DIBENZOPHENAZINE AND QUINOXALINE DERIVATIVES AS NOVEL VISIBLE PHOTOSENSITIZERS FOR DIARYLIODONIUM SALTS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

MERVE KOLAY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMISTRY

JULY 2011

Approval of the thesis:

DIBENZOPHENAZINE AND QUINOXALINE DERIVATIVES AS NOVEL VISIBLE PHOTOSENSITIZERS FOR DIARYLIODONIUM SALTS

submitted by **MERVE KOLAY** in partial fulfillment of the requirements for the degree of **Master of Science in Chemistry Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. İlker Özkan
Head of Department, **Chemistry**

Prof. Dr. Levent Toppare
Supervisor, **Chemistry Dept., METU**

Assist. Prof. Dr. Umut Bulut
Co-Supervisor, **Chemistry Dept., METU-NCC**

Examining Committee Members:

Prof. Dr. Jale Hacaloğlu
Chemistry Dept., METU

Prof. Dr. Levent Toppare
Chemistry Dept., METU

Assist. Prof. Dr. Umut Bulut
Chemistry Dept., METU-NCC

Assoc. Dr. Yasemin Arslan Udum
Institute of Science and Technology
Dept. of Adv. Tech., Gazi University

Assist. Prof. Dr. Ali Çırpan
Chemistry Dept., METU

Date: 20.07.2011

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: MERVE KOLAY

Signature

ABSTRACT

DIBENZOPHENAZINE AND QUINOXALINE DERIVATIVES AS NOVEL VISIBLE PHOTOSENSITIZERS FOR DIARYLIODONIUM SALTS

Kolay, Merve
M. Sc., Department of Chemistry
Supervisor: Prof. Dr. Levent Toppare
Co-Supervisor: Assist. Prof. Dr. Umut Bulut

July 2011, 49 pages

This study is focused on the use of visible light in photoinitiated cationic polymerization. Photoinitiated polymerization of oxiranes, vinyl ethers, and other vinyl monomers was achieved. In doing so, (2-(2,3 dihydrobenzo [b][1,4]dioxin-6-yl)-3-(2,3-dihydrobenzo[b]-[1,4]dioxin-7-yl)-5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-8-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7yl) quinoxaline) (DBQEd) and poly(2,3,5,8-tetra(thiophen-2-yl)quinoxaline) (TTQ), two dibenzo[a,c]phenazine derivatives; 10,13-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)dibenzo[a,c] phenazine (PHED) and 10,13-bis(4-hexylthiophen-2-yl)dibenzo[a,c]phenazine (PHEHT) were utilized as the photosensitizers for diaryliodonium salt photoinitiators. Novel dyes based on the dibenzo[a,c]phenazine and quinoxaline skeleton were shown to be efficient in carrying out the cationic photopolymerizations of a wide variety of epoxide, oxetane, and vinyl monomers at room temperature upon irradiation with long-wavelength UV and visible light. The polymerizations were initiated at room temperature in the presence of diphenyliodonium hexafluorophosphate ($Ph_2I^+PF^-_6$) and monitored by optical pyrometry (OP). The photopolymerization of an epoxide monomer via solar irradiation was also demonstrated.

Keywords: Cationic Polymerization, Diaryliodonium Salts, Photopolymerization, Photosensitization, Dibenzophenazine Derivatives, Quinoxaline Derivatives, Ring-Opening Polymerization.

ÖZ

DİBENZO[A,C]FENAZİN VE KİNOKZALİN GRUBUNA SAHİP OLAN MONOMERLERİN FOTOSENSİTİZER OLARAK, DİFENİLİYODONYUM FOTOBAŞLATICISI İLE FOTOPOLİMERİZASYONLARI

Kolay, Merve
Yüksek Lisans, Kimya Bölümü
Tez Yöneticisi: Prof. Dr. Levent Toppare
Ortak Yöneticisi: Yrd.Doç.Dr Umut Bulut

Temmuz 2011, 49 sayfa

Bu çalışmada fotobaşlatıcı katyonik polimerizasyonun gün ışığında gerçekleştirilmesi amaçlanmıştır. Donör olarak EDOT ve tiyofen ve akseptör olarak “dibenzo[a,c]fenazin” ve “kinokzalin” grubuna sahip olan monomerler oksiran ve vinil monomerlerinin fotobaşlatici katyonik polimerizasyonunda sensitizer görevi yapmıştır. Sensitizerlerin spektroskopik çalışmaları sırasında maksimum soğurma dalga boyu değeri ve UV-Vis-NIR bölgelerindeki soğurma bantları incelenmiştir. Floresans çalışmaları sırasında ise yine maksimum soğurma dalga boyu değeri ölçülmüş ve Stern Volmer grafiği çizilmiştir. Yapılan çalışmada “dibenzo[a,c]fenazin” ve “kinokzalin” esaslı farklı donör gruplar içeren monomerler fotosensitizer olarak, difeniliyodonyum hegzaflorofosfat ($Ph_2I^+PF^-_6$) fotobaşlatıcısı kullanılarak epoksit ,Okseten ve vinil monomerlerinin UV ve görünür bölgede irradyasyonla fotopolimerizasyonları gerçekleştirilmiştir. Oda sıcaklığında gerçekleşen bu polimerizasyon Optik Pirometre cihazıyla gözlemlenmiştir. Buna ek olarak monomerlerin güneş ışığında fotopolimerizasyonları da gerçekleştirilmiştir.

Anahtar kelimeler: Katyonik Polimerizasyon, Difeniliyodonyum Tuzları, Fotopolimerizasyon, Fotosensitizasyon, Dibenzofenazin Türevleri, Kinokzalin Türevleri.

To My Family

ACKNOWLEDGEMENTS

I would like to express my sincere thanks to my supervisor Prof. Dr. Levent Toppare not only for his invaluable guidance but also for his enthusiasm and inspiration through the years of my graduate studies. It was an immense pleasure to work with someone like him.

I would like to thank to Assist. Prof. Umut Bulut for her guidance, support, encouragement, patience, valuable discussions and helping me in many ways.

I would like to express my special thanks to Simge Tarkuç and Yasemin Udum Arslan for their endless helps besides their kind friendship. And I am grateful to Yusuf Nur and Özlem Türkarslan. They are my surrogate family.

I would like thank to all Toppare Research Group members for their cooperation and their kind friendship.

Many thanks to Gönül, Hava, Seda, Gözde, and Doğukan for always being there for me, for their true friendship.

Words fail to express my eternal gratitude to my family to whom I dedicate this thesis. I am indebted to my parents Nermin and Mehmet Kolay and my little sister Şeyda for their endless love, support, and motivation throughout my whole life. They are the reason I am who I am today.

Finally, I would like to express my special thanks to Emre Onat for his continuous love, patience and inexhaustible tolerance since we met. His love made my life more meaningful.

TABLE OF CONTENTS

CHAPTERS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

LIST OF ABBREVIATIONS

CP	Conducting Polymer
DCM	Dichloromethane
EDOT	3,4-Ethylenedioxythiophene
LED	Light Emitting Diode
NMR	Nuclear Magnetic Resonance
P3AT	Poly(3-hexylthiophene)
$\mathbf{Ph_2^+PF_6^-}$	Diphenyliodonium hexafluorophosphate
PEDOT	Poly(3,4-ethylenedioxythiophene)
PTh	Polythiophene
PS	Photosensitizer
PI	Photoinitiator

CHAPTER 1

INTRODUCTION

1.1 Introduction to Photoinitiated Polymerization

The technology and science of polymerizations have improved considerably. Today, the technology is applied to the fabrication of products which are used in our everyday life. Prevalent research continues to improve the technology and progress new functions for photoinitiated polymerizations.

In recent years, photoinitiated polymerization has become a powerful industrial process as it spread in a wide range of economic and ecological areas. Photopolymerization is mainly a process which converts a monomer into polymer by a chain reaction initiated by reactive species such as free radicals or ions [1]. These reactive species generally originate from photosensitive compounds; namely photoinitiators and photosensitizers. The process is widely used in various applications including coatings, printing inks, dental fillings, and adhesive applications [2-5].

Although the photopolymerization can be initiated radically, cationically or anionically, free radical and cationic UV curing are the two major applications of photoinitiated polymerizations employed in industrial processes.

1.1.1 Photoinitiated Free Radical Polymerization

Light induced polymerization reactions are widely used in a wide range of commercial applications. Photoinitiated free radical polymerization is one of the most widely used beat techniques in industry. Being applicable to a wide range of formulations makes free radical polymerizations an important industrial method [6]. The method is useful in wide range of formulations such as acrylates, polyurethanes and unsaturated polyesters. Moreover, photoinitiators used in free radical polymerization have spectral sensitivity in the long wavelength UV and visible range.

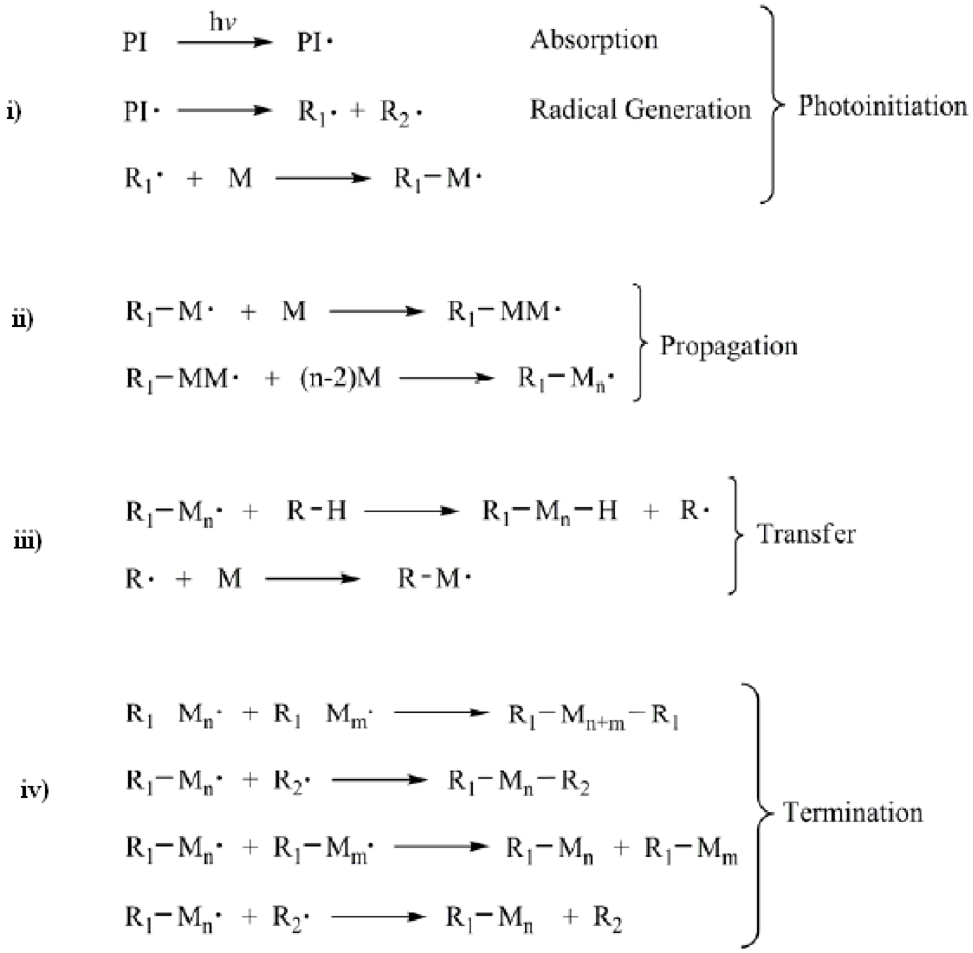


Figure 1.1 The general mechanism for the free radical polymerization**.**

Photoinitiated free radical polymerization consists of four discrete steps:

i) photoinitiation step;

In this step a photosensitive compound absorbs light or it takes electronic excitation energy from a light absorbing sensitizer. Homolytic bond cleavage leads to the formation of radicals that react with a monomer unit.

ii) propagation step;

This step involves recursive addition of monomer units to the chain radical produces the polymer backbone.

iii) chain transfer step;

In this step termination of growing chains by hydrogen abstraction and formation of new radicals are denoted.

iv) termination step;

Termination of chain radicals occur by recombination or disproportionation reactions with some other radicals involving primary radicals which are produced by the photoreaction.

Much effort has been assigned to free radical systems mainly due to the availability of the high reactivity of acrylate based monomers. In addition, extensive investigation was gathered for photoinitiators [3, 7]. On the other hand, although the most popular industrial applications are based on free radical polymerization, there are serious drawbacks related to the free radical polymerization [8-10]. Post cure limitations and the inhibition effect of oxygen are some examples to these effects. Therefore the development of photoinitiated cationic polymerization has become an important subject.

1.1.2 Photoinitiated Cationic Polymerization

Until the discovery of onium salt photoinitiators, photoinitiated free radical polymerizations attracted more attention than photoinitiated cationic polymerizations. Discovery of photochemically active onium salts has led to the rapid increase of photoinitiated cationic polymerization in many areas. In this study, we have focused mainly on photoinitiated cationic polymerizations.

1.2 Cationic Photoinitiation

1.2.1 Advantages and Applications of Photoinitiated Cationic Polymerization

Photoinitiated polymerization has found use in a number of areas since it has several advantages over other comparable methods such as rapid through cure, room temperature treatment, non-polluting and solvent-free formulations, low energy requirements and low cost [11,12].

