitiators and the subsequently formed oligomers to make atom transfer radical polymerization occur as phenylphenothiazine does. Detailed mechanism has been depicted in Figure 1.1.2.5

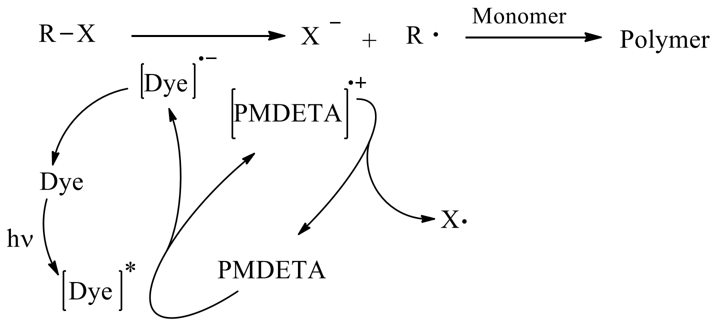
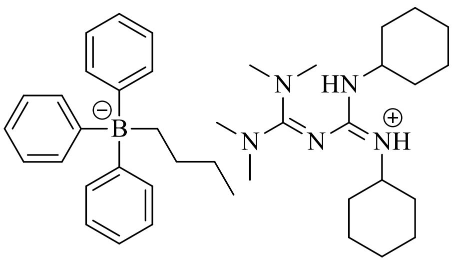


Figure 1.2 : NIR light induced radical polymerization initiated by halogen transfer using organodyes.

1.2 Photoinduced Anionic Polymerizations

Photoinduced anionic polymerizations have been investigated scarcely compared to the alternatives since preserving the ongoing reaction is harder in this polymerization method. Living anions tend to react with air or humidity more aggressively to stop the polymerization yielding byproducts, short chains and high dispersity. However, by using photobase generators, thiol-ene click reactions and thiol-epoxy click reactions can be catalyzed efficiently to obtain polymers benefiting from the characteristics of the mentioned reactions. The earliest examples of photobase generators are dating back to 1997 which utilize the use of tungsten and chromium pentacarbonyl pyridine complexes that releases pyridine after irradiation to initiate polymerization. More modern approaches utilize the excitation of chromophore groups which triggers the release of carbon dioxide from the bonded carboxylic acid part with a methylene bridge to trigger the generation of aggressive carbanions instead of carboxylates. These carbanions are acting as bases or nucleophiles to initiate the anionic polymerization. Some commercial photobases are given in Figure 1.2.1.1 and the mentioned reaction mechanism has been depicted in Figure 1.2.1.2.



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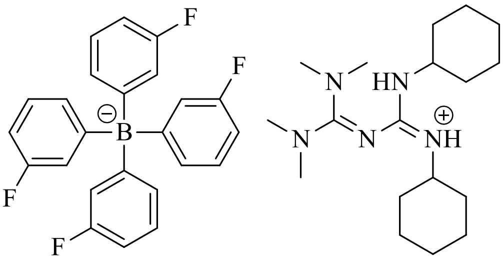

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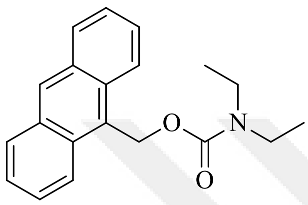

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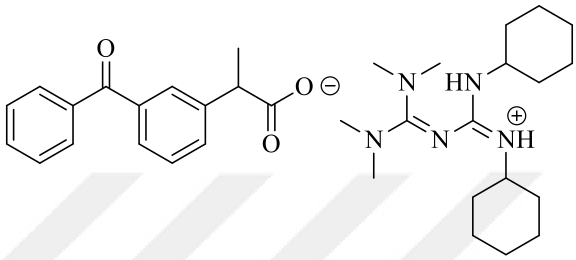

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Figure 1.3 : Commercially available photobase generators.

Our research group successfully managed to make polymer functionalizations utilizing photobase generators in collaboration with Zhiquan Li's research group. That approach involves the mentioned thiol epoxy click reactions to yield grafts, blocks and chain extensions utilizing thioxanthone carboxylic acid derivatives as the photo base generator.

1.3 Photoinduced Cationic Polymerizations

Cationic polymerization is a well-established technique that plays an important role in industry. Even the earliest example of the commercial polymers, which is a phenol formaldehyde resin, has been synthesized by cationic polymerization by Leo Baekeland in 1907. Before photoinitiated approaches, several Lewis acids were examined by the industry and scientists across the globe to obtain the best results. Even though, increasing the reactivity of the Lewis acid has a positive effect on the yield, it has created more dangerous reactions to handle. In addition to danger, it has also increased the costs of the chemicals and the required precautions for the reaction to be conducted successfully. Arising from these challenges, photochemistry offers the ideal solutions for these problems using photoacid generators or photooxidizers.

The development of methods that use the most common onium salt, namely iodonium salts in photochemistry dates back to 1977. Initial efforts have been made by Lam and Crivello to obtain direct cationic photopolymerization. They have successfully conducted cationic chain polymerization and ring opening polymerizations using a variety of onium salts. As they have suggested, using a non-nucleophilic counteranion for the onium salt is a must for the cationic polymerization to occur. Otherwise, the nucleophilic counteranion reacts with the living cationic chain to result in non-polymerizable polymer chains with a bromine chain end. The same thing applies to the other onium salts too. *N*-alkoxypyridinium and triarylsulfonium salts are also can be seen in several applications of photochemically initiated cationic polymerizations. Combining the stability in room temperature with the reactive nature when excited, mentioned onium salts are finding themselves a crucial role in the polymerization field. Widely used and some commercially available onium salts are given in Figure 1.4.

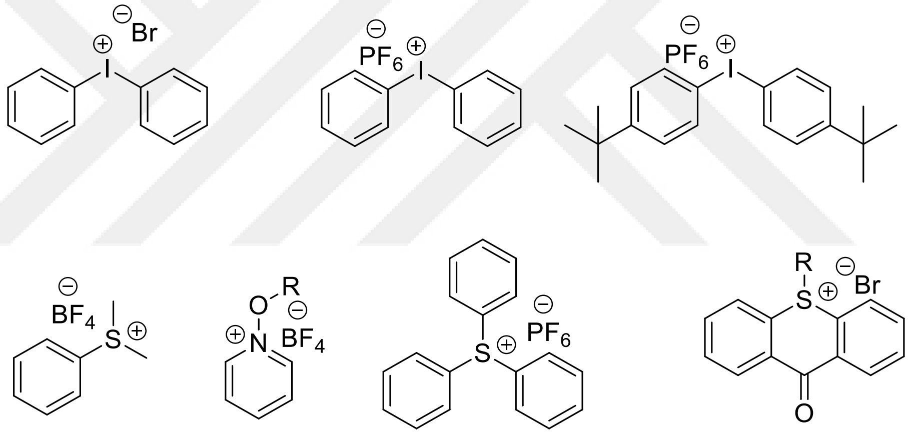


Figure 1.4 : Widely used onium salts.

A variety of applications can be performed using onium salts from frontal polymerization to 3D printing. They can also react with the generated radicals by the above mentioned paths and excited photosensitizers at different wavelengths which open new horizons for applications. Therefore initiating systems using onium salts can be divided into three regarding their reaction mechanism for creating the reactive species.

1.3.1 Direct initiation systems

Direct initiation of cationic polymerization using onium salts utilizes generally UV lights since in the early stages of development, onium salts could only contain relatively smaller chromophore groups. That actually had a positive impact on shelf life and made it possible to be stored at room temperature. By their molecular structure most commonly used onium salts can be divided into three as pyridinium salts, sulfonium salts and iodonium salts. Their molecular structures are given in Figure 1.5.

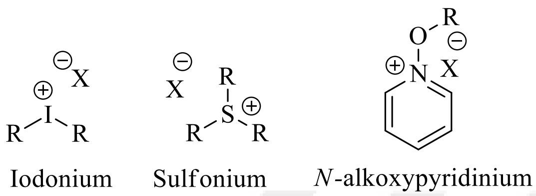


Figure 1.5 : Common types of onium salts

In some cases, since they are producing acids after the irradiation they can be referred as photo acid generators.

1.3.1.1 Pyridinium salts

N-alkoxypyridinum salts amongst this group are well-known and established over time. However, due to its lower reactivity compared to alternatives, the focus of the scientists shifted over iodonium and sulfonium salts more. There are still contributions on literature involving pyridinium salts can be seen that underlines the need for such chemistry in the polymerization field. The mechanism of direct initiation of *N*-alkoxypyridinium salts involves the absorption of light, excitation of the onium salt and than subsequent homolytic cleavage occurring on N-O bond to yield alkoxy radical and pyridine radical cation. Pyridine radical cation undergoes the required electron transfer from the environment to initiate the cationic polymerizations. The detailed mechanism has been depicted in Figure 1.6.

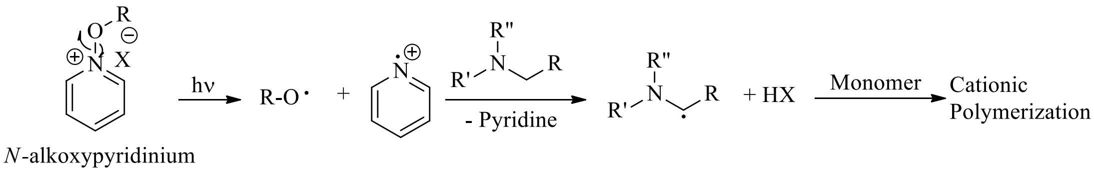


Figure 1.6 : Photoinduced acid generation and cationic polymerization by *N*-alkoxypyridinium salts.

1.3.1.2 Sulfonium Salts

Photochemically used sulfonium salts refer to trivalent sulfur atoms that are on the cationic state. They find themself use in the field of radical and cationic polymerizations. Several approaches make use of sulfonium salts to generate oxidative radical species that can undergo electron transfer reactions to promote cationic chain polymerizations.

As mentioned previously, photochemically triggered reactions and the formation of a charge transfer complex is possible between electron donor species and sulfonium salts to make electron transfer happen between the salt and the photosensitizer molecule. Mentioned reaction mechanism has been shown in Figure 1.7.

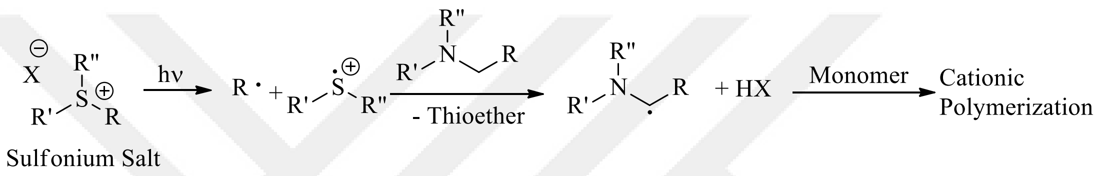


Figure 1.7 : Photoinduced acid generation and cationic polymerization by sulfonium salts

Our research groups have successfully synthesized derivatives of sulfonium salts previously for the initiation of both cationic or radical polymerizations involving different kinds of reaction mechanisms.

1.3.1.3 Iodonium Salts

Iodonium salts are the most reactive yet still stable alternative amongst the onium salts. They enable the scientists to develop several applications including 3D printing and frontal polymerization by taking advantage of the reactive nature of the iodonium salts. Initial development was made by Law and Crivello in 1977. As mentioned previously, they have successfully synthesized a variety of iodonium salts and applied them in cationic polymerization by using suitable wavelengths to irradiate them. Commonly used iodonium salts are given in Figure 1.8.

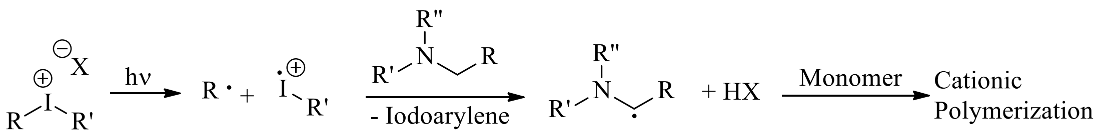


Figure 1.8 : Photoinduced acid generation and cationic polymerization bu iodonium salts

Since they are the most reactive onium salts in the literature, scientists across the globe are trying to develop novel iodonium salts to bring their absorption range to the visible to NIR area. Visible light induced direct cationic polymerizations are possible with that advancement, which can further develop 3D printing field involving only cationically polymerizable monomers.

After the irradiation, the excited iodonium salt directly decomposes between I-C bond to yield in an organo radical and iodoaryl radical cation. Which has an immense oxidation potential to initiate polymerization reactions. If suitable hydrogen donors are provided in the reaction media, subsequently happening electron transfer and hydrogen transfer results in superacid generation depending on the counteranion of the iodonium salt as explained previously.

1.3.2 Indirect initiation systems

Indirect photoinitiation systems involve different approaches. Either a photosensitized system or a free radical promoted cationic polymerization system can be considered as an indirect initiation system.

1.3.2.1 Photosensitized systems

Photosensitized systems consist of two different components involving an oxidizing salt and a photosensitizer. Photosensitizer is responsible for the absorption of light. The electron transfer reaction between the excited photosensitizer and the onium salt is accounted for the initiation of the polymerization reaction. Some of the common photosensitizers are given below in Figure 1.9.

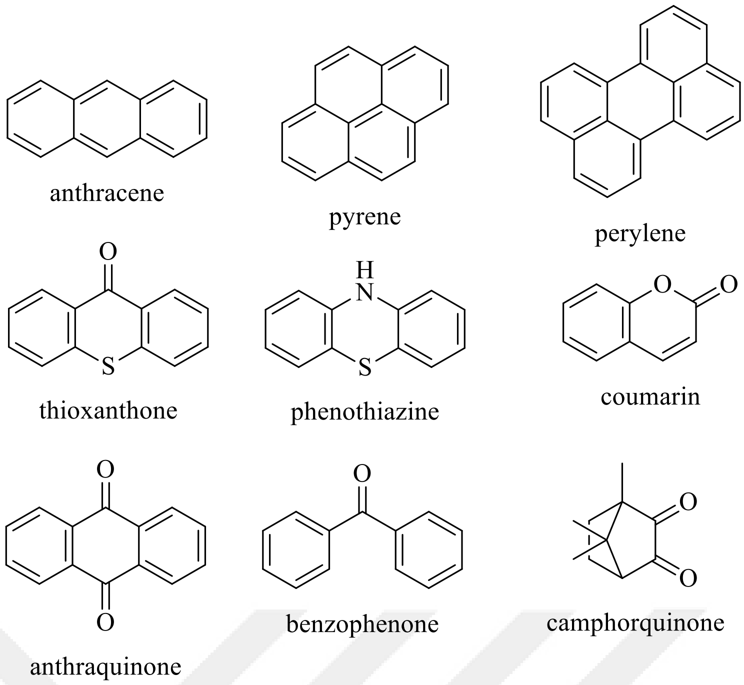


Figure 1.9 : Commercially available and mostly used photosensitizers.

