SUBSTITUTED QUINOXALINE AND BENZIMIDAZOLE CONTAINING MONOMERS AS LONG WAVELENGTH PHOTOSENSITIZERS FOR DIARYLIODONIUM SALT INITIATORS IN PHOTOPOLYMERIZATION

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ABSTRACT

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In this study; ferrocenyl and naphthalenyl substituted quinoxaline derivatives; 5,8- bis (2,3- dihydrothieno [3,4-b] [1,4] dioxin-5-yl)-2- (naphthalen-2-yl)- 3- ferrocenyl-4a,8a-dihydroquinoxaline; 5,8- bis (2,3-dihydrothieno [3,4-b] [1,4]dioxin-5-yl) -2- (phenyl) -3-ferrocenylquinoxaline; 5,8-bis (2,3-dihydrothieno [3,4-b] [1,4]dioxin-5-yl) -2,3- di(naphthalen-2-yl)quinoxaline and trihexylthiophene and thiophene coupled benzimidazole derivatives; 4-(tert-butyl)-4,7-bis(4-hexylthiophen-2-yl)spiro[benzo[d]imidazole-2,1-cyclohexane] and 4-(tert-butyl)-4, 7-bis(thiophenyl)spiro[benzo[d]imidazole-2,1-cyclohexane] were used as photosensitizers to broaden the active area of diaryliodonium salts. Both quinoxaline and benzimidazole derivatives are expected to be efficient in cationic photopolymerization with a variety of vinyl and oxide monomers at room temperature upon long wavelength UV irradiation. Photopolymerization will be initiated by diphenyliodonium salts and monitored with Optical Pyrometry. Characterization will be completed with optical absorption, flourescence studies and photopolymerization under solar irradiation.

Keywords: Cationic polymerization, Diaryliodonium salts, Photopolymerization, Photosensitization, Photosensitizers, Quinoxaline, Benzimidazole

ÖZ

TÜREVLENDİRİLMİŞ KİNOKSALİN VE BENZİMİDAZOL MONOMERLERİNİN FOTODUYAR OLARAK DİFENİLİYODONYUM BAŞLATICILARI İLE FOTOPOLİMERİZASYONDA KULLANILMASI

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Ocak 2013, 62 sayfa

Bu çalışmada ferosenil ve naftalenil içeren kinoksalin türevleri ve triheksil tiyofen ve tiyofen ile kenetlendirilmiş benzimidazol monomerleri fotopolimerizasyon sırasında aktif spektral bölgeyi görünür bölgeye genişletmek amacıyla fotoduyar olarak kullanılmıştır. Kinoksalin ve benzimidazol türevlerinin verimliliğini kanıtlarken fotobaşlatıcı olarak difeniliyodonyum tuzları kullanılarak vinil ve oksit monomerlerle oda sıcaklığında UV ışınlarında fotopolimerleşme gerçekleştirilmiştir. Monitörleme Optik Pirometri yöntemi ile yapılmıştır, bunun yanı sıra moleküllerin soğurma özellikleri, floresan çalışmaları gercekleştirilmiş, güneş ışığında da fotopolimerleşmenin olabileceği kanıtlanmıştır.

Anahtar kelimeler: Katyonik polimerleşme, Diariliyodoniyum tuzları, Fotopolimerleşme, Fotoduyar moleküller, Kinoksalin, Benzimidazol

To Sevi Kiper &
In the memory of Cavide Çorakçı

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I would like to thank all my family members and friends, whose names are not mentioned here, but always been in my heart.

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BPADGE	2,2’-(((propane-2,2-diylbis(4,1-phenylene)) bis(oxy))bis(methylene))bis(oxirane)
CEVE	(2-chloroethoxy) ethane
CHO	7-oxabicyclo [4.1.0] heptane
COI	Coinitiator
DCM	Dichloromethane
DVE- 3	1, 2-bis (vinyloxy) ethane
EDOT	3,4-Ethylenedioxythiophene
LED	Light Emitting Diode
NMR	Nuclear Magnetic Resonance
P3HT	Poly(3-hexylthiophene)
$\mathbf{Ph_2^+ PF_6^-}$	Diphenyliodonium hexafluorophosphate
PI	Photoinitiator
PS	Photosensitizer
Th	Thiophene
VCHDO	3-(oxiran-2yl)-7-oxabicyclo [4.1.0] heptanes

CHAPTER 1

INTRODUCTION

Polymer science has progressed significantly. Today, polymers are in our everyday lives. Scientists continue to improve the technology and discover new polymerization processes. Initiation of polymerization is an important step for industrial applications. There are a variety of initiation methods such as thermal, photochemical, and redox processes. [1] Photochemical initiation has become popular in the last decade. Radicals, cations and anions can be produced by UV or visible irradiation of a pure monomer or of a monomer which contains a catalyst or a photosensitizer. [2]

1.1 Photo – Induced Polymerization

Photoinduced polymerization of multifunctional monomers gives the formation of crosslinked polymers. [3], [4] Generally, UV radiation is used for polymeric initiation. Under intense radiation, initiation leads to very high polymerization rates and phase change occurs rapidly from liquid to solid state. [4] High rates and the exothermic effect may bring some irregularity in the resulting polymer. These deformities may direct to alternation of physical properties. [3] As result, over the last 30 years photoinitiated polymerization is widely used in industrial applications. [5] More traditionally photopolymerization technique is used in coatings, printing inks, adhesives, and microelectronics. [6–8] There are also some other modern applications of photopolymerization, such as curing of dental fillings [9] and polymeric photo optical control materials. [5]

Photoinitiated polymerization is a chain reaction. It is initiated by irradiation of a pure monomer. There are different types of this chain process. Initiated species and polymeric chain ends can be radicals, [10] cations [11] or anions, weak bases. [12]

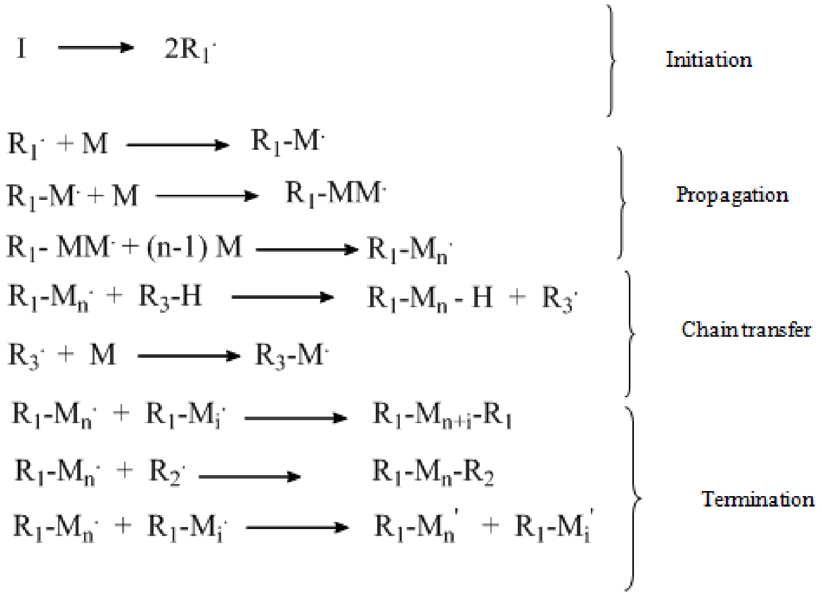
Photoinduced polymerization proves to be more advantageous compared to other polymerization techniques. It is a rapid and energy efficient process, which can be conducted at room temperature with low costs.[13] Besides, photoinitiated polymerizations provide micro- and macro- spatial control over a broad range of domain spaces. [14] Photoinitiated polymerization can proceed at low temperature, so monomers with low ceiling temperature can be utilized, and the rate of depolymerization would not exceed that of polymerization. Moreover, when polymerization reactions progress at low temperature, side reactions like chain transfer are minimized. As a result, syndiotactic configuration can be obtained by photopolymerization. Last of all, photopolymerization can be applied to larger surfaces easily, whereas this is not the case for thermal polymerization.

1.1.1 Free – Radical Photopolymerization

1.1.1.1 General Information about Free Radical Polymerization

Free radical polymerization is a preferred way to synthesize commercial polymers. It is used for the production of more than 50 % of all plastics in the world. There are various different methods for vinyl polymer syntheses through radical polymerization. [15], [16] Polymerization reactions with free radical polymerizable monomers take place under fairly simple conditions, which require absence of oxygen. Humidity does not terminate free radical polymerizations. Polymerization is carried out within a convenient temperature range, between 0 - 100˚C. [15]

The mechanism of free radical polymerization, suggested by Taylor and Bates [16], is described below. (Scheme 1.1) Free radical polymerization proceeds through initiation, growth, termination and transfer steps.



Scheme 1.1: The General Mechanism of Free – Radical Polymerization

Generation of free radicals is the major step in initiation of free radical polymerization. Carbon – carbon double bond has low stability particularly susceptible to attack by a free radical. As a result of this attack, radical adds to a double bond of the vinyl type monomer resulting in the generation of new radical. [17] After active center was obtained by initiation, generated radical attacks to the monomer and increases the number of repeating units on the polymer chain. [2] As the last step in free radical polymerization either chain transfer or termination step take place. Transfer step is the name of process when the termination of a polymer chain leads to the initiation of a new polymer chain. [15]

Free radical polymerization has various advantages. First of all, it is easy to perform for a numerous types of monomers under mild conditions using convenient equipment. Side reactions are limited and some initiator molecules are left unreacted. Free radical polymerization reactions are often reproducible. One drawback of free radical polymerization is the lack of control over termination and transfer reactions. Propagation step involves short – lived intermediates. This directly affects the precise control of molar mass and leads to a broad polydispersity. Oligomer concentration in this type of polymerization is quite high. Free radical polymerization can be considered as diffusion controlled but fast termination reaction makes diffusion hard to control even for small radicals. [15]

1.1.1.2 Photoinitiation of Free Radical Polymerization

Photoinitiation of free radical polymerization starts with generation of initiating species. The difference of this type of free radical polymerization is the role of light. Light absorption is involved in the very first step of the reaction. As seen in the mechanism below (Scheme 1.2), photosensitive compound absorbs light (photoinitiator) and transfers its energy to another compound. That compound shifts to its excited state with the energy obtained from light absorbing sensitizer. This energy transfer leads to homolytic breakage of the chemical bond and generation of radical. After radicals are generated, the reaction between those radicals and monomer, namely propagation, termination and transfer are thermal processes, and they are not affected by light. [18]

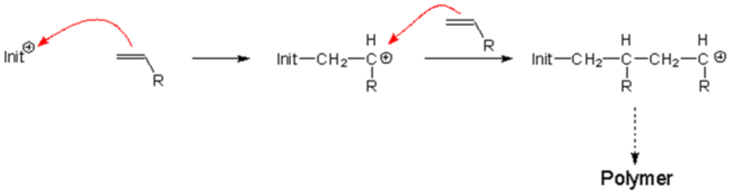
$$\left.\begin{array}{l} PI \longrightarrow PI^* \\ PI^* \longrightarrow R_1^{\cdot} + R_2^{\cdot} \\ R_1^{\cdot} + M \longrightarrow R_1\text{-}M^{\cdot} \end{array}\right\} \quad \text{Photoinitiation}$$

Scheme 1.2: Photoreactions in Free Radical Photopolymerization

1.1.2 Cationic Photopolymerization

1.1.2.1 Basic Information About Cationic Polymerization

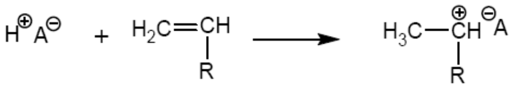
Cationic polymerization can be defined as a reaction initiated by a carbocation in the propagation step derived from a monomer and an initiator. For cationic initiation strong electron acceptors are needed as initiators. In the literature, aprotonic acids (Lewis acid or Friedel-Crafts halides), protonic acids (Brønsted acid) or stable carbenium ion salts are used for this purpose. Cationic active species are formed in the initiation step, reaction starts when a cation interacts with the first monomer, forming a carbenium ion on the monomer and nucleophilic attack is observed for the propagation. Carbenium ion is the chain carrier in this reaction. At the propagation step, reformation of carbenium ion occurs as long as the nucleophilic attacks continue to monomer. Polymer chain grows in a "head to tail" configuration. [17] The mechanism of cationic polymerization can be seen at Scheme 1.3:



Scheme 1.3: General mechanism of cationic polymerization

As mentioned before, cationic polymerization reactions can be initiated by means of Brønsted acids, Lewis acids or some other catalysts and methods for the formation of carbenium ion. [2] Initiation via protonic (Brønsted) acids and aprotonic (Lewis) acids will be focused in this section.

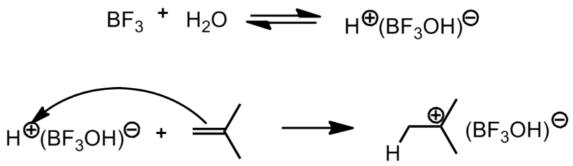
In the initiation via Brønsted acids, hydrogen abstraction is the main step. (Scheme 1.4) After the monomer is protonated, cationic polymerization commences. Acid should be strong enough to produce reasonable concentration of cationic active species. Meanwhile, the anion of the acid should be non-nucleophilic so that termination by combination does not occur at an unexpected stage. [19]Cationic photopolymerization might be terminated by chain transfer reaction and a proton for initiating a new chain will be generated.[20]



$$H^{\oplus}A^{\ominus} + H_2C{=}\underset{R}{CH} \longrightarrow H_3C{-}\underset{R}{\overset{\oplus}{CH}}\;{}^{\ominus}A$$

Scheme 1.4: Initiation of cationic polymerization via Brønsted acid

Initiation by Lewis acid is another method for cationic polymerization. (Scheme 1.5) Lewis acid initiators are often used to obtain high molecular weight polymers at low temperatures. Friedel – Crafts catalysts, like $AlCl_3$, [25, 26] BF_3, [23] and $SnCl_4$ [28, 29] are widely used for this purpose, however, Lewis acids require cocatalysts that act as a proton donor. Water, an organic acid or an organic hydrocarbon can be used as a co – catalyst in this case. [2] Lewis acid catalysts have some drawbacks. It is hard to handle Lewis acids due to their corrosive nature and the difficulty of separating the catalyst from product at the end of the reaction. [26]



Scheme 1.5: Initiation of cationic polymerization via Lewis acid

1.1.2.2 Photoinitiation of Cationic Polymerizations

Free radical photopolymerization is preferred over cationic polymerization in industry, therefore, scientists focused on free radical polymerization more. However, epoxy monomers and some vinyl monomers cannot be polymerized by free radical polymerization. Thus, research on photoinitiated cationic polymerization has increased in the recent years. The discovery of onium salts is particularly significant for this trend.

The initiation step is the only step that is dependent on light, and once the active centers are produced, they propagate without any further interaction with light. The reaction mechanism of photoinitiation depends on the structure of photoinitiator being used. There are two main types of initiator systems. Certain type of initiators starts the reaction immediately whereas some other types of initiators are dormant species. This type is called as externally stimulated initiators. This is a very useful property for cationic polymerization because crosslinking or polymerization can take place at the desired time with a specific rate. Externally stimulated initiators are generated via heat or light. [11] Some initiators used in cationic photopolymerization are examples to these dormant species, thus, activated upon irradiation. This means, the starting time of the reaction is easy to control. Non-nucleophilic counter anion prevents the termination of a growing polymer chain. [19] Classical cationic initiators have some disadvantages. First of all, initiator concentration is not constant throughout the reaction, since initiator is added in either solid form or as a concentrated solution. It initiates the reaction instantaneously. Therefore, initiator concentration decreases as reaction proceeds. Secondly, reaction is very exothermic and starts immediately. Thus, starting temperature should be comparatively low. [11]

1.1.3 Comparison Of Free Radical Photopolymerization And Cationic Photopolymerization

1.1.3.1 Comparison of Ionic and Free – Radical Polymerization

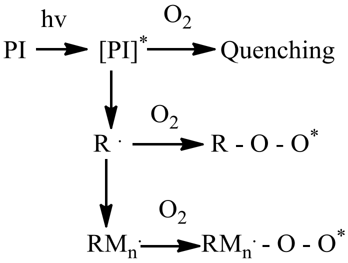
Polymerization types can be mainly classified as ionic (cationic, anionic) and free radical polymerization. Some types of photopolymerization have been discussed in the previous sections in detail. Ionic polymerization has several advantages over free radical polymerization.

Ionic polymerizations can proceed at lower temperatures with good efficiency. Their activation energies are lower than those of free radical polymerizations. In addition, chain termination in free radical polymerization happens only with joint annihilation of two polymeric radicals, which will not be the case in ionic polymerization. One important concept for ionic polymerization is the effect of solvent on reaction mechanism. Solvent assists electric charge separation in ionic polymerization whereas free radical polymerization mechanism is unaffected. In ionic polymerization, dissociation constant of solvent plays a significant role, as solvents with high dissociation constants carry polymerization on free ions, where solvents with low dissociation constants propagate either through free ions or ion pairs. Kinetics of ionic polymerization depends on solvent type, because solvent species are also involved in the mechanism. [27]

1.1.3.2 Comparison of Cationic Photopolymerization and Free Radical Polymerization

Even though free radical polymerization is generally used in industrial applications, cationic photopolymerization has several superior properties over free radical polymerization.

Free radical photopolymerization is limited to olefinic monomers. Monomers in the group of vinyl ethers and epoxides cannot be polymerized via free radical photopolymerization, but can easily be polymerized through cationic photopolymerization with good rheological properties. [5] In addition, cationic photopolymerization does not require use of solvent [28] which satisfies one of the 12 principle of green chemistry. [29] Cationic photopolymerization is not inhibited by oxygen, thus, does not require special conditions for curing.(Scheme 1.6) [30]



Scheme 1.6: Inhibition of Photoinitiated Polymerization Reaction by Oxygen

In the absence of moisture, thick films can be produced. Termination rate of cationic photopolymerization is very low in dry environment. [31] Cationically polymerizable monomers are not volatile and do not have high toxicity or irritation power. [13]

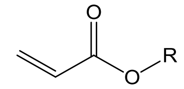
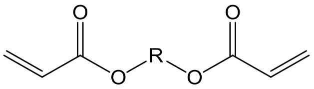
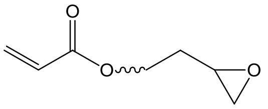
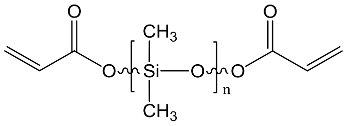
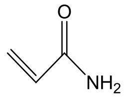
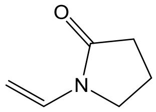
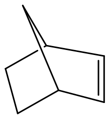
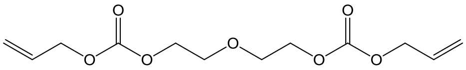
Another advantage of cationic polymerization is the dark cure or post – polymerization. As discussed, chain transfer in free radical polymerization is more possible than it is in cationic polymerization. In cationic polymerization, if this is a photoinduced one, counter ion of photoinitiator can also combine with the propagating chain and terminate the reaction. However, this probability is very unlikely to happen. For this reason, cationic photopolymerization can be considered as a non – terminating process. [4], [20], [32] As a consequence, reaction continues for an extremely long time even after irradiation has stopped. Almost all of the monomer has been polymerized and this is called as dark cure or post – polymerization. [32] Lastly, volume shrinkage is an issue for free radical photopolymerization that can be minimized with ring opening process in cationic photopolymerization. When the list of advantages is considered for cationic photopolymerization, it is realized that it can be integrated in industry more.