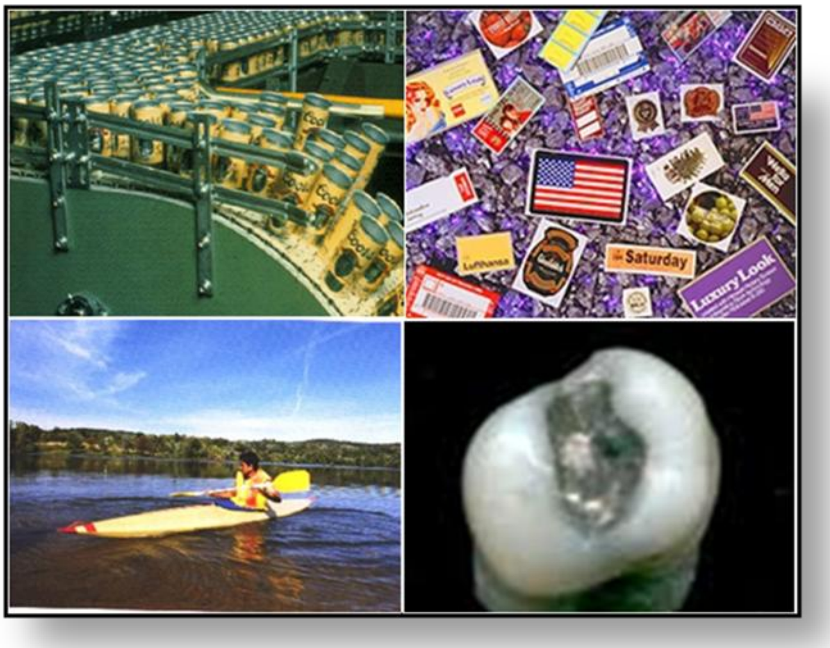


Figure 1.2 Applications of Photoinitiated Cationic Polymerization**.**

The method is also becoming popular due to its low shrinkage, high mechanical performance and good adhesion of resulting polymer. The process can be controlled by regulating the intensity of the light source. Contrary to other commonly used techniques, oxygen does not inhibit the cationic photopolymerization [13]. Cationic polymerization of vinyl and epoxide based monomers activated by near-UV and visible light is widely employed in commercial applications and continuously growing in industry [14]. Photopolymerization processes can be utilized in numerous applications such as coatings, adhesives, printing inks and photo curable dental fillings. In addition, sun light is used as energy source in fabrication of building panels and roofing, boats, catheters, water storage and delivery systems, and casts [15-17]. A number of epoxide and vinyl ether monomers were polymerized via cationic mechanism [18,19].

1.2.2 Monomers Used in Photoinitiated Cationic Polymerization

Depicted in Figure 1.3 are the cationically polymerizable monomers and their resulting polymers [20]. The typical monomers that may undergo photoinitiated cationic polymerization are heterocyclic monomers involving sulfur, oxygen, nitrogen atoms in their rings and vinyl and alkoxy vinyl monomers. Vinyl ether and epoxide monomers usually found use in UV-curing applications.

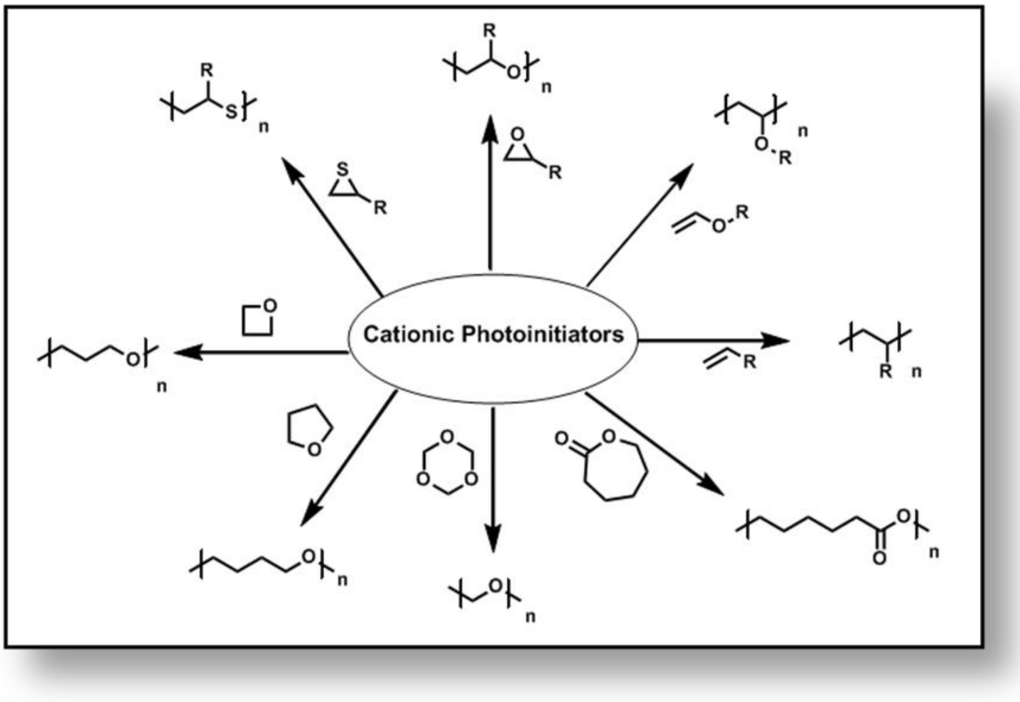


Figure1.3 Photo induced cationic polymerization of various monomers.

Although there is a variety of cationically polymerizable monomers employed in industry, need from many industrial applications encourage formulation of new monomers with high polymerization efficiency. For this reason, several studies have been devoted to the design for new monomers in recent years, especially for epoxides, with high reactivity as well as monomers possessing functional groups. This allows the design of the special polymers since nature of the monomers affects the physical and mechanical properties of the resulting polymer.

1.2.3 Photoinitiated Ring-Opening Polymerization of Epoxides

Illustrated in Figure 1.4 is the commonly accepted mechanism for the photoinitiated cationic ring-opening polymerization of epoxides. The mechanism is for the use of a diaryliodonium salt but can also be applied to all cyclic ether monomers and triarylsulfonium salt photoinitiators.

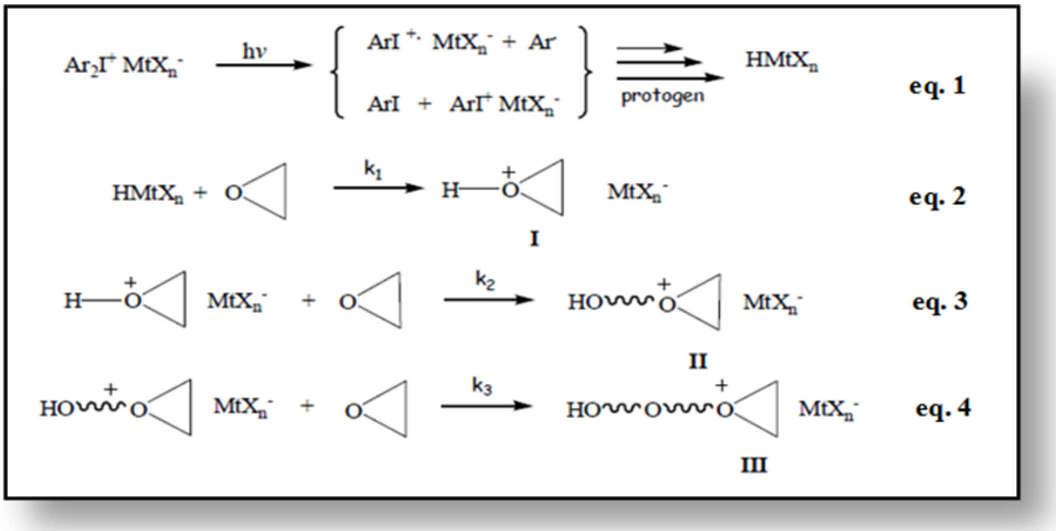


Figure 1.4 Photoinitiated Cationic Polymerization of Epoxide Monomers

Four discrete steps can be discerned for the mechanism of photoinitiated polymerization. First step involves UV irradiation of the diaryliodonium salt (eq 1). This results in the excitation and photo fragmentation of the initiator into a various cationic and radical species. Further reaction of these cationic and radical species yields the Brønsted acid. The resulting photogenerated superacids protonate the cyclic ether very rapidly (eq 2). The secondary oxonium species (I) undergo S_N2 attack by the nucleophilic cyclic ether monomer to yield the tertiary oxonium species (II) as a result of ring opening of the heterocyclic ring (eq 3). Finally, repetitive attack by a cyclic ether on the tertiary oxonium ion (eq 4) leads to chain growth (III).

1.2.4 Onium Salt Initiators

Among a variety of factors which influence the efficiency of polymerization reactions, the photoinitiator plays an important role [21, 22]. Onium salts are the most widely used cationic photoinitiators. Significant advances in the photoinitiated cationic polymerization have been achieved with the use of these photochemically active onium salts. Iodonium and sulfonium salts are commonly employed as photoinitiators due to their thermal stability, solubility in a variety of monomers, and efficiency in generating reactive species during the polymerization process [23]. These onium salts give an irreversible photochemical reaction in response to UV excitation. So far the most common onium salts are diaryliodonium and triarylsulfonium salts with nonnucleophilic counterions [24, 25]. In this thesis, diaryliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) salt was used as the photoinitiator.

Figure 1-5 a) Diaryliodonium salt, b) triarylsulfonium salt photoinitiators

1.3 Photosensitization of Cationic Photoinitiators

The use of photosensitizers is important for the success of cationic polymerizations in many applications. Onium salts used in cationic photopolymerization, essentially absorb between 225 and 350 nm as illustrated in Figure 1.6. These photoinitiators are either poorly responsive or completely inactive in visible region since they do not absorb at wavelengths above 350 nm. There are many applications such as home and boat building in which cationic polymerization is conducted under direct solar irradiation [26]. In addition, many current imaging light sources deliver monochromatic radiation in the long-wavelength UV and visible regions where onium salts are not responsive [27]. For practical applications, these photoinitiator-monomer systems are expected to absorb at longer wavelengths.

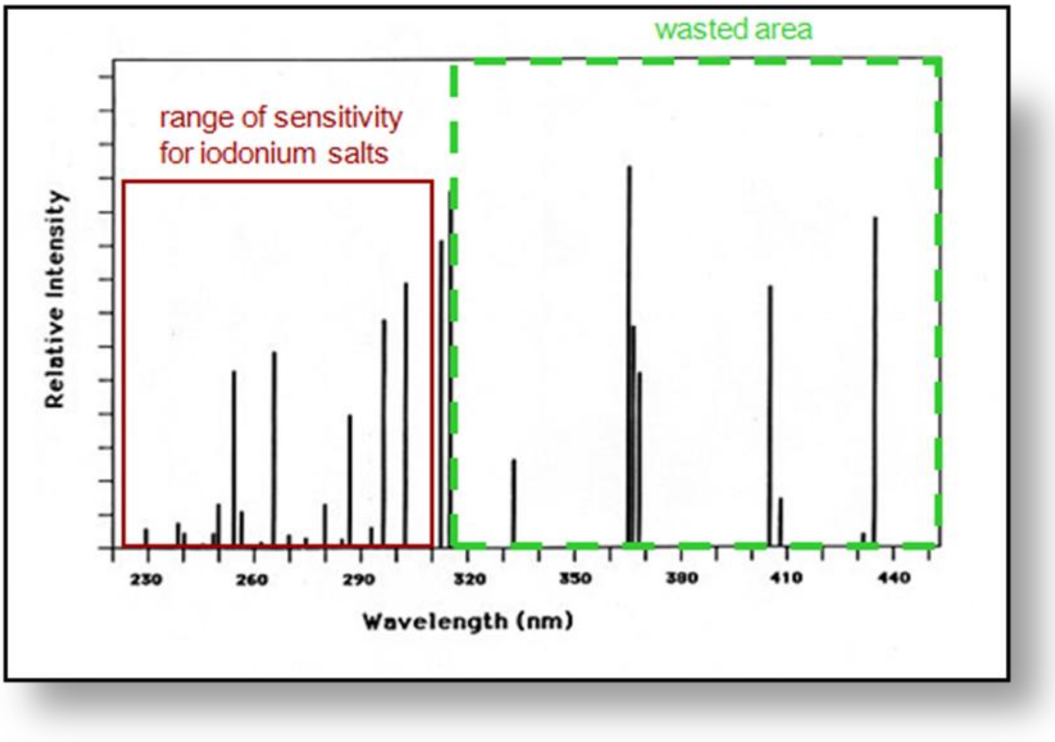


Figure 1.6 Spectral distribution for Mercury Arc Lamps.

At this point, a strategy commonly employed to broaden the spectral sensitivity of the onium salts is the use of electron-transfer photosensitization [28,30]. A photosensitizer plays a major role to absorb the luminous energy at a wavelength where initiator is unable to start the reaction. Photosensitizer transfers the excitation to initiator and the cationic polymerization takes place. A large number of systems allow extending the spectral sensitivity to long wavelength UV and visible region.

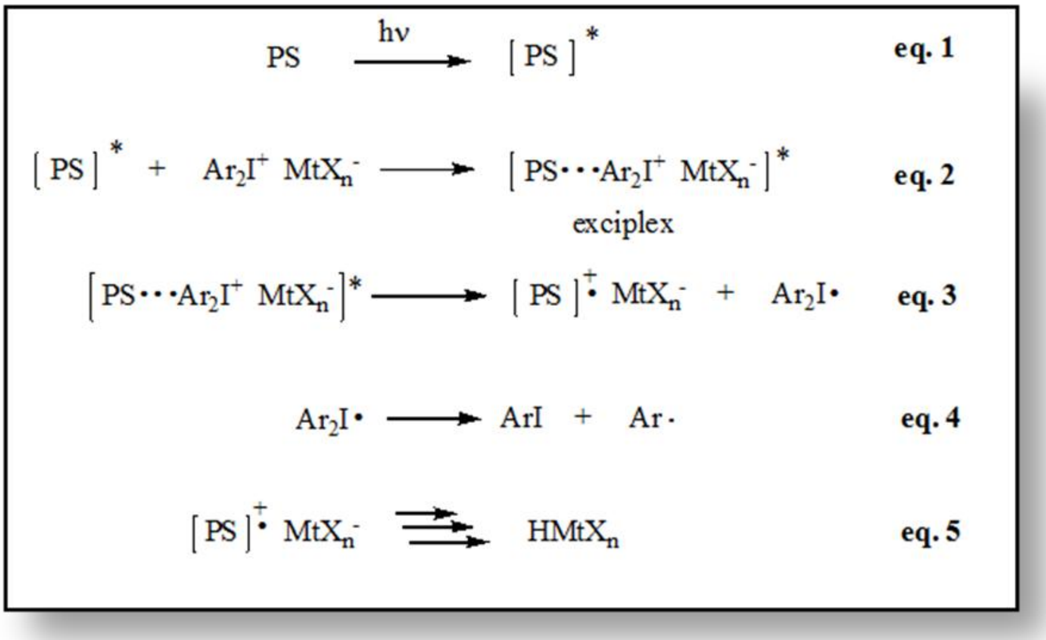


Figure 1.7 Electron-transfer Photosensitization.