Different photosensitizers can result in different polymerization kinetics. There is some research that investigates the photosensitizers photoinitiating capabilities by adding and subtracting electron acceptor and donor moieties in the molecular structure. Recently developed iodonium salts are highly active in the photopolymerization of vinyl ethers and epoxides even under visible light irradiation. Detailed investigations done by laser flash photolysis and cyclic voltammetry experiments revealed increasing nucleophilicity of the counter anion and donor–π–acceptor nature of the chromophores increasing the efficiency of the onium salts.

1.3.2.2 Free radical promoted cationic polymerization systems

Initial reports on free-radical promoted cationic polymerizations date back in 1978. This innovation broadened the horizon for the development of novel cationic polymerization routes. Since thermally and photochemically generated radicals can readily be oxidized by onium salts to the corresponding cations, this property brings new possibilities to initiate cationic polymerizations. A vast number of light sources including UV, visible, and NIR light can be adapted into free radical promoted cationic polymerization.

Free radical promoted cationic polymerization systems were proven to be useful to broaden the spectral response of the all onium salts. The wide variety of photoinitiators and salts allow the researchers to tune the absorption characteristics of the polymerization reaction. The molecular structures of the most common visible light photoinitiators including acyl germanes, acyl phosphine oxides and acyl silanes that undergo homolytic cleavages after irradiation to yield radicals are given in Figure 1.10. Also, conventional UVC absorbing photoinitiators including benzophenone or acetophenone can be utilized as a photoinitiator for free radical promoted cationic polymerization.

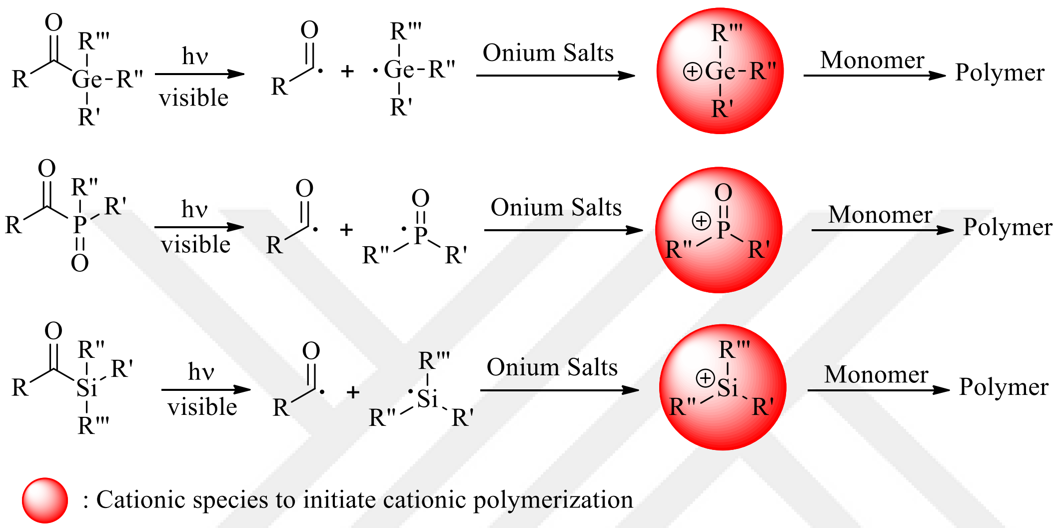


Figure 1.10 : Free-radical promoted cationic polymerizations using different initiators.

Since the number of NIR absorbing photoinitiators are low, upconverting nanoparticles have been utilized by our research group previously to conduct polymerization with the same mechanism. The approach involve the use of upconverting nanoparticles to convert NIR light into the visible light inside the reaction media to conduct free radical promoted cationic polymerization.

Even though some of the resulting radicals generated by photocleavage are not capable to be oxidized by onium salts, they may have a tendency to abstract hydrogen or halogen. Subsequently formed radicals can also be oxidized to promote cationic polymerization. Dimanganese decacarbonyl chemistry is actually belongs in this group. Polymerization initiates after the oxidation of the resulting radical after the halogen abstraction. Detailed mechanisms of the mentioned initiating systems are shown in Figure 1.3.2.2.2.

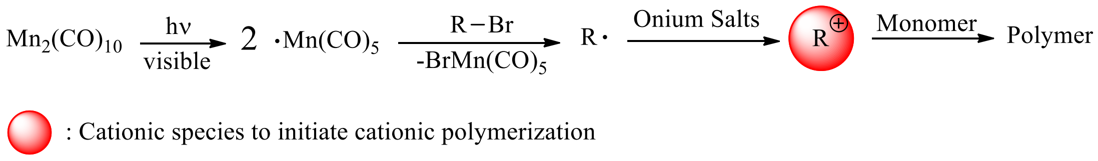


Figure 1.11 : Free-radical promoted cationic polymerization using dimanganesedecacarbonyl as the photoinitiator

1.4 Photoinduced Chain-Growth Polymerizations

Chain-growth polymerization mechanism is fundamentally different from the step-growth polymerization. In chain-growth polymerizations, a reactive specie is generated either by heat or light, and when used with a suitable monomer polymerization occurs. Chain-growth polymerization reactions can involve any mechanism namely radical, anionic, or cationic. Just like in the thermal route, photoinduced chain-growth polymerizations involve a suitable combination of monomer and the photoinitiator for the polymerization. Initial developments on photochemically promoted chain-growth polymerizations mainly involve radical polymerizations.

Radical polymerization is a well-established technique to yield a wide variety of styrenic and acrylic polymers. These polymers are widely used in several applications arising from their advantages over other materials. Since the radical polymerization is easy to conduct and can be adapted to several fields, recent technological advancement in additive manufacturing industry took advantage of it to build advanced 3D-VAT printing systems.

Chain polymerization initiates really fast compared to step-growth alternatives. And polymerization continues through the reactive sides of the active molecules. Inconvenience in the initiation step may result in a high dispersity of obtained polymers. In order to get rid of this high dispersity problem occurring in the free radical polymerization, two different techniques namely atom-transfer radical polymerization and reversible addition fragmentation chain-transfer methods were proposed by Matyjaszewski and Rizzardo respectively.

By atom-transfer radical polymerization, Matyjaszewski's research group interfered with the propagation step and adjust the resulting dispersity of the obtained polymers. Copper metal was utilized as the coinitiator and also plays the role of the deactivator and the reactivator of the propagating chain. By this strategy, they have successfully obtained polymers with very low dispersity that found their use in several different fields including material science to drug delivery. A typical simplified mechanism of atom-transfer radical polymerization involving copper salt has been illustrated in Figure 1.12.

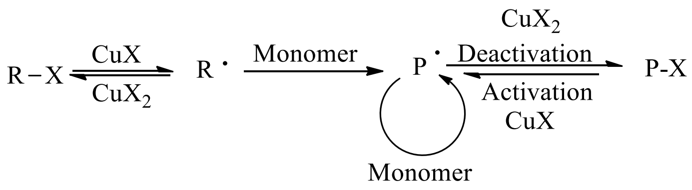


Figure 1.12 : Simplified atom-transfer radical polymerization mechanism

A similar approach is taken by reversible addition fragmentation chain transfer methods. Instead of copper complexes, now dithiocarboxylate derivatives are utilized for the chain transfer. A detailed explanation of reversible addition fragmentation chain transfer method is observable in Figure 1.13.

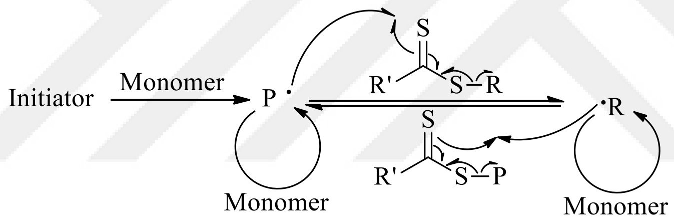


Figure 1.13 : Simplified reversible addition fragmentation atom transfer polymerization mechanism

Photoinduced approaches that take advantage of the previously mentioned radical polymerization methods were initially developed by our research group. Prof. Yagci successfully developed photoinitiated atom-transfer radical polymerization by employing photochemical reduction of copper(II) anion inside the reaction media to obtain copper(I) which can be used to perform atom-transfer radical polymerization.

In the field of cationic chain polymerizations, conventionally obtained ring opening polymerizations of cyclic ethers, caprolactone, siloxanes and direct cationic polymerization of vinyl ethers were done by using acid catalysts. By employing photoacid generators with a non-nucleophilic counteranion physical properties of the obtained polymers can be altered. Using onium salts are also favorable since transportation and storing superacids are challenging tasks for sustainability and economy. Bringing storage conditions to the room temperature and under air atmosphere is highly beneficial.

1.5 Photoinduced Step-Growth Polymerizations

Step-growth polymerizations involve a different approach than chain growth polymerizations. Bifunctional monomers are employed instead of an initiator molecule and polymerizable monomer combination. Polymer chains do not propagate from a reactive end, instead, every molecule contains at least two reactive sites. This alters the polymerization kinetics of the step-growth polymerization. Unlike chain polymerization, in step-growth polymerization at the beginning dimerization and oligomerization occurs and over time those oligomers react with each other to create polymer. In chain polymerization the other hand, rapid reactions occur subsequently between the reactive chain end and the monomers to result in the polymer. Overall kinetics can be illustrated in Figure 1.14.

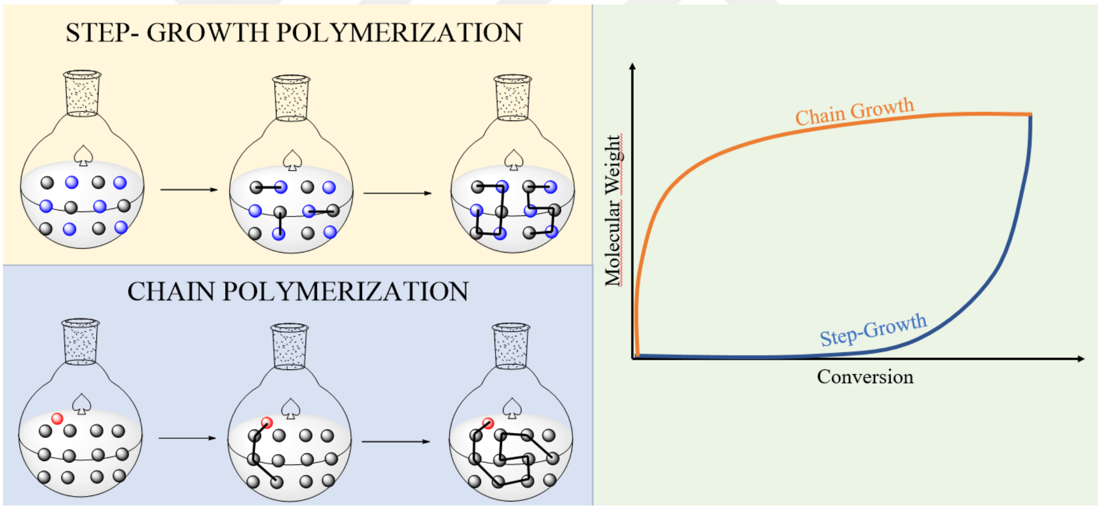


Figure 1.14 : Illustrations of chain-growth and step-growth polymerizations to underline the effect of the mechanism on the final product.

Industrially important polymers namely, polyesters, polycarbonates, polyamides, polyurethanes, some epoxides, polyimides and polyureas are being synthesized by step-growth polymerizations. Even though most of them use conventional acids to catalyze the reactions, photochemical approaches are developing in this field rapidly.

Introduction of photochemistry opened new horizons for the step-growth methods of synthesizing conducting polymers in one pot without requiring any premodification. Our research group under the management of Prof. Yagci had successfully developed novel methods on this topic. These methods made the polymerization of polythiophenes, polycarbazole and polypyrene derivatives possible under room temperature using photooxidizers. The method was also coined as photooxidative polymerization of conjugated monomers. Possible reaction mechanism to yield polethylcarbazole has been given below in Figure 1.15.

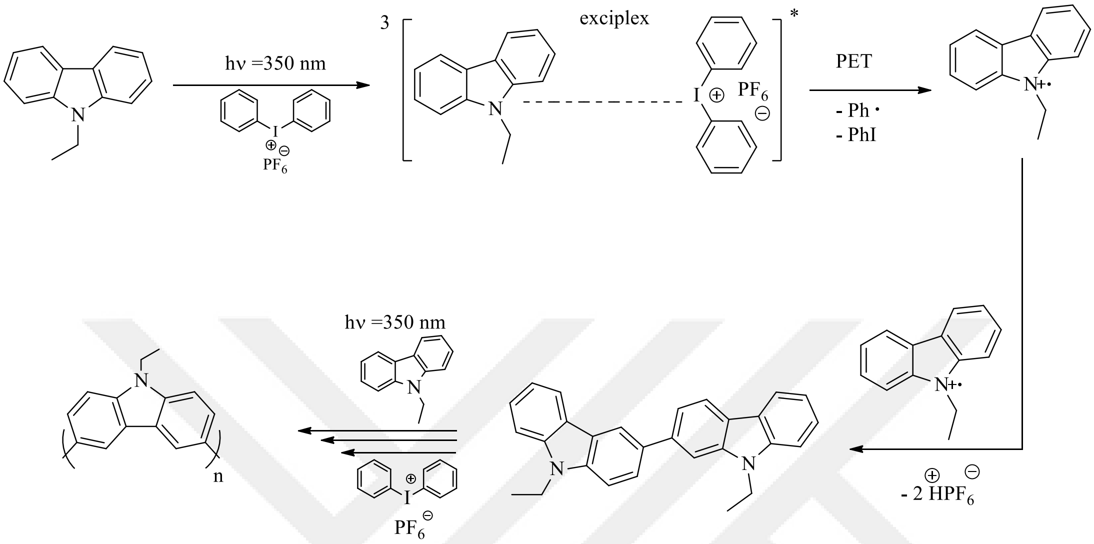


Figure 1.15 : Different routes for photooxidative polymerization to obtain conjugated polymers.