1.2 Monomers

1.2.2 Monomers for Free – Radical Photopolymerization

Free radical polymerization has a specific monomer range. Carbon – carbon double bond containing monomers are used widely. Free radical polymerization proceeds through the free radical active center. Opening of carbon-carbon double bond forms the active center and polymer chain grows by its addition to monomers. Most unsaturated monomers are employed for radical photopolymerization because propagating species, free radicals, are neutral and do not require electron–donating or electron–withdrawing substituents to delocalize charge on polymer chain. The reactivity of monomers is important for commercial applications. Acrylate and methacrylate monomers are the most commonly used monomers. More examples can be found in Table 1.1. Mentioned monomers have very high reaction rates. Therefore, acrylates are particularly amenable to high speed processes into films and coatings. [20] Multiacrylates have good mechanical strength and solvent resistance since they form crosslinked polymers; where prepolymer mixture of monoacrylates can be processed easier due to reduction in viscosity. [20], [33] Shrinkage is a well-known problem in acrylate polymerization. Covalent bonding between monomers leads to this problem. If Van der Waals forces were formed between compounds then the distance would be halved and problem would be solved. One solution for this is oligomer formation, which is not a good approach for industrial production.

Table 1.1: Structures of Free Radical Polymerizable Monomers

Monomers	**Structure**
Alkyl acrylates	
Alkoxy diacrylates	
Epoxy acrylates	
Silicone acrylates	
Acyl amides	
N-vinylpyrrolidinone	
Norborane	
Diallyldiglycolcarbonte	

1.2.3 Monomers for Cationic Photopolymerization

Photoinitiated cationic polymerization solved polymerization problem of complex structured monomers. Vinyl, alkoxy vinyl and heterocyclic (bearing sulphur, oxygen or nitrogen atom in their rings) monomers can easily be polymerized via cationic photopolymerization; because electron donating groups are needed for cationic polymerization to proceed. Sulphur, oxygen and nitrogen increases the electron density on the double bond as a result of inductive effect. Some examples can be seen in Figure 1.1. [34]

Even though cationic photopolymerization is applicable for a broader variety of monomers, it is not preferred in industry. As scientist started to investigate more on this topic, new monomer designs with high polymerization rates and improved characteristics have been discovered and demand for cationic photopolymerization has become higher. Difunctional epoxide and vinyl ether monomers are employed in UV curing applications.

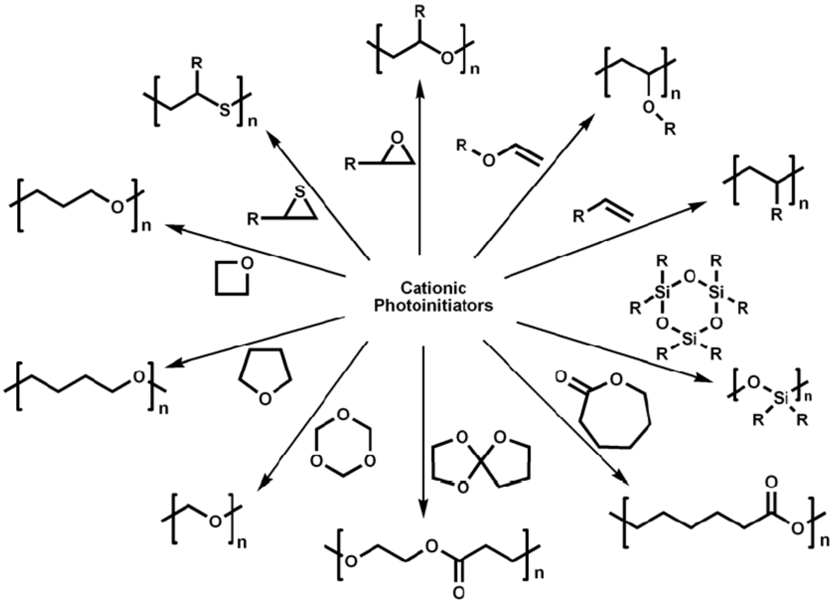
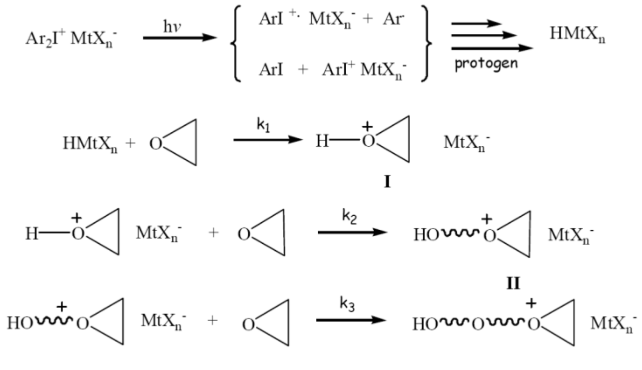


Figure 1.1: Structures of Cationic Polymerizable Monomers

1.2.3.1 Polymerization of Epoxides

Polymerization of epoxides has been studied by various research groups. Crivello and co-workers pioneered cationic polymerization of epoxides by using onium salts. [35] In chain growth polymerization of epoxides, cation or anion formation occurs after initiation step. Once active sides are generated, polymerization continues by addition of monomers. Polymer structure is controlled by the following parameters: functionality of monomers, molar ratio between initiator and monomer, temperature, and the concentration of species in chain transfer step. These influence relative rates of different steps. [36]



Scheme 1.7: Mechanism of Cationic Polymerization of Epoxide Monomers

As a result, it is seen that epoxide polymerizations do not suffer from volume shrinkage problem and attribute exceptional adhesion to many different types of substrates. Cross-linked polymer is observed with cationic polymerization of epoxides. The oxidative and thermal resistivity of those polymers is noticeably better than the ones with free radical polymerization of acrylate monomers. Good mechanical and electrical properties of epoxides are mentioned above. In this study, three different epoxides monomers are used. (Figure 1.2) [37]

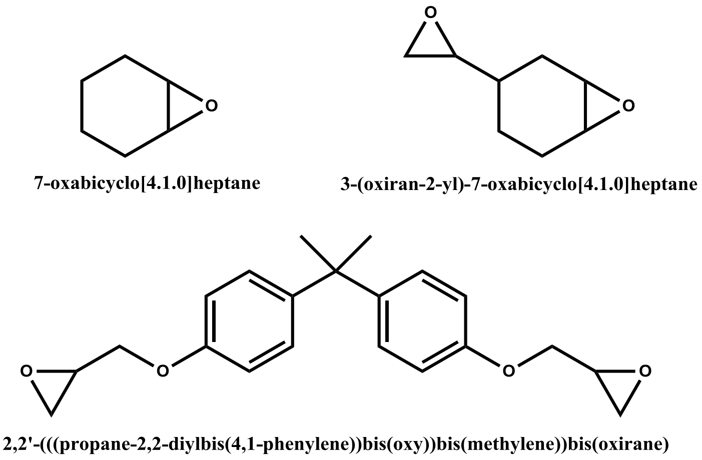
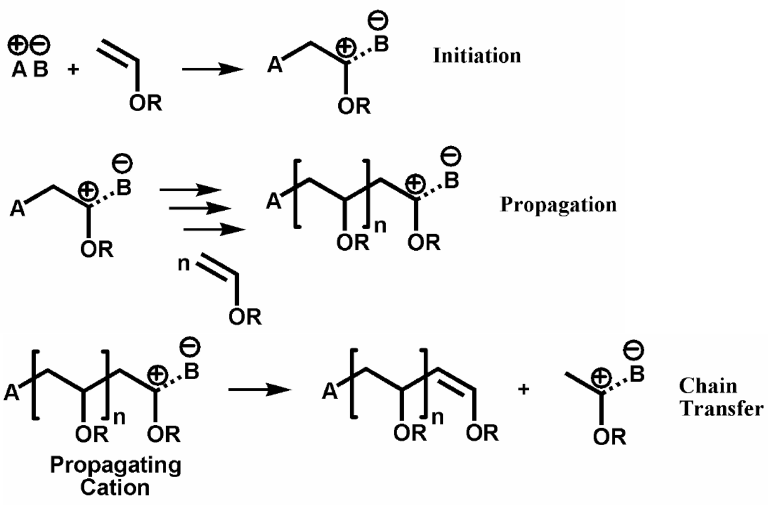


Figure 1.2: Structures of Epoxide Monomers Used in This Study

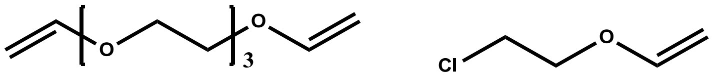
1.2.3.2 Polymerization of Vinyl Ethers

Vinyl ethers have very high reactivity towards cationic polymerization in the presence of protonic acids. This is one of reasons for vinyl ethers to be popular in industrial polymerization. [30], [38], [39] Significant variety of polymers and copolymers can be achieved using vinyl ether monomers because of strong electron donating oxygen present in air. [40]



Scheme 1.8: Mechanism of Cationic Polymerization of Vinyl Ethers

When vinyl ether polymerization is initiated, the reaction goes fast and extensive. Reactivity of vinyl ether monomer depends on the nature of side chain R group. If alkyl substituent is branched or electron–donating, then polymerization rate is very fast. On the other hand, aromatic vinyl ethers are not as reactive as alkyl ones due to possible side reactions. [40]
The photopolymerization of monomers below are the part of this study. (Figure 1.3)



1,2-bis(vinyloxy)ethane **(2-chloroethoxy)ethene**

Figure 1.3: Structures of Vinyl Ether Monomers Used in This Study

1.3 Photoinitiator

Initiation in photoinduced polymerizations occurs via photoinitiators. Photoinitiator is a molecule that absorbs light induced energy and launches polymerization. (Scheme 1.9) As system is exposed to light, concentration of photoinitiator decreases. This process can take place either directly or indirectly. If photoinitiation mechanism proceeds with absorption of light by photoinitiator molecule, this is called as direct photoinitiation.

$$\mathrm{PI} \longrightarrow \mathrm{H}^{+} + \mathrm{R}^{\cdot +} + \text{Other Products}$$

$$\mathrm{R}^{\cdot +} + \mathrm{M} \longrightarrow \text{Polymer}$$

$$\mathrm{H}^{+} + \mathrm{M} \longrightarrow \text{Polymer}$$

Scheme 1.9: General scheme for direct photolysis

Mostly, some other molecules are involved in photoinitiation and those molecules undergo a series of complex reactions to form initiating species. These molecules can be photosensitizers, free radicals, activators, or coinitiators. (Scheme 1.10) [41] Photosensitizers will be discussed in detail in next chapter.

$$\mathrm{S} \longrightarrow \mathrm{S}^{*}$$

$$\mathrm{S}^{*} + \mathrm{I} \longrightarrow \mathrm{S} + \mathrm{I}^{*}$$

Scheme 1.10: General scheme for indirect photolysis

Ideal photoinitiation systems should have high molar absorption coefficient in the absorption range under study, because as stated in the first law of photochemistry, only absorbed light by a molecule is successful to create a photochemical change. [42] Besides, photoinitiators should have high quantum yield, since one other role of photoinitiators in reaction is the control of reaction rate. Moreover, to reach high initiation rates, their singlet and triplet excited states should have short lifetimes to avoid self-quenching. (Figure 1.4) [43]

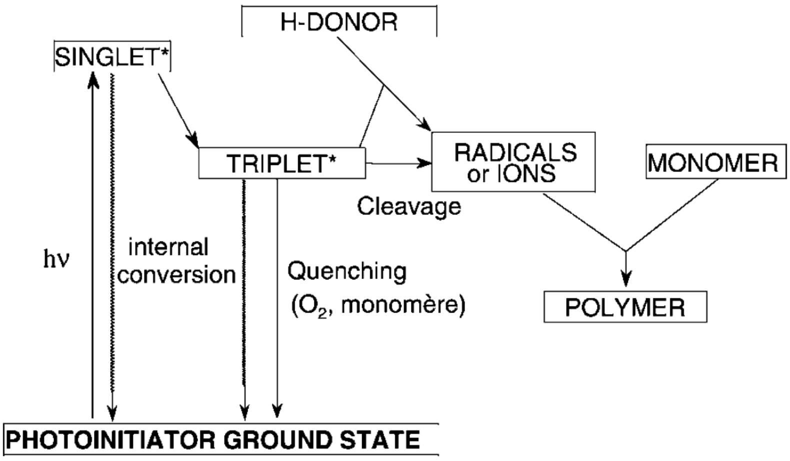
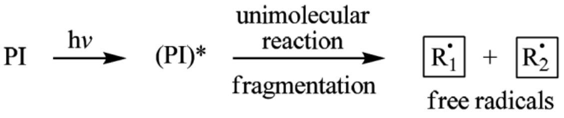


Figure 1.4: Various deactivation pathways for the excited photoinitiator (39)

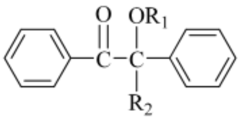
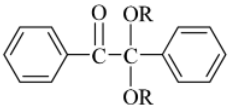
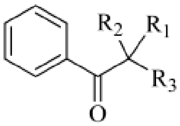
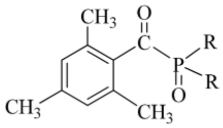
Free radical photoinitiators generate free radicals when they absorb light and those free radicals work as propagating group in the polymerization. Free radical photoinitiators have two main classes:

a. **Cleavage (Type I) initiators:** Aromatic carbonyl compounds with suitable substitution are classified as type I photoinitiators. They undergo α–cleavage reaction. They have high quantum efficiencies, but they exhibit thermal instability. That’s why they are not preferred in most applications. Benzoin and its derivatives, such as benzyl ketals, acetophenones, and amino alkyl phenones can be given as example. (Table 1.2) [5], [44], [45]

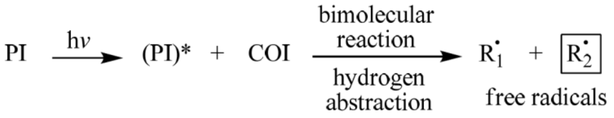


Scheme 1.11: Mechanism of Direct Photoinitiation of Free – Radical Polymerization

Table 1.2: Structures of Type I Photoinitiators

Photoinitiators	Structure	λ_{max} (nm)
Benzoin ethers		323
Benzil ketals		365
Acetophenones		340
Acylphosphineoxides		380

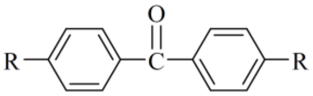
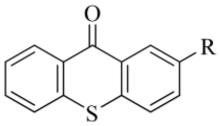
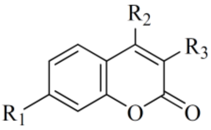
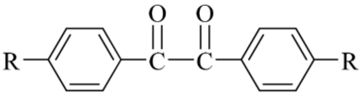
b. **H–Abstraction (Type II) initiators:** Aromatic ketones, such as benzophenone, thioxanthones, benzyl and quinones can be named as type II photoinitiators. (Table 1.3) The initiation mechanism is bimolecular which is the reason of slow curing of type II initiators when compared with type I initiators. [5] In bimolecular initiation, H- abstraction competes with other side reactions. In order to eliminate this problem, coinitiator systems can be used. (Scheme 1.12) [46]



$$PI \xrightarrow{h\nu} (PI)^* + COI \xrightarrow[\text{hydrogen abstraction}]{\text{bimolecular reaction}} \underbrace{R_1^\bullet + \boxed{R_2^\bullet}}_{\text{free radicals}}$$

Scheme 1.12: Mechanism of Indirect Photoinitiation of Free Radical Polymerization

Table 1.3: Structures of Type II Photoinitiators

Photoinitiators	Structure	λ_{max} (nm)
Benzophenones		335
Thioxanthones		390
Coumarins		370
Benzils		340

1.3.1 Cationic Photoinitiators

Cationic photoinitiators lead the polymerization through a cation. Classical initiators are separated into one initiating cation and a counter anion. In externally stimulated initiators, cation is released when stimulation is applied. For this reason, initiation time and rate can be specified. [11] Well known examples for cationic initiators are as follows:

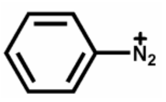
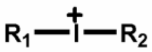
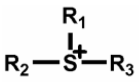
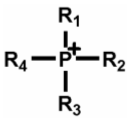
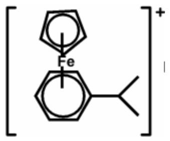
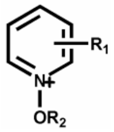
- Onium salts (aryldiiodonium salts, diazodoium salts, trisulfonium salts…)
- Thiopyrylium salts
- Sulfonic esters of hydroxyketones
- Perhalogenides
- Metallocenes
- Prototropic nitro compounds

The most effective and extensively used cationic photoinitiators are onium salts, particularly diaryliodonium salts and triarylsulfonium salts.

1.3.1.1 Onium Salts:

Onium salts are the most well-known photoinitiators used in the research of photoinduced polymerization. A Brønsted acid is formed after irradiation of onium salts. These salts can yield two types of initiation, direct or indirect initiation. In direct initiating system, onium salts absorb the energy and are decomposed to initiating species. Energy is absorbed by an additional compound in indirect initiating systems. Excited additional compound might react with onium salt or transfer its energy to onium salt for polymerization to be carried out. [6], [8], [47]–[50] Some examples of onium salts are given on Table 1.4. The nature of an onium salt influences polymerization mechanism. Cationic part decides how photochemistry will progress and anionic part determines how polymer chemistry will proceed. Cationic part affects molar absorbance coefficient, as well as λ_{max}, quantum yield, and thermal stability. Photosensitization properties are also established by cationic part of the salt. Anionic part plays role on acidic strength, initiation, and propagation rates of polymerization and the nucleophilicity of the ions formed. As mentioned before, non–nucleophilic ion species are desired to prevent fast combination with positively charged species and retardation or complete suppression of polymerization reaction. [51] Commercialization of onium salts progresses due to their several advantages in applications. For instance, solvent-free formulas eliminate air or water pollution as well as the initial costs related to their use and recovery. In addition, these polymerizations have high production yields and energy efficiencies compared to thermal processes. [52]

Table 1.4: Structures of Common Onium Salts

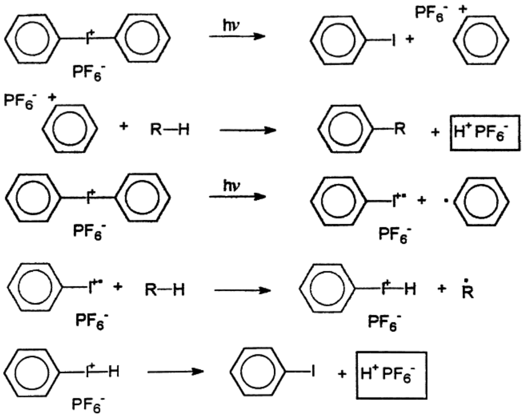
Photoinitiators	Structure of the cationic part	Structure of the anionic part
Aryldiazonium Salts		BF_4^-
Iodonium Salts		
Sulphonium Salts		PF_6^-
Phosphonium Salts		SbF_6^-
Ferrocenium Salts		AsF_6^-
N – alkoxy pyridinium Salts		

1.3.1.1.1 Diaryliodonium Salts:

General structure of diaryliodonium salts are shown in Table 1.4. If R_1 is equal to R_2, then salt is referred as symmetrical; if R_1 is not equal to R_2 that means salt is asymmetrical. In this study, diphenyliodonium hexafluorophosphate salt, $Ph_2I^+PF^-_6$, is preferred, since no chemoselectivity problems arise in symmetric diaryliodonium salts. [53]

Iodine has an extraordinary hypervalent structure, which imparts good stability to diaryliodonium salts. Chloronium and bromonium analogs of iodonium salts were synthesized; however, they were thermally unstable and had a difficult synthetic route. [51] Quantum efficiencies of diaryliodonium salts vary from 0.7 – 0.9. Aromatic rings are responsible for absorption range in UV–Vis region. Diaryliodonium salts absorbs between 230 – 300 nm in general. (Scheme 1.13) [51]

The reaction mechanism of diaryliodonium salts has been investigating by some research groups. [51], [54], [55]



Scheme 1.13: The Mechanism of Photochemical Reaction of Onium Salts

Mechanism of diaryliodonium salts is quite complicated. Both homolytic and heterolytic cleavages occur. Three different species are formed; cationic, cation-radical, and free-radical parts are present after photo-excitation of the diaryliodonium salt. All these fragments are highly reactive and instantaneously react with solvent molecules, monomers, or impurities and yield Brønsted acids. Protonic acid ions are primarily initiators for cationic polymerization.