Figure 1.7 is the general illustration of the photosensitization mechanism with diaryliodonium salts. The reaction sequence starts with the absorption of a photon by the photosensitizer (eq. 1). An excited state complex is usually formed between the initiator and the sensitizer (eq. 2). Then, the onium salt is reduced by one electron transfer between two species, followed by the formation of a diaryliodine free radical and the photosensitizer radical cation (eq. 3). The next step is irreversible since the rapid decomposition of the resulting unstable diaryliodine free radical (eq. 4) which prevents back electron transfer. The photosensitizer radical cations from eq.3 initiate cationic polymerizations through a variety of pathways, such as releasing a Brønsted acid (eq.5).

Cationic polymerizations can be initiated by photosensitizer radical cations by several mechanisms, as shown in Figure 1.8.

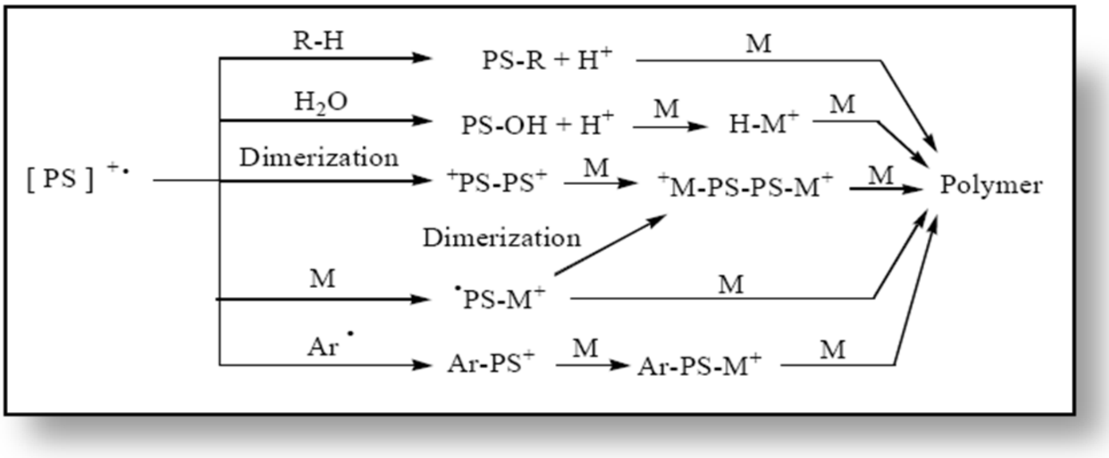


Figure 1.8 Photosensitization Mechanisms

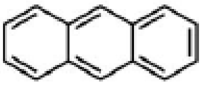
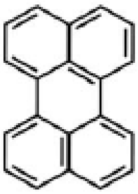
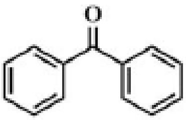
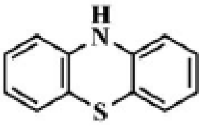
The Rehm-Weller equation illustrates (section 3.1) that photosensitizers must be electron-rich units with strong absorption characteristics in the long wavelength spectral region that become good electron-donors in their excited states.

In addition, low oxidation potential of the photosensitizer dye molecules; make free energy change more negative. The more negative free energy change values give more efficient PET reaction.

The use of fused aromatic molecules as photosensitizers has been proven to be one of the effective ways to design these systems due to their low oxidation potentials.

Aromatic hydrocarbons undergo efficient photosensitization with onium salt photoinitiators [31-33]. Anthracene, perylene, benzophenone and phenothiazine are the most commonly used photosensitizers. However, these hydrocarbons have some serious drawbacks that limit their use [33]. Having poor solubitiy, toxicity, limited wavelength and high cost are some of these drawbacks, which increase the need for new photosensitizers.

Table 1.1 Structures, oxidation potentials, excitation energies and absorption characteristics of some common photosensitizers.

Photosensitizer	E^{ox}_{sens} (V)	E^{*}_{sens} (kJ·mol^{-1})	λ_{max} (nm)
 **Anthracene**	1.1	319 (E_S)	252 356 374
 **Perylene**	0.9	277 (E_S)	252 435
 **Benzophenone**	2.7	290 (E_T)	252 333 342
 **Phenothiazine**	0.6	239 (E_T)	254 318

1.3.1 Dibenzophenazine Derivatives as Novel Visible Photosensitizers for Diaryliodonium Salts

Highly conjugated molecules have been shown to be convenient systems to promote cationic polymerization at above 400 nm, as they are capable of absorbing light in the visible region. A number of systems allow for the expansion of the spectral sensitivity to the visible region [34-38]. An excellent example of such materials is dibenzo[a,c]phenazine derivatives, since these derivatives absorb at long wavelengths. Moreover, they have good solubility in monomers used in cationic polymerization. Molecules containing dibenzo[a,c]phenazine moieties are shown to be efficient photosensitizers in free radical polymerizations [39-41].

1.3.2 Quinoxaline Derivatives as Long Wavelength Photosensitizers in Photoinitiated Cationic Polymerization of Diaryliodonium Salts

As mentioned in section 1.3, extension of the spectral sensitivity can be achieved by electron transfer photosensitization [42]. The photosensitizer plays a major role in absorbing the luminous energy at a wavelength where the initiator is unable to start reaction. A large number of systems allow extending the spectral sensitivity to long wavelength UV and visible region. Quinoxaline derivatives are one of these systems.

Quinoxaline derivatives have aroused attention for their use as photosensitizers due to their interesting electrochemical and optical properties. Several derivatives found use in free radical polymerizations as visible light absorbing photoinitiators [43-44]. They are electron rich species with low oxidation potentials and absorption peaks in visible region. They were also employed as visible photoinitiators for free-radical/cationic hybrid photopolymerizations [45]. Substituted quinoxaline derivatives were used as efficient photosensitizers for cationic photopolymerizations by Toppare Research Group [37].

The monomers used in this study have low oxidation potentials, and also they have absorption peaks in visible region. Quinoxaline derivatives are electron rich species which make DBQEd and TTQ an important building block of a wide variety of materials for electronic and optical applications [47,48].

1.4 Aim of This Work

In this study, the use of visible light in photoinitiated cationic polymerization is highlighted. Photoinitiated polymerization of oxiranes, vinyl ethers, and other vinyl monomers is achieved. In doing so (2-(2,3 dihydrobenzo [b][1,4]dioxin-6-yl)-3-(2,3-dihydrobenzo[b]-[1,4]dioxin-7-yl)-5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-8-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7yl) quinoxaline) (DBQEd) and poly(2,3,5,8-tetra(thiophen-2-yl)quinoxaline) (TTQ), two dibenzo[a,c]phenazine derivatives; 10,13-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)dibenzo[a,c]phenazine (PHED) and 10,13-bis(4-hexylthiophen-2-yl)dibenzo[a,c]phenazine (PHEHT) were utilized as the photosensitizers for cationic polymerizations. Novel dyes of the dibenzo[a,c]phenazine and quinoxaline skeleton are expected to be efficient in carrying out the cationic photopolymerizations of a wide variety of epoxide, oxetane, and vinyl monomers at room temperature upon irradiation with long-wavelength UV and visible light.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

All starting materials, monomers, and reagents were purchased from the Aldrich Chemical (Milwaukee, WI). The photosensitizers PHED (10,13-bis(2,3-dihydrothieno[3,4-b] [1,4]dioxin-5-yl) dibenzo[a,c]phenazine) and PHEHT (10,13-bis(4-hexylthiophen2yl)dibenzo[a,c] phenazine) ,DBQEd (2-(2,3 dihydrobenzo [b][1,4]dioxin-6-yl)-3-(2,3-dihydrobenzo[b]-[1,4]dioxin-7-yl)-5-(2,3-dihydrothieno [3,4-b][1,4]dioxin-5-yl)-8-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl) quinoxaline) and TTQ (2,3,5,8-tetra(thiophen-2-yl)quinoxaline) were synthesized by Toppare Research Group as detailed in the literature [38, 39]. All monomers, reagents, and starting materials, hexafluorophosphate ($Ph_2I^+PF_6^-$) (as photoinitiator)**,** cyclohexene oxide (CHO), vinylcyclohexene diepoxide (VCHDE), 2-choloroethylvinylether (CEVE), neopentylglycol diglycidyl ether (NPGDGE) and 3,4-epoxycyclohexylmethyl 3’,4’-epoxycyclohexanecarboxylate (ERL-4221E) were purchased from the Aldrich Chemical Co. (Milwaukee, WI) , and were reagent quality. The poly(propylene) films used in optical pyrommetry studies were corona-treated and they were kindly supported as gifts by Superfilm Co. Gaziantep, Turkey. Varian Cary 5000 Spectrometer was used to illustrate UV spectrum of the photosensitizer.

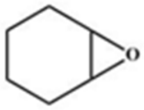
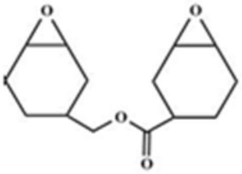
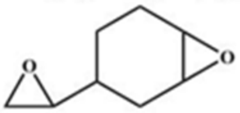
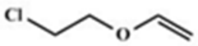
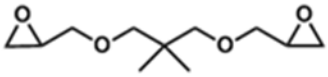
Epoxide and Vinyl monomers	
Cyclohexene Oxide (CHO)	
3,4epoxycyclohexylmethyl3,4-epoxycyclohexanecarboxylate) (ERL-4221E)	
Vinyl Cyclohexene Diepoxide (VCHDE)	
2-Chloroethylvinylether	
Neopentylglycol diglycidyl ether (NPGDGE)	

Figure 2.1 Monomers used in this thesis study.

2.2 Synthesis of photosensitizers

Substituted dibenzo[a,c]phenazine and quinoxaline derivatives DBQEd and TTQ, two dibenzo[a,c]phenazine derivatives; PHED and PHEHT were synthesized by Toppare Research Group. [13]

2.2.1 Syntheses of Quinoxaline Derivatives

2.2.1.1 Synthesis of DBQEd

Synthesis of DBQEd involved cross coupling of the dibromoquinoxaline derivative with tributyl(thiophen-2-yl)stannane and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane catalyzed by palladium, $Pd(PPh_3)_2Cl_2$ as depicted in Figure 2.2. A mixture of HBr/Br_2 was used to brominate 2, 1, 3-benzothiadiazole (1) Excess quantity of $NaBH_4$ were used for reduction of the resulting compound and 3,6-dibromo- 1,2-phenyldiamine (2) was achieved. Condensation reaction of 3,6-dibromo-1,2-phenyldiamine (3) and 1-(2,3- dihydrobenzo[b][1,4]dioxin-6-yl)-2-(2,3-dihydrobenzo[b][1,4]dioxin- 7-yl)ethane-1,2-dione (5) was performed in ethanol by adding catalytical amount of paratoluenesulfonic acid (PTSA). Tributyltin substituted EDOT was produced in order to synthesize DBQEd, (8). The coupling reaction of quinoxaline product (1 mmol) with tributyl(2,3-dihydrothieno[3,4- b][1,4]dioxin-5-yl)stannane (7 mmol) in THF (100 mL) yields the resulting product DBQEd. Column chromatography (silica, DCM/hexane, 3/1) gave DBQEd as a red solid. The synthetic route of the monomer is shown in Figure 2.2.

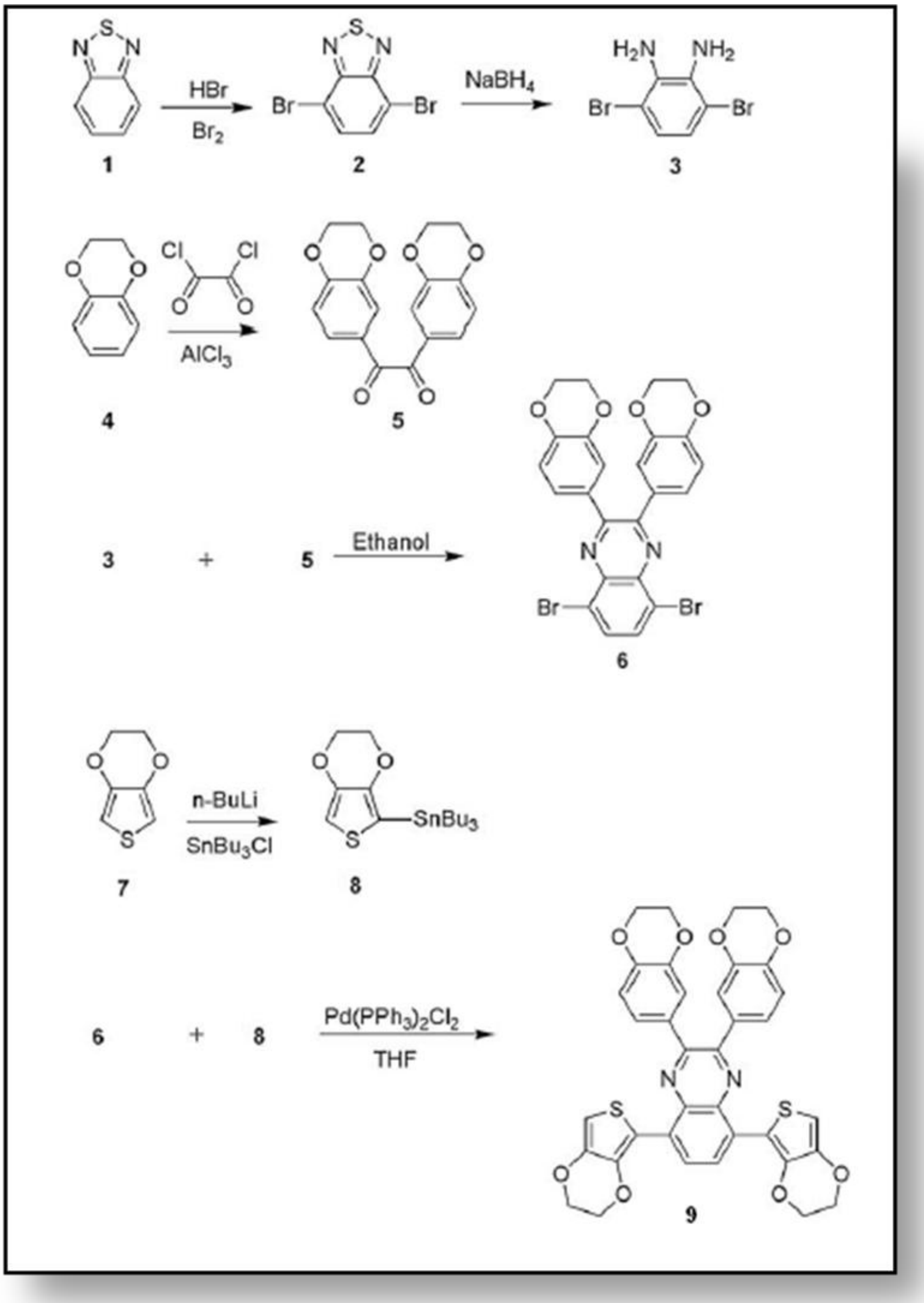


Figure 2.2 Synthesis mechanism of the DBQEd.