In the scope of the thesis, the horizon will be further extended into the photoinduced substitution reactions to yield polymers including Friedel-Crafts type electrophilic aromatic substitutions.

1.6 Purpose of the Thesis

The objective of this thesis is to develop novel photoinduced step-growth polymerizations and investigate the possible applications of both the method and the synthesized polymers. Novel photoinduced polymerization techniques involving photoinduced substitution reactions, Friedel-Crafts type electrophilic aromatic substitution reactions and possible mechanistic transformation to chain polymerization have been investigated. To investigate the kinetics of the photopolymerization reactions, spectroscopic techniques including nuclear magnetic resonance, Fourrier Transform infrared, UV-Visible and fluorescence spectroscopy together with gel permeation chromatography, differential scanning calorimetry and thermogravimetric analysis have been used. The thesis is written in a way to include their own introduction and discussion parts.

2. VISIBLE LIGHT INDUCED STEP-GROWTH POLYMERIZATION BY SUBSTITUTION REACTIONS

2.1 Abstract

A new visible light induced step-growth polymerization of dibromoxylene, and diols using dimanganese decacarbonyl and diphenyliodonium salt is described. The polymerization is suggested to proceed by substitution reaction between dixylenium cations formed upon visible light irradiation in the presence of dimanganese decacarbonyl and diphenyl iodonium salt. For the described substitution reaction with diols as nucleophilic component, the scope of the process is studied. Furthermore, the presence of halide groups at the chain ends of the resulting polymers provided the possibility of initiating subsequent free radical and free radical promoted cationic resulting in the formation of polyether-based block copolymers.

2.2 Main Text

Light induced strategies provide unique advantages in comparison to conventional processes such as spatial and temporal control, rapid reaction rates, and no solvent requirements.[22], [23] The low energy requirement, reduction of polymerization time, and chemical consumption underline the importance of such systems as green processes.[24] Moreover, they provide in situ processable materials at room temperatures, which cannot be obtained by thermal means.[25], [26] After such advantages have been realized, many polymerization processes as well as polymer modifications have been adapted to light induced procedures. Free radical, cationic, and anionic polymerizations have been extensively performed by photochemical means.[12], [27], [28], [29], [30], [31], [32], [33], [34], [35] This way, a wide range of structurally different polymers can successfully be prepared under irradiation at a broad wavelength range including near infra-red region. However, the corresponding light-induced step-growth polymerization has scarcely been investigated.[11], [36], [37], [38], [39], [40] By taking advantage of the advanced state of the conventional approaches, recent research interest in synthetic polymer chemistry is directed to adapt photoinduced reactions to step-growth polymerization. Generally, applied light induced strategies include cycloaddition and selected organic reactions or consequential electron transfer and radical coupling processes.[36], [37], [38], [39],

[40], [41] The latter can be achieved by the use of conjugated aromatic structures as monomers and onium salts with appropriate oxidation potentials and non-nucleophilic counter ions as oxidants. The mechanism considers an electron transfer from the electron-rich aromatic compound to the onium salt to yield the corresponding radical cation of the monomer. After a series of proton release and radical coupling steps, conjugated step-growth polymers can be readily obtained. The latest reports from our laboratory demonstrated the possibility of the syntheses of polycarbazoles, polythiophenes, and polypyrenes using this strategy.[42], [43], [44], [45], [46], [47] Figure 2.1 shows the overall process in the example of the polymerization of N-ethylcarbazole.

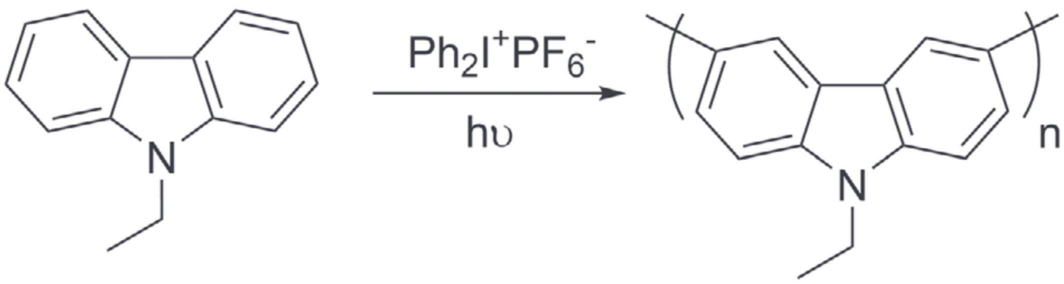


Figure 2.1 : Synthesis of poly(*N*-ethylcarbazole) by light induced step-growth polymerization.

In another study, it was shown that conventional step-growth polymers can be prepared to benefit from dimanganese decacarbonyl ($Mn_2(CO)_{10}$) chemistry. For that purpose, bisbenzylbromide compounds having ester, amide or urethane skeletons as inner structures act as monomers to give polyesters, polyamides, and polyurethanes, respectively under visible light irradiation.[48] Figure 2.2 shows the overall synthetic approach on the example of the formation of polyesters.

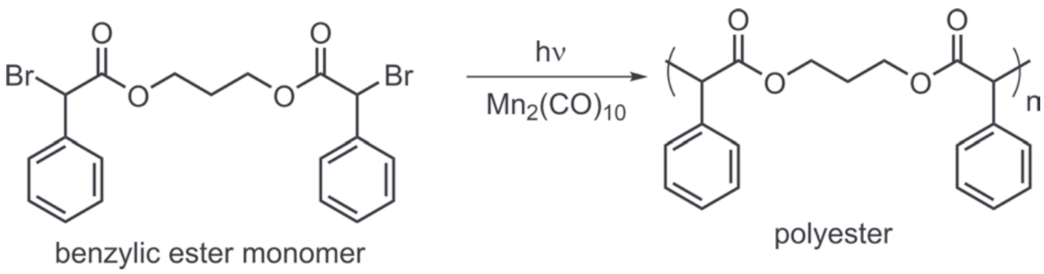


Figure 2.2 : Synthesis of polyesters by light induced step-growth polymerization.

In this study, we extend the $Mn_2(CO)_{10}$ photochemistry to generate cationic species and present a new nucleophilic substitution methodology for the synthesis of polyethers. $Mn_2(CO)_{10}$ is known to generate radicals from alkyl halides through halogen abstraction under visible light. Since the quantum yield of $Mn_2(CO)_{10}$ for initiation is close to unity at high halogen concentrations, the reacting species can be easily generated.[49], [50] Thus formed radicals are generally used for the free radical polymerization of various monomers. In addition, these radicals are also oxidized to their corresponding cations to initiate free radical promoted cationic polymerization.[8], [51], [52] In this work, we employed $Mn_2(CO)_{10}$ for the generation of bisbenzylic cations, which react with diols to form polyethers successfully. Diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) is used as an oxidant for the generation of benzylic cations, which are more prone to nucleophilic attack in comparison to benzyl halides.

Polymerizations were performed using α,α′-dibromo-p-xylene (DBX) and 1,2-ethanediol, 1,3-propanediol or 1,6-hexanediol, and glycerol.

As can be seen from Table 2.1, both 1,2-ethanediol and 1,3-propanediol gave polyethers with similar molecular weight characteristics (runs 1 and 2). Notably, diols with short alkyl chains are essential for the polymerization to occur; no polymer is formed when 1,6-hexanediol is used as the diol component under our reaction conditions (run 3). An affordable polymer was obtained only at prolonged irradiation times, which might be attributed to the limited interaction of the hydroxyl groups having longer spacer groups with the cationic centers (run 4). Convincing evidence for the polymerization mechanism was obtained from the crosslinking monomer glycerol. Because of the presence of three diol groups, this monomer readily crosslinks and ultimately forms gelled systems (run 5).

Table 2.1 : Visible light induced step-growth polymerization using DBX and various alcohols in the presence of $Mn_2(CO)_{10}$ and Ph_2IPF_6

Run	Alcohol	Polymer	t (h)	Conv. (%)	M_n (g mol^{-1})	$Đ$
1	Ethanediol	P(DBX-ED)	12	32	2050	1.5
2	Ethanediol	P(DBX-ED)	24	0	-	-
3	Propanediol	P(DBX-PD)	12	18	1950	1.6
4	Hexanediol	P(DBX-HD)	12	3	-	-
5	Hexanediol	P(DBX-HD)	72	48	3450	2.4
6	Glycerol	P(DBX-G)	12	55	∞	nd

a)[DBX]:[Diol]:[$Mn_2(CO)_{10}$]:[Ph_2IPF_6] = 1:1:1:2, [$Mn_2(CO)_{10}$] = 0,28 mol L–1, λ =400–500 nm; b)determined gravimetrically; c)determined by GPC using polystyrene standards; d)experiment is performed in dark; e)crosslinked polymer is formed.

The structures of the polymers were investigated by ^{1}H-NMR spectroscopy. The broad peaks around 6.8–7.4 ppm evidence the presence of the aromatic groups. The etheric signals appear around 2.8 ppm further evidencing the structures of the polymers (Figure 2.3).

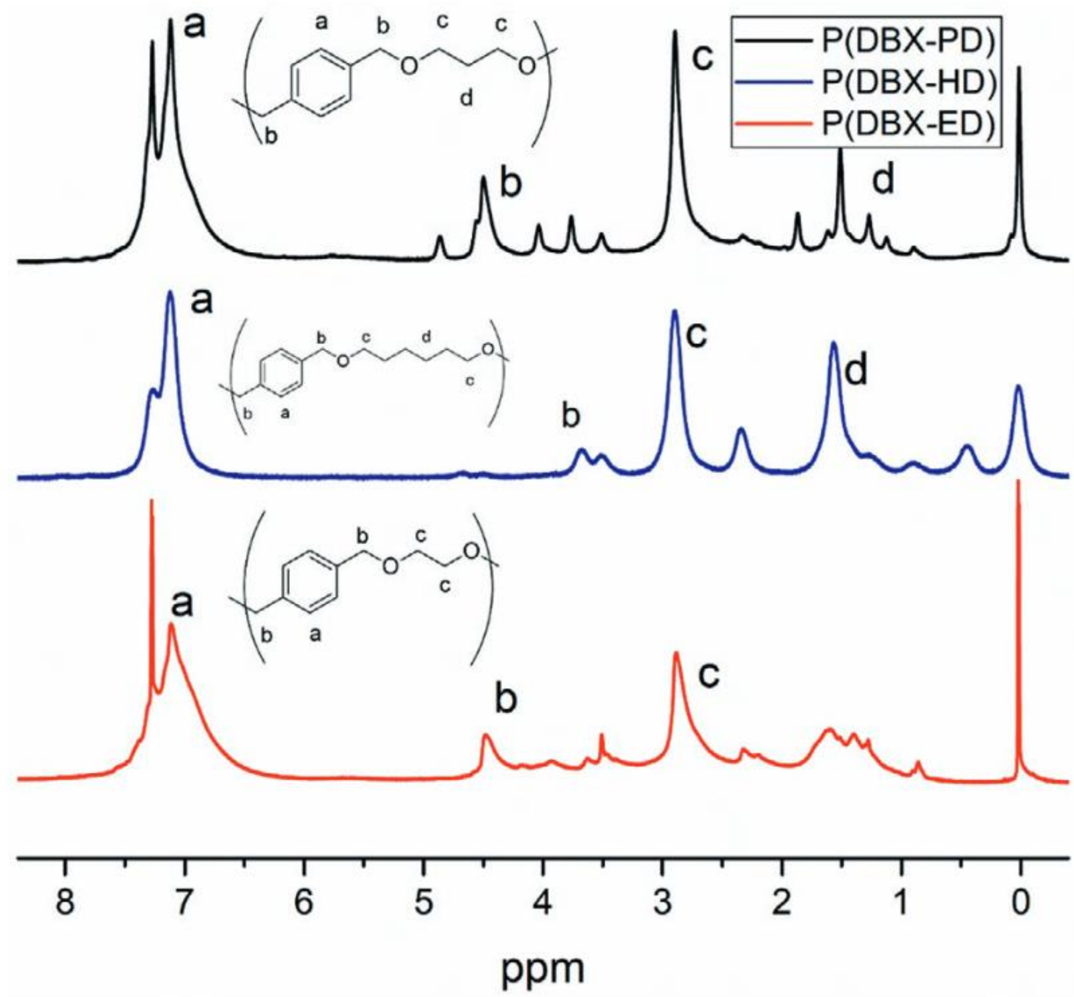


Figure 2.3 : ^{1}H-NMR spectra of the polymers obtained by photoinduced substitution reactions.

In order to confirm that the initial step involves radical generation mechanism, a model reaction was conducted. Thus, benzyl bromide was irradiated in the presence of $Mn_2(CO)_{10}$ and stable radical, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), under visible light. The benzylic radical generated this way was scavenged by TEMPO. The formed adduct was characterized by ^{1}H-NMR analysis (see Supporting Information for the reaction and ^{1}H-NMR analysis of the product).

The kinetics of the polymerization was also investigated. A typical polymerization using DBX and 1,2-ethanediol together with $Mn_2(CO)_{10}$ and $Ph_2I^+PF_6^-$ was conducted in a glass tube with a rubber septum under visible light exposure. Aliquot samples were taken out by a syringe under nitrogen gas in certain time intervals and precipitated in methanol to obtain polymers for molecular weight characterization. Figure 2.4 shows the M_n versus time plots for this polymerization.