1.4 Photosensitizers

A photosensitizer can be described as a molecule which facilitates the excitation of secondary molecule, in this case photoinitiator, by absorbing and transferring energy upon irradiation. [41] Photosensitizers enhance the absorptivity of photoinitiator salts by absorbing light energy on their behalf. Improvement in spectral activity increases the rates of photoinitiated cationic polymerization of epoxides and vinyl ethers in the presence of onium salts as initiators.

The spectral distribution of mercury vapor lamp can also be seen in Figure 1.5. The absorption range of iodonium salts does not cover the spectral region used in industry. Visible region is also missing in iodonium salts spectral sensitivity area. In the future, polymerization in visible region might gain importance in industry. For this reason, photosensitizer concept is introduced to enlarge absorption region of photoinitiator salts.

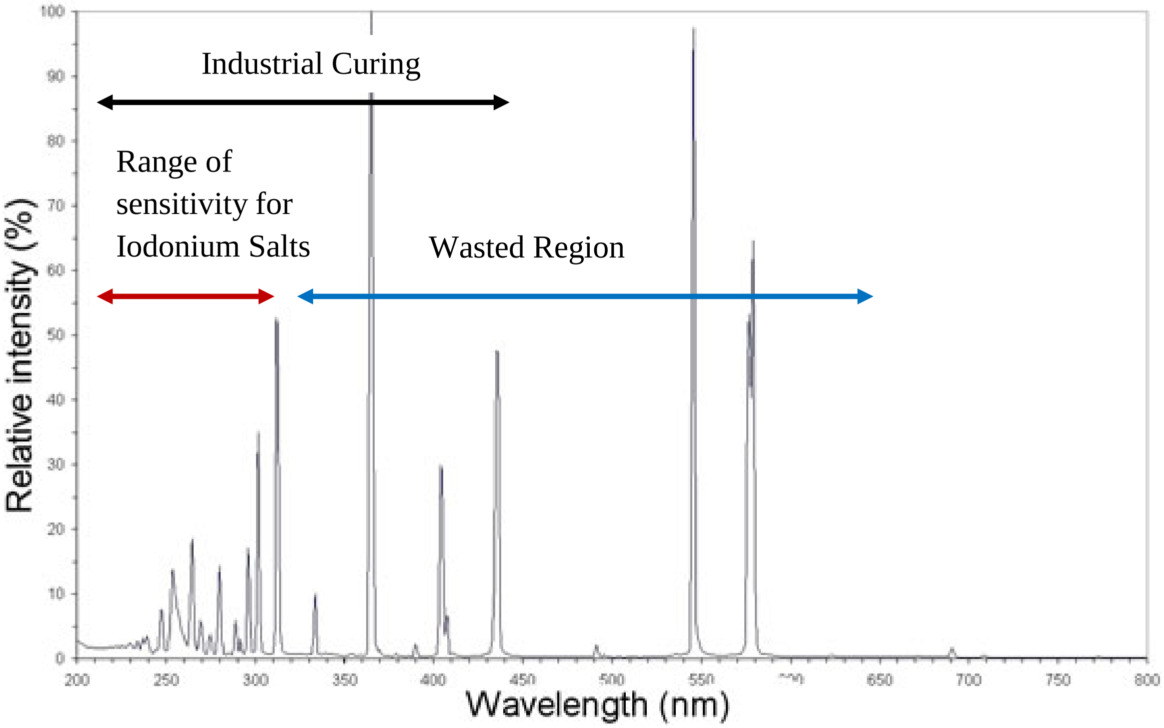
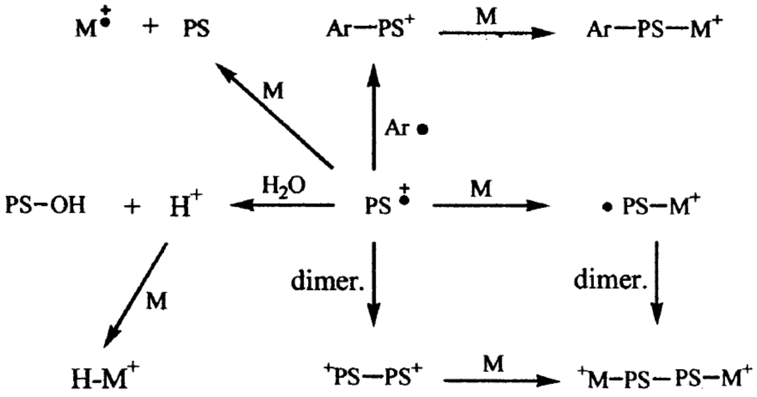


Figure 1.5: Spectral distributions of Hg lamps

When photosensitizer is added in to the monomer system, there are many different ways that polymerization can proceed through. These are shown in Scheme 1.14. [56]



Scheme 1.14: Possible ways of photosensitization

According to suggested mechanism in the literature, photoinitiator salt and photosensitizer forms an exciplex. The mechanism of photosensitization of cationic polymerization can be seen at Scheme 1.15. This process is named as oligomeric and polymeric electron transfer. [35]

$$\mathrm{PS} \xrightarrow{h\nu} [\mathrm{PS}]^{*} \qquad \textbf{eq. 1}$$

$$[\mathrm{PS}]^{*} + \mathrm{Ar_2I^{+}\ MtX_n^{-}} \longrightarrow \underset{\text{exciplex}}{[\mathrm{PS}\cdots\mathrm{Ar_2I^{+}\ MtX_n^{-}}]^{*}} \qquad \textbf{eq. 2}$$

$$[\mathrm{PS}\cdots\mathrm{Ar_2I^{+}\ MtX_n^{-}}]^{*} \longrightarrow [\mathrm{PS}]^{+\bullet}\ \mathrm{MtX_n^{-}} + \mathrm{Ar_2I}^{\bullet} \qquad \textbf{eq. 3}$$

$$\mathrm{Ar_2I}^{\bullet} \longrightarrow \mathrm{ArI} + \mathrm{Ar}^{\bullet} \qquad \textbf{eq. 4}$$

$$[\mathrm{PS}]^{+\bullet}\ \mathrm{MtX_n^{-}} \rightrightarrows \mathrm{HMtX_n} \qquad \textbf{eq. 5}$$

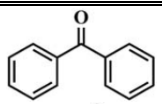
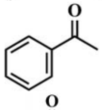
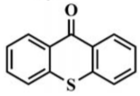
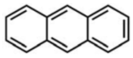
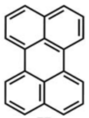
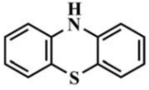
Scheme 1.15: Photosensitization Mechanism of Cationic Polymerization

According to the mechanism, photosensitizer is excited as it absorbs light. (Eq 1) After this step, the excited photosensitizer molecule may form an exciplex (excited-state complex) with the photoinitiator salt. (Eq 2) Exciplex formation has been suggested by Rodrigues and Neumann. [57], [58] This exciplex is very unstable, therefore electron transfer occurs between initiator salt and sensitizer molecule. Photoinitiator salt is reduced in this step. (Eq 3) Meanwhile, unstable free radicals are formed from the rapid decomposition. Their formation avoids back electron–transfer and makes overall process irreversible. (Eq 4) In the end Brønsted acid ($HMtX_n$) is formed to initiate polymerization. (Eq 5)

Most of the onium salts have narrow absorption bands around short wavelength region; an important part of emitted light is wasted. Photosensitizers possess a broader spectral sensitivity; they capture higher portion of the spectral distribution of light source. When outcomes are compared with only photoinitiator, monomer containing experiments, photolytic process is more efficient due to the increase in the number of initiating species formed. When number of active species is increased, rate of polymerization accelerates accordingly. [59] This increases productivity and lower concentration of photoinitiator is needed. By decreasing the concentration of photoinitiator, cost of process is also reduced. Photosensitizers are also capable of polymerizations carried out under sunlight, which is a promising advantage for future applications. [56]

Polynuclear aromatic compounds have been popular in photosensitization studies. (Table 1.6) Anthracene, [56] pyrene [60] and perylene [61] gave good results in terms of polymerization rate and conversion efficiency with diaryliodonium salts and triarylsulfonium salts. However, they have some disadvantages. They are poorly soluble in many cationic polymerizable monomer systems due to their fused benzene rings. They are volatile organic compounds which increases the possibility of mass loss during or before reaction occurs. Furthermore, which is more important drawback, they are considered as toxic and potentially carcinogenic materials; therefore, their uses in commercial applications are not preferable. [59]

Table 1.5: Structures, oxidation potentials, triplet or singlet excitation energies and absorption characteristics of some common photosensitizers.

Photosensitizers	Structure	$E_{1/2}^{ox}$ (PS)	λ_{max} (nm)
Benzophenone		290 (E_T)	252 333 342
Acetophenone		308 (E_T)	242 279 318
Thioxanthone		277 (E_T)	219 255 298
Anthracene		319 (E_S)	252 356 374
Perylene		277 (E_S)	252 435
Phenothiazine		239 (E_T)	254 318

1.4.1 Quinoxaline Derivatives As Photosensitizers

A quinoxaline contains a benzene ring and a pyrazine ring. They can be also called as benzopyrazine. Their heterocyclic structures are obtained as a result of a reaction between diamine unit fused on benzene ring and 1, 2 substituted diketone. [62]

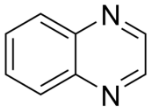
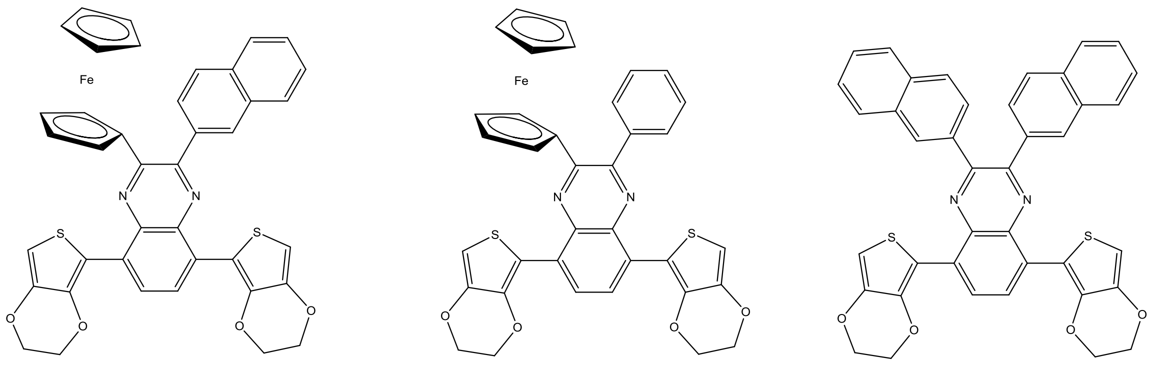


Figure 1.6: Structure of Quinoxaline

Quinoxaline derivatives are proposed as photosensitizers due to their good spectral properties as a result of their extended conjugation and high electron density. There are examples of quinoxaline derivatives used as photoinitiators in free radical polymerization. They have electron rich moieties which lower their oxidation potential. [63], [64] The lower the oxidation potential, more spontaneous the polymerization become according to Rehm – Weller equation. Depending on the substituted unit, they show good visible absorption.

Three different substituted quinoxaline derivatives were synthesized by Toppare Research Group and their electrochemical properties were studied. [65], [66] Their potential as photosensitizers in cationic photopolymerization has been investigated in this study.

(Figure 1.7)



FcNp (PS 1)

FcPh (PS 2)

NpNp (PS 3)

Figure 1.7: Substituted quinoxaline derivatives as prospective photosensitizers

1.4.2 Benzimidazole Derivatives As Photosensitizers

Benzimidazole is a fused benzene ring in combination with an imidazole. They are promising photoactive bicyclic compounds for photosensitization studies. Owing to their stability and light absorptivity, benzimidazole derivatives are also important in dye chemistry and organic electronics. [67]

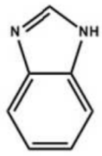
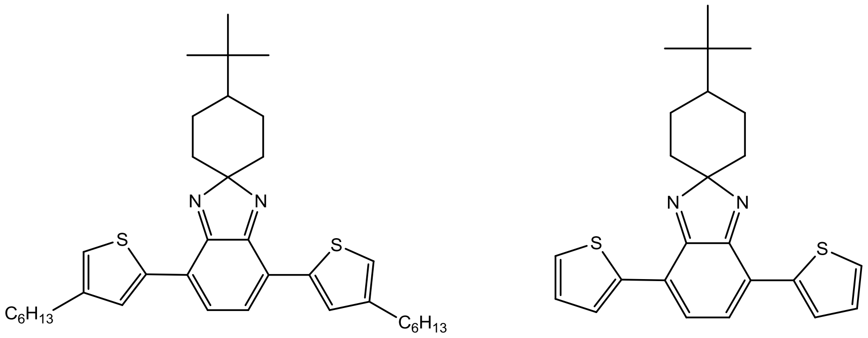


Figure 1.8: Structure of Benzimidazole

Two different substituted benzimidazole derivatives were synthesized by Toppare Research Group and their electrochemical properties were studied. [68] The effect of change in donor unit is tested with these two molecules. Their cationic photopolymerization potentials have been investigated in this study. Their lower oxidation potentials and broad absorption spectrum make them good candidates for photosensitization of cationic polymerization. (Figure 1.9)



BIHT (PS 4)

BIT (PS 5)

Figure 1.9: Substituted benzimidazole derivatives as prospective photosensitizers

1.5 Fluorescence

The emission of light is an outcome of an energy transferred to compound. Fluorescence spectrum is the processed data form of obtained emission values after irradiation of sample with a specific wavelength (maximum absorption wavelength). Both qualitative and quantitative data can be obtained. When sample is irradiated with a certain wavelength, it transfers to an excited state. This could be a vibrational state in one of the excited electronic state. This state is usually the first excited electronic state. During relaxation from this state, several different processes can take place. [69] These are summarized on Jablonski diagram. (Figure 1.10)

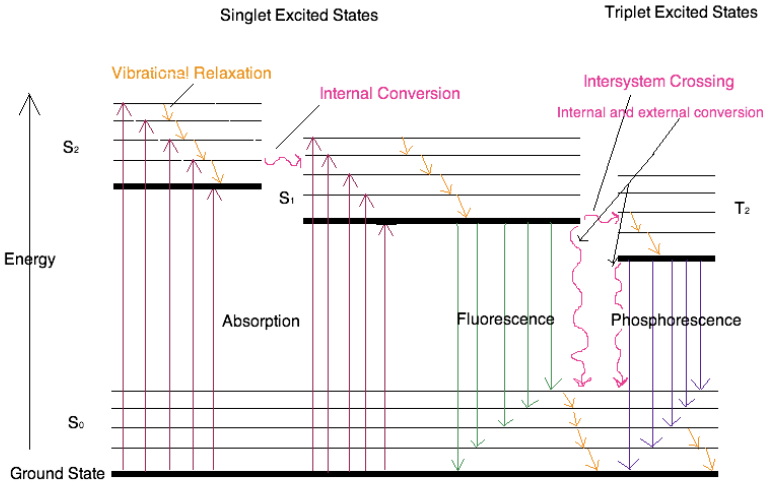


Figure 1.10: Jablonski Diagram

As seen in Jablonski diagram, other processes compete with fluorescence, such as isomerization, photoionization, photodissociation and acid-base equilibria. Besides, fluorescence intensity may decrease or diminish with formation of other complexes. This is called quenching. [69]

Fluorescence quenching is an important method to explore the energetic of excited states. It refers to any kind of processes, where decrease in the fluorescence intensity is pronounced. The reasons for lost in fluorescence are many different types of molecular interactions. Some examples of these interactions are excited state reactions, energy transfers, molecular rearrangements, ground – state complex formation and excited state complex formation. Mainly two types of fluorescence quenching mechanisms are studied in solutions. The first one is collisional quenching (dynamic quenching). In dynamic quenching, complex forms at their excited state. Fluorophore and quencher collide and yields to an exciplex after excitation. The second type of quenching mechanism is called as static quenching. It requires the formation of ground state complex between fluorophore and quencher. Formed complexes are non – fluorescent which is the main reason of the decrease in fluorescence emission of solution. [69]

1.6 Aim Of This Work

In this study, photopolymerization of several vinyl ether and epoxide monomers in the presence of proposed photosensitizers have been explored. Substituted quinoxaline derivatives and benzimidazole derivatives have been used as photosensitizers for diaryliodonium salt photoinitiators. Highly conjugated compounds with good absorption bands in long wavelength UV and visible region are presented. These versatile intermediates; such as exciplex, facilitate photoinitiated cationic polymerization of commercially critical monomers such as cyclic ethers and vinyl epoxides. Polymerizations were carried out using long wavelength UV light in the presence of diphenyliodonium hexafluorophosphate ($Ph_2I^+PF^-_6$). The polymerizations were monitored by optical pyrometry (OP). In addition, we also demonstrate that it was possible to initiate photopolymerization under solar irradiation in the presence of these photosensitizers.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

All chemicals were used without any purification. All polymerization experiments were conducted at NTP.

5, 8-Bis (2, 3-dihydrothieno [3, 4-b][1,4]dioxin-5-yl)-2-(naphthalen-2-yl)-3-ferrocenyl-4a,8a-dihydroquinoxaline [65] (PS1), 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-(phenyl)-3-ferrocenylquinoxaline [66] (PS2), 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(naphthalen-2-yl) quinoxaline [66] (PS3), 4'-(tert-butyl)-4,7-bis(4-hexylthiophen-2-yl)spiro[benzo[d]imidazole-2,1-cyclohexane] [68] (PS4) and 4'-(tert-butyl)-4,7-bis(thiophenyl)spiro[benzo[d]imidazole-2,1-cyclohexane] [70] (PS5) were synthesized as described in literature.

7-oxabicyclo[4.1.0]heptane (CHO), 2-chloroethyl vinyl ether (CEVE), 3-(oxiran-2yl)-7-oxabicyclo[4.1.0]heptane (VCHDO), 1,2-bis(vinyloxy)ethane (DVE-3), 2,2’-(((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(methylene))bis(oxirane) (BPADE), diphenyliodonium hexafluorophosphate ($Ph_2I^+ PF_6^-$), dichloromethane (DCM), chloroform ($CHCl_3$), and all other chemicals mentioned in the synthetic route of PS1, PS2, PS3, PS4, and PS5 were purchased from Aldrich Chemical Co. (Milwaukee, WI) unless otherwise indicated. The corona-treated poly (propylene) films were supplied as a gift from Superfilm Co. Gaziantep, Turkey.