2.2.1.2 Synthesis of 2,3,5,8-tetra(thiophen-2-yl) quinoxaline (TTQ)

For the preparation of the monomer, namely 2,3,5,8-tetra(thiophen-2-yl) quinoxaline (TTQ), tributyl(thiophen-2-yl)stannane (2.2 mmol) and 5,8-Dibromo-2,3-di(thiophen-2-yl)quinoxaline (0.440 mmole) were dissolved in dry THF (80 mL). Then, under argon atmosphere the solution was purged and palladium catalyst $PdCl_2(PPh_3)_2$ (0.045 mmol) was added at room temperature. Then, again under argon atmosphere, mixture was stirred at 100 ^{0}C for overnight. The solution was cooled, and the solvent was vaporized in the rotary evaporator. The column chromatography (DCM-Hexane 3:1) was applied for the residue in order to afford an orange solid (136 mg, yield: 68%). The characterization of the monomer was done with 1H NMR, 13C NMR. Synthesis mechanism of the monomer is shown in Figure 2.3.

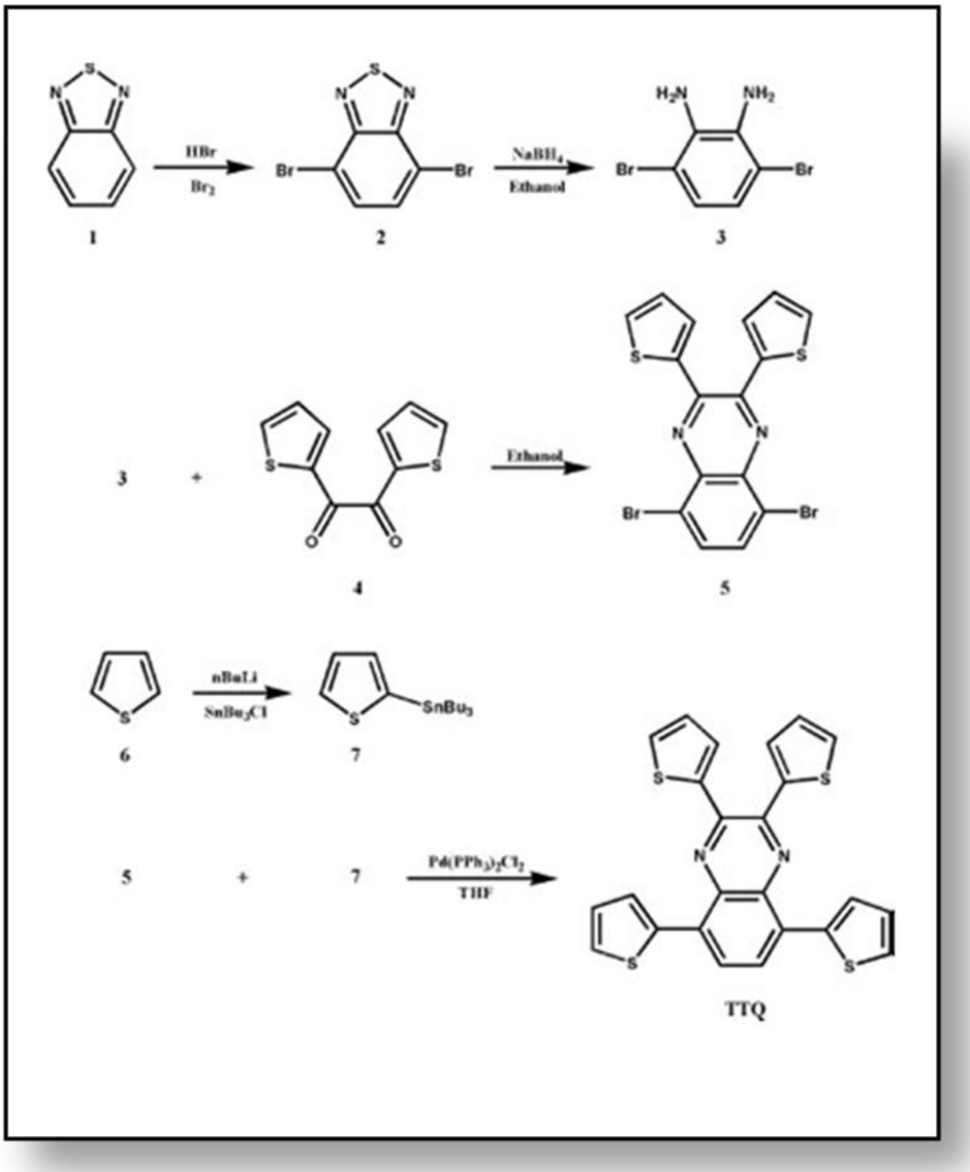


Figure 2.3 Synthetic route of the TTQ.

2.2.2 Synthesis of Dibenzo[a,c]phenazine Derivatives

2.2.2.1 Synthesis of 10,13-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5 yl)dibenzo [a,c]phenazine (PHED)

Synthesis of PHED involved the reduction reaction of 4,7-dibromo-2,1,3-benzothiadiazole (2) to afford 3,6-dibromo-1,2-phenyldiamine (3) in the presence of excess $NaBH_4$. The daimine product with phenanthrene-9,10-dione was subjected to condensation reaction with paratoluene sulfonic acid (PTSA) as the catalyst, in ethanol. Addition of equimolar n-BuLi, as strong base, and addition of $SnBu_3Cl$ were promoted the stannylation of EDOT. Compounds 5 and 7 were subjected to Stille coupling with the catalytical amount of $Pd(PPh_3)_2Cl_2$ to give the resulting molecule PHED (8). Column chromatography on silica gel was applied for purification and dark red solid, PHED was obtained. Synthesis mechanism of the monomer is shown in Scheme 2.3.

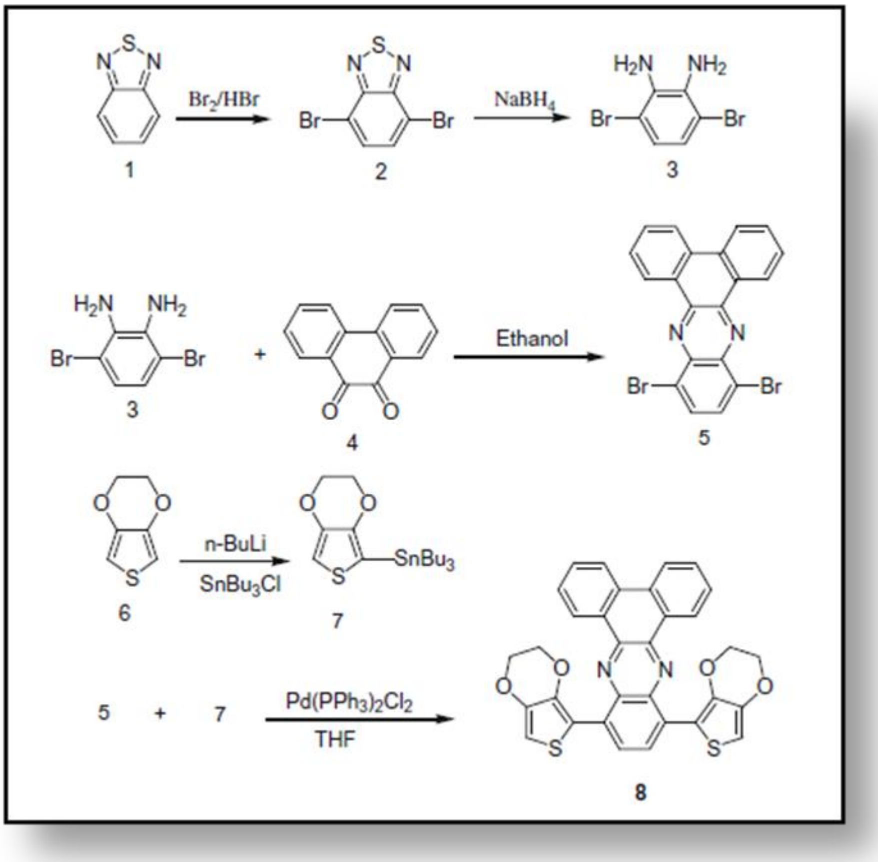


Figure 2.4 Synthetic route of the PHED.

2.2.2.2 Synthesis of 10,13-bis(4-hexylthiophen-2-yl)dibenzo[a,c]phenazine (PHEHT)

Access to the monomer, namely 10,13-bis(4-hexylthiophen-2-yl)dibenzo[a,c]phenazine was achieved by brominating benzo[c][1,2,5]thiadiazole (**1**) with Br_2 in HBr solution at 150^{o}C in order to give the dibromo compound. Reaction of 4,7-dibromobenzo[c][1,2,5]thiadiazole (**2**) with excess amount of $NaBH_4$ gave 3,6-dibromo-1,2- phenyl-diamine (**3**) by one-pot reduction. The condensation reaction between the diamine compound (**3**) and phenanthrene-9,10-dione (**4**), (**5)** was obtained (Scheme 2).

To a solution of (**5**) (0.72 mmol) in 100 mL of anhydrous THF, tributylstannane derivative (**7**) (2.88 mmol) was added. After the solution purged with argon, palladium catalyst, dichlorobis(triphenylphosphine)palladium(II) (0.12 mmol) was added at room temperature. The mixture was refluxed for overnight under argon atmosphere. Solution was concentrated on rotary evaporator. The residue was purified by column chromatography over silica gel, eluting with 1:1 (dichloromethane/hexane) and gave orange solid, PHEHT (**8**).

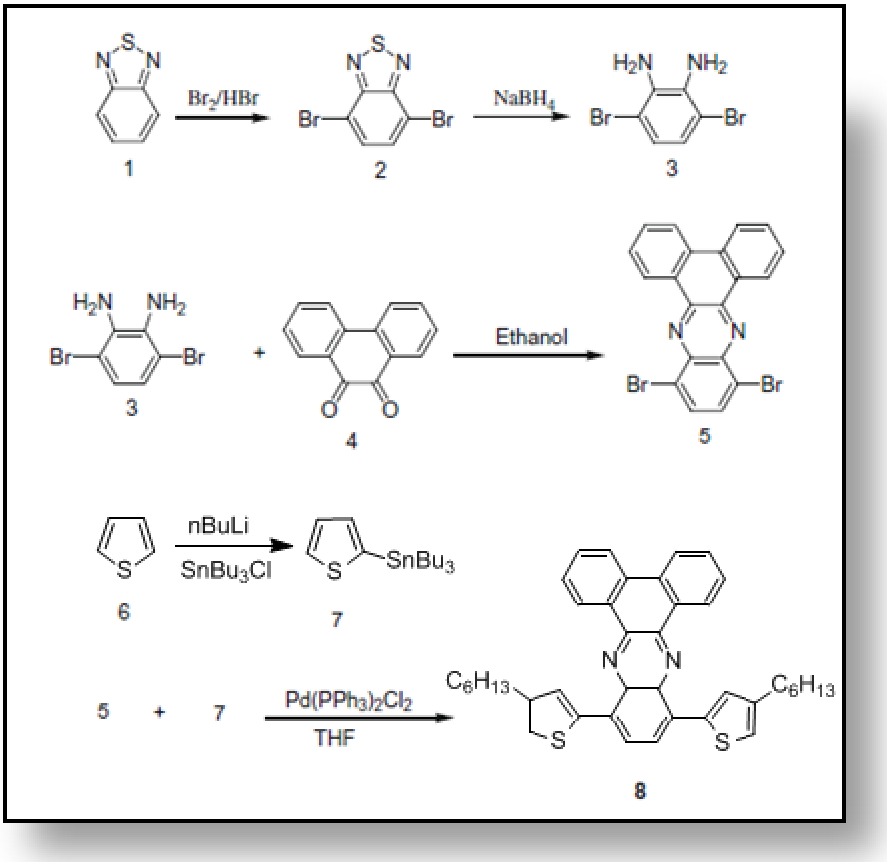


Figure 2.5 Synthetic route of the PHEHT

2.3 Fluorescence Quenching Studies.

Varian Cary Eclipse Fluorescence Spectrometer was used for all fluorescence quenching studies. An excitation wavelength of 332 nm was used and the fluorescence emission band at 651 nm was monitored for PHED. At 314 nm excitation wavelength, the fluorescence emission maximum 625 nm was observed for PHEHT. Both PHED and PHEHT concentrations were 1 x 10^{-4} M in dichloromethane.

DBQEd and varying concentrations of $Ph_2I^+PF_6^-$ in dichloromethane were subjected to an excitation wavelength of 321 nm. The fluorescence emission band at 579 nm was noted. For TTQ, an excitation wavelength of 314 nm was used, and the fluorescence emission maximum at 576 nm was observed. Both the DBQEd and the TTQ concentrations were 2 x 10^{-5}M in dichloromethane.