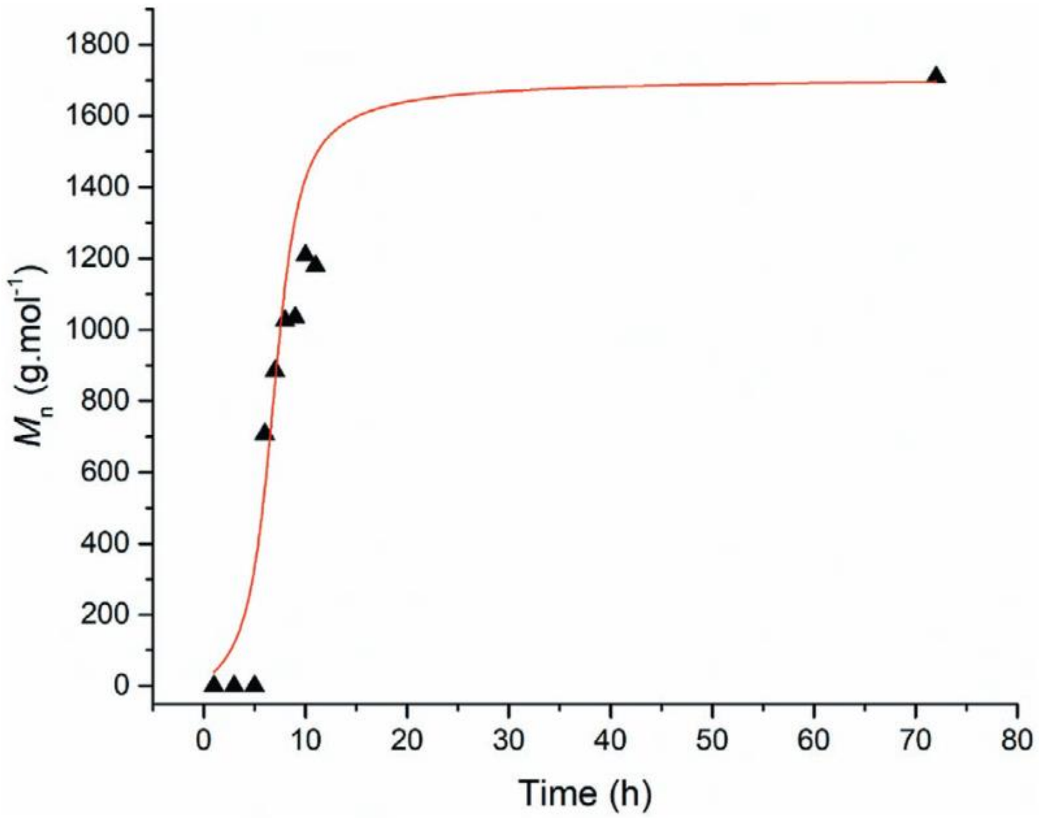


Figure 2.4 : Molecular weight versus time plot for the light induced polymerization of DBX and 1,2-ethanediol in the presence of $Mn_2(CO)_{10}$ and $Ph2I^+PF6^-$

In early stages, no precipitable polymer was obtained. Molecular weight increases by prolonged irradiation, which is in accordance with the usual behavior of step-growth polymerization. However, the regime follows a leveling off after 12 h of irradiation as a result of the precipitation of the polymer from the solvent. This might also be attributed to lower initiation efficiency at lower halide concentrations, which is consumed during the halogen abstraction steps.

The general mechanism is shown in Figure 2.5.

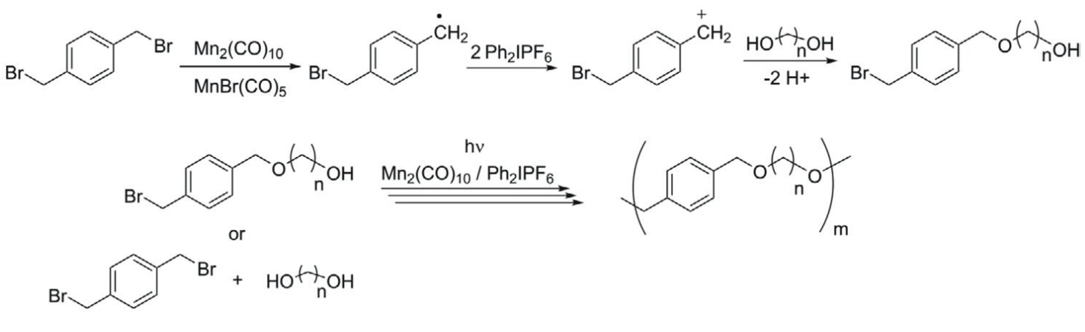


Figure 2.5 : Visible light induced step-growth polymerization by using DBX and diols in the presence of $Mn_2(CO)_{10}$ and $Ph2I^+PF6^-$.

Since the polymerizations follow a halogen abstraction step, the synthesized polymers are likely to have a halogen terminus. Therefore, the synthesized polymers can be used as precursors for block copolymerization by taking advantage of the halogen chain-end functionalities. For this purpose, the polyether synthesized by using ethanediol was subjected to visible light irradiation in the presence of $Mn_2(CO)_{10}$ together with methyl methacrylate or $Ph_2I^+PF_6^-$ and cyclohexane oxide for the free radical and cationic. This way, block copolymerizations were performed by free radical or free radical promoted cationic polymerization mechanisms, respectively. The overall strategy is presented in Figure 2.6.

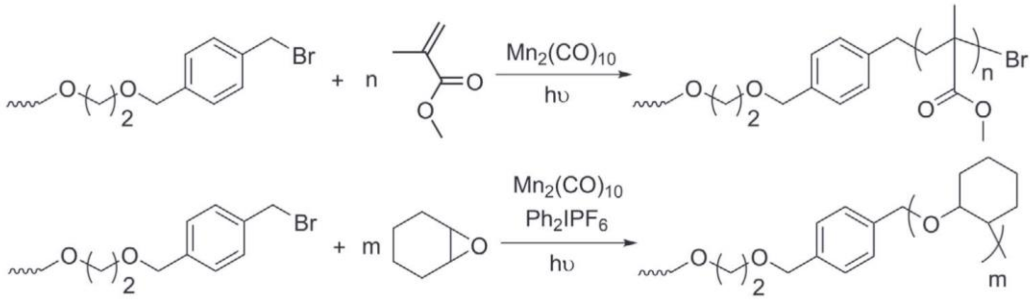


Figure 2.6 : Visible light induced free radical and cationic block copolymerizations.

The structures of the block copolymers were investigated by ^{1}H-NMR spectroscopy. The emergence of the new peaks at 3.6 ppm and 3.4 ppm evidence the formation of the poly methyl methacrylate (PMMA) and poly cyclohexeneoxide (PCHO) segments, respectively (Figure 2.7).

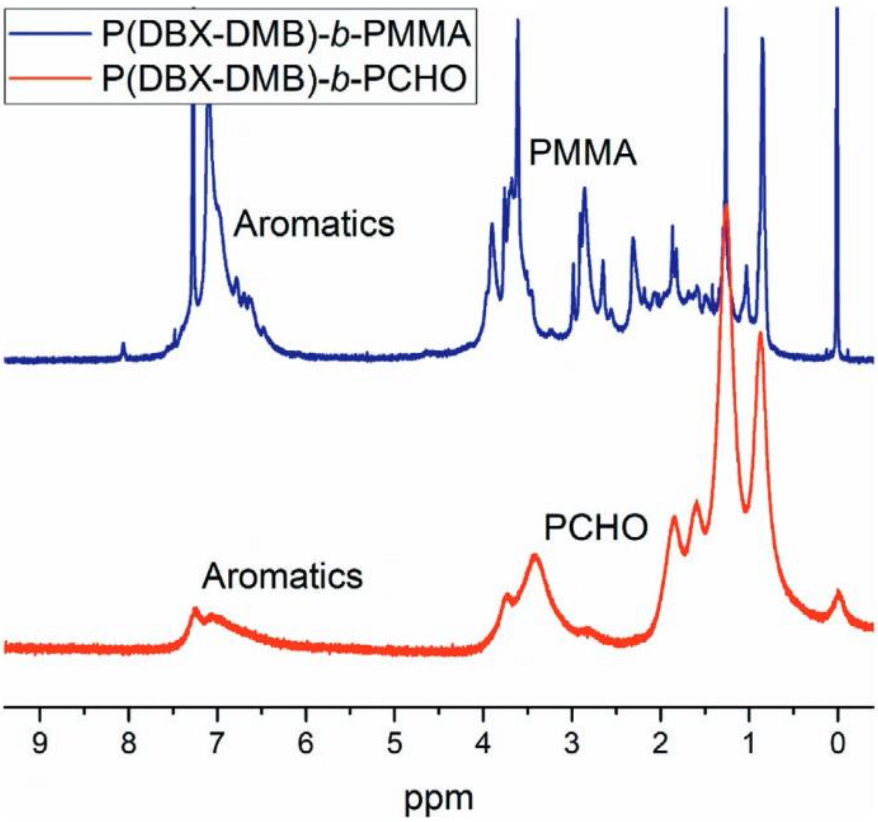


Figure 2.7 : [1]H-NMR spectra of P(DBX-ED)-*b*-PMMA and P(DBX-ED)-*b*-PCHO.

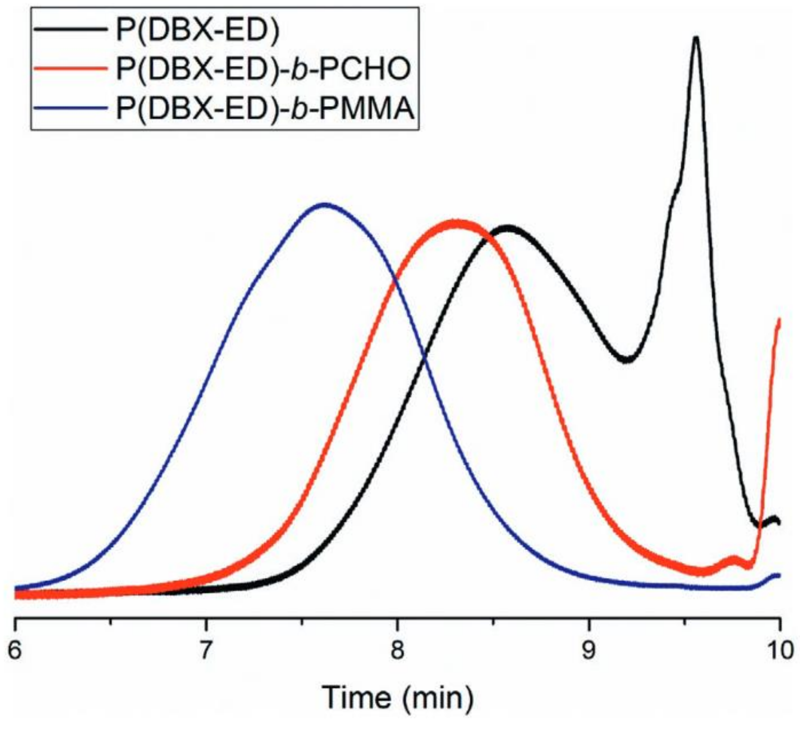


Figure 2.8 : GPC traces of the precursor polymer and the block copolymers.

Figure 2.8 shows the comparison of the gel permeation chromatography (GPC) traces of the precursor polymer and the block copolymers. Although the precursor polymer displays a bimodal regime as a consequence of the nature of the step-growth polymerization, both block copolymers obtained have unimodal molecular weight distribution. More importantly, there is a clear shift to a higher molecular weight region without a detectable contamination of a precursor polymer, which further confirms successful block copolymerizations.

2.3 Conclusion

In conclusion, in this paper we have established a new synthetic approach for the visible light induced step-growth polymerization using dibromoxyelene and diols in the presence of $Mn_2(CO)_{10}$ and $Ph_2I^+PF_6^-$. Upon irradiation, the benzylic radicals formed by halide abstraction are oxidized to the carbocations capable undergoing nucleophilic substitution with diols to form aromatic polyethers. The synthetic route developed is capable of extension to combine with the other polymerization routes such as free radical and free radical cationic polymerizations. In view of the design flexibility offered by commercially available di- and multi-functional alcohols and possibility to form networks and block copolymers by the combination of step-growth polymerization with chain polymerization processes, this synthetic approach could be a potent method for producing complex macromolecular structures for various applications.

2.4 Experimental Section

2.4.1 Materials

$Mn_2(CO)_{10}$ (98%, Sigma-Aldrich), DBX (97%, Sigma-Aldrich), diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$, 98%, Sigma-Aldrich), anisole (99.7%, Sigma-Aldrich), benzyl alcohol (≥98% Sigma-Aldrich), 1,4-dimethoxybenzene (99%, Sigma-Aldrich), and methanol (95%, Merck) were used as received. TEMPO (98%) was sublimated before use. Propylene carbonate (99%, Sigma-Aldrich) was stored in molecular sieves prior to use. MMA (99%) was passed through basic alumina prior to use. CHO (98%) was purified by vacuum distillation.

2.4.2 Typical Photopolymerization Procedure

$Mn_2(CO)_{10}$ (110 mg, 0.28 mmol), DBX (75 mg, 0.28 mmol), $Ph_2I^+PF_6^-$ (240 mg, 0.56 mmol), and corresponding alcohol (0.28 mmol) were taken in a Schlenk tube containing propylene carbonate (1 mL) under nitrogen atmosphere. The tube was sealed and exposed to visible light irradiation (λ = 400–500 nm) for 12 h. The reaction mixture was poured into tenfold excess methanol to precipitate the polymer. The resulting polymer was precipitated by pouring the media into methanol. Then, the precipitate was filtered off and dried under the vacuum at 50 °C. Conversions were determined by gravimetrical method.

2.4.3 Block Copolymerizations Using Methyl Methacrylate

$Mn_2(CO)_{10}$ (10 mg, 0.025 mmol), the precursor polyether (P(DBX-ED), 50 mg, 0.017 mmol) were dissolved in MMA (2 mL, 18.8 mmol) in a Schlenk tube under nitrogen atmosphere. The reaction mixture was exposed to visible light for 12 h. Then, the reaction mixture was precipitated into tenfold methanol to obtain P(DBX-ED)-*b*-PMMA (Mn: 17 200 g mol–1, M_w/M_n: 2.76).

2.4.4 Block Copolymerizations Using Cyclohexene Oxide

$Mn_2(CO)_{10}$ (10 mg, 0.025 mmol), the precursor polyether (P(DBX-ED), 50 mg, 0.017 mmol), and $Ph_2I^+PF_6^-$ (12 mg, 0.028 mmol) were dissolved in CHO (2 mL, 20 mmol) in a Schlenk tube under nitrogen atmosphere. The reaction mixture was exposed to visible light for 12 h. Then, the reaction mixture was precipitated into tenfold methanol. The obtained polymer was reprecipitated from tetrahydrofuran (THF)/hexane mixture to obtain pure P(DBX-ED)-*b*-PMMA (M_n: 5100 g mol–1, M_w/M_n: 2.14).