2.2 Synthesis Of Photosensitizers

2.2.1 Synthesis of Quinoxaline Derivatives

2.2.1.1 Synthesis of 5, 8-bis (2, 3-dihydrothieno [3, 4-b] [1, 4] dioxin-5-yl)-2-(naphthalen-2-yl)-3-ferrocenyl-4a, 8a-dihydroquinoxaline (PS1)

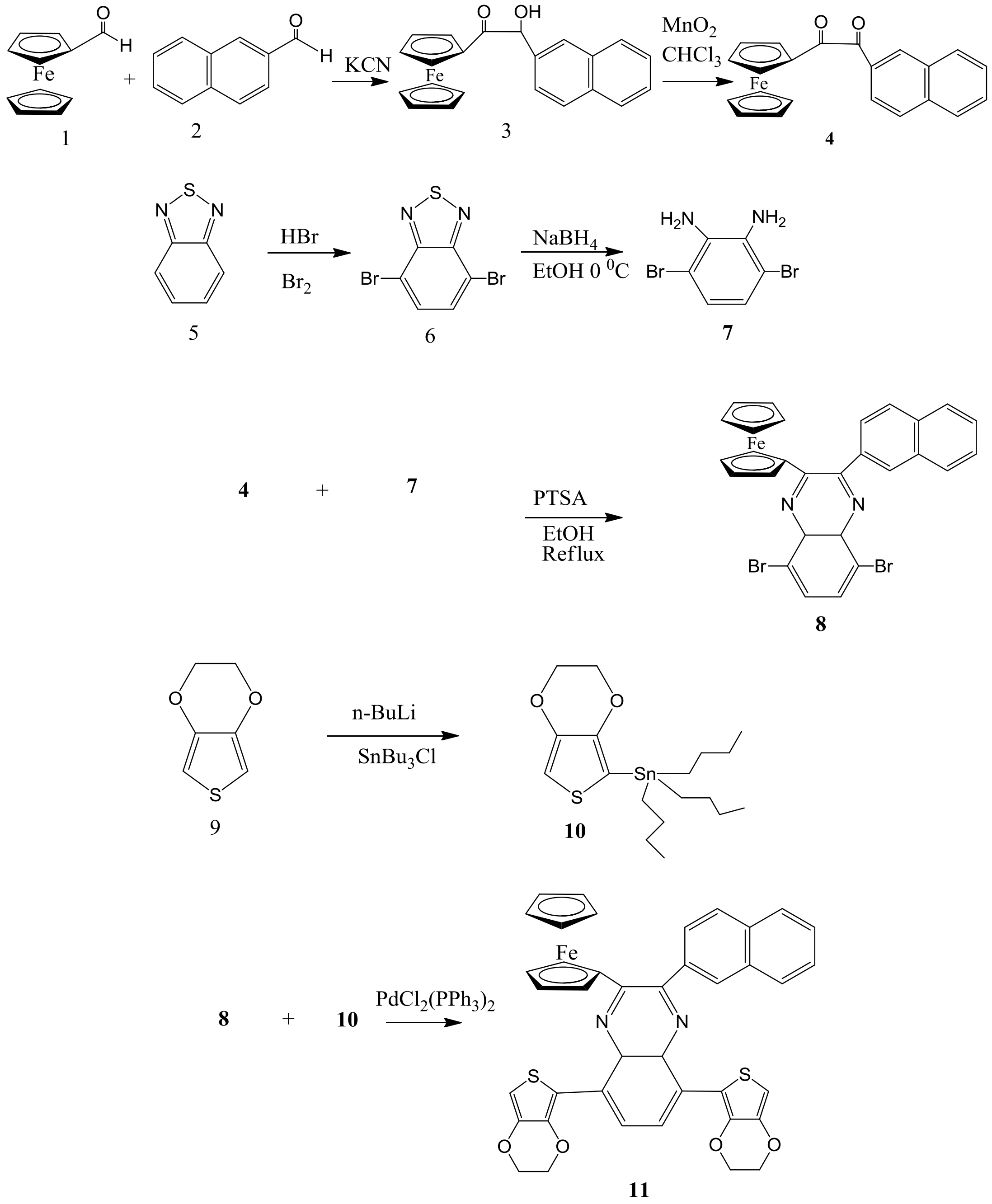
2-Hydroxy-1-(naphthalen-2-yl)-2-ferrocenylethanone, [71] 1-ferrocenyl-2-naphthylethanedione, [71] 4,7-dibromo-2,1,3-benzothiadiazole,3,6-dibromo-1,2-phenylenediamine, [72] 5,8-dibromo-2-(naphthalen-2-yl)-3-ferrocenyl-4a,8a-dihydroquinoxaline [73] tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane, tributyl(4-hexylthiophen-2-yl)stannane and tributyl(thiophen-2-yl)stannane [74] were synthesized from previously recorded studies.

3,6-Dibromo-1,2-phenylenediamine and 1-ferrocenyl-2-naphthylethanedione solution was refluxed overnight in ethanol. P-toluene sulfonic acid (PTSA) was used as catalyst. The reaction medium was cooled down to 0^{o}C. The precipitate was filtrated, and then cleansed with cold ethanol.[65]

5,8-Dibromo-2-(naphthalen-2-yl)-3-ferrocenyl-4a,8a-dihydroquinoxaline and tributyl (2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane were dissolved in dry THF. The catalytic amount of $Pd(PPh_3)_2Cl_2$ was added under argon atmosphere. The mixture was stirred at 100^{o}C for 15 h, cooled, and concentrated on the rotary evaporator. The residue was purified with column chromatography (silica gel, $CHCl_3$: hexane, 2:1). Red solid product was isolated.

^{1}H NMR ($CDCl_3$) δ 3.91 (s, 5H), 4.24–4.19 (m, 2H), 4.25 (dd, J = 4.9 and 2.9 Hz, 2H), 4.30–4.26 (m, 2H), 4.34–4.30 (m, 2H), 4.40–4.35 (m, 2H), 4.76–4.70 (m, 2H), 6.42 (s, 1H), 6.61 (s, 1H), 7.52–7.44 (m, 2H), 7.75 (dd, J = 8.5 and 1.6 Hz, 1H), 7.89–7.83 (m, 3H), 8.23 (s, 1H), 8.63 – 8.49 (m, 2H).

^{13}C NMR ($CDCl_3$) δ 64.35, 64.39, 64.96, 65.01, 70.04, 70.06, 71.87, 77.21, 82.32, 102.78, 103.10, 113.47, 126.26, 126.67, 127.01, 127.56, 127.67, 127.71, 127.81, 128.01, 128.66, 128.90, 129.63, 133.10, 133.39, 135.95, 136.90, 137.48, 140.23, 140.32, 141.32, 141.49, 150.10, 151.99.



Scheme 2.1: Synthetic Route of 5, 8-bis (2, 3-dihydrothieno [3, 4-b] [1, 4] dioxin-5-yl)-2-(naphthalen-2-yl)-3-ferrocenyl-4a, 8a-dihydroquinoxaline (PS1) [65]

2.2.1.2 Synthesis of 5, 8-bis (2,3-dihydrothieno [3, 4-b] [1, 4] dioxin-5-yl)-2-(phenyl)-3-ferrocenylquinoxaline (PS2)

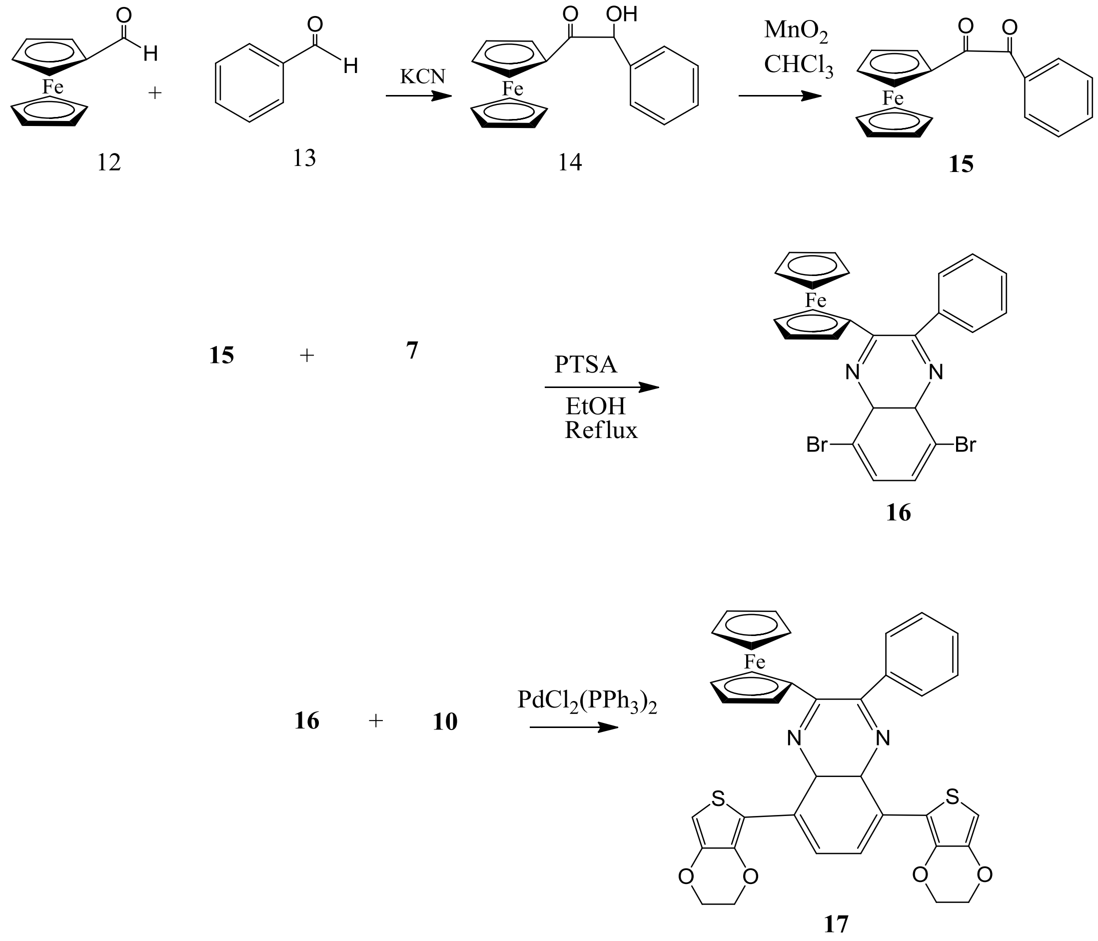
2-Hydroxy-2-phenyl-1-ferrocenylethanone [71], 1-ferrocenyl-2-phenylethanedione [71], 4,7-dibromo-2,1,3- benzothiadiazole [75], 3,6-dibromo-1,2-phenylenediamine [72], 5,8-dibromo-2-phenyl-3-ferrocenylquinoxaline [73] and tributyl(2,3-dihydrothieno-[3,4-b][1,4]dioxin-5-yl)stannane [74] were synthesized according to procedures in literature.

A solution of 3, 6-dibromo-1, 2-phenylenediamine and 1-ferrocenyl-2-phenylethanedione in ethanol was refluxed overnight. P-toluene sulfonic acid (PTSA) was the catalyst of this reaction. The mixture was cooled to 0^{o}C and concentrated on the rotary evaporator. The remainder was separated in column chromatography (silica gel, hexane: Ethanol, 10:1). Middle group was obtained as a purple solid.

5,8-Dibromo-2-phenyl-3-ferrocenylquinoxaline and tributyl (2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-stannane were solved in dry THF. The reactants were purged with argon for 90 minutes and $Pd(PPh_3)_2Cl_2$ were added. The mixture was stirred at 100^{o}C for 18 h, cooled to room temperature. Then reaction solution was concentrated on the rotary evaporator. The residue was purified with column chromatography (silica gel, $CHCl_3$: hexane, 2:1). PS2 was obtained as a red solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 5H), 4.27 (dd, J = 4.1 Hz, 2H), 4.31 (dd, J = 3.7 Hz, 2H), 4.34–4.32 (m, 2H), 4.37 (dd, J = 5.2, 2.4 Hz, 2H), 4.41 (dd, J = 5.2, 2.4 Hz, 2H), 4.79–4.76 (m, 2H), 6.49 (s, 1H), 6.65 (s, 1H), 7.46 (dd, J = 8.0, 3.0 Hz, 3H), 7.78–7.70 (m, 2H), 8.55 (d, 1H), 8.63 (d, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 64.3, 64.9, 70.0, 71.8, 82.3, 102.7, 103.1, 113.4, 126.6, 127.0, 127.5, 127.6, 127.7, 127.8, 128.0, 128.6, 128.9, 129.6, 133.1, 133.3, 135.9, 136.9, 137.5, 140.2, 140.3, 141.3, 141.4, 150.1, 151,9.



Scheme 2.2: Synthetic Route of 5, 8-bis (2, 3-dihydrothieno [3, 4-b] [1, 4] dioxin-5-yl)-2-(phenyl)-3-ferrocenylquinoxaline (PS2) [66]

2.2.1.3 Synthesis of 5, 8-bis (2, 3-dihydrothieno [3, 4-b] [1, 4] dioxin-5-yl)-2,3-di(naphthalen-2-yl)quinoxaline (PS3)

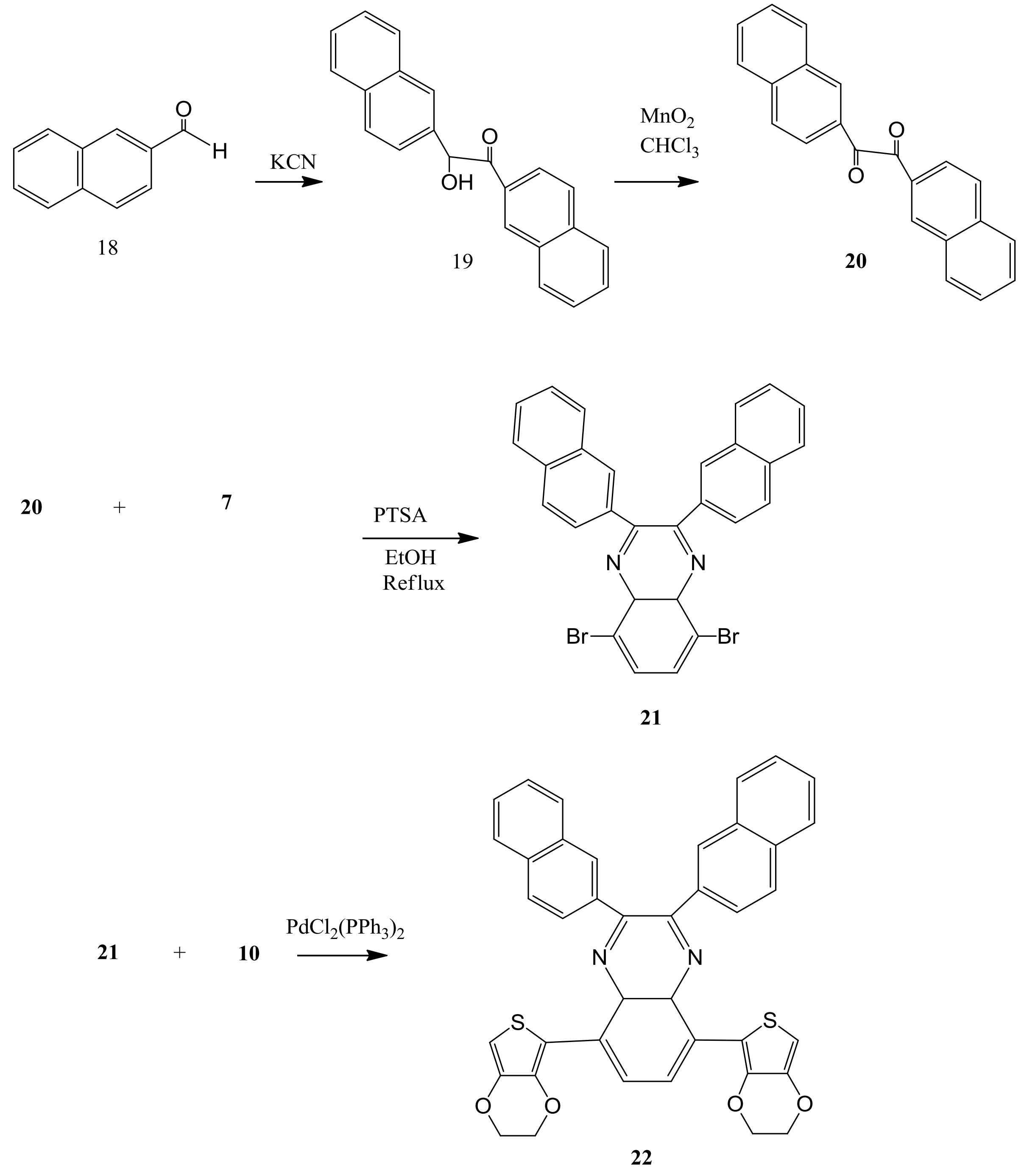
2-Hydroxy-1,2-di(naphthalen-2-yl)ethanone [71], 1,2-di(naphthalen-2-yl)ethane-1,2-dione [71], 4,7-dibromo-2,1,3- benzothiadiazole [75], 3,6-dibromo-1,2-phenylenediamine [72], 5,8-dibromo-2,3-di-(naphthalen-2-yl)quinoxaline [73] and tributyl(2,3-dihydrothieno-[3,4-b][1,4]dioxin-5-yl)stannane [74] were synthesized as described in literature.

A solution of 3, 6-dibromo-1, 2-phenylenediamine and 1,2-di(naphthalen-2-yl)ethane-1,2-dione in ethanol was prepared and refluxed overnight with a catalytic amount of p-toluene sulfonic acid (PTSA). The mixture was cooled to $0^{o}C$. The precipitate was isolated by filtration and washed with ethanol several times then the residue was subjected to column chromatography (silica gel, $CHCl_3$: hexane, 1:1) to get the acceptor unit as a yellow solid.

5,8-Dibromo-2,3-di(naphthalen-2-yl)quinoxaline and tributyl (2,3-dihydrothieno[3,4-b][1,4]dioxin-5- yl)stannane were dissolved in dry THF. The reaction was proceeded at argon atmosphere for 30 min. and $Pd(PPh_3)_2Cl_2$ was added. The mixture was stirred at $100^{o}C$ under argon atmosphere for 18 h, cooled and concentrated on the rotary evaporator. The purification was completed with column chromatography (silica gel, $CHCl_3$: hexane, 2:1) PS3, a red solid, was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (dd, J=3.78, 4H), 4.35 (dd, J=3.55, 4H), 6.51 (s, 2H), 7.59–7.39 (m, 2H), 8.38–7.60 (m, 8H), 9.23–8.44 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 64.3, 65.0, 103.4, 112.1, 123.2, 124.3, 124.9, 125.1, 125.9, 128.9, 129.01, 131.1, 134.3, 135.4, 137.4, 139.1, 140.6, 141.4, 146.4, 148.9.