2.4 Kinetic Characterization of Photopolymerizations by Optical Pyrometry (OP).

Optical pyrometry (OP), a method remotely senses the temperature changes was employed to determine the progress of cationic photopolymerizations. The instrument operates by remotely monitoring the temperature of a sample while it undergoes a photoinduced exothermic polymerization. The observed rise in temperature is directly proportional to the conversion of the monomer undergoing polymerization. The equipment and method utilized to illustrate the cationic photoinitiated polymerizations reported in this study by OP were explained in detail in an article from Crivello’s group.

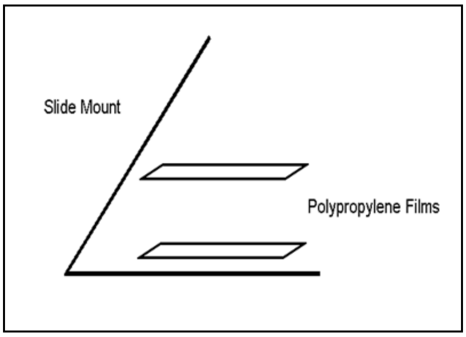


Figure 2. 6 Sample Preparation

Sample preparation is as follows: Homogeneous solutions of the selected monomer and the photoinitiator were prepared with and without the photosensitizer. Liquid samples were sandwiched between two 10-µm corona-treated polypropylene films. The resulting samples were mounted in a 2.0 cm x 2.0 cm plastic slide holder and placed in the optical pyrometer.

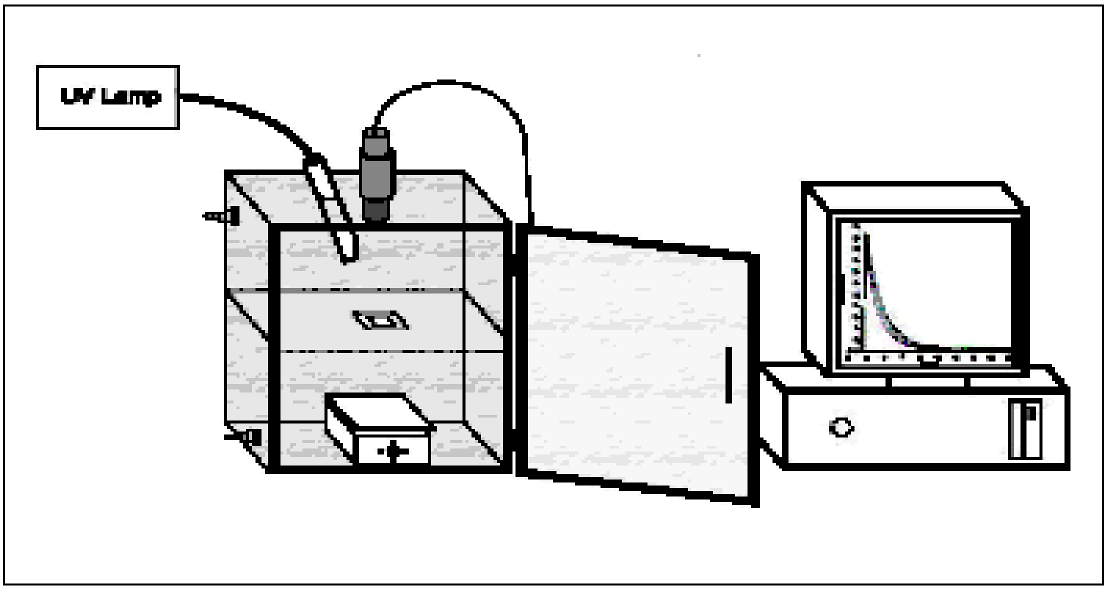


Figure 2.7 Optical Pyrometer

As illustrated in Figure 2.7, samples were irradiated with ‘‘cold’’ UV light. UVEXS model SCU-110 mercury arc lamp (Sunnyvale, CA) provided with a liquid optic cable, was used for all optical pyrometry studies. Three kinetic runs were carried out for each photopolymerizable system and the average values of these runs reported in results chapter. All optical pyrometry experiments were performed at ambient temperatures (25–28^{o}C).

2.5 Solar Irradiation Induced Polymerization.

ERL-4221 solutions containing 1.0 mol % $Ph_2I^+PF_6^-$ and 0.1 mol% PHED, 0.1 mol% PHEHT, 0.1 mol% DBQEd or 0.1 mol% TTQ were prepared. Then these solutions spread onto a glass slide. The solutions were subjected to direct solar irradiation at METU Campus, Ankara on July 20, 2010 initiated at 09:00 h, where the ambient temperature was 27^{o}C.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Electron-Transfer Photosensitization of Onium Salts

According to the Rehm-Weller equation, electron transfer from the excited sensitizer to onium salt is feasible if the change in free energy (ΔG) is negative. Based on the oxidation potential (E^{ox}_{sens}) and active excitation energy (E^{*}_{sens}) of the photosensitizer and the reduction potential (E^{red}_{onium}) of the initiator, the free energy change (ΔG) for the photoinduced electron transfer process is estimated.

$$\Delta G = (E^{ox}_{sens} - E^{red}_{onium}) - E^{*}_{sens} \qquad \text{(eq.1)}$$

It can be predicted that compounds with an extended conjugation bearing electron rich moieties will have low oxidation potentials and will become good electron donors in their excited states, therefore, will be promising candidates for the photosensitization of onium salts.

Dibenzo[a,c]phenazine is a fully conjugated compound with its fused pentacyclic system, which has two absorption maxima at 373 and 393 nm. Incorporation of electron rich 3,4-ethylenedioxythiophene (EDOT) or 6-hexylthiophene units affords low oxidation potential values and imparts strong absorption characteristics in the long wavelength UV and visible spectral regions.

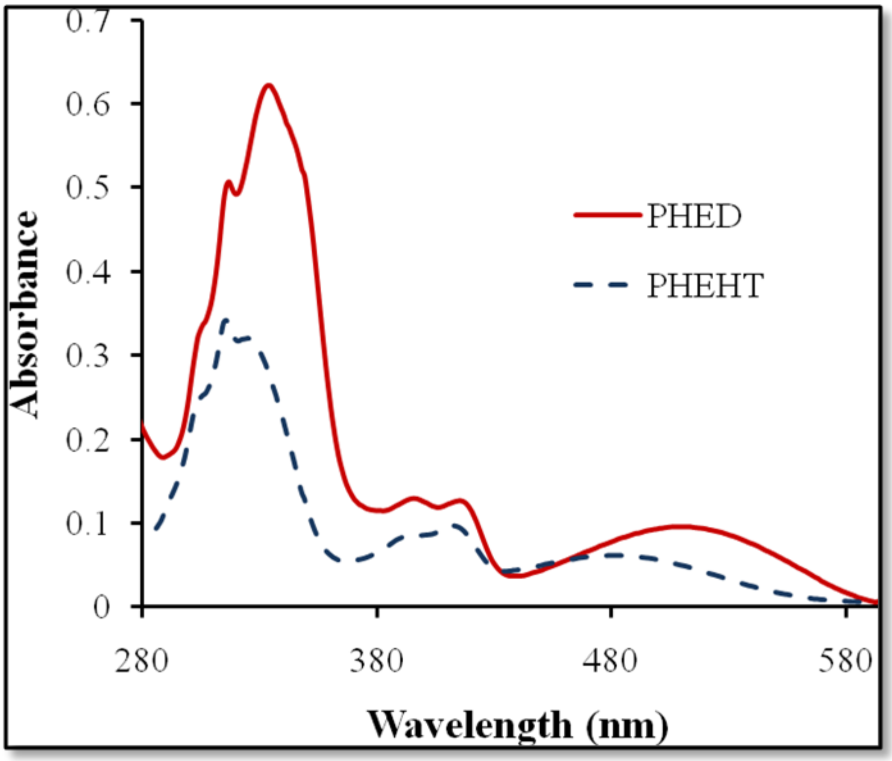


Figure 3.1 UV-Vis spectra of 2 x 10^{-6} mol L^{-1} PHED (—) and 2 x 10^{-6} mol L^{-1} PHEHT (---) in CH_2Cl_2

The oxidation potentials of the molecules were determined by cyclic voltammetry and found as + 0.86 V for PHED and + 1.1 V for PHEHT versus Ag wire. As seen in Figure 3.1, both molecules reveal strong absorptions in the visible region of the spectrum covering between 400 and 600 nm, where iodonium salts are completely transparent. Moreover, the photosensitizers are highly soluble in the monomers of interest, which is crucial for the choice of photosensitizers.

Quinoxaline is a highly conjugated compound with its fused aromatic system. Substituted quinoxaline derivatives were synthesized by Toppare research group for the synthesis of conducting polymers [23-29]. Since they are soluble in various monomers and have low oxidation potentials, these molecules are good candidates as phosensitizers for PET reactions with aryliodonium salts. (2-(2,3 dihydrobenzo[b][1,4]dioxin-6-yl)-3-(2,3-dihydrobenzo[b]-[1,4]dioxin-7-yl)-5-(2,3-dihydro thieno[3,4-b][1,4]dioxin-5-yl)-8-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-

yl)quinoxaline) (DBQEd) and (2,3,5,8-tetra(thiophen-2-yl)quinoxaline) (TTQ) are novel quinoxaline derivatives, which were tested as the electron transfer photosensitizers.

These substituted quinoxaline derivatives possess long wavelength absorption in the visible region of the spectrum covering the range between 400 and 520 nm, where iodonium salts are transparent in this region. As illustrated in Figure 3.2, DBQEd has two UV absorption peaks at 321 and 406 nm, and TTQ has two strong UV absorption peaks at 321 and 406 nm.

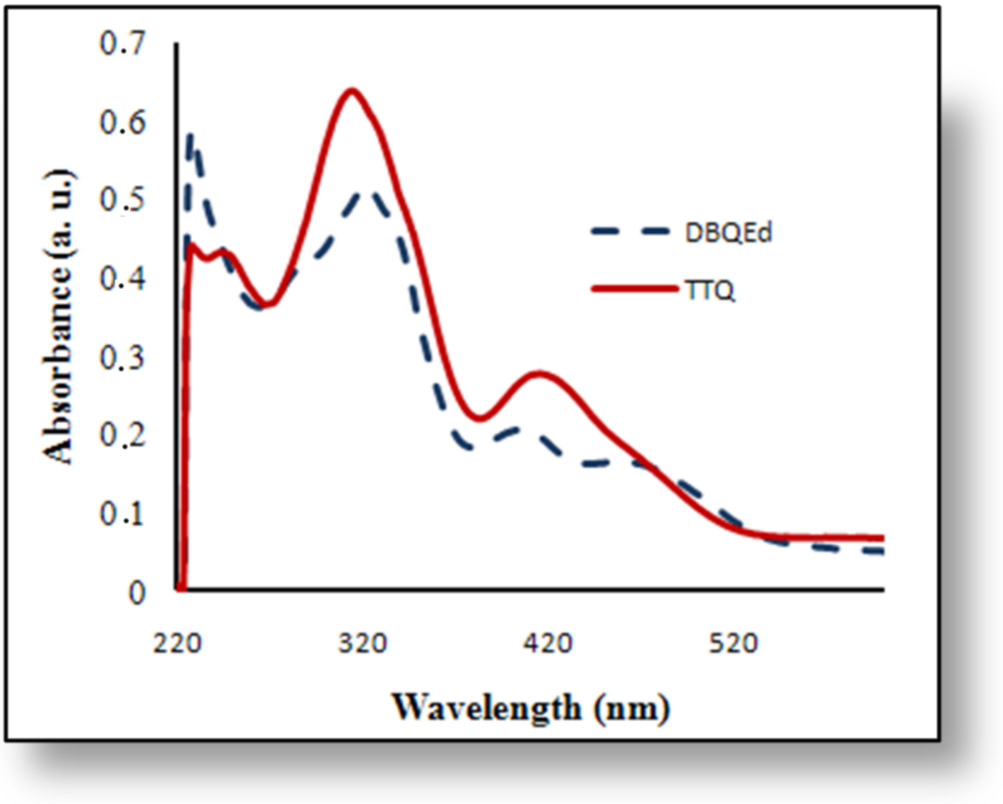


Figure 3.2 UV-Vis spectrum of 2 x 10^{-5}M mol L^{-1} TTQ (—) and 2 x 10^{-5}M mol L^{-1} DBQEd (---) in CH_2Cl_2

Furthermore, the presence of electron rich donor groups in the molecule backbone enhance the electron density of the photosensitizer molecule. Oxidation potentials of the molecules were determined via cyclic voltammetry. The oxidation potential of

DBQEd was found as +0.80 V and it was +1.0 V for PHEHT versus Ag wire. It was found that the oxidation potential of DBQEd is lower than that of TTQ as expected. This can be explained by higher electron density of ethylenedioxythiophenyl substituent compared to thiophene.

3.2 Fluorescence Quenching Study of Photosensitizers

The efficiency of the electron transfer from the photosensitizer to the photoinitiator determines the efficiency of the polymerization. Accordingly, we carried out a fluorescence quenching study by increasing iodonium salt concentration. Figure 3.3 and Figure 3.4 illustrate a typical Stern-Volmer plot. The linear relationship demonstrates that the fluorescence intensity of the photosensitizer decreases as the photoinitiator concentration increases.