2.4.5 Modal Reaction

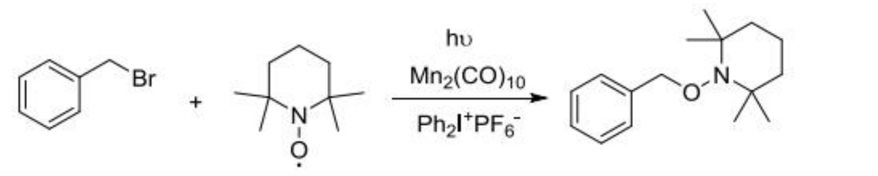
Benzyl bromide (12 µL, 0.1 mmol), TEMPO (16 mg, 0.1 mmol), and $Mn_2(CO)_{10}$ (20 mg, 0.05 mmol) were dissolved in propylene carbonate (1 mL) in a Schlenk tube under nitrogen atmosphere. The tube was exposed to visible light irradiation for 24 h. After the reaction was completed, the product was purified by preparative TLC using ethyl acetate/hexane (1/4 by volume).

2.4.6 Characterization

GPC analyses were performed by a TOSOH EcoSEC GPC system including an autosampler system, a column oven, temperature-controlled pump, a degasser unit, TSKgel superhZ2000 4.6 mm ID × 15 cm × 2 cm column, and a refractive index detector. As an eluent, THF was used with a flow rate of 1.0 mL min−1 at 40 °C. Refractive index detector was calibrated with polystyrene standards. Eco-SEC Analysis software was used to analyze the data. UV−vis analyses were recorded with Shimadzu UV-1601 double-beam spectrometer equipped with deuterium lamp and a 50 W halogen lamp that can emit light between 190 and 1100 nm. ^{1}H-NMR spectra were recorded in deuterated chloroform (CDCl3) with an internal standard tetramethylsilane with 500 MHz Agilent VNMRS spectrometer. Fourier-transform infrared spectra were taken via PerkinElmer Spectrum One spectrometer with ATR accessory and a mercury cadmium telluride detector.

2.5 Supporting Information

(a)



(b)

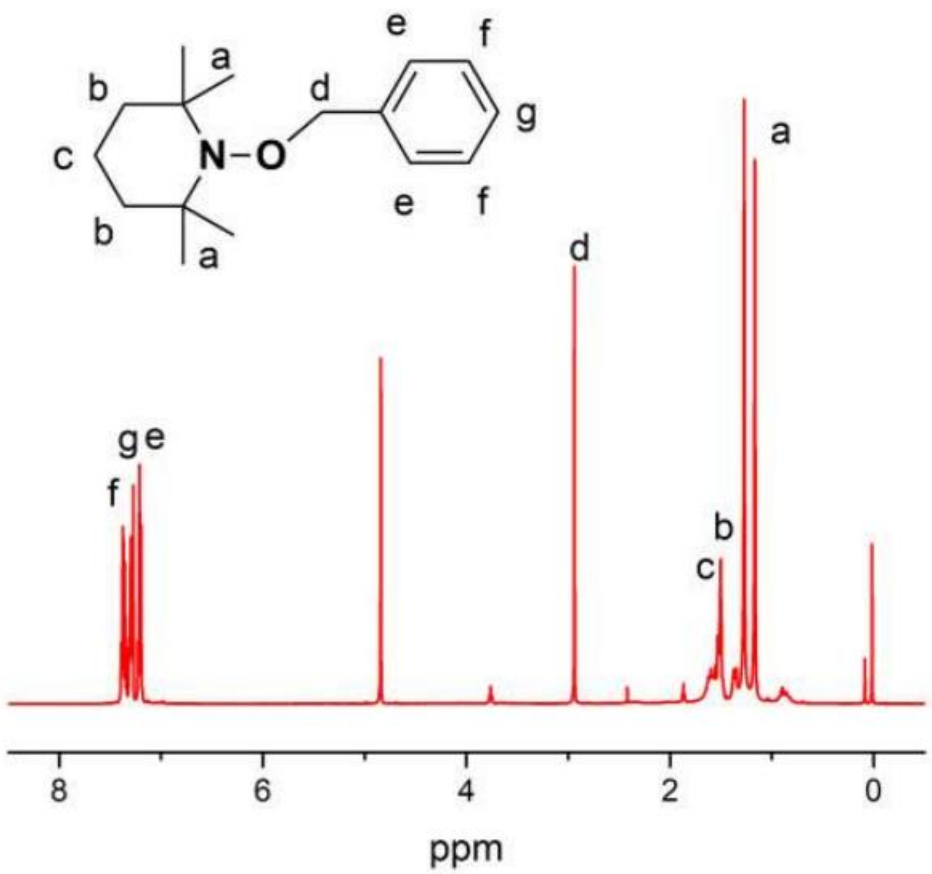


Figure 2.9 : a) Reaction scheme and b) ^{1}H-NMR spectra of the obtained product of the modal reaction.

3. VISIBLE LIGHT INDUCED STEP-GROWTH POLYMERIZATION BY ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS

3.1 Abstract

A novel visible light induced step-growth polymerization to form poly(phenylene methylene) by electrophilic aromatic substitution reactions is described. The effect of different nucleophilic aromatic molecules on polymerization has been investigated. The possibility of combining step-growth polymerization with conventional free radical and free radical promoted cationic polymerizations through photoinduced chain-end activation has been demonstrated. Highly fluorescent fibers of the resulting block copolymers were obtained using the electrospinning technique. The versatile photoinduced step-growth polymerization process reported herein paves the way for a new generation of polycondensates and their combination with chain polymers that cannot be obtained by conventional methods.

3.2 Introduction

There has been growing interest in utilizing photochemistry for existing conventional synthetic procedures, especially after its distinguished advantages have been realized.[9], [22] These advantages include temporal and spatial control, high reaction rates, and lower energy and chemical consumption.[23], [53], [54] Since these advantages are directly in line with the main objective of green chemistry, photochemical techniques provide unique opportunities to move towards a more sustainable world.[55]

Photoinduced reactions have come to the forefront in synthetic polymer chemistry.

Photochemical processes are commonly used in free radical, cationic, and controlled polymerization systems and click chemistry.[11], [31], [32], [52], [56], [57], [58], [59], [60], [61], [62], [63], [64], [65], [66], [67], [68], [69], [70], [71] Recently, photopolymerization has also been used in the preparation of step-growth polymers, which brings a breath of fresh air to synthetic polymer chemistry as polycondensates still represent the majority of polymer production.[11] Previous studies from our laboratory showed that polythiophenes, polycarbazoles and polypyrenes could be prepared by step-growth polymerization, where the typical mechanism involves photoinduced electron transfer and radical coupling steps.[42], [44], [45], [72] Other conventional polycondensates, namely polyethers, polyesters, polyamides and polyurethanes, were also prepared by light induced step-growth polymerization through dimanganese decacarbonyl ($Mn_2(CO)_{10}$) chemistry.[48], [73]

Poly(phenylene methylene) (PPM) derivatives represent a unique class of functional materials with a beneficial combination of properties such as remarkable resistance to oxidants, high hydrophobicity and a very high decomposition temperature of around 470 °C even in the ambient atmosphere.[74], [75] Additionally, they exhibit photoluminescence (PL) at around 400–600 nm, with a solid-state quantum efficiency of around 0.41 and a lifetime of >8 ns, which is an excellent property for a polymer that has no direct π-conjugation system along the chain.[76] Because of these properties, PPM and its derivatives are widely used in several fields, such as optical fibers, corrosion-resistant coatings and encapsulation laminates. [77]

Although various visible light photoinitiating systems exist for different modes of polymerization processes, ($Mn_2(CO)_{10}$) in conjunction with organic halides appears to be an ideal photoinitiating system for the preparation of polymers with various topologies.[78], [79] Typical applications include free radical polymerization, promotion of cationic polymerization, graft copolymerization, atom transfer radical polymerization, iodine degenerative transfer polymerization, mechanistic transformation, preparation of telechelics and hyperbranched polymers, and step-growth polymerization by coupling reactions. [80], [81], [82], [83], [84]

3.3 Experimental

3.3.1 Materials

Dimanganesedecacarbonyl (98%, Sigma-Aldrich), α,α′-dibromo-*p*-xylene (97%, Sigma-Aldrich), diphenyliodonium hexafluorophosphate (≥98%, Sigma-Aldrich), anisole (≥99 %, Sigma-Aldrich), 1,4-dimethoxybenzene (99%, Sigma-Aldrich), propylene carbonate (99%, Sigma-Aldrich).

3.3.2 Characterization

Gel permeation chromatography (GPC) analyses were performed by a TOSOH EcoSEC GPC system including an autosampler system, a column oven, temperature-controlled pump, a degasser unit, TSKgel superhZ2000 4.6 mm ID × 15 cm × 2 cm column and a refractive index detector. As an eluent, tetrahydrofuran (THF) was used with a flow rate of 1.0 mL min^{-1} at 40 °C. Refractive index detector had calibrated with polystyrene standards which have narrow molecular-weight distribution. Eco-SEC Analysis software was used to analyze data coming from SEC (size- exclusion chromatography). UV−Vis analyses were recorded with Shimadzu UV-1601 double-beam spectrometer equipped with deuterium lamp and a 50 W halogen lamp that can emit light between 190 nm and 1100 nm. Fluorescence spectra were recorded via PerkinElmer LS55 spectrometer which can work between 200 nm and 900 nm wavelengths with a slit width of 10 nm. ^{1}H-NMR spectra were recorded in deuterated chloroform ($CDCl_3$ with an internal standard tetramethylsilane) with 500 MHz Agilent VNMRS 500 spectrometer. Fourier-transform infrared (FT-IR) spectra were taken via PerkinElmer Spectrum One spectrometer with ATR accessory and a mercury cadmium telluride (MCT) detector.

3.3.3 Polymerization Procedures

Dimanganesedecacarbonyl ($Mn_2(CO)_{10}$) (110 mg, 0.28 mmol), α,α′-dibromo-*p*-xylene (DBX) (75 mg, 0.28 mmol), diphenyliodonium hexafluorophosphate (240mg 0.56 mmol) and corresponding nucleophile (0.28 mmol) was dissolved in propylene carbonate (1 mL) in a Schlenk tube under nitrogen atmosphere. The reaction medium was irradiated for 12 hours via photoreactor containing 12 fluorescent lamps that emit visible light (λ = 400-500 nm). The Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2021 resulting polymer was precipitated in methanol, filtered off and dried under vacuum at 50 ºC. Conversions were determined gravimetrically. Electrospinning In order to achieve the beadless electrospun microfibers, P(DMPMPM)-*b*-PMMA polymer (375 mg) was dissolved directly with THF (2 mL) vigorously magnetic stirrer until homogeneity. Thus prepared solution was loaded in a plastic syringe equipped with a 21-gauge metal needle on a syringe pump (NE-500, New Era Pump Systems Inc., Turkey). Typical electrospinning process was applied by using high voltage power supply (Elektrosis, PW1010, Turkey) on glass slides stuck on mobile aluminium collector in a transparent chamber (NE-100, Inovenso, Turkey) and process parameters were adjusted as;

applied voltage = 15 kV, tip-to-collector distance = 10 cm and the solution flow rate = 2 ml/h. Laboratory temperature and relative humidity were kept constant at 24.5 °C and %40 throughout the electrospinning, respectively

3.4 Results and Discussion

Herein, we present a novel strategy for the synthesis of PPM derivatives by means of light induced step-growth polymerization. For this purpose, aromatic compounds with different reactivities, namely methoxybenzene (MB), *p*-dimethoxybenzene (DMB), *p*-dihydroxybenzene (DHB), and *α,α′*-dibromo-*p*-xylene (DBX), were irradiated under visible light in the presence of $Mn_2(CO)_{10}$ and diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$). The experimental conditions and molecular weight characteristics of the resulting polymers are presented in Table 3.1.

Table 3.1 : Visible light induced step-growth polymerization

Comonomer	Conversion (%)	M_n (g mol^{-1})	$Đ$
Methoxybenzene	48	∞	nd
p-dimethoxybenzene	37	2400	1.8
Hydroquinone	0	-	-

[DBX] : [Comonomer] : [$Mn_2(CO)_{10}$] : [$Ph_2I^+PF_6^-$] = 1 : 1 : 1 : 2, time: 12 h, [$Mn_2(CO)_{10}$] = 0.28 mol L^{-1} . λ = 400–500 nm. b Determined gravimetrically. c Determined by GPC using the polystyrene standards

Experiments with MB yield a crosslinked polymer, while a linear polymer is formed by using DMB. The observed crosslinking in the case of MB is due to the presence of three reactive sites with low steric hindrance. In the case of DHB, however, no polymerization is observed, despite the strong electron donating character of the hydroxyl groups. This can be attributed to the radical scavenging activity of phenolic hydroxyls, which also confirms the involvement of the radical species in the first step of the process. Moreover, radical formation by photoinduced halide abstraction was previously evidenced by a radical trapping experiment. The radicals formed from DBX by photochemically generated $Mn(CO)_5$ are readily oxidized to benzylic cations by the strong oxidant iodonium salt. The thus-formed cations react with aromatic comonomers with high electron densities according to Friedel–Crafts alkylation. The successive halide abstraction, oxidation and substitution reactions essentially yield PPM. The overall mechanism is presented in Scheme 1 with the DMB comonomer as an example.

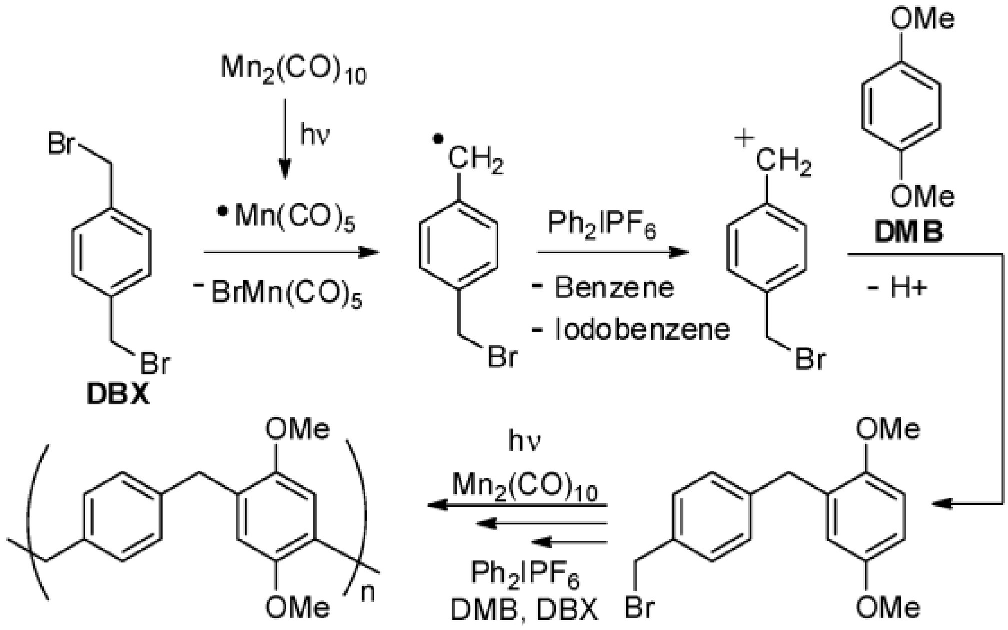


Figure 3.1 : Visible light induced step-growth polymerization of DBX and DMB in the presence of $Mn_2(CO)_{10}$ and $Ph_2I^+PF_6^-$

The kinetics of polymerization were also investigated. For this purpose, aliquot samples were taken by a syringe from the polymerization mixture at certain time intervals and precipitated in methanol. The polymers obtained were analyzed by GPC, and the increase in molecular weight with increasing irradiation time was observed in accordance with the general behavior of step-growth polymerization (Figure 3.2).