Scheme 2.3: Synthesis of 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(naphthalen-2-yl)quinoxaline (PS3) [66]

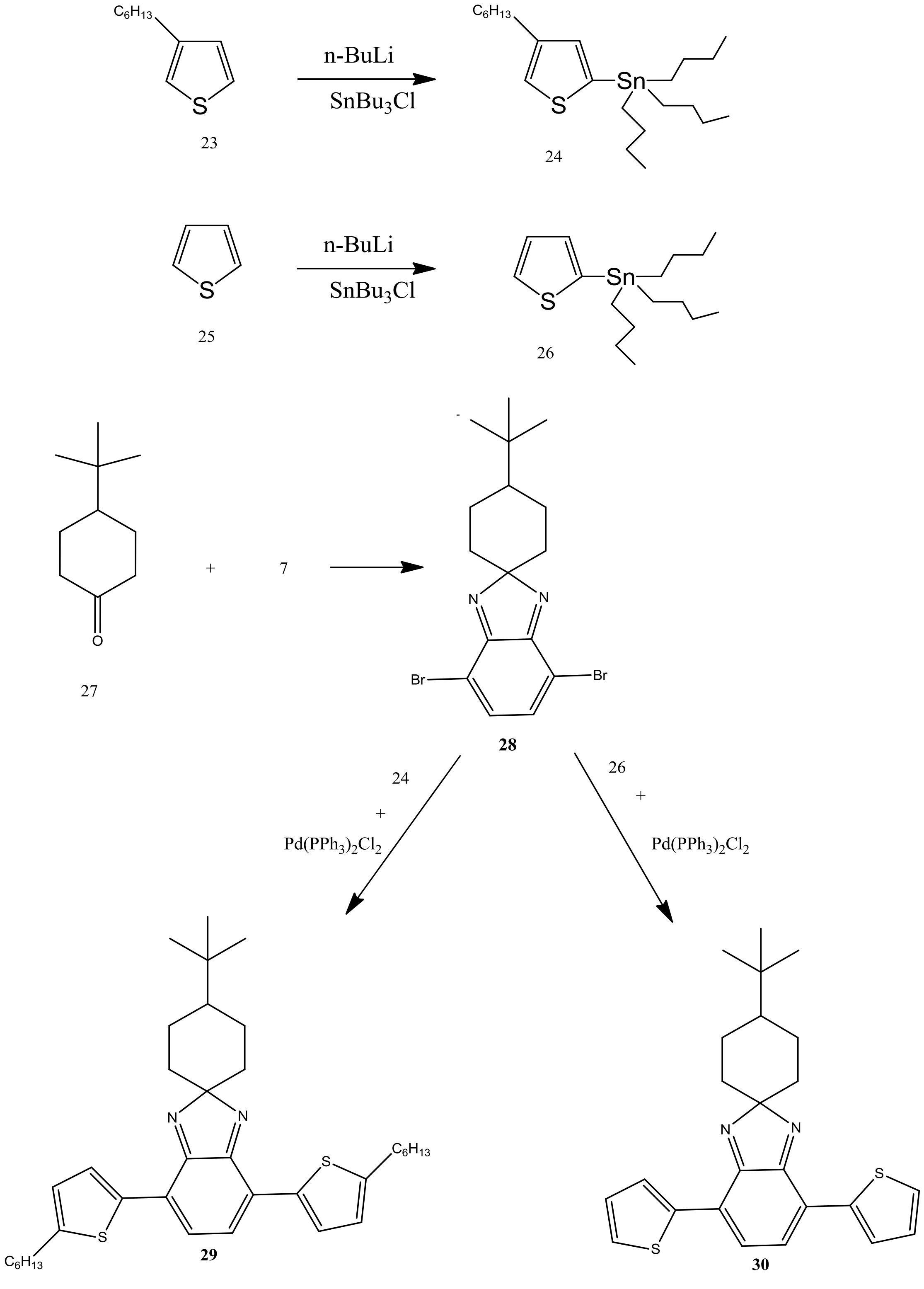
2.2.2 Synthesis of Benzimidazole Derivatives

2.2.2.1 Synthesis of 4'-(tert-butyl)-4,7-bis(4-hexylthiophen-2-yl)spiro[benzo[d]imidazole 2, 1-cyclohexane] (PS4) and 4'-(tert-butyl)-4, 7-bis(thiophenyl)spiro [benzo[d]imidazole-2, 1-cyclohexane] (PS5)

A solution of 3,6-dibromobenzene-1,2-diamine, 4-tert-butylcyclohexanone and toluene was stirred at 130^{o}C for 24 hours in argon atmosphere. Then the solvent was removed. The crude product was dissolved in dichloromethane and stirred at room temperature under argon atmosphere. To this solution, 85 % activated manganese (IV) oxide was added. After stirring at room temperature for 4 hours, the reaction mixture was filtered, diluted with dichloromethane, washed with distilled water, and dried over $MgSO_4$. After removing the solvent with rotary evaporator, the residue was subjected to column chromatography using hexane:ethylacetate (10:1). 4,7-Dibromo-4'-(tert-butyl)spiro[benzo[d]imidazole-2,1'-cyclohexane] was obtained as a yellow oil.

A solution of 4’,7’dibromo-4-(tert-butyl)spiro[cyclohexane-1,2’-indene] and tributyl(4-hexylthiophen-2-yl)stannane was refluxed in THF at 100^{o}C under argon atmosphere. After 12 h, solvent was removed under rotary evaporator and the purification was done by column chromatography using dichloromethane-hexane (1:3) as the eluent. 5,5'-(4-(Tert-butyl)spiro[cyclohexane-1,2'-indene]-4',7'-diyl)bis(3-hexylthiophene) (PS4) was obtained as a orange - pink solid.

A solution of 4’, 7’dibromo-4-(tert-butyl) spiro [cyclohexane-1, 2’-indene] and tributyl (thiophenyl)stannane was refluxed in THF at 100^{o}C under argon atmosphere. After 12 h, solvent was removed under rotary evaporator and the residue was purified by column chromatography using dichloromethane-hexane (1:3) as the eluent. 5,5'-(4-(Tert-butyl)spiro[cyclohexane-1,2'-indene]-4',7'-diyl)bis(thiophene) (PS5) was obtained as a pink solid.



Scheme 2.4: Synthetic route of 4'-(tert-butyl)-4,7-bis(4-hexylthiophen-2-yl)spiro[benzo[d]imidazole-2,1-cyclohexane] (PS4) and 4'-(tert-butyl)-4,7-bis(thiophenyl)-spiro[benzo[d]imidazole-2,1-cyclohexane] (PS5) [68, 70]

2.3 Characterization

2.3.1 UV – Vis Spectroscopy

Common UV irradiation sources are used in investigation of photopolymerization. In UV – Vis spectroscopy, wavelength from 190 to 800 nm are investigated (190 – 400 UV wavelength range; 400 – 800 visible wavelength range). In this study, UV – Vis spectrum was used to understand absorption behavior of prospective photosensitizers. UV Spectra of photosensitizers were recorded on a Varian Cary 5000 Spectrometer. Absorption spectrum is plotted by observing emission as the wavelength of excitation radiation is changed.

2.3.2 Fluorescence Quenching Studies

In this study, exciplex formation of the excited state of photosensitizer and photoinitiator salt has been analyzed.

Fluorescence quenching studies of PS1, PS2 and PS3 were carried out on Varian Cary Eclipse Fluorescence Spectrometer. Excitation wavelengths were chosen as 335 nm since their absorption wavelengths were 323 nm, 322 nm, and 325 nm while the fluorescence emission bands were 590 nm, 607 nm, and 602 nm respectively. The PS1, PS2, and PS3 concentrations were $1x10^{-4}$ M in dichloromethane and quencher (diphenyliodonium hexafluorophosphate, $Ph_2I^+PF^-_6$) concentrations were $1x10^{-4}$ M, $2x10^{-4}$ M and $3x10^{-4}$ M.

Fluorescence quenching studies of PS4 and PS5 were also carried out on Varian Cary Eclipse Fluorescence Spectrometer. Excitation wavelengths were chosen as 510 nm since their absorption wavelengths were 491 nm and 503 nm while the fluorescence emission bands were 619 nm and 606 nm respectively. The PS4 and PS5 concentrations were $1x10^{-4}$ M in dichloromethane and quencher (diphenyliodonium hexafluorophosphate, $Ph_2I^+PF^-_6$) concentrations were $1x10^{-4}$ M, $2x10^{-4}$ M and $3x10^{-4}$ M.

2.3.3 Optical Pyrometry

In photoinitiated polymerization, liquid substrates transforms to insoluble polymers in a very short time, such as seconds to minutes. That is why the mechanism of photopolymerization has been difficult to analyze.

There are several different techniques studied in the literature. Differential Scanning Photocalorimeter (DSP) and Real-Time Fourier Transform Infrared Spectroscopy (RT-FTIR) are two mostly used analytical methods. DSP relies on the fact that all studied polymerizations are exothermic. Unfortunately it has very poor reproducibility because its data depends on sample size and concentration. Also, DSP does not provide much information about the chemistry of photopolymerization. [76] On the other hand, RT- FTIR gives great information about the chemistry going on in polymerization, but lacks information about the environmental and physical changes in the sample. For instance, exact value for temperature rise of photopolymerization cannot be obtained from RT-FTIR measurements. [77] Both of these techniques are good to work with only simple one or two monomers mixtures. When reaction medium gets more complex with photoinitiators or some other co-initiators, these methods became difficult to work with. [78] In addition, they are both very expensive.

Crivello and his collaborators invented Optical Pyrometry (OP) for analyzing both physical changes in the reaction and mechanism of polymerization. [79] It operates by directly recording the temperature of polymerization. Even though photoinitiated polymerizations have very short induction time, OP is able to trace each step in the polymerization. The observed rise in temperature is proportional to the amount of the monomer undergoing polymerization. OP is a multipurpose instrument for monitoring photopolymerization with several advantages.

These advantages are its lost cost, rapid data process, reproducibility, and sensitivity. OP is a very user friendly instrument. Interpretation of graphs is easy and gives lots of different information about the process. By interpreting graphs, one can observe the rate of reactions. OP can be used by itself or it can be combined with RT-FTIR. [78] If it is joined with infrared spectroscopy, it provides scientific and practical information such as instantaneous temperature and chemical conversion profiles of polymerizations. Device can also be connected to a personal computer to store data for further analysis.

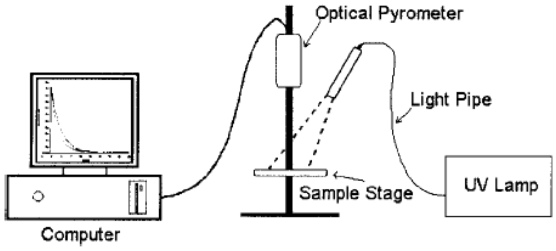


Figure 2.1: Instrumentation of Optical Pyrometry [78]

Homogeneous solutions of monomers in the presence of diphenyliodonium hexafluorophosphate salt were prepared with/without photosensitizers, and placed between two thin films (10 μm) of oriented and corona-treated poly(propylene). Then, the resulting assembly was placed in plastic slide frames (2 cm × 2 cm) and put in the sample holder. Samples were exposed to UV light using UVEX model SCU-110 mercury lamp (Sunnyvale, CA) equipped with a liquid optic cable. The liquid optic cable allows UV light to function only between 300 and 750 nm, blocking the transmission in the infrared region.

All OP experiments in this investigation were carried out at constant temperature (18^{o}C). With the onset of UV irradiation, temperature data were collected at a rate of one measurement per second and recorded with personal computer for analysis. Three kinetic runs were performed for every polymerization and the graphs were plotted using average values of these runs.

Table 2.1: Experimental set up (Quinoxaline Derivatives)

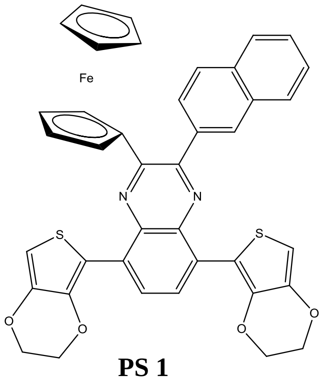
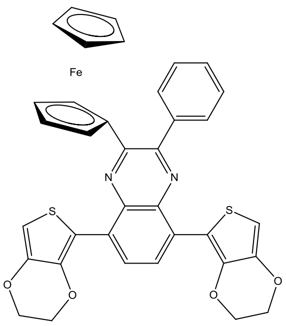
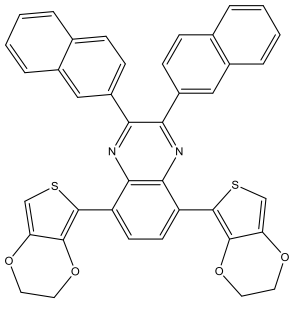
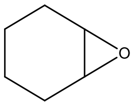
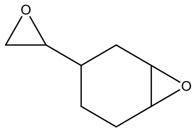
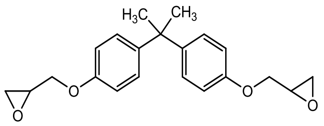
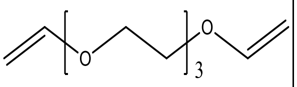
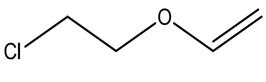
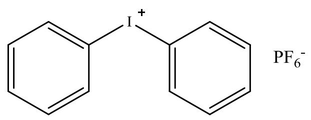
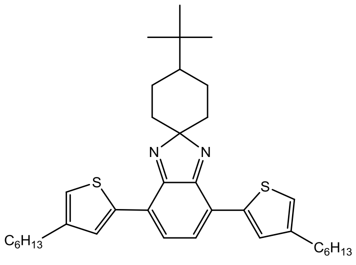
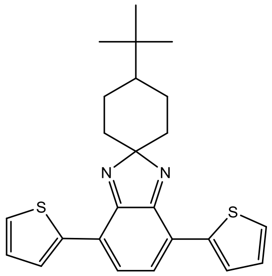
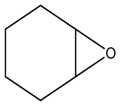
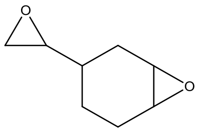
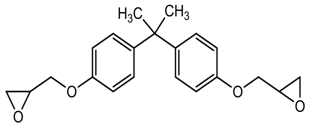
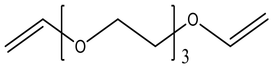
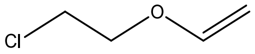
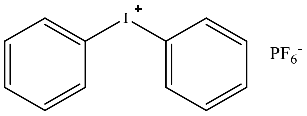
Photosensitizers	Monomers	Photoinitiator Salt
 **PS 1**  **PS 2**  **PS 3**	 **CHO**  **VCHDO**  **BPADGE**  **DVE -3**  **CEVE**	 **Diphenyliodonium Hexafluorophosphate**

Table 2.2: Experimental set up (Benzimidazole Derivatives)

Photosensitizers	Monomers	Photoinitiator Salt
 **PS 4**  **PS 5**	 **CHO**  **VCHDO**  **BPADGE**  **DVE -3**  **CEVE**	 **Diphenyliodonium Hexafluorophosphate**

2.3.4 Solar Irradiation Induced Polymerization

A solution of 7-oxabicyclo[4.1.0]heptane (CHO) containing 1.0 mol % $Ph_2I^+PF_6^-$ with 1.0 mol % of each photosensitizer (PS1, PS2, PS3, PS4, or PS5) was prepared and spread onto corona-treated poly(propylene) films between plastic film slides. Solutions were exposed to Atlas Materials Testing Systems solar simulator AM 1.5G. After 5 minutes of continuous irradiation, initial colors of solutions became dark and sticky polymer films were formed on the corona-treated poly (propylene) films.

CHAPTER 3

RESULTS AND DISCUSSION

Quinoxaline derivatives have been synthesized as precursor monomers for the synthesis of conducting polymers. [80], [81] These molecules appear to be good candidates for electron transfer photosensitization reactions for aryliodonium salts due to their extended conjugation, low oxidation potentials, and high solubility in various cationically polymerizable monomers. As described in Introduction, an electron transfer will take place from the excited photosensitizer to the diaryliodonium salt photoinitiator. With this energy transfer, onium salt is rapidly decomposed and the radical formed retards back electron transfer making the overall process irreversible.

Photoinduced electron transfer mechanism is facilitated when the free energy change (ΔG) has to be smaller than zero. Free energy change of this reaction is estimated by the Rehm-Weller equation : [82]

$$\Delta G = (E^{ox}_{sens} - E^{red}_{onium}) - E^{*}_{sens} \qquad \textbf{eq 6.}$$

where E^{red}_{onium} is the reduction potential of the onium salt, E^{ox}_{sens} is the oxidation potential of the photosensitizer and E^{*}_{sens} is its excited-state energy. The Rehm-Weller equation demonstrates that the electron transfer process is more effective as the oxidation potential values of photosensitizer dye monomers become smaller, because the free energy change becomes more negative.

3.1 Quinoxaline Derivatives As Photosensitizers

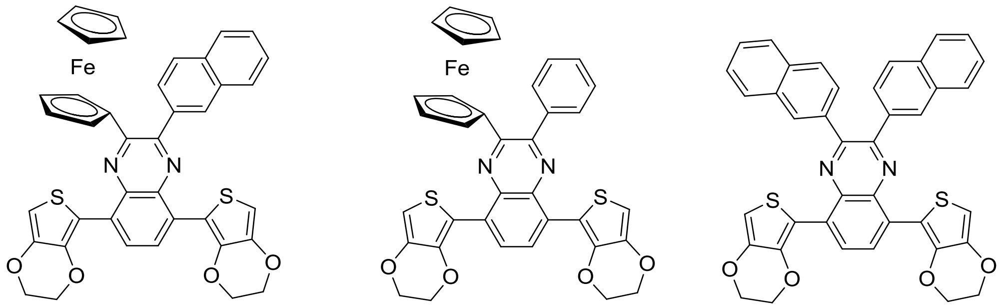
In this study, ferrocenyl, naphthanyl, and phenyl substituted quinoxaline derivatives were investigated as photosensitizers. Four different studies were conducted:

1. Broad absorption band of each molecule was confirmed by using UV–Vis spectroscopy.

2. As mentioned in Figure 1.20, exciplex formation should occur between photoinitiator salt and photosensitizer molecule to have an efficient polymerization. In order to prove this statement, fluorescence quenching studies were performed.
   Stern – Volmer plots were drawn to understand the interaction mechanism between the photoinitiator salt and the photosensitizer molecule.

3. Cationic photopolymerization mechanism was clarified with optical pyrometry. Each polymerization was different in terms of their induction times, polymerization rates, the highest temperature values during polymerization and polymerization times. The nature of monomer and photosensitizer determine the efficiency.

4. Photosensitized cationic polymerizations are known to be energy efficient processes. Because these kinds of polymerizations do not need an artificial energy source for polymerization. Intensity of solar irradiation is usually sufficient to carry out this process. Responses of proposed photosensitive molecules were tested under solar irradiation as the last step.



PS1 PS2 PS3

Figure 3.1: Quinoxaline derivatives as photosensitizer

3.1.1 UV – Vis Spectra Of PS1, PS2 & PS3

Quinoxaline molecules are derivatized by substituting electron rich moieties such as ferrocene and/or naphthanyl as well as ethylenedioxythiophene (EDOT) donor groups to extend the conjugation and increase electron density. As a result, the photosensitizer molecules become good electron-donors in their excited states. As seen in Figure 3.2, all photosensitizers under investigation have broad absorption bands between 320 nm and 470 nm. Thus, photosensitization can occur in a wider spectral area than photoinitiators alone can achieve. Moreover, the oxidation potential values of photosensitizers are lowered with enhanced electron density in the photosensitizer molecules leading to a more apparent efficacy of the polymerizations. The oxidation potentials of PS1, PS2 and PS3 are determined as 1.1 V [65], [66] , 0.98 V, [66] and 0.85 V [66] respectively by cyclic voltammetry. Low oxidation potentials facilitate electron transfer between photosensitizers and diphenyliodonium salt. This concept is explained with Rehm – Weller equation.