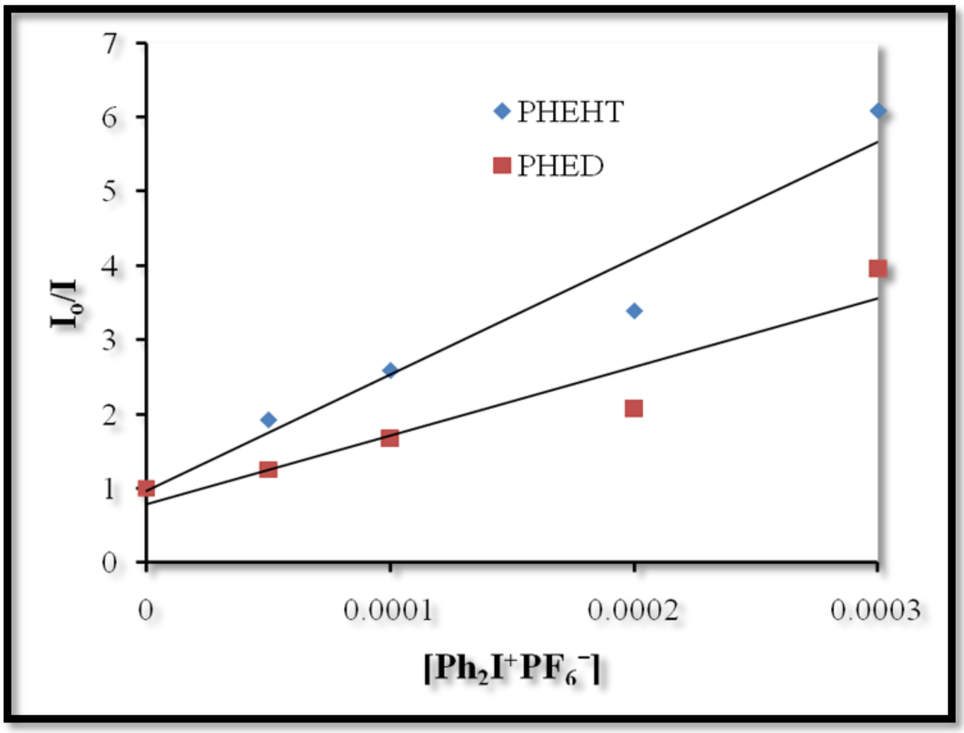


Figure 3.3 Stern-Volmer plot of the quenching of PHED (□) (1 x 10^{-4} M) and PHEHT (◊) (1 x 10^{-4} M) by diphenyliodonium hexafluorophosphate ($Ph2I^+PF6^-$) in

dichloromethane. (Excitation wavelength 332 nm for PHED and 314 nm for PHEHT)

Further evidence for the electron transfer mechanism was provided by running polymerizations where either $Ph_2I^+PF_6^-$ or the dye molecules were eliminated from the sample mixture. It was concluded that the presence of both the iodonium salt and the photosensitizer together was imperative since polymerization did not commence even after prolonged irradiation time in the absence of either components.

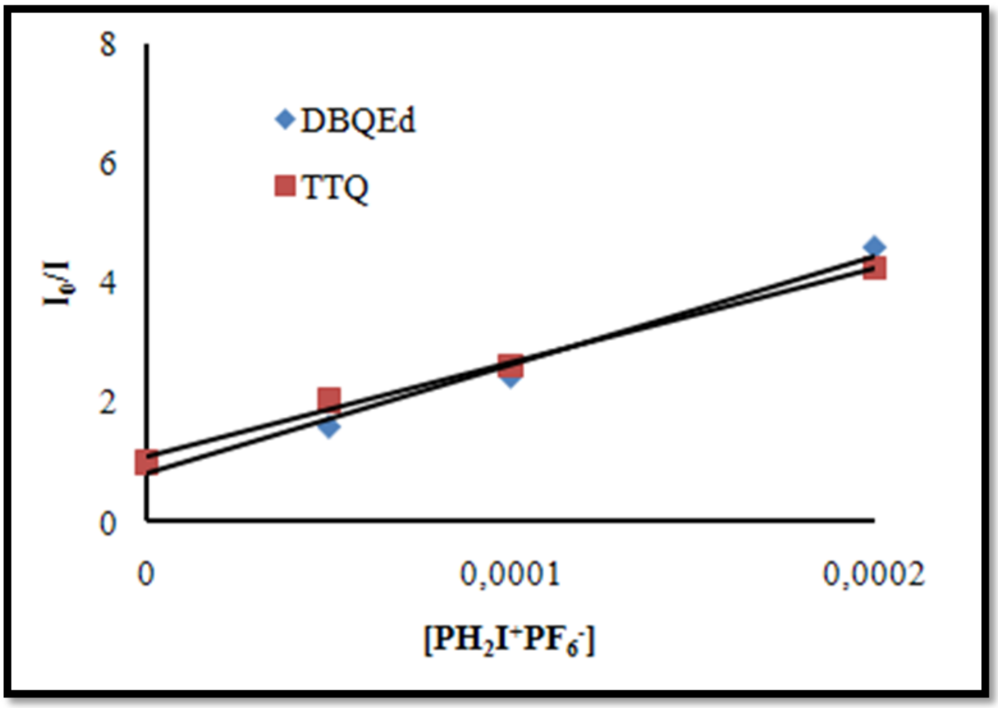


Figure 3.4 Stern-Volmer plot of the quenching of DBQEd (◊) (2 x 10^{-5}M) and TTQ (□) (2 x 10^{-5}M) by diphenyliodonium hexafluorophosphate ($Ph2I^+PF6^-$) in dichloromethane. (Excitation wavelength 321 nm for DBQEd and 314 nm for TTQ)

3.3 Optical Pyrometry Study of Photosensitizers

In order to monitor the progress of a photopolymerization, there are several methods. The two common methods are real time IR spectroscopy and differential scanning photocalorimetry (8, 15). In addition to these methods, optical pyrometry has been widely used and it is an easier and more convenient method than the others, since one can monitor the photopolymerizable mixtures under various reaction conditions at speed. An optical pyrometer remotely monitors the temperature of a sample while it goes into photoinitiated exothermic polymerization. The detected temperature increment directly corresponds to the amount of the monomer that polymerized in the sample. (15) The illumination intensity and wavelength can be controlled within this new method. Formulation and the reaction conditions are very important for the efficiency of polymerization. By optical pyrometry, these effects on the rate of photopolymerizations can also be determined.

3.3.1 Optical Pyrometry Study of Photosensitizers PHED and PHEHT

In this thesis, we accomplish the utilization of two dibenzo[a,c]phenazine derivatives; 10,13-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)dibenzo [a,c]phenazine (PHED) and 10,13-bis(4-hexylthiophen-2- yl)dibenzo[a,c]phenazine (PHEHT) for the photosensitization reaction of onium salt photoinitiators in cationic polymerizations of a variety of epoxide, oxetane, and vinyl monomers at room temperature upon irradiation with long wavelength UV and visible light.

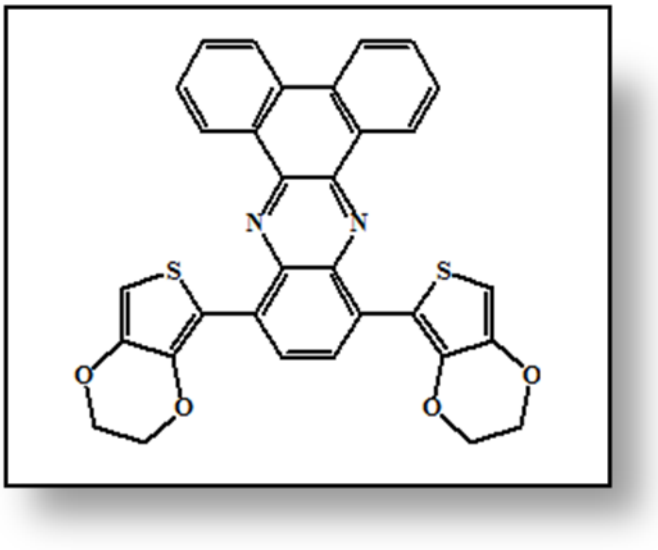


Figure 3.5 10,13-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)dibenzo[a,c]phenazine.

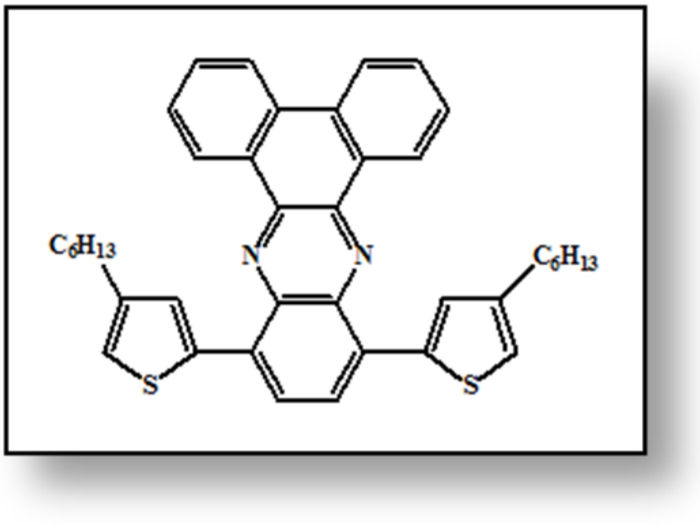


Figure 3.6 10,13-Bis (4-hexylthiophen-2- yl)dibenzo[a,c]phenazine.

Optical pyrometry (OP) provides a facile method to test the potential photosensitizers by monitoring the heat released during polymerizations. Using this technique, photosensitizers were examined in several cationically polymerizable monomers such as the monofunctional epoxide (CHO), difunctional epoxide (VCHDE), vinyl ether (CEVE), and glycidyl ether (NPGDGE) in the presence of diaryliodonium salt photoinitiator. The photopolymerizations are compiled in Figures 3.5, 3.6, 3.7 and 3.8.

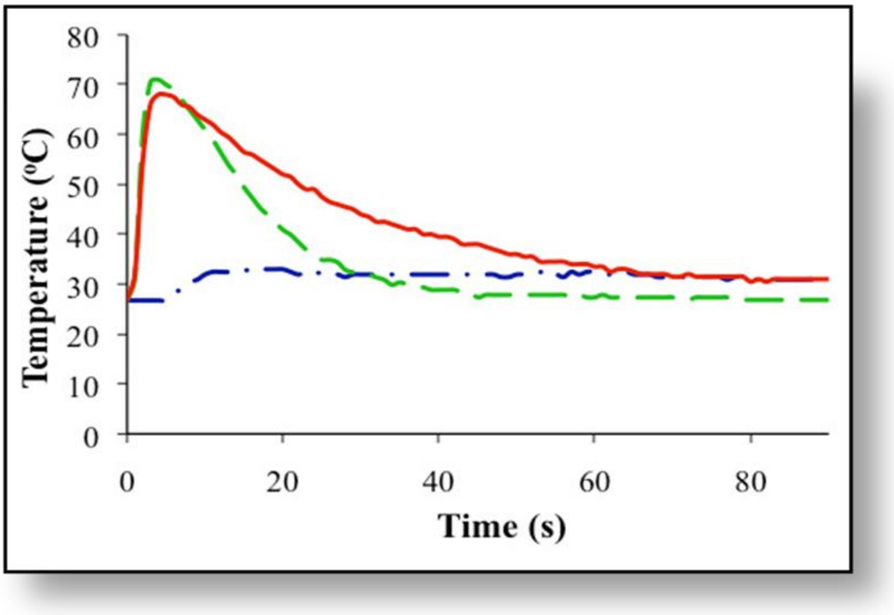


Figure 3.7 Optical pyrometry study of cationic polymerization of cyclohexene oxide (CHO) in association with 1.0 mol% $Ph_2I^+PF_6^-$ in the absence of a photosensitizer (− · −), in the presence of 0.1 mol% PHED photosensitizer (—) and 0.1 mol% PHEHT photosensitizer (---). (Light intensity 15 mW cm$-^2$)

Polymerization of cyclohexene oxide started immediately in the presence of PHED and polymerization started in the first seconds in the presence of PHEHT, whereas there is no or very little polymerization without the photosensitizers. Resulting polymer was hard and non-sticky.

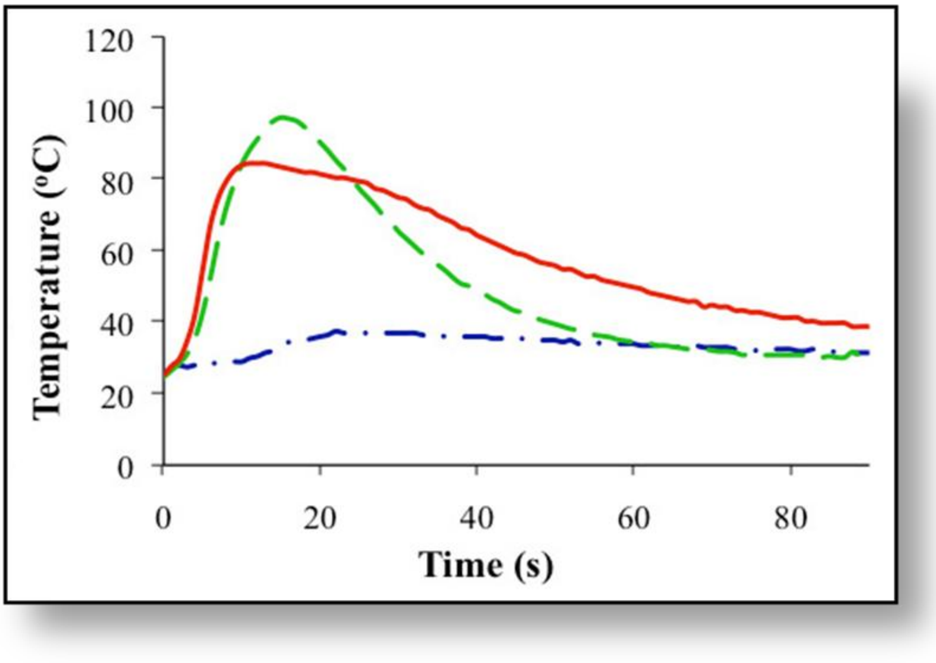


Figure 3.8 Optical pyrometry study of cationic polymerization of vinylcyclohexenediepoxide (VCHDE) in association with 1.0 mol% $Ph_2I^+PF_6^-$ in the absence of a photosensitizer (− · −), in the presence of 0.1 mol% PHED photosensitizer (—) and 0.1 mol% PHEHT photosensitizer (---). (Light intensity 15 mW cm^{-2})

Polymerization of VCHDE has started in the first seconds in the presence of PHED and PHEHT whereas there is no polymerization without the photosensitizers. Resulting polymers were hard, brittle, and nonsticky.