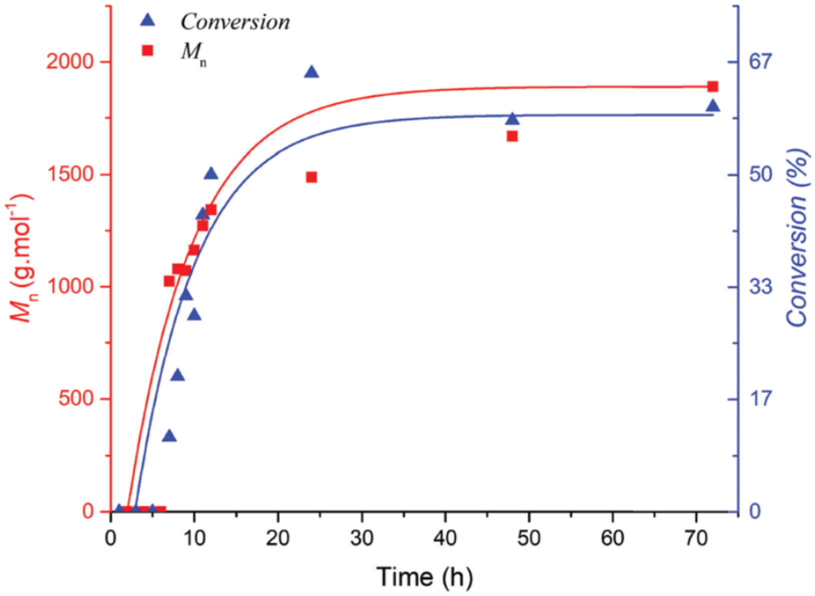


Figure 3.2 : Molecular weight and conversion versus time plot for visible light induced step-growth polymerization of DBX and DMB (see Table 3.1 for experimental details)

The observed leveling off is due to the precipitation of the polymer with relatively high molecular weights. The synthesized polymers exhibit a photoluminescence feature arising from homoconjugation along the chain as observed with the other PPM type polymers. The UV and fluorescence spectra and the visual appearance under UV irradiation of the linear polymer and cross-linked polymer are shown in Figure 3.3.

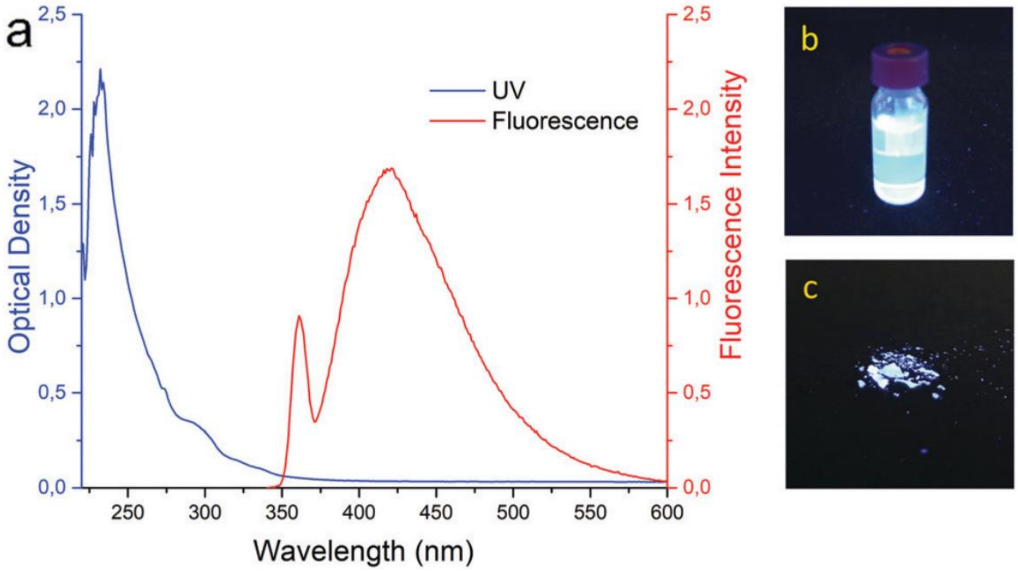


Figure 3.3 : The UV absorption and fluorescence emission spectra (λ_{ex} 365 nm) of P(DMPMPM) (a) and the visual appearance of the polymer solution (b) and solid form (c) under UV irradiationigure 2

In order to test the chain-end fidelity of P(DMPMPM) and take advantage of the halide functionality for the preparation of complex polymeric structures, we performed block copolymerizations via radical and cationic routes using described $Mn_2(CO)_{10}$ photochemistry. The radicals formed at the chain ends by the usual photoinduced halide abstraction process initiated the free radical polymerization of methyl methacrylate (MMA) to yield P(DMPMPM)-*b*-PMMA block copolymers.

The process was also adapted to the cationic mode. In the presence of iodonium salt, the terminal radicals are oxidized to the corresponding polymeric cations capable of initiating the cationic polymerization of cyclohexene oxide (CHO) to produce a P(DMPMPM)-*b*-PCHO block copolymer (Figure 3.4). Table 3.1 summarizes photoinduced block copolymerization with both modes.

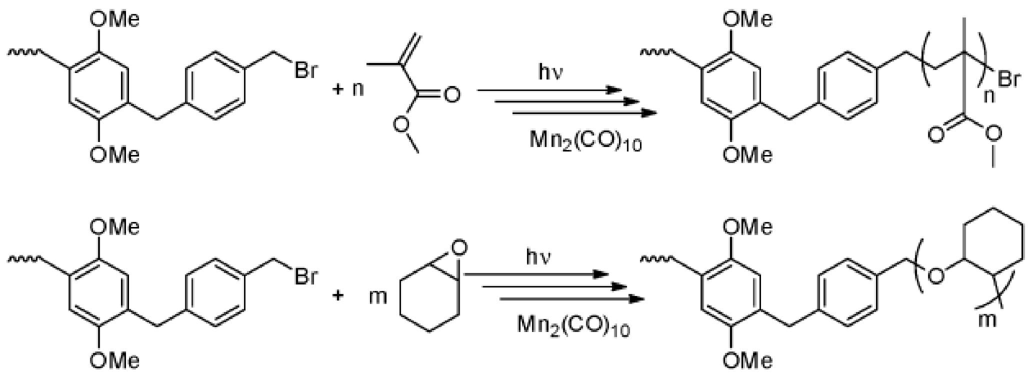


Figure 3.4 : Visible light induced radical and cationic polymerizations of MMA and CHO with P(DMPMPM)

The structures of the polymers were characterized by ^{1}H-NMR and FT-IR analyses. The ^{1}H-NMR spectrum of PDMPMPM displays aromatic peaks between 6.5 and 7.4 ppm. In addition, broad peaks associated with methoxy hydrogens around 3.6 ppm and methylene bridge protons at 2.8 ppm were observed. After block copolymerization, the characteristic bands of the PMMA segment at 3.6 ppm and the aliphatic peaks of the PCHO segment at 1.3 ppm were detected, proving the success of the processes (Fig. 3a). The FT-IR spectra of the polymers further confirm the structures. The aromatic stretching bands at 1400 cm^{-1} and C–H stretching bands at 3000 cm^{-1} were observed in all cases. After block copolymerization, the strong stretching of ester carbonyl appeared at 1730 cm^{-1} (Figure 3.5). The GPC chromatograms of the polymers also reveal the success of the blocking process. Following the incorporation of the PMMA segment, there is a clear shift to the higher molecular weight region.

Notably, prolonged irradiation results in a higher increase in the molecular weight (Table 3.2 and Figure 3.5).

Table 3.2 : Visible light induced block copolymerization of P(DMPMPM) with MMA and CHO in propylene carbonate

Monomer	Mode	Time (h)	Conv. (%)	M_n (kg mol^{-1})	ΔM_n (%)	$Đ$	Block
MMA	Radical	24	44	36.9	1437.5	3.7	P(DMPMPM)-*b*-PMMA1
MMA	Radical	72	53	166.8	6850.0	1.9	P(DMPMPM)-*b*-PMMA2
CHO	Cationic	24	3	2.6	8.3	1.8	P(DMPMPM)-*b*-PCHO

a $[Mn_2(CO)_{10}]$ = 1.3 x 10^{-1} mol L^{-1} , [MMA] = 4.7 mol L^{-1} . b $[Mn_2(CO)_{10}]$ = 1.3 x 10^{-1} mol L^{-1} , $[Ph_2I^+PF_6^-]$ = 2.6 x 10^{-1} mol L^{-1} , [CHO] = 4.95 mol L^{-1} . c Determined by GPC using polystyrene standards. d Determined gravimetrically

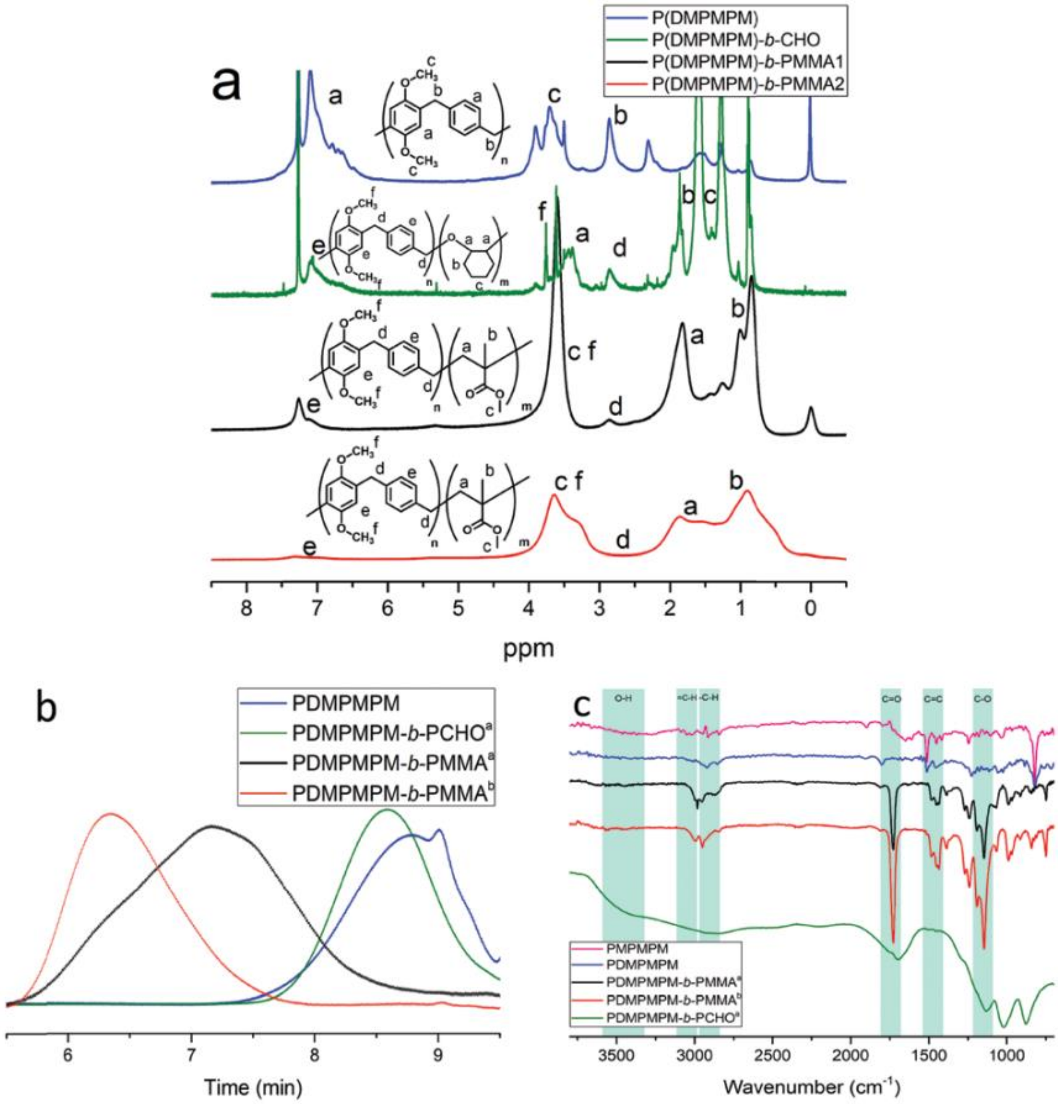


Figure 3.5 : F1

Figure 3.6 : ^{1}H-NMR spectrum (a), GPC chromatograms (b) and FT-IR spectrum (c) of PPM and block copolymers.

The high molar mass P(DMPMPM)-b-PMMA is transformed into microfiber forms by the electrospinning method. The surface morphology and average diameter of the microfibers obtained by the electrospinning process were evaluated on an environmental SEM (JEOL-JSM-5600) operated at 7.5 kV and 10.3 mm working distance. As can be easily seen from Fig. 4, microscale cylindrical, uniform and bead free morphologies with average diameters ranging from 2 to 6 μm were observed. A fluorescence microscope (OLYMPUS CK40-F200) was also used to image the fluorescence features of the electrospun microfibers. These results show that fluorescent polymers with microfiber properties, which may find applications in biomedical imaging technologies and colorimetric/optical sensors, can be obtained by the described synthetic methodology.