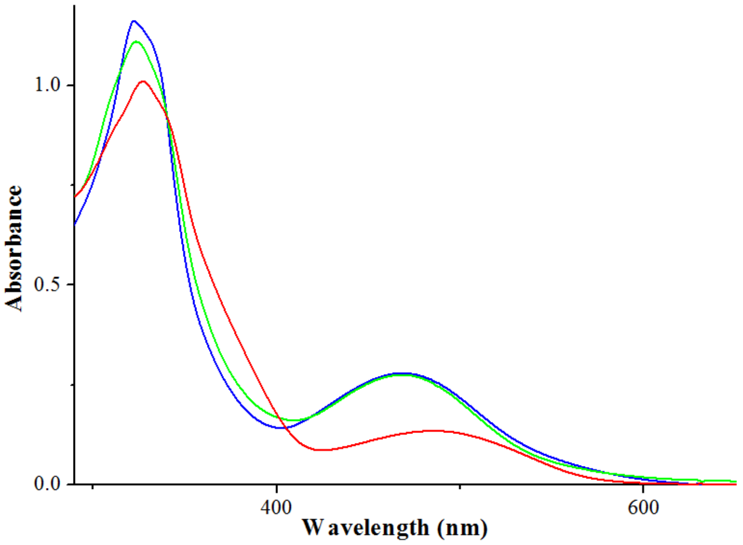


Figure 3.2: UV–Vis spectrum of 1 x 10^{-5}mol L^{-1} PS1 (🟩), 1 x 10^{-5}mol L^{-1} PS2 (🟦) and 1 x 10^{-5}.mol L^{-1} PS3 (🟥) in CH_2Cl_2.

3.1.2 Fluorescence Quenching Of PS1, PS2 & PS3

According to UV – Vis spectrum of all prospective photosensitizer molecules absorb in a broader range than diphenyliodonium salts. In this study, photosensitizer is excited and emits fluorescence. Specific wavelengths were chosen during fluorescence quenching study. Fluorescence spectrum was taken at 335 nm PS1, PS2 and PS3. Excitation wavelength was chosen 15 nm larger than their absorption maxima. Because, after absorption, Stoke’s shift occurs due to non-radiative transitions, and emission spectra are red shifted. In order to prevent overlap between absorption and emission spectra, excitation wavelength was selected 10-15 nm longer than absorption maximum. Moreover, if photosensitizer molecules were excited at their absorption maximum, emission spectrum would be obtained at a lower intensity.

There are lots of different ways that cause the reduction in fluorescence intensity as there are various pathways that cation–radical and photosensitive molecule can go. Proposed exciplex formation shown in Figure 1.20 was proven by fluorescence quenching studies of the photosensitizer solutions as a function of diaryliodonium salt concentration, and a typical Stern-Volmer graph was plotted. The photosensitizer emits less fluorescence as it is quenched more by the increasing photoinitiator concentration, which is confirmed by the increase in the Stern-Volmer plot (Figure 3.3).

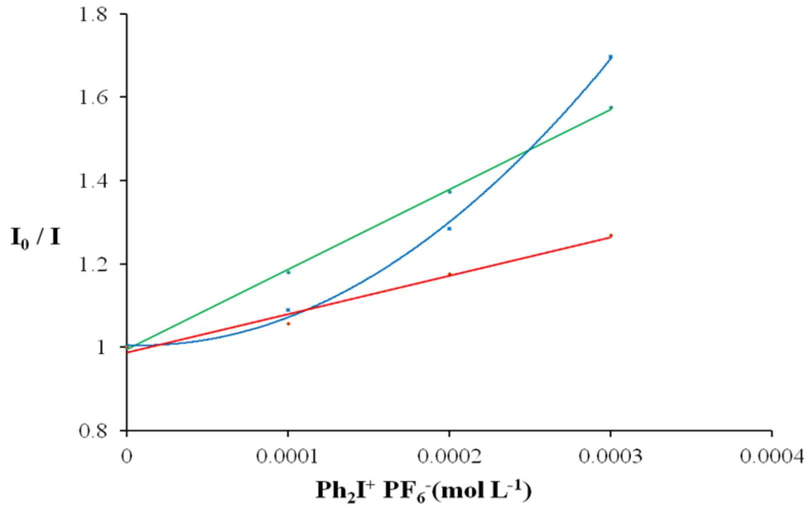


Figure 3.3: Stern-Volmer plot of the quenching of PS1 (—) ($1x10^{-4}$M), PS2 (—) ($1x10^{-4}$ M) and PS3 (—) by diphenyliodonium hexafluorophosphate (Ph_2I^+ PF_6^-) in dichloromethane (excitation wavelength 335nm) (I_0 = fluorescence intensity of PS solutions; I = fluorescence intensity of PS solutions in the presence of $Ph_2I^+PF_6^-$).

When we examine the Stern-Volmer graph, it was observed that PS1 and PS3 have a constant slope, which shows a dynamic quenching in the reaction medium. Static quenching occurs when fluorophore interacts with another molecule and forms a stable complex. This clearly demonstrates the exciplex formation between photoinitiator salt and sensitizer molecules. Equation for static quenching is shown below:

$$I_0/I = 1 + K_{SQ}[Q] \qquad \textbf{eq. 7}$$

An exponential increase is observed in the Stern–Volmer graph of PS2, which shows both a static quenching and a dynamic quenching, also known as collisional quenching occurs in the reaction medium. PS2 forms complex at its ground state, which is called as static quenching. Dynamic quenching takes place when the excited fluorophore contacts with an atom or molecule. As a consequence of this contact, non-radiative transitions are experienced and stable complex formation is not seen. The relationship for dynamic quenching is shown below:

$I_0/I = 1 + k_{DQ}\,\tau_0\,[Q]$ **eq. 8**

When both dynamic quenching and static quenching takes place at the same time, equation turns into the following form:

$I_0/I = (1 + k_{DQ}\,\tau_0\,[Q_1]\,) \times (1 + K_{SQ}[Q_2]\,)$ **eq. 9**

As a result, we can conclude that the non-linear correlation of the Stern-Volmer graph of PS2 mean that both static and dynamic quenching takes place in reaction medium. [83], [84]

3.1.3 Optical Pyrometry Studies Of PS1, PS2 & PS3

Optical pyrometry was used to optimize reaction conditions and examine the progress of cationic photopolymerizations. A temperature rise within a short period of time is expected with the initiation of photopolymerization. Low or modest temperature rise show that polymerization proceeds slowly. In general, most addition polymerizations are rapid and have high exothermicities where bulk polymerizations are characterized from large temperature differences. [76]

Cyclohexene oxide (CHO) was chosen as the monomer for optimization of light intensity and photosensitizer concentration due to its moderate reactivity compared to other monomers under investigation. Also, CHO polymerizes only by cationic mechanisms and does not polymerize with radical mechanism.

Solution were prepared and investigated at OP. Optimization studies are shown for PS1 molecule. (Figure 3.4) PS2 and PS3 displayed similar results (Figure 3.5, Figure 3.6). Light intensity optimization studies showed that both initiation and propagation steps of photopolymerizations were much faster with increased intensity of light as expected. An intensity of 15.1mWcm^{-2} was sufficient as the induction period was eliminated. Similarly, it was observed that the polymerization rate increased as concentration of the photosensitizer was increased, again as expected, and 0.1 % mol photosensitizer was sample to eliminate the induction period. Consequently, all OP experiments were conducted in the presence of 0.1 % mol photosensitizer under UV light of an intensity of 15.1mWcm^{-2} unless otherwise indicated.

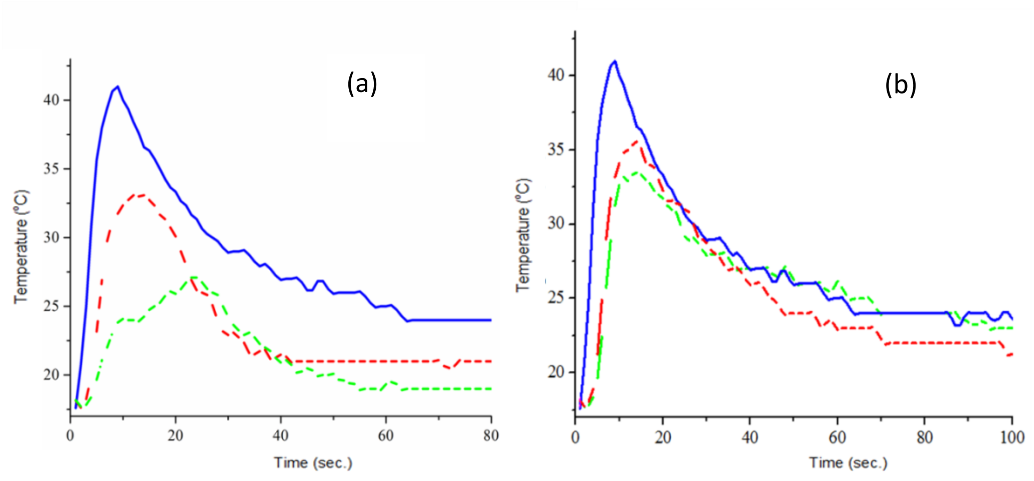


Figure 3.4: Optimization of (a) Intensity [9.2 mWcm^{-2}(•••), 12.1 mWcm^{-2} (▬), 15.1 mWcm^{-} (▬)], (b) Concentration [0.01 mol% PS1 (••••), 0.05 mol% PS1 (▬), 0.1 mol% PS1(▬)] with 1.0 mol % $Ph_2I^+ PF_6^-$ in 7-oxabicyclo[4.1.0]heptane (CHO) solution.

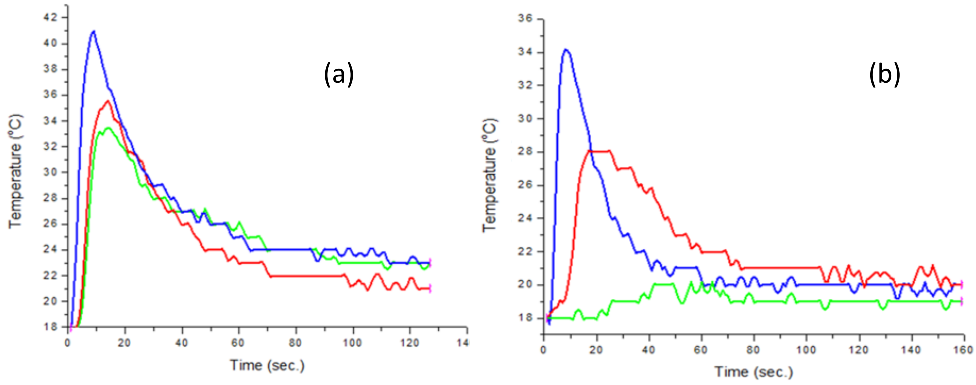


Figure 3.5: Optimization of (a) Intensity [9.2 mWcm^{-2}(••••), 12.1 mWcm^{-2} (▬), 15.1 mWcm^{-2}(▬)], (b) Concentration [0.01 mol% PS2 (•••), 0.05 mol% PS2 (▬), 0.1 mol% PS2(▬)] with 1.0 mol % $Ph_2I^+ PF_6^-$ in 7-oxabicyclo[4.1.0]heptane (CHO) solution.

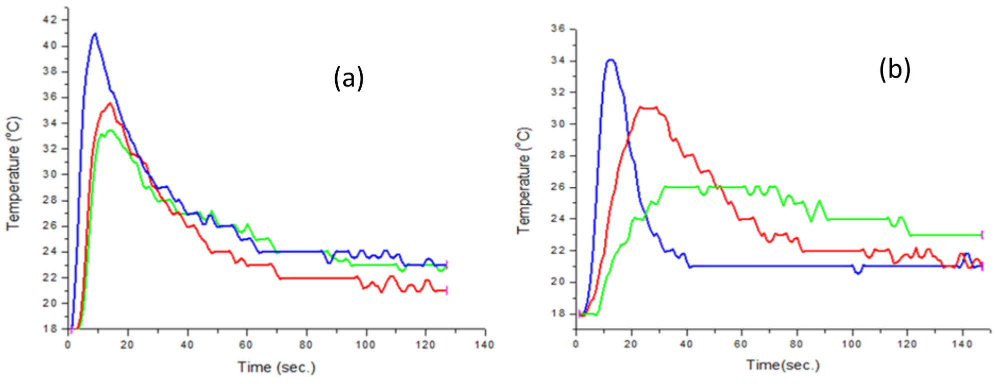


Figure 3.6: Optimization of (a) Intensity [9.2 mWcm^{-2}(•••), 12.1 mWcm^{-2} (▬), 15.1 mWcm^{-2}(▬)], (b) Concentration [0.01 mol% PS3 (••••), 0.05 mol% PS3 (▬), 0.1 mol% PS3(▬)] with 1.0 mol % $Ph_2I^+ PF_6^-$ in 7-oxabicyclo[4.1.0]heptane (CHO) solution.

Solutions were prepared with different monomers in the presence and absence of both photosensitizer and photoinitiator. It was established that the presence of the photoinitiator was critical since no polymerization was observed when photoinitiator was absent in the solutions. All photosensitizers were completely soluble in various cationically polymerizable monomers. The OP technique was further used to examine the progress of polymerization. Figure 3.7, 3.8, 3.10 - 3.12 illustrate the photopolymerizations of a monofunctional epoxide (CHO), a difunctional epoxide (VCHDO), vinyl ether monomers (CEVE and DVE-3), and difunctional glycidyl ether (BPADGE) in the presence of diaryliodonium salt photoinitiator. In the presence of the photosensitizers, polymerizations proceeded with a short induction time, whereas little or no polymer was obtained in their absence.

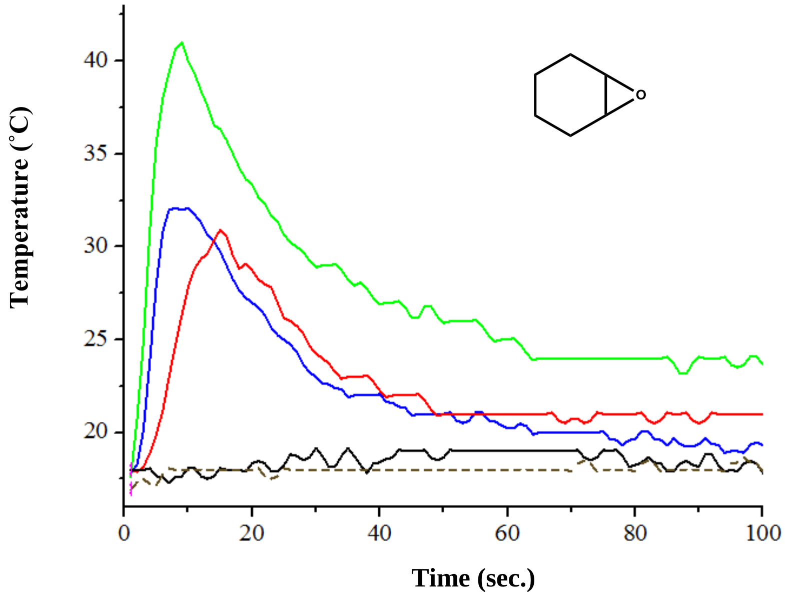


Figure 3.7: Cationic photopolymerization of 7-oxabicyclo [4.1.0] heptane (CHO) with $Ph_2I^+PF^-_6$ in the absence of a photosensitizer (▬), with photosensitizer in the absence of $Ph_2I^+PF^-_6$ (····), in the presence of 0.1 mol % PS1 (▬), 0.1 mol % PS2 (▬) and 1.0 mol % PS3 (▬) (light intensity: 15.1 mW cm^{-2}).

If we compare reactivities of vinyl ethers and epoxides, it fits well that vinyl ethers give a higher temperature rise than epoxides. Fast polymerization of divinyl ether monomers leads to the formation of three-dimensional polymer network but epoxy monomers are rigid and lack of bond rotation. [85]

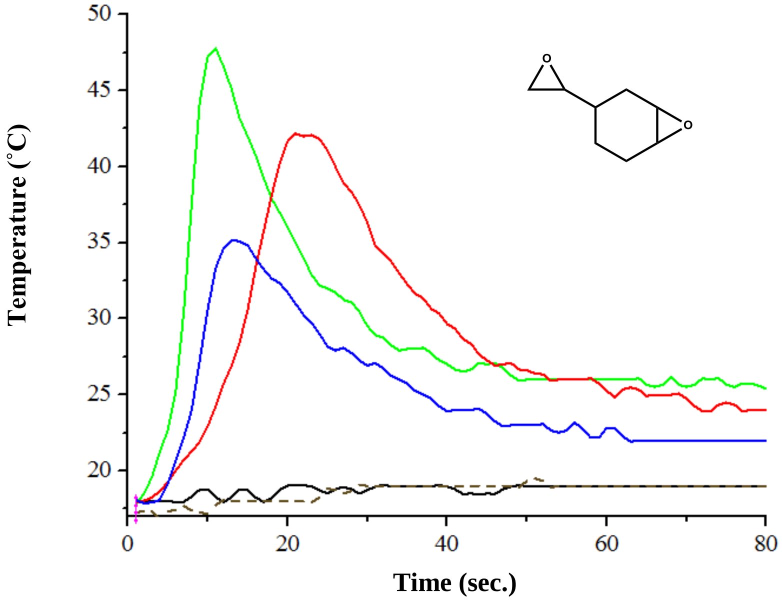


Figure 3.8: Cationic photopolymerization of 3-(oxiran-2yl)-7-oxabicyclo[4.1.0]heptane (VCHDO) with $Ph_2I^+PF^-_6$ in the absence of a photosensitizer (▬),with photosensitizer in the absence of $Ph_2I^+PF^-_6$ (••••), in the presence of 0.1 mol % PS1 (▬) , 0.1 mol % PS2 (▬) and 1.0 mol % PS3 (▬) (light intensity: 15.1 mW cm^{-2}).

Vinyl ethers (CEVE and DVE-3) were able to polymerize in the absence of photosensitizers due to their high reactivity. However, a higher temperature rise was observed in the presence of the each photosensitizer, as expected by the exothermic polymerization. It can be seen that PS1 was more reactive towards epoxides (CHO, VCHDO). This can be interpreted as the effect of ferrocene. According to the literature [11, 88], molecules containing ferrocenyl group are used to increase efficiency of photopolymerization of epoxide monomers. When ferrocene interacts with light, upper cyclopentyl ring of ferrocenium ion dissociates and initiates the photochemical reaction as described in Figure 3.9. [11], [86]

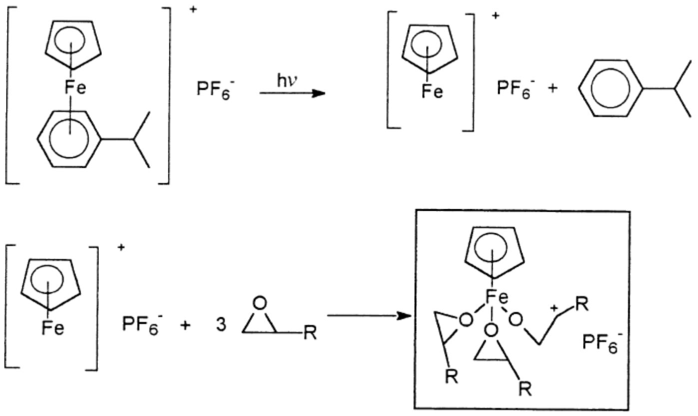


Figure 3.9: Mechanism of ferrocenium salt upon light exposure

PS3 reacted vigorously with vinyl ether type monomers (CEVE, DVE-3). High conjugation density of naphthanyl group increases the efficiency of photoinitiated polymerization with vinyl type monomers.