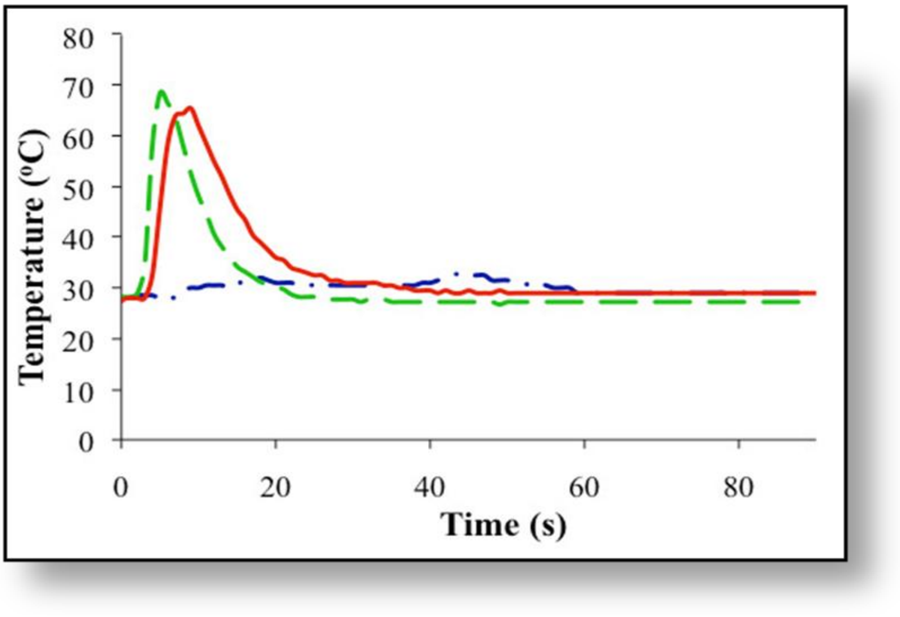


Figure 3.9 Optical pyrometry studies of cationic polymerization of 2-chloroethylvinylether (CEVE) in association with 1.0 mol% $Ph_2I^+PF_6^-$ in the absence of a photosensitizer (− · −), in the presence of 0.1 mol% PHED photosensitizer (—) and 0.1 mol% PHEHT photosensitizer (---). (Light intensity 15 mW cm^{-2})

A very rapid polymerization of 2-chloroethylvinylether monomer with the photosensitizers was observed, whereas there was no polymerization without the photosensitizers.

The photosensitizers displayed similar behavior in the polymerization of the reactive monomers. The polymerizations of CHO, VCHDE, and CEVE took off promptly in the presence of the photosensitizers. On the other hand, in their absence, there is little or no polymerization (Figures 3.5, 3.6, and 3.7). The distinction between the two photosensitizers becomes apparent in the polymerization studies with NPGDGE (Figure 3.8) due to the lower reactivity of NPGDGE compared to other monomers.

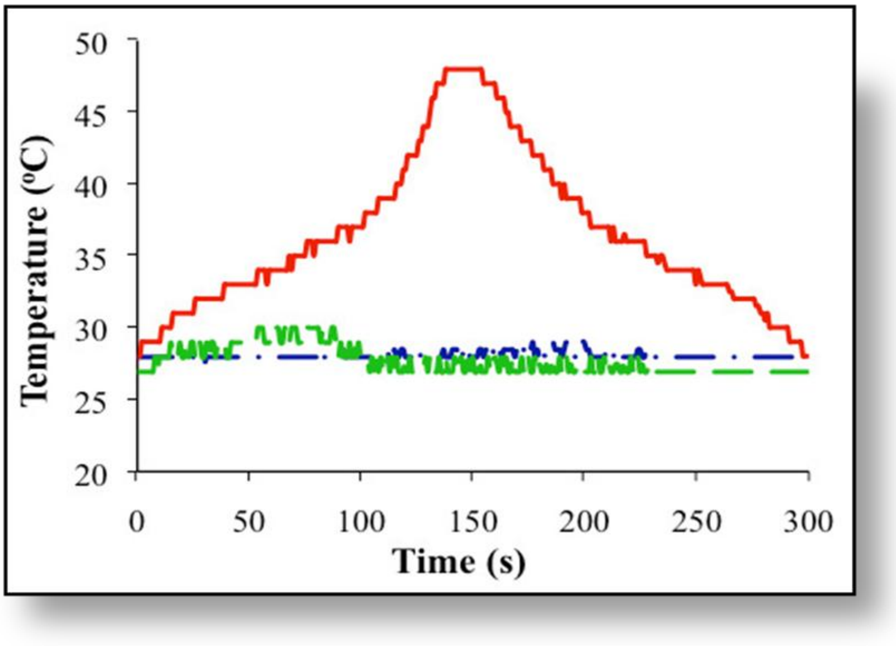


Figure 3.10 Optical pyrometry studies of cationic polymerization of neopentylglycol diglycidyl ether (NPGDGE) in association with 1.0 mol% $Ph_2I^+PF_6^-$ in the absence of a photosensitizer (− · −), in the presence of 0.1 mol% PHED photosensitizer (—) and 0.1 mol% PHEHT photosensitizer (---). (Light intensity 15 mW cm^{-2})

The polymerization is quite sluggish with PHEHT whereas a faster polymerization is observed in the presence of PHED reaching high temperatures, indicative of a more efficient process than that of PHEHT containing batch. This result is in agreement with the lower oxidation potential of PHED as discussed previously in this section.

3.3.2 Optical Pyrometry Study of Photosensitizers DBQEd and TTQ

In this thesis, we outlined the application of two novel quinoxaline derivatives, namely (2-(2,3 dihydrobenzo [b][1,4]dioxin-6-yl)-3-(2,3-dihydrobenzo[b]-[1,4]dioxin-7-yl)-5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-8-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl) quinoxaline) (DBQEd) and (2,3,5,8-tetra(thiophen-2-yl)quinoxaline) (TTQ) for the onium salt photosensitization and photopolymerization of several types of cationically polymerizable monomers.

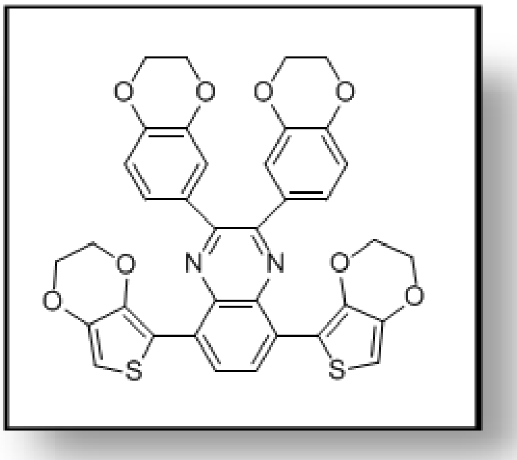


Figure 3.11 2-(2,3 Dihydrobenzo [b][1,4]dioxin-6-yl)-3-(2,3-dihydrobenzo[b]-[1,4]dioxin-7-yl)-5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-8-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl) quinoxaline.

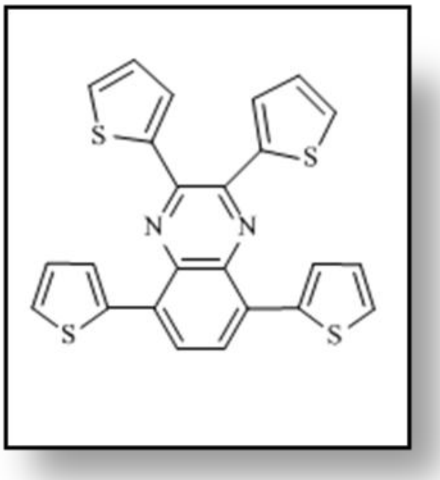


Figure 3.12 2,3,5,8-tetra(thiophen-2-yl)quinoxaline.

By optical pyrometry, photosensitizers were tested for several cationically polymerizable monomers in the presence of diaryliodonium salt initiators. Figures below, illustrate the photopolymerizations of some representative monomers such as the monofunctional epoxide (CHO), the difunctional epoxides (ERL-4221E and VCHDE), and vinyl ether (CEVE).

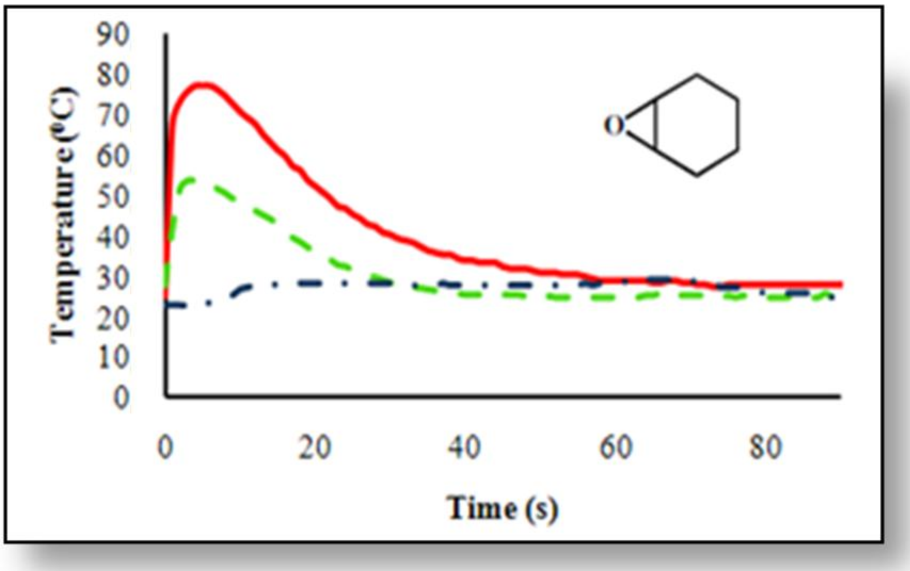


Figure 3.13 Optical pyrometry study of cationic polymerization of cyclohexene oxide (CHO) in association with 1.0 mol% $Ph_2I^+PF_6^-$ in the absence of a photosensitizer (− · −), in the presence of 0.1 mol% PHED photosensitizer (—) and 0.1 mol% PHEHT photosensitizer (---). (Light intensity 15 mW cm^{-2})

Polymerization of CHO started immediately in the presence of DBQEd and polymerization started in the first seconds in the presence of TTQ, whereas there was no or very little polymerization without the photosensitizers. Resulting polymer was brittle and tack-free.

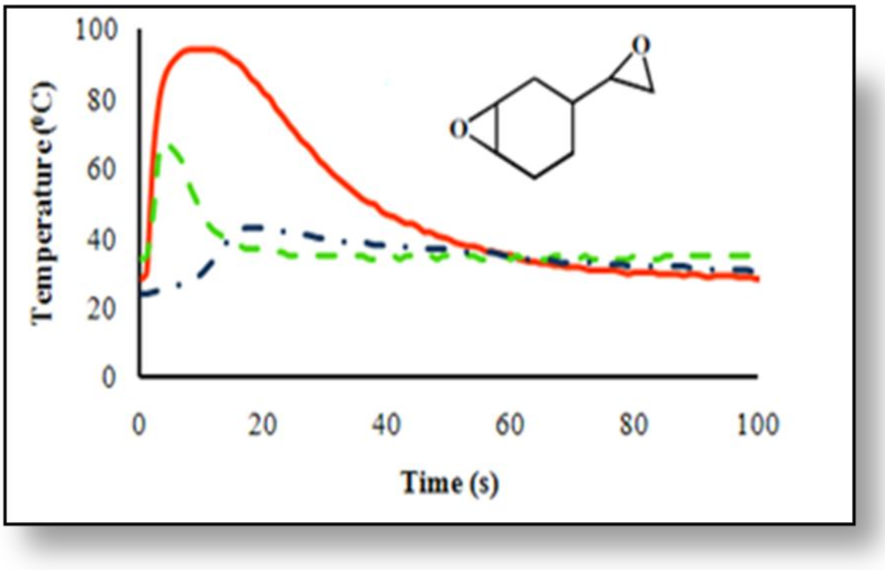


Figure 3.14 Optical pyrometry study of cationic polymerization of vinylcyclohexenediepoxide (VCHDE) in association with 1.0 mol% $Ph_2I^+PF_6^-$ in the absence of a photosensitizer (− · −), in the presence of 0.1 mol% PHED photosensitizer (—) and 0.1 mol% PHEHT photosensitizer (---). (Light intensity 15 mW cm^{-2})

Polymerization of VCHDE has started in the first seconds in the presence of DBQEd and TTQ whereas there was no polymerization without photosensitizers. Resulting polymers were hard, brittle and nonsticky.

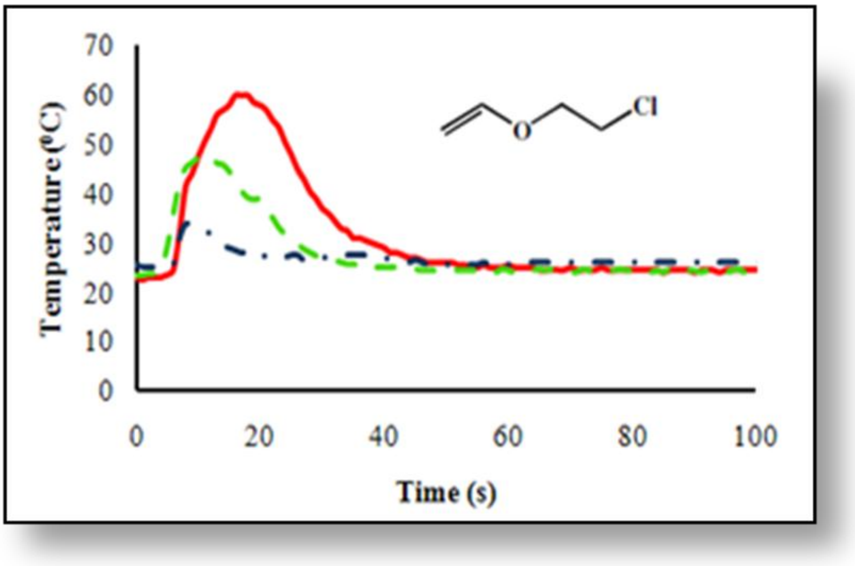


Figure 3.15 Optical pyrometry study of cationic polymerization of 2-chloroethylvinylether (CEVE) in association with 1.0 mol% $Ph_2I^+PF_6^-$ in the absence of a photosensitizer (− · −), in the presence of 0.1 mol% PHED photosensitizer (—) and 0.1 mol% PHEHT photosensitizer (---). (Light intensity 15 mW cm^{-2})

Polymerization of 2-chloroethylvinylether monomer started immediately in the presence of photosensitizers whereas there was no polymerization without the photosensitizers. Resulting polymers were nonsticky and brittle.