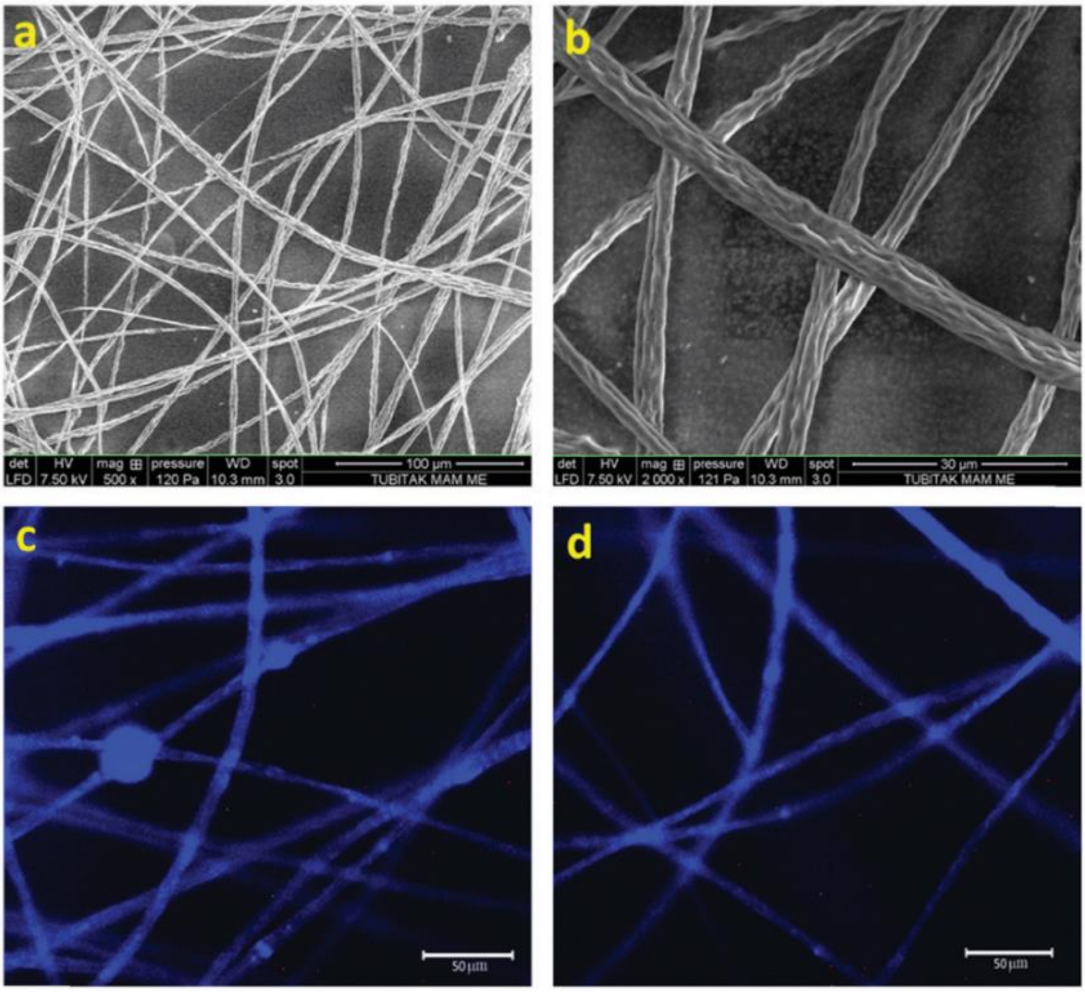


Figure 3.7 : Environmental scanning electron microscope (ESEM) and fluorescence optical microscopy images of the electrospun PDMPMPM-*b*-PMMA microfiber; scale bars indicate (a) 100 mm, (b) 30 mm, and (c and d) 50 mm.

3.5 Conclusion

In conclusion, we have successfully accomplished the first photoinduced step-growth synthesis of PPM derivatives by electrophilic aromatic substitution reactions. The key steps of the polymerization are successive visible light induced radical generation by halide abstraction, oxidation of the radicals thus formed and electrophilic aromatic substitution processes. Depending upon the nature of the electron donor aromatic monomers, linear and crosslinked polymers are formed. The chain ends of the polymers obtained can be activated in the same way to initiate radical and cationic polymerizations to form the corresponding block copolymers, which may lead to new possibilities for the incorporation of chain polymers into polycondensates. The resulting block copolymers can form highly fluorescent fibers by the electrospinning technique.

4. VISIBLE LIGHT INDUCED CONVENTIONAL STEP-GROWTH AND CHAIN-GROWTH CONDENSATION POLYMERIZATIONS BY ELECTROPHILIC AROMATIC SUBSTITUTION

4.1 Abstract

A novel visible light induced step-growth polymerization by electrophilic aromatic substitution between photochemically generated carbocations and dimethoxybenzene nucleophile is described. Conventional step-growth polymerization and chain-growth condensation polymerization (CCP) mechanisms are presented. It is found that by changing the molar ratios of the monomers slightly, the CCP mechanism becomes operative and relatively higher molecular weight polymers are obtained because of the higher reactivity of the end groups of the intermediates and oligomers than that of the monomers. The possibility of grafting onto polymers containing epoxide at their side chains by photoinduced chain end activation of poly(dimethoxyphenylene methylene) is demonstrated. This study is expected to promote potential applications of the combination of photoinduced electron transfer reactions and CCP in macromolecular synthesis and material science.

4.2 Introduction

The interest in utilizing photochemistry in conventional procedures is rapidly growing as the advantages of photochemical methods are realized.[9], [22] Some of the most prominent advantages include high reaction rates, lower energy and chemical consumption, and spatiotemporal control.[23], [24], [85] Photoinduced systems offer great opportunities as their advantages are directly in line with green chemistry. [86]

Photo-induced approaches to polymer chemistry have recently received remarkable interest as they are successfully conveyed to radical, cationic, controlled polymerizatio n and click processes.[12], [27], [31], [32], [51], [54], [59], [61], [70], [87], [88], [89], [90], [91], [92], [93], [94] Recently, interest has been expanding to apply photo-induced systems in step-growth polymerization. In our laboratory, we showed that polythiophenes, polythienothiophenes, polycarbazoles, poly(phenylene methylene) (PPM) derivatives, polyethers and polypyrenes could be prepared by photoinduced step-growth polymerization techniques.[42], [43], [44], [45], [73], [95], [96], [97] Also, traditional polycondensates, namely polyurethanes and polyesters were prepared by step-growth polymerization by taking advantage of dimanganese decacarbonyl ($Mn_2(CO)_{10}$) photochemistry and electron transfer reactions.[48], [98], [99]

PPM derivatives exhibit unique properties such as high thermal stability, resistance against oxidants and hydrophobicity.[74], [75], [76] These materials also show photoluminescence (PL) activity at around 400-600 nm, with a lifetime of 8 ns and solid state quantum efficiency of 0.41. As they have no direct π–conjugation, the observed PL activity is due to the homoconjugation along the polymer chain. Such properties make PPMs as alternative candidates for corrosion resistant coatings, optical fibers and laminates.

Conventional step-growth polymerization requires absolute stoichiometric balance of the antagonist functional groups of the monomers to obtain polymers with sufficient conversion and molecular weight.[100] Recently, a new approach, chain-growth condensation polymerization (CCP)[101], [102], [103] utilizing a slight imbalance of the molar ratios the functional monomers in step-growth polymerization was introduced. In the process, the higher reactivity of the end groups of the oligomers than that of the monomers results in the formation of polymers with relatively higher molecular weights. [104]

4.3 Results and Discussion

In order to extend photoinduced electron transfer reactions in macromolecular synthesis, we herein report a novel strategy for the synthesis of PPM derivatives by visible light induced Friedel-Crafts electrophilic aromatic substitution. In the process, visible light activated halide abstraction from dibromomethane (DBM) or dichloromethane (DCM) forms the respective radicals capable of being oxidized by diphenyl iodonium salt ($Ph_2I^+PF_6^-$) to generate cations. Thus formed cations undergo Friedel-Crafts electrophilic aromatic substation reaction with electron rich aromatic monomer, dimethoxybenzene (DMB). Successive radical generation, oxidation and electrophilic aromatic substation reactions essentially yield poly(dimethoxyphenylene methylene) (PDPM).

In the process, the amount of the halide monomer granted two synthetic pathways: conventional step-growth and CCP. The conventional method using balanced amounts of DBM and DMB yielded polymer with a molecular weight of 1640 g mol-1. Notably, using DCM as the halide monomer, no precipitable polymer was obtained under identical experimental conditions due to the less favorable halide abstraction reaction. When the organo halide concentration is increased to 1.8 equivalents, a different situation is encountered. A significant increase in the molecular weight observed can be attributed to the higher reactivity of initially formed α-halidexylene end groups than dihalidomethane monomers. The increased reactivity of oligomers compared to DMB arising from the slight electron donating nature of methylene bridges also contributes to the observed molecular weight increase. In this case, the polymerization proceeds according to the CCP mechanism (Scheme 1). Further increase in the halide concentration, i.e. without additional solvent, results in the formation of polymers with higher molecular weights. It should be noted that using DBM as solvent, the polymerization was not successful as the components of the system were not soluble in neat DBM: The overall results are presented in Figure 4.1 and Table 4.1.

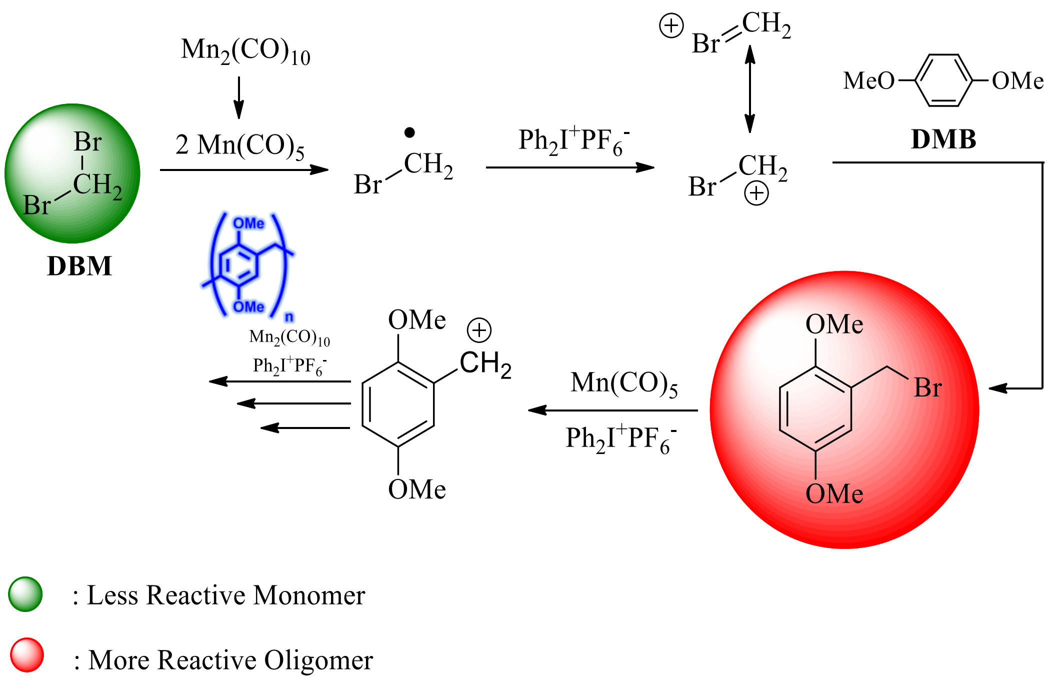


Figure 4.1 : Visible light induced step-growth polymerization by the reaction of DBM and electron-rich DMB in the presence of $Mn_2(CO)_{10}$ and $Ph_2I^+PF_6^-$.

Table 4.1 : Synthesis of polyphenylene methylene derivatives by visible light induced step-growth polymerization.

Comonomer [a)]	Molar ratio of [Comonomer]: [DMB]	Solvent	Conv.[b)] [%]	M_n[c)]	$Đ$[c)]
DBM	1	PC	27	1640	1.4
DCM	1	PC	-	-	-
DBM	1.8	PC	52	2000	1.5
DCM	1.8	PC	31	1500	1.3
DBM	50	DBM	-	-	-
DCM	57	DCM	32	2650	1.7

[a)] $[DMB]:[Mn_2(CO)_{10}]:[Ph_2I^+PF_6^-]$ = 1:1:2. time: 24h, $[Mn_2(CO)_{10}]$ = 0,28 mol L^{-1}; [b)] Determined gravimetrically; [c)] Determined by GPC using polystyrene standards

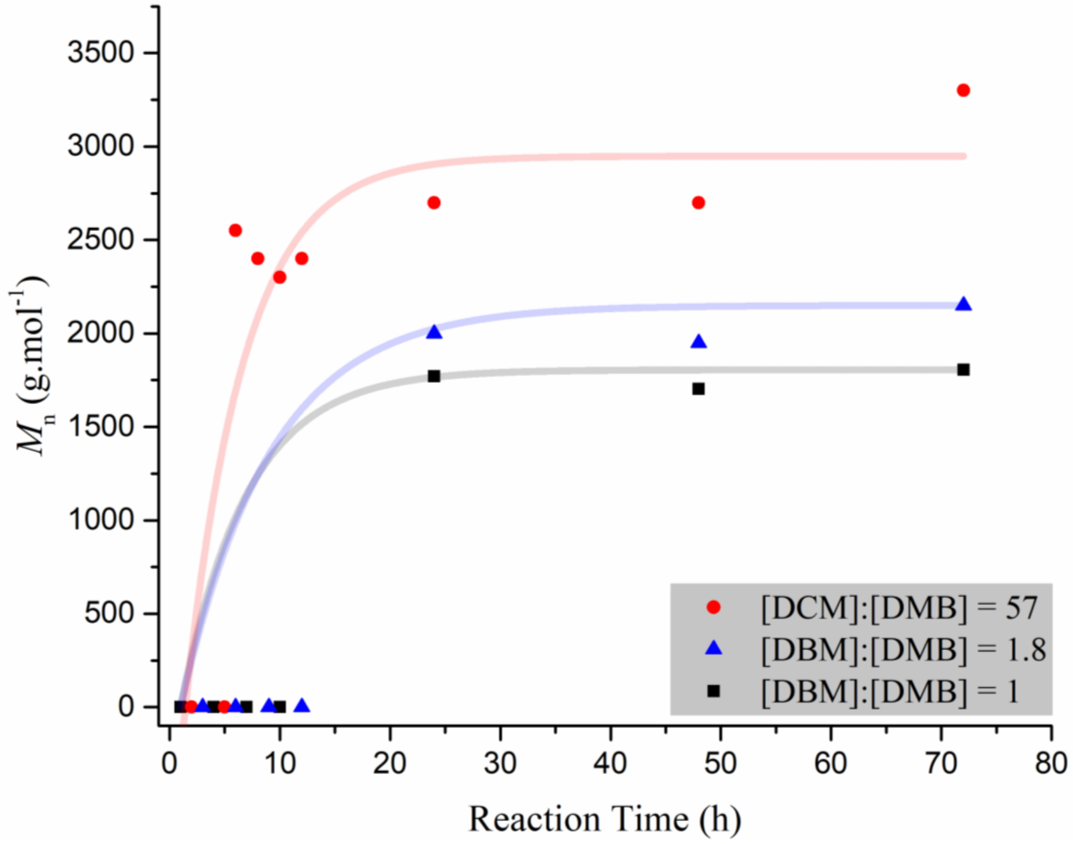


Figure 4.2 : M_n versus reaction time plots for visible light induced step-growth polymerization (see Table 1 for experimental details).