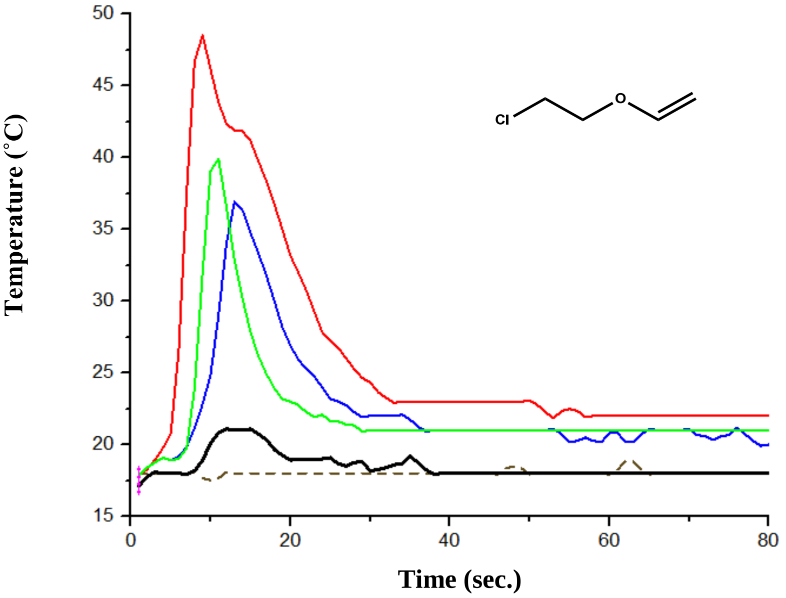


Figure 3.10: Cationic photopolymerization of (2-chloroethoy) ethane (CEVE) with $Ph_2I^+PF^-_6$ in the absence of a photosensitizer (▬), with photosensitizer in the absence of $Ph_2I^+PF^-_6$ (•••), in the presence of 0.1 mol % PS1 (▬), 0.1 mol % PS2 (▬) and 1.0 mol % PS3 (▬) (light intensity: 15.1 mW cm^{-2}).

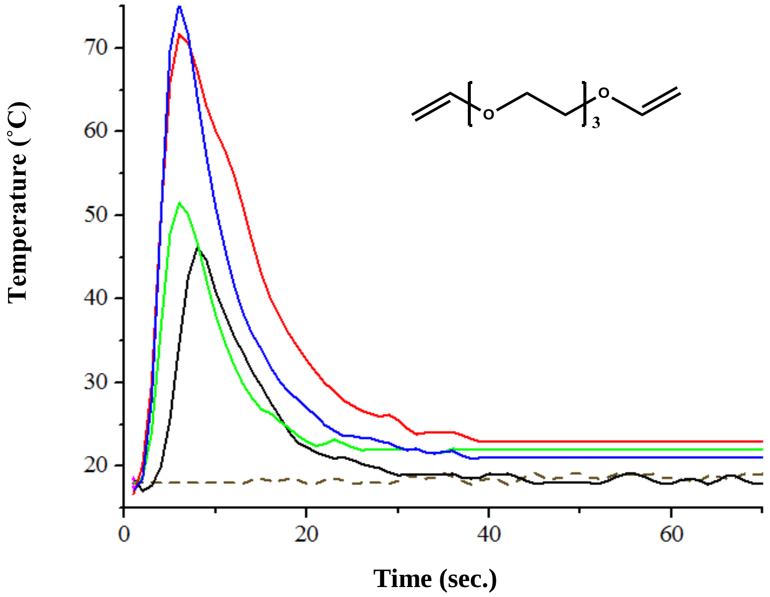


Figure 3.11: Cationic photopolymerization of 1,2-bis(vinyloxy)ethane (DVE-3) with $Ph_2I^+PF^-_6$ in the absence of a photosensitizer (▬), with photosensitizer in the absence of $Ph_2I^+PF^-_6$ (•••), in the presence of 0.1 mol % PS1 (▬) , 0.1 mol % PS2 (▬) and 1.0 mol % PS3 (▬) (light intensity: 15.1 mW cm^{-2}).

It is expected that glycidyl ethers undergo cationic polymerization with a lower rate when compared with vinyl ethers. [87] BPADGE polymerize very slowly without the aid of photosensitizers. Its polymerization rate increased to some extent with the help of photosensitizers where slow termination rate remained as it is.

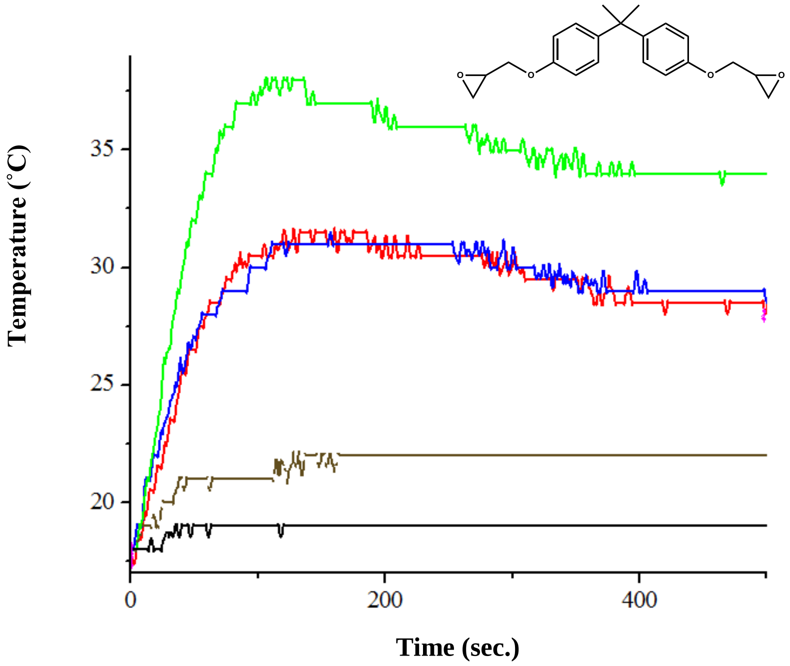


Figure 3.12: Cationic photopolymerization of 2,2’-(((propane-2,2-diylbis(4,1-phenylene)) bis(oxy))bis(methylene))bis(oxirane) (BPADGE)with Ph$_2$I$^+$PF$^-_6$ in the absence of a photosensitizer(▬) with photosensitizer in the absence of Ph$_2$I$^+$PF$^-_6$ (•••), in the presence of 0.1 mol % PS1 (▬) , 0.1 mol % PS2 (▬) and 1.0 mol % PS3 (▬)
(light intensity: 15.1 mW cm^{-2}).

It is concluded that quinoxaline derivative photosensitizer molecules are very efficient in markedly increasing the overall rate of cationic polymerization of the monomers.

3.1.4 Solar Irradiation Induced Poylmerization Of PS1, PS2 & PS3

As discussed in Section 3.1.1, the photosensitizers absorb light in visible region. So we examined their efficiencies in the photopolymerization of CHO using solar irradiation. Samples containing PS1, PS2 or PS3 were prepared and exposed to solar irradiation via AM 1.5G solar simulator as described in experimental section. PS1 containing solution with an orange color changed into dark brownish orange after 5 minutes (Figure 3.13). For PS2 containing solution the film surface changed color in 5 minutes to turn into dark green from orange (Figure 3.14). Finally, when PS3 containing solution was exposed to solar irradiation, its pinkish orange color changed to greenish dark yellow in 5 minutes (Figure 3.15). All of the polymer films were tack-free to touch.


(a) (b)

Figure 3.13: CHO / $Ph_2I^+PF_6^-$ / PS1 mixture **(a)** before exposure to solar irradiation, and **(b)** after 5 minutes of exposure.

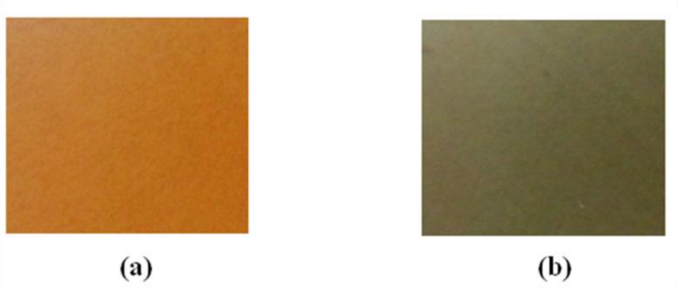

(a) (b)

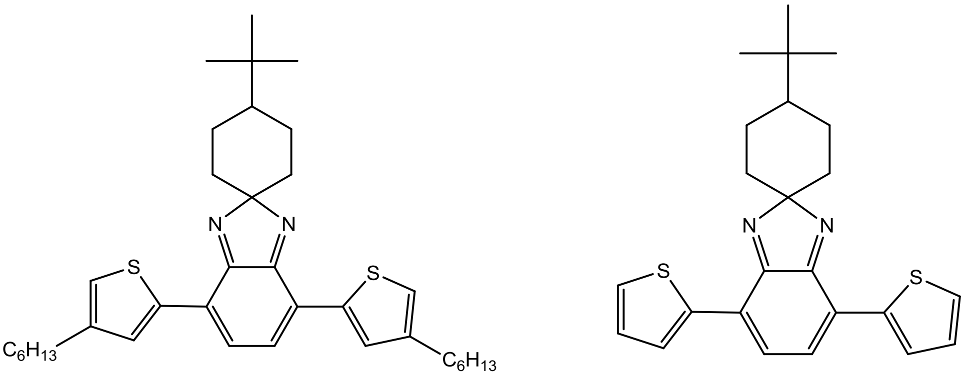
Figure 3.14: CHO / $Ph_2I^+PF_6^-$ / PS2 mixture **(a)** before exposure to solar irradiation, and **(b)** after 5 minutes of exposure.


(a) (b)

Figure 3.15: CHO / $Ph_2I^+PF_6^-$ / PS3 mixture **(a)** before exposure to solar irradiation, and **(b)** after 5 minutes of exposure.

3.2 Benzimidazole Derivatives As Photosensitizers

Structures of benzimidazole derivatives are given in Figure 3.16. Same procedure that has been explained in Section 3.1 was applied to demonstrate their potential as photosensitizers in the presence of diphenyliodonium salts.



BIHT (PS 4)

BIT (PS 5)

Figure 3.16: Benzimidazole derivatives as photosensitizers

3.2.1 UV – Vis Spectra Of PS 4 & PS 5

Benzimidazole molecules are derivated with a stereogenic carbon unit. Acceptor units in molecules are the same whereas the donor unit is different. Alkylated thiophenyl unit is expected to increase the solubility of molecules in different monomers. Since electron transfer occurs from thiophenyl unit to benzimidazole unit, their absorption range does not differ much. As seen in Figure 3.14, all photosensitizers under investigation have broad absorption bands between 350 nm and 560 nm. As a result of this data, photosensitization can occur in a wider spectral area than photoinitiators alone can achieve. Moreover, the oxidation potential values of photosensitizers are lowered with enhanced electron density in the photosensitizer molecules leading to more efficient polymerizations. The oxidation potentials of PS4 and PS5 are determined as 1.04 V [68] and 1.1 V [70] respectively by cyclic voltammetry. Low oxidation potentials facilitate electron transfer between photosensitizers and diphenyliodonium salt as explained previously by the Rehm-Weller equation, since the reaction will have a more negative free energy.

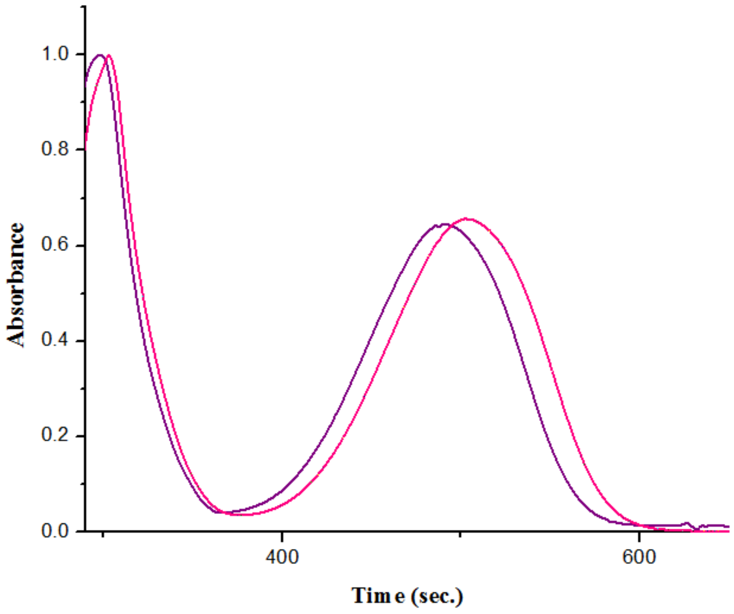


Figure 3.17: UV–Vis spectra of 1x 10^{-5}mol L^{-1} PS4 (▬), 1x 10^{-5}mol L^{-1} and PS5 (▬) in CH_2Cl_2.

3.2.2 Fluorescence Quenching Of PS 4 & PS 5

Proposed benzimidazole derivatives have a broader absorption range as seen in Figure 3.17. As a second step, exciplex formation is examined with Stern – Volmer graphs.

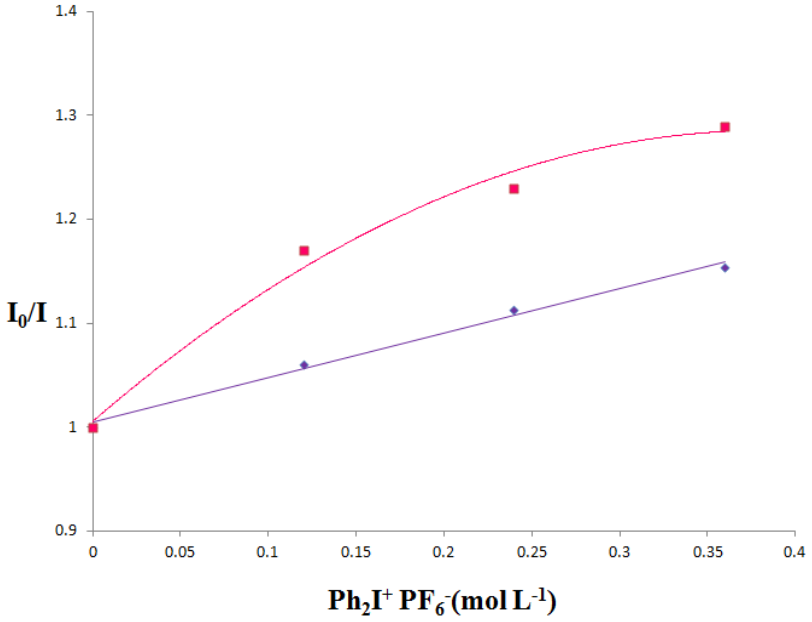


Figure 3.18: Stern-Volmer plot of the quenching of PS4 (▬) ($1x10^{-4}$M) and PS5 (▬) ($1x10^{-4}$ M) by diphenyliodonium hexafluorophosphate (Ph_2I^+ PF_6^-) in dichloromethane (excitation wavelength 510 nm) (I_0 = fluorescence intensity of PS containing solutions without $Ph_2I^+PF_6^-$, I = fluorescence intensity of PS solutions in the presence of $Ph_2I^+PF_6^-$).

As discussed earlier, linear correlation is an indication of dynamic quenching mechanism. A linear correlation is observed for PS 5. Exciplex formation in the reaction medium of PS 5 was proven with this graph. However, PS 4 has a non-linear increasing slope, which shows less accessibility of the excited fluorophore. Some sensitizer molecules are accessible and some are less accessible according to that graph. Donor unit of PS 4 has hexyl groups on its both sides. Those hexyl groups are supposed to increase the solubility of the molecule. At the same time, they might prevent the formation of a complex (exciplex). [83]

3.2.3 Optical Pyrometry Studies Of PS 4 & PS 5

Optical pyrometry experiments were conducted to study the photosensitization behavior of PS 4 and PS 5. All OP experiments were conducted in the presence of 0.1 % mol photosensitizer under UV light of an intensity of 15.1 mWcm^{-2} unless otherwise indicated.

Solutions were prepared with different monomers in the presence and absence of both photosensitizer and photoinitiator. The essentiality of the photoinitiator was confirmed again since no polymerization was observed when photoinitiator was absent in the solutions. All photosensitizers were completely soluble in various cationically polymerizable monomers. The OP technique was used to monitor the progress of polymerization. Figure 3.19 –Figure 3.23 illustrates the photopolymerizations of CHO, VCHDO, CEVE, DVE-3, and BPADGE using diaryliodonium salt photoinitiator. In the presence of the photosensitizers, polymerizations proceeded with a short induction time, whereas little or no polymer was obtained in their absence.

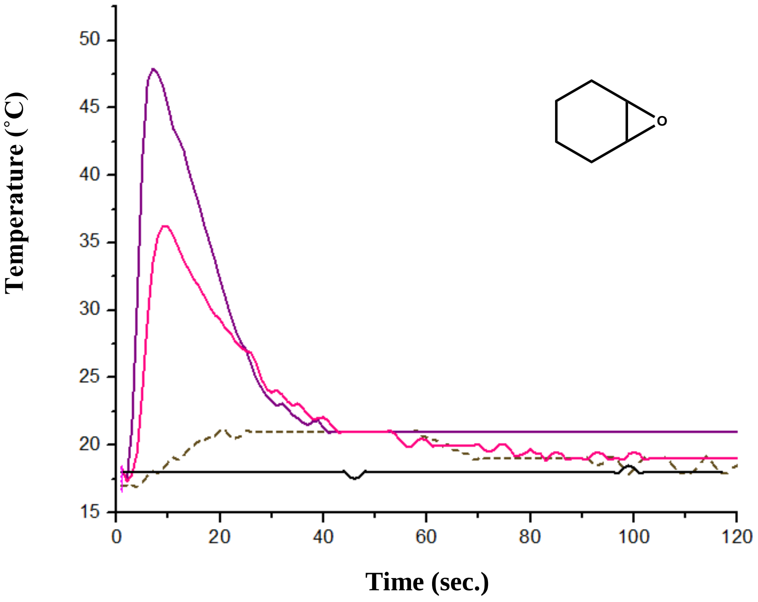


Figure 3.19: Cationic photopolymerization of 7-oxabicyclo [4.1.0] heptane (CHO) with $Ph_2I^+PF^-_6$ in the absence of a photosensitizer (—), with photosensitizer in the absence of $Ph_2I^+PF^-_6$ (•••), in the presence of 0.1 mol % PS4 (—) and 0.1 mol % PS5 (—) (light intensity: 15.1 mW cm^{-2}).