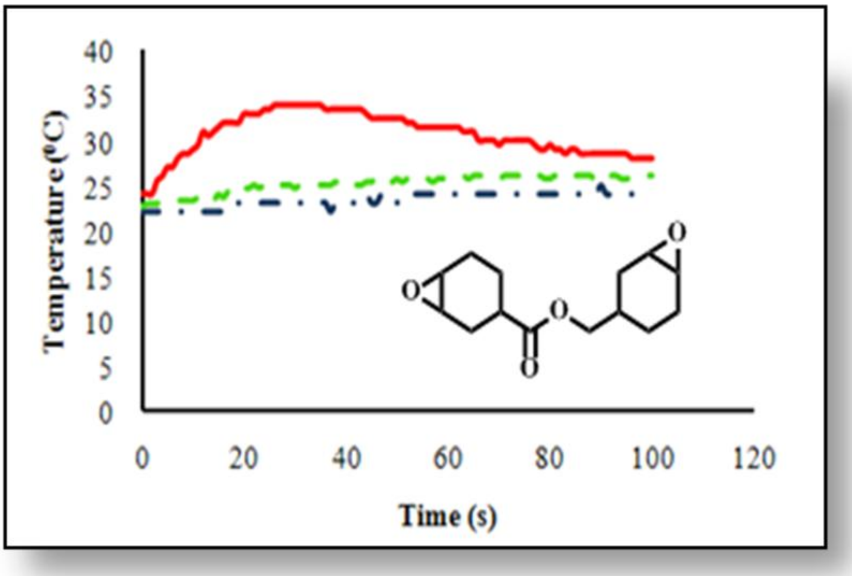


Figure 3.16 Optical pyrometry study of cationic polymerization of 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate (ERL-4221E), with 1.0 mol% $Ph_2I^+PF_6^-$ in the absence of a photosensitizer (− · −), in the presence of 0.1 mol% PHED photosensitizer (—) and 0.1 mol% PHEHT photosensitizer(---). (Light intensity 15 mW cm^{-2})

The polymerizations of CHO, VCHDE, and CEVE in the presence of photosensitizers showed similar behavior. The rapid polymerizations of aforementioned monomers were observed in the presence of photosensitizers whereas in their absence there was little or no polymerization. Compared to other monomers, polymerization was quite slow for ERL-4221E due to the low reactivity of this monomer. Polymerization with DBQEd was more efficient with respect to TTQ. As illustrated in Figures 3.9, 3.10, 3.11 and 3.12, faster polymerizations reaching high temperatures were observed, highlighting a more competent photosensitization system. The reason behind this is the lower oxidation potential of DBQEd, as discussed previously.

3.4 Photopolymerizations Under Solar Irradition

As depicted in Figures 3.13, 3.14, 3.15 and 3.16, all photosensitizers (PHED, PHEHT, DBQEd and TTQ) reveal considerable absorption in the visible region. Therefore, the behavior of the photosensitizers under solar irradiation was studied.

3.4.1 Photopolymerizations with PHED and PHEHT under Solar Irradition

Finally, the photosensitizers were examined under solar irradiation. A solution of ERL- 4221 containing 1.0 mol % $Ph_2I^+PF_6^-$and 0.1 mol% PHED was prepared and spread onto a glass slide. After 30 seconds of continuous irradiation, the pinkish red-colored solution spread on a glass slide surface (Figure 3.13 A) was transformed to a dark brown film (Figure 3.13 B).

(A) **(B)**

Figure 3.17 ERL4221E/ $Ph_2I^+PF_6^-$/PHED mixture (A) upon exposure to solar irradiation, (B) after 5 minutes of irradiation.

Similarly, 1.0 mol % $Ph_2I^+PF_6^-$ and 0.1 mol% PHEHT were dissolved in ERL-4221 affording the orange-colored solution (Figure 3.14 A) turned to a dark orange film (Figure 3.14 B). It took 5 minutes of continuous irradiation for the solutions to become fully cured.

Figure 3.18 sub-captions: (A) (B)

Figure 3.18 ERL4221E/ $Ph_2I^+PF_6^-$ /PHEHT mixture (A) before exposure to solar irradiation, (B) after 5 minutes of irradiation.

3.4.2 Photopolymerizations with DBQEd and TTQ Under Solar Irradition

Figure 3.2 illustrates that both DBQEd and TTQ have considerable absorption in the visible region. Therefore, photosensitizers were both tested for solar irradiation induced polymerization. Glass surface permeated with a solution of ERL-4221 containing 1.0 mol % $Ph_2I^+PF_6^-$ and 0.1 mol% DBQEd was exposed to direct solar irradiation. After 30 seconds the brown-yellow colored solution on a glass surface (Figure 3.15) turned to a dark green film.

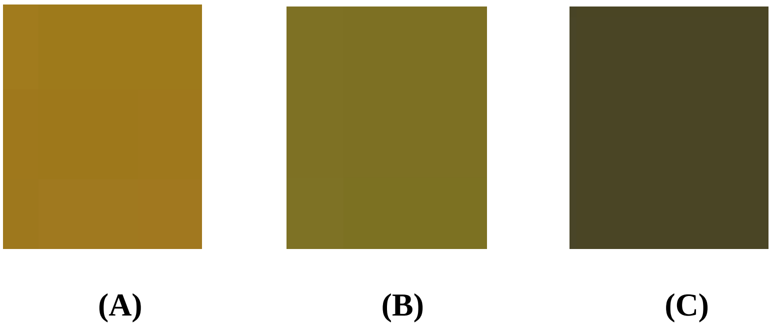


Figure 3.19 ERL4221E/ $Ph_2I^+PF_6^-$/DBQEd mixture (A) upon exposure to solar irradiation, (B) after 30 seconds of irradiation, and (C) after 2 minutes of irradiation.

Similarly 1.0 mol % $Ph_2I^+PF_6^-$ and 0.1 mol% TTQ dissolved in ERL-4221, the yellow-colored solution (Figure 3.16) turned to a dark yellow film. After 2 minutes of continuous irradiation, the solutions became fully cured.

(A) **(B)** **(C)**

Figure 3.20 ERL4221E/ $Ph_2I^+PF_6^-$/DBQEd mixture (A) upon exposure to solar irradiation, (B) after 30 seconds of irradiation, and (C) after 2 minutes of irradiation.

CHAPTER 4

CONCLUSION

Electron transfer photosensitization of diaryliodonium salts was carried out using four molecules, which have dibenzo[a,c]phenazine backbone with EDOT or 3-hexylthiophene pendant groups and novel quinoxaline derivatives with EDOT and thiophene pendant groups. The fully conjugated compounds effectively polymerized epoxide and vinyl ether monomers. Cationic polymerization of oxetane and vinyl ether monomers were successfully carried out under long wavelength UV light as well as solar irradiation. The polymerizations were followed by optical pyrometry. The photosensitizers revealed excellent polymerization under solar irradiation. The compounds possess significant absorption at long wavelengths due to extended conjugation, which make them useful for visible light applications.

A part of this study was published in the Journal of Polymer Science Part A: Polymer Chemistry, 49, 3299 (2011).

REFERENCES

1- M. U. Kahveci, A. G. Yilmaz, Y. Yagci, Photoinitiated Cationic Polymerization: Reactivity and Mechanistic Aspects, In *Photochemistry and Photophysics of Polymer Materials*, ed.; N. S. Allen, Ed.; John Wiley & Sons, Inc., New Jersey. 2010.

2- J. V. Crivello, Photo- and thermal catalysts for cationic polymerization In *Ring-Opening Polymerization*; ed.; D. J. Brunelle, Ed.; Hanser: Munich, 1993.

3- J.P. Fouassier, In *Photoinitiation, Photopolymerization and Photocuring: Fundamentals and Applications*; Ed.; Hanser Gardner Publications: Cincinnati, OH, 1995.

4- J.P. Fouassier, In *Photoinitiated Polymerisation: Theory and Applications*, Ed.; Rapra Technology Ltd.: Shawbury, 1998.

5- J.P. Fouassier, X. Allonas, D. Burget, *Progress in Organic Coatings* 2003, 47, 16–36.

6- Y. Yagcı, S. Jockusch, N. J. Turro, *Macromolecules* 2010, *43*, 6245–6260.

7- Y. Yagcı, M. K. Mishra, In *Handbook of Radical Vinyl Polymerization*. ed.; Marcel Dekker, Ed.; Inc., New York, 1998.

8- A. K. O’Brien, C. N. Bowman, *Macromolecules* 2006, 39, 2501–2506

9- C. Decker, *Makromol. Chem*. 1979, 180, 2027–2030

10- M. Biernat, G. Rokicki, *Polimery,* 2005, 50, 633–645

11- C. G.Roffey In *Photopolymerization of Surface Coatings*, Ed.;Wiley, New York. 1989.

12- R.S.Davidson, In *Exploring the Science, Technology and Applications of UV and E.B. Curing,* Ed.; SITA Technology Ltd. London 1998.

13- J. Narewska, R. Strzelczyk, R. Podsiadły, *J Photoch Photobio A: Chem.* 2010, 212, 68-74.

14- B. Aydogan, B. Gacal, A. Yildirim, N. Yonet, Y. Yuksel, Y. Yagci, Wavelength Tunability in Photoinitiated Cationic Polymerization, in Photochemistry and UV

Curing: New Trends. In *Photochemistry and Photobiology Research Signpost*, ed.;Fouassier, JP, Ed.; Trivandrum: E-Publishing Inc., 2006.

15- J.V. Crivello, U. Bulut, *J Polym Sci Part A: Polym Chem* 2005, 43, 5217–5231.

16- B. Aydogan, G. Gunbas, A. Durmus, L. Toppare, Y. Yagcı, *Macromolecules* 2010, 43, 101–106

17- U. Bulut, G. Gunbas, L. Toppare, *J Polym Sci Part A: Polym Chem* 2010, 48, 209–213.

18- R. Podsiad1y *Dyes Pigments* 2009; 80:86–92

19- B. Falk, S.M. Vallinas, J.V. Crivello, *J Polym Sci Part A: Polym Chem* 2003, 41:579-596.

20- J. V. Crivello, K. K. Dietliker, In *Photoinitiators for Free Radical Cationic and Anionic Photopolymerisation*, ed.; Bradley, G., Ed.; SITA Technology Ltd., London. 1998.

21- J. V. Crivello, *Chemtech* 1980, 10, 624–628.

22- J. V. Crivello, J.H.W. Lam, *J Polym Sci Part A: Polym Chem* 1996; 34, 3231–3253.

23- J. V. Crivello, J.H.W. Lam, *Macromolecules* 1977, 10(6), 1307-1315

24- J.P. Fouassier, D. Burget, J. V. Crivello, *J. Macromol. Sci. Pure Appl. Chem.* 1994, 31(6), 677-701.

25- J. V, Crivello, J. H. W. Lam, J. *Polm. Sci. C Polm. Symp.* 1976, (56) 383-395.

26- J. V. Crivello, In *UV Curing Science and Technology*; ed.; S. P. Pappas, Ed.; Technology Marketing: Stamford, CT, 1978.

27- J. V. Crivello, U. Bulut, *Macromol. Symp.* 2006, 240, 1–11.

28- Y. Y. Durmaz, N. Moszner, Y. Yagcı, *Macromolecules* 2008, 41, 6714-6718.

29- R. Podsiad1y, *Dyes and Pigments* 2009, 80, 86–92

30- J. V. Crivello, K. D. Jo, *J. Polym. Sci. Part A: Polym. Chem.*1993, 31, 2143–2152.

31- G. Manivannan, J.P. Fouassier, J. V. Crivello, *J. Polym. Sci. Part A: Polym. Chem.*1992, 30, 1999–2001.

32- ,J. V. Crivello, M. Jang, *J. Photochem. Photobiol.* 2003, 159, 173–188.

33- J. V. Crivello, J. H. W. Lam, *J. Polym. Sci., Polym. Chem. Ed.* 1979, 17, 1059–1065.

34- B. Aydogan, G. Gunbas, A. Durmus, T. Toppare, Y. Yagcı, *Macromolecules* 2010, 43, 101–106.

35- Y. Bi, D.C. Neckers, *Macromolecules* 1994, 27, 3683–3693.

36- Y. Yagci, Y. Hepuzer, *Macromolecules* 1999, 32, 6367–6370.

37- U. Bulut, G. Gunbas, L. Toppare, *J. Polym. Sci. Part A: Polym. Chem.*2010, 48, 209-213.

38- U. Bulut, A. Balan, C. Caliskan, *J. Polym. Sci. Part A: Polym. Chem.* 2011, 49, 729-733.

39- Z. Kucybala, A. Kosobucka, *Polym. Bull.* 2006, 56, 321-329.

40- S. Tarkuc, Y. Arslan Udum, L. Toppare, *J. Electroanal. Chem.* 2010, 643, 89–93.

41- S. Tarkuc, Y. Arslan Udum, L. Toppare, 2011 *Thin Solid Films* (submitted).

42- R. Podsiadly, A.M. Szymczak, K. Podemska, *Dyes Pigments* 2009, 82, 365–371.

43- Z. Kucybala, A. Kosobucka, J. Paczkowski, *J Photochem Photobio, A* 2000, 136, 227–234.

44- B. Przyjazna, Z. Kucybala, J. Paczkowski, *Polymer* 2004, 45, 2559–2566.

45- R. Podsiadły, K. Podemska, A. M. Szymczak , *Dyes and Pigments* 2011, 91, 422–426.

46- S. Tarkuc, Y. Arslan Udum, L. Toppare, *Polymer* 2009, 50, 3458–3464.

47- Y. Arslan Udum, E. Yıldız, G. Gunbas, L. Toppare. *J Polym Sci Part A: Polym Chem,* 2008, 46, 3723–3731.

48- B. Valeur, In *Molecular Fluorescence Principles and Applications,* Ed.; Wiley-VCH, Germany. 2002.

49- J. R. Lakowicz, In *Principles of Fluorescence Spectroscopy,* Ed.; Kluwer Academic/Plenum, New York. 1999.

50- K. K. Rohatgi-Mukherjee, In *Fundamentals of Photochemistry, Ed.;* New Age International, Calcutta. 1986.