The structural characterization of the obtained PDPM is accomplished by spectral analyses. The ^{1}H-NMR spectrum of PDPM displays aromatic peaks between 6.5 and 7.6 ppm. Aromatic peaks appear on the shielded side due the electron rich character of the polymer. Additionally, methylene bridge and methoxy protons were observed at 3.0-3.5 ppm and 3.5-4.0 ppm, respectively as broad bands (Figure 2a). PDPM possesses photoluminescence properties as confirmed by its fluorescence spectrum and visual observation analogous to the reported examples (Figure 3).

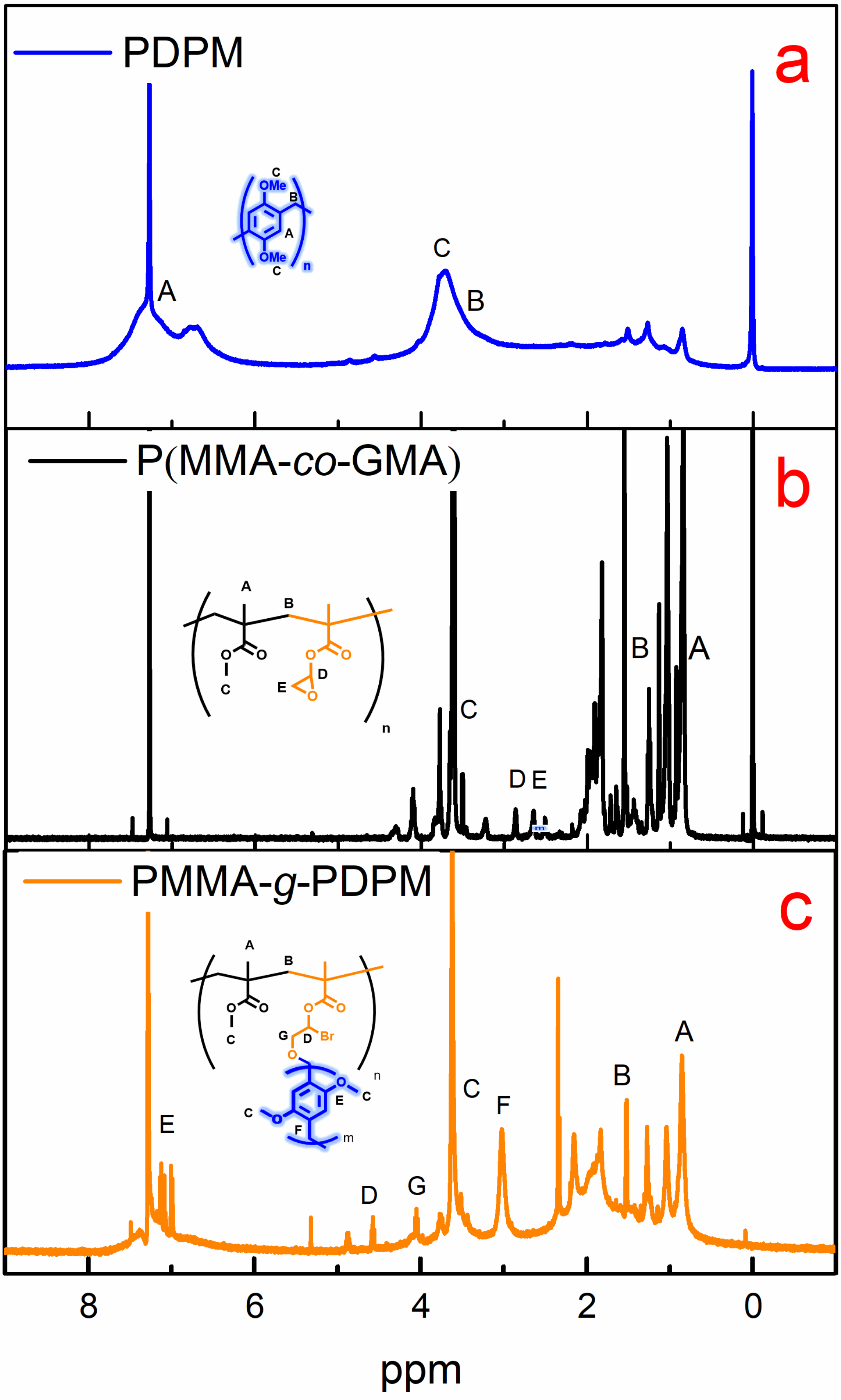


Figure 4.3 : a) ^{1}H-NMR Spectra of PDPM, b) P(MMA-*co*-GMA) and c) PMMA-*g*-PDPM graft copolymer.

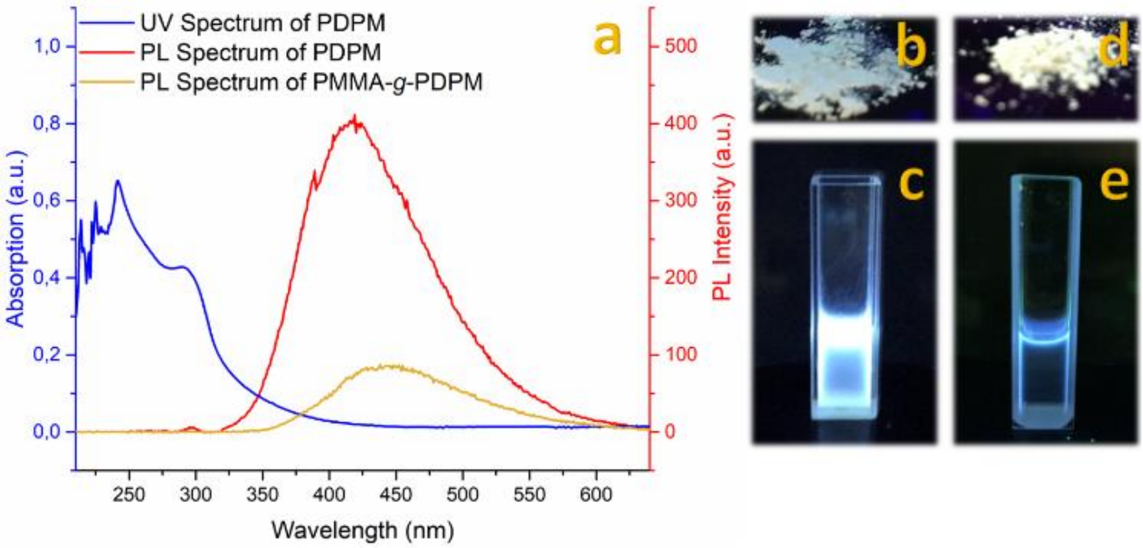


Figure 4.4 :
a) UV absorption and fluorescence emission spectra (λ_{ex} 295 nm) of PDPM and PMMA-*g*-PDPM; b) Visual appearance of PDPM in solid state and c) in solution under 365nm UV light; d) Visual appearance of PMMA-*g*-PDPM in solid state and e) in solution under 365nm UV light.

As the polymers possess benzyl halide end groups, it seemed appropriate to take advantage of the chain-end fidelity for the preparation of graft copolymers. For this purpose, first, epoxy side chain functional polymer, poly(methyl methacrylate-co-glycidyl methacrylate) copolymer (P(MMA–co-GMA) was synthesized by atom transfer radical polymerization (ATRP) (see supporting information for details). Upon visible light irradiation of the solutions containing PDPM, P(MMA–co-GMA), $Mn_2(CO)_{10}$ and $Ph_2I^+PF_6^-$, radicals formed by halide abstraction by Mn(CO)5 at the chain-ends of the PDPM were oxidized by the iodonium ions in the usual manner. The nucleophilic attack of the pendant epoxy groups to the cations formed eventually yielded PMMA-g-PDPM graft copolymer (Scheme 2). The structural and molecular weight characteristics of the precursor polymers and graft copolymer are presented in Figure 2 and Table 2.

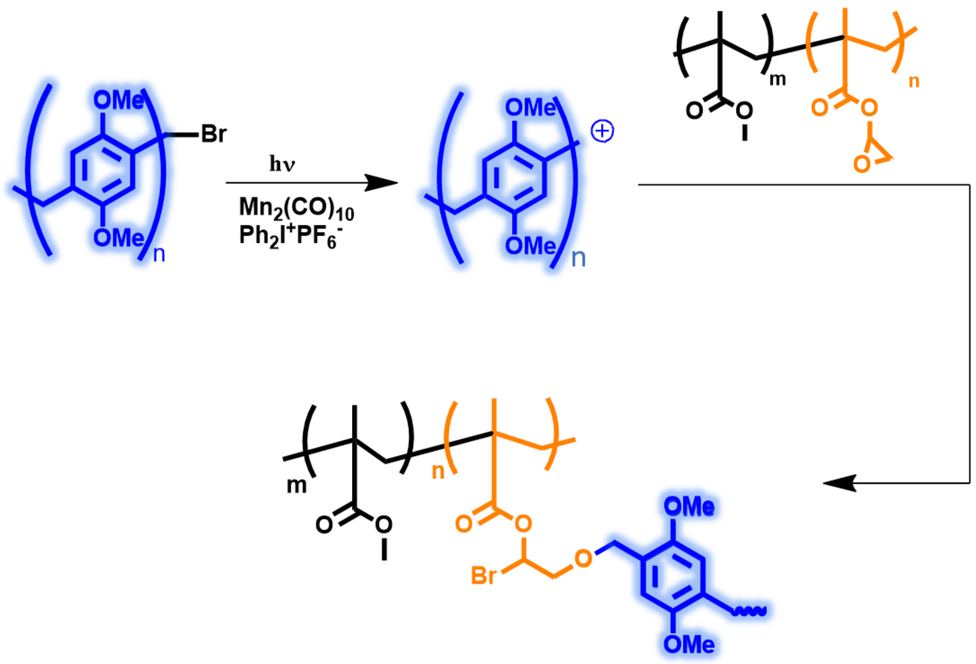


Figure 4.5 : Visible light induced grafting in the presence of $Mn_2(CO)_{10}$ and $Ph_2I^+PF_6^-$.

In the ^{1}H-NMR spectrum of P(MMA-co-GMA) copolymer, the characteristic ester peak of MMA is observed around 3.6 ppm, also epoxide peaks belonging to GMA are observed around 2.8 and 3.0 ppm. Integration ratio of these peaks were in line with the molar ratios of MMA and GMA (MMA/GMA = 10). As can be seen from Figure 2b and Figure 2c, after the grafting process, hydrogen peaks belonging to epoxide groups were disappeared, confirming the occurrence of the grafting process. The agreement of the molecular weights obtained by GPC and ^{1}H-NMR analyses further verifies the successfulness of the grafting.

Table 4.2 : Photoinduced grafting of PDPM to P(MMA-*co*-GMA) by visible light induced electrophilic aromatic substitution reaction.

Polymer	M_n[b)]	$Đ$[b)]
P(MMA-*co*-GMA)	4400	1.3
PDPM	1640	1.4
PMMA-*g*-PDPM[a)]	8500	1.6

[a)][PDPM]:[$Mn_2(CO)_{10}$]:[$Ph_2I^+PF_6^-$] = 1:1:2, PC as solvent. time: 24h, [$Mn_2(CO_{10})$] = 0,28 mol·L^{-1}; [b)]Determined by GPC using polystyrene standards

4.4 Conclusion

In conclusion, we herein reported a straightforward and economical light induced synthetic route to produce PPM derivatives using simple and inexpensive reactants. The approach also provides environmental benefits and operational simplicity. The applied photoinduced step-growth polymerization is based on the generation of free radicals by visible light halide abstraction from DBM or DCM followed by cation formation using the strong oxidant iodonium ion. The formed cations undergo electrophilic aromatic substitution reaction with the electron donor monomer DMB to yield PDPM. Depending on the stoichiometric variations of the monomers used, polymerizations proceed via conventional step-growth or CCP mechanisms. While at equimolar ratios the conventional mechanism is dominant, at higher molar ratios of the dihalide monomer, CCP becomes operative. The higher molecular weights attained in the latter case is due to the higher reactivity of the oligomers compared to the monomers. Photochemical activation of the benzyl halide functionality of the polymer chain ends provides a powerful synthetic strategy to prepare graft copolymers. It is also noteworthy that both PDPM homopolymer and the graft copolymer formed therefrom exhibit high fluorescence properties. This new method would dramatically extend the applications of PPM based complex macromolecular structures by specifically selected combinations.

5. CONCLUSION

As conclusion, the harmony between the dimanganesedecacarbonyl and the diphenyliodonium salts has been adapted to the step-growth polymerization involving different mechanisms. Approaches included mainly photoinitiated substitution reactions. Initially diols were selected as the nucleophiles for the substitutions. Having extraordinarily good results from the polymerizations to obtain polyethers, the nucleophilic strength of the comonomer has been decreased for the subsequent approach. Electron rich aromatic compounds were selected as the nucleophiles to perform Friedel-Crafts type electrophilic aromatic substitution reactions. Fluorescent and telechelic poly(phenylene methylene) polymers were obtained by the developed method which had been further extended to obtaining fibers after the copolymerizations with methylmethacrylate. Furthermore, as the third approach the electrophilicity of the dibromoxylene was decreased in order to see the limits of the offered polymerization method. Now dihalidomethane derivatives were offered as a cheaper and better alternative contrary to the reactivity it has. A novel reaction mechanism involving named chain-growth condensation polymerization happened in the reaction to yield better results arising from the fact that the resulting oligomers are more reactive than the monomers. This study was the very first example of the chain-growth condensation polymerization using photoinduced approaches.

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PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

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