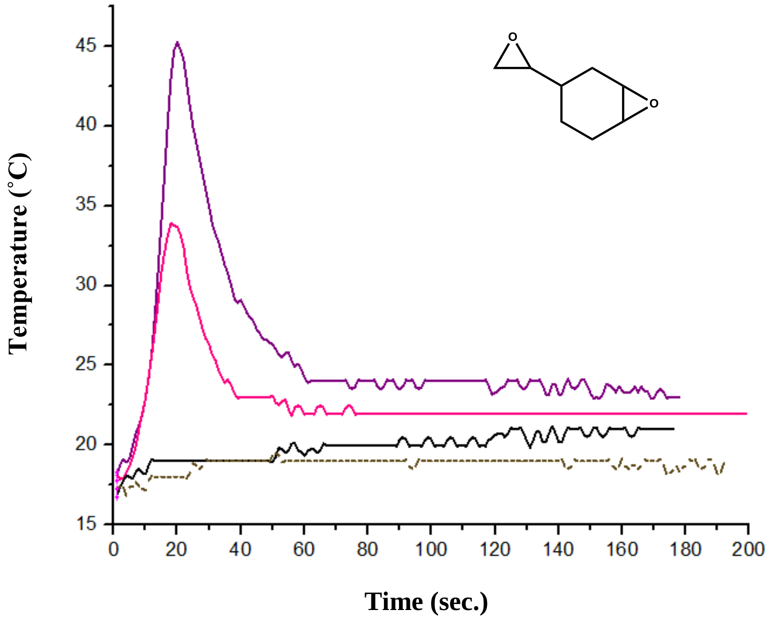


Figure 3.20: Cationic photopolymerization of 3-(oxiran-2yl)-7-oxabicyclo [4.1.0] heptane (VCHDO) with $Ph_2I^+PF^-_6$ in the absence of a photosensitizer (—), with photosensitizer in the absence of $Ph_2I^+PF^-_6$ (•••), in the presence of 0.1 mol % PS4 (—) and 0.1 mol % PS5 (—) (light intensity: 15.1 mW cm^{-2}).

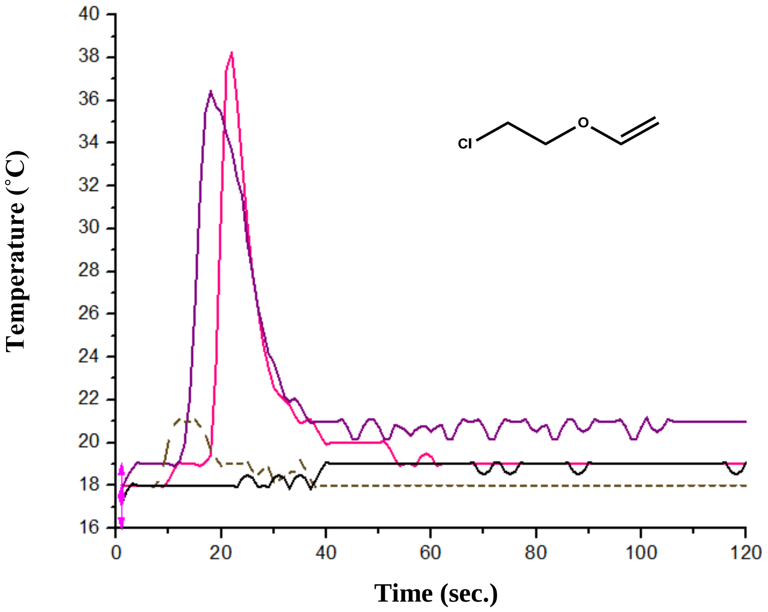


Figure 3.21: Cationic photopolymerization of (2-chloroethoxy) ethane (CEVE) with $Ph_2I^+PF^-_6$ in the absence of a photosensitizer (—), with photosensitizer in the absence of $Ph_2I^+PF^-_6$ (•••), in the presence of 0.1 mol % PS4 (—) and 0.1 mol % PS5 (—) (light intensity: 15.1 mW cm^{-2}).

As mentioned earlier, vinyl ethers (CEVE and DVE-3) reveal polymerization even in the absence of photosensitizers; however, much higher polymerization rates were obtained with the use of photosensitizers.

PS 5 yielded an even higher temperature rise compared to PS 4. It can be seen that PS 5 was more reactive towards epoxides (CHO, VCHDO). The reason for this difference is the lack of exciplex formation in PS 4 reaction medium. [69]

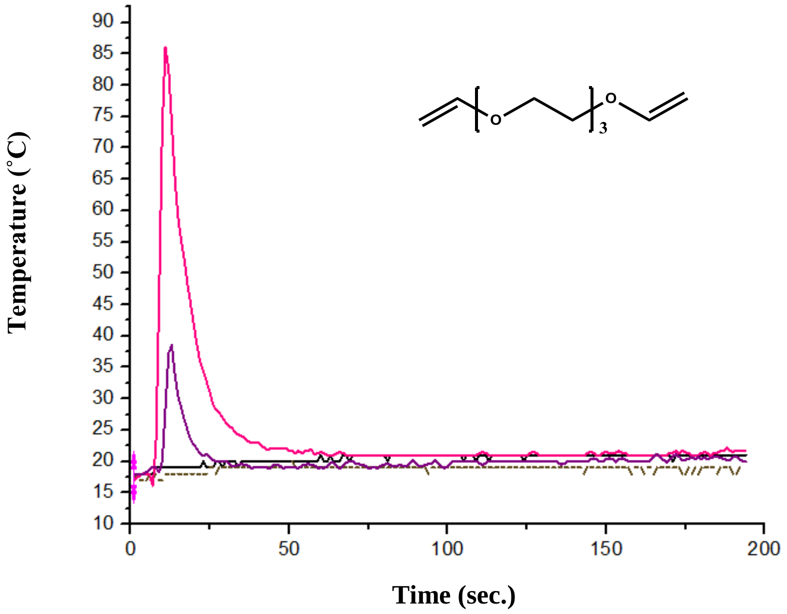


Figure 3.22: Cationic photopolymerization of 1, 2-bis (vinyloxy) ethane (DVE-3) with $Ph_2I^+PF^-_6$ in the absence of a photosensitizer (━), with photosensitizer in the absence of $Ph_2I^+PF^-_6$ (•••), in the presence of 0.1 mol % PS4 (━) and 0.1 mol % PS5 (━) (light intensity: 15.1 mW cm^{-2}).

BPADGE polymerize very slowly without the aid of photosensitizers. Its polymerization rate increased to some extent with the help of photosensitizers whereas the termination rate remained slow.

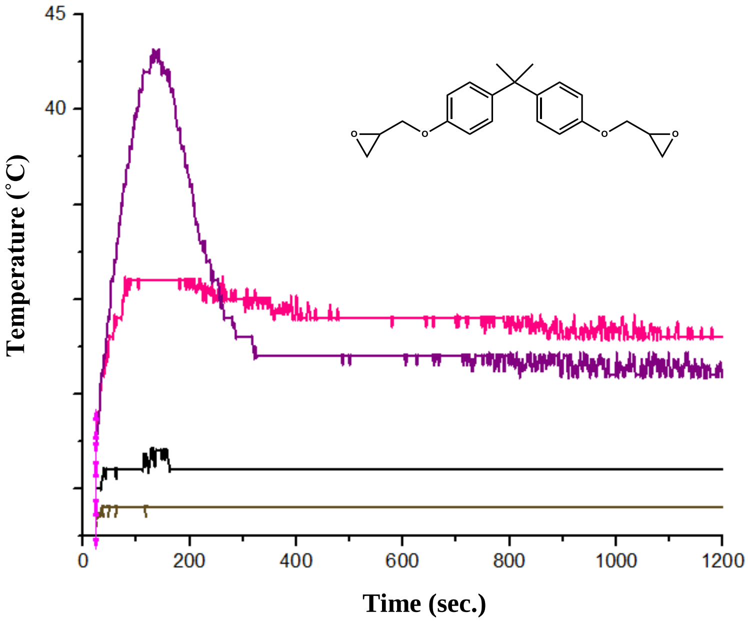


Figure 3.23: Cationic photopolymerization of 2,2’-(((propane-2,2-diylbis(4,1-phenylene)) bis(oxy))bis(methylene))bis(oxirane)(BPADGE)with $Ph_2I^+PF^-_6$ in the absence of a photosensitizer (—), with photosensitizer in the absence of $Ph_2I^+PF^-_6$ (•••), in the presence of 0.1 mol % PS4 (—) and 0.1 mol % PS5 (—) (light intensity: 15.1 mW cm^{-2}).

It is concluded that photosensitizer molecules are very efficient in markedly increasing the overall rate of cationic polymerization of the monomers.

3.2.4 Solar Irradiation Induced Photopolymerization Of PS 4 & PS 5

As discussed in Section 3.2.1, the photosensitizers absorb light in visible region. Hence, we examined their efficiencies in the photopolymerization of CHO using solar irradiation. Samples containing PS 4 or PS 5 were prepared and exposed to solar irradiation via AM 1.5G solar simulator as described in Experimental. PS 4 containing solution with a light pink color changed to a dark reddish pink after 2 minutes irradiation (Figure 3.24). Color of the PS 5 containing solution changed in 2 minutes to turn into brownish purple from bright pink. (Figure 3.25)


(a) (b)

Figure 3.24: CHO / $Ph_2I^+PF_6^-$ / PS4 mixture **(a)** before exposure to solar irradiation, and **(b)** after 2 minutes of exposure.

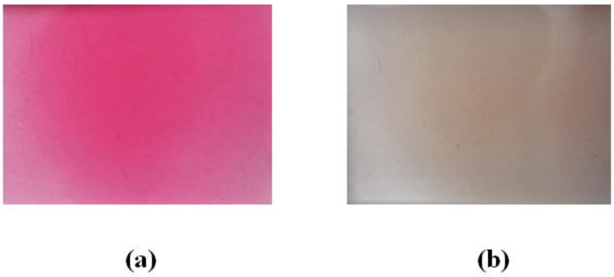
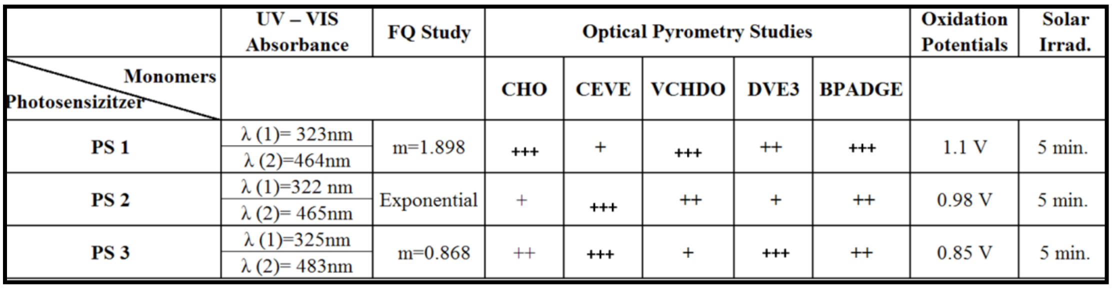

(a) (b)

Figure 3.25: CHO / $Ph_2I^+PF_6^-$ / PS5 mixture **(a)** before exposure to solar irradiation, and **(b)** after 2 minutes of exposure.

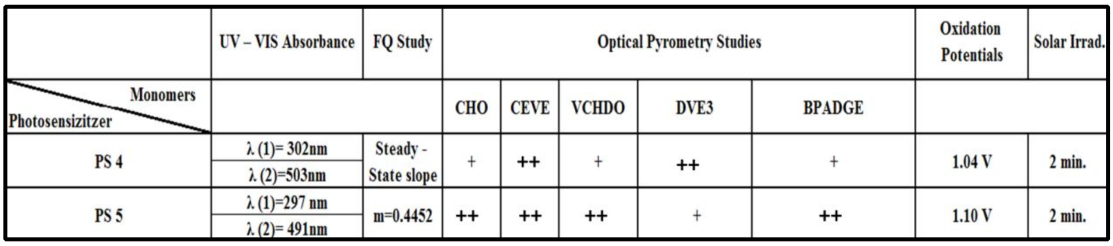
3.3 Comparison of Photosensitizers

Table 3.1: Comparison of PS1, PS2 and PS3



	UV – VIS Absorbance	FQ Study	Optical Pyrometry Studies					Oxidation Potentials	Solar Irrad.
Monomers / Photosensizitzer			CHO	CEVE	VCHDO	DVE3	BPADGE		
PS 1	λ (1)= 323nm λ (2)=464nm	m=1.898	+++	+	+++	++	+++	1.1 V	5 min.
PS 2	λ (1)=322 nm λ (2)= 465nm	Exponential	+	+++	++	+	++	0.98 V	5 min.
PS 3	λ (1)=325nm λ (2)= 483nm	m=0.868	++	+++	+	+++	++	0.85 V	5 min.

Table 3.2: Comparison of PS4 and PS5



	UV – VIS Absorbance	FQ Study	Optical Pyrometry Studies					Oxidation Potentials	Solar Irrad.
Monomers / Photosensizitzer			CHO	CEVE	VCHDO	DVE3	BPADGE		
PS 4	λ (1)= 302nm λ (2)=503nm	Steady - State slope	+	++	+	++	+	1.04 V	2 min.
PS 5	λ (1)=297 nm λ (2)= 491nm	m=0.4452	++	++	++	+	++	1.10 V	2 min.

CHAPTER 4

CONCLUSION

This study aimed to understand photosensitization mechanism in cationic photopolymerization and proposed five different molecules to be used as photosensitizers. Prospective molecules were separated into two different sets.

In the first set, quinoxaline derivatives, the effect of mid group was investigated. Three quinoxaline derivatives, functionalized with ferrocene, naphthanyl and benzyl units combined with EDOT donor group were utilized as photosensitizers for diphenyliodonium salts to facilitate cationic polymerization. The effect of ferrocenyl was pronounced during the polymerization of epoxide monomers upon irradiation. According to the proposed mechanism, ferrocenyl group was divided in two parts and led more efficient polymerization. When photopolymerization of vinyl ether type monomers were investigating in the presence of photosensitizers, increased electron density on naphthanyl units gave higher temperature rise, so faster polymerization.

The second set of molecules, benzimidazole derivatives, was studied to understand the effect of donor units of the molecules. Two benzimidazole units, functionalized with tert -butyl cyclohexyl unit coupled with thiophene and trihexyl thiophene donor groups were used as photosensitizers during photopolymerization in the presence of diphenyliodonium salt. Photosensitizers displayed extended spectral sensitivity, low oxidation potential, and excellent solubility in a variety of monomers. It was shown that photopolymerizations became faster, revealing little or no induction time, and more efficient under both long wavelength UV light and solar irradiation in the presence of suggested photosensitizers.

To sum up all molecules are good candidates as photosensitizers. Further studies, such as their stability and rheology properties can be investigated before introducing into industrial applications.

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APPENDIX A

NMR DATA

NMR spectra were recorded on a Bruker DPX 400.
Chemical shifts δ are reported in ppm relative to $CHCl_3$ (^{1}H: δ=7.27), $CDCl_3$ (^{13}C: δ=77.0) and CCl4 (^{13}C: δ=96.4) as internal standards.
^{1}H and ^{13}C NMR spectra of products are given below.

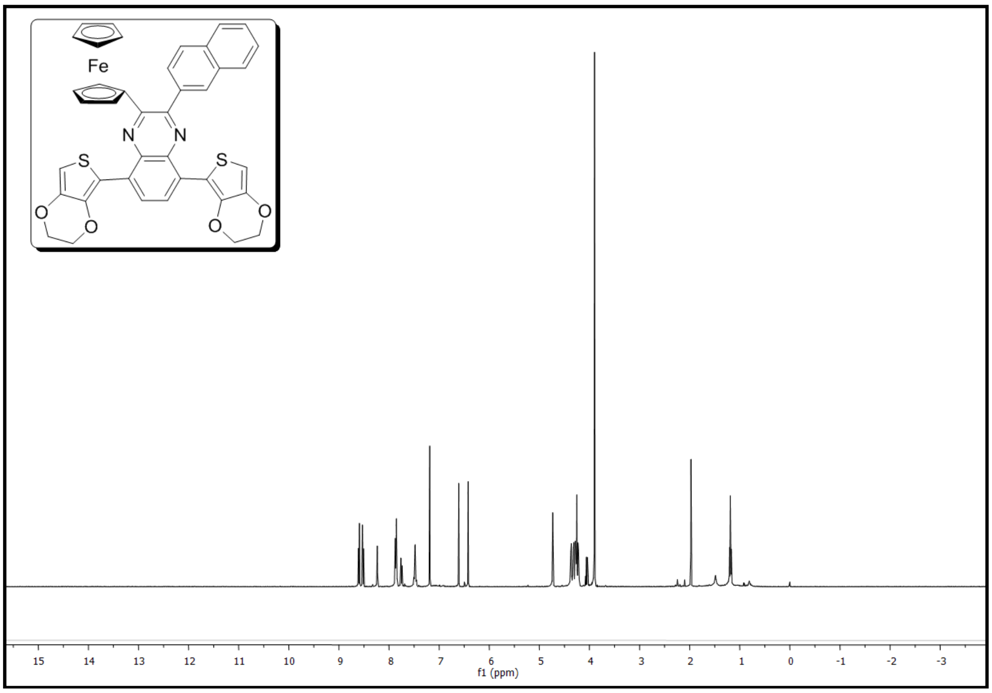

Figure A. 1 ^{1}H-NMR spectrum of 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-(naphthalen-2-yl)-3-ferrocenyl-4a,8a-dihydroquinoxaline (PS1)

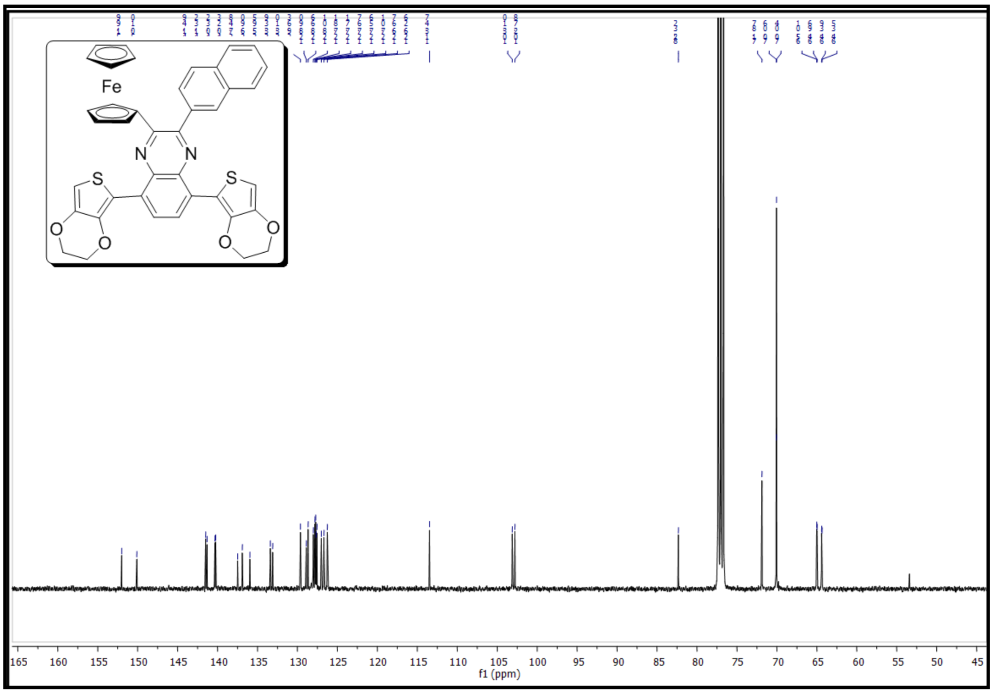

Figure A. 22 ^{13}C-NMR spectrum of 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-(naphthalen-2-yl)-3-ferrocenyl-4a,8a dihydroquinoxaline (PS1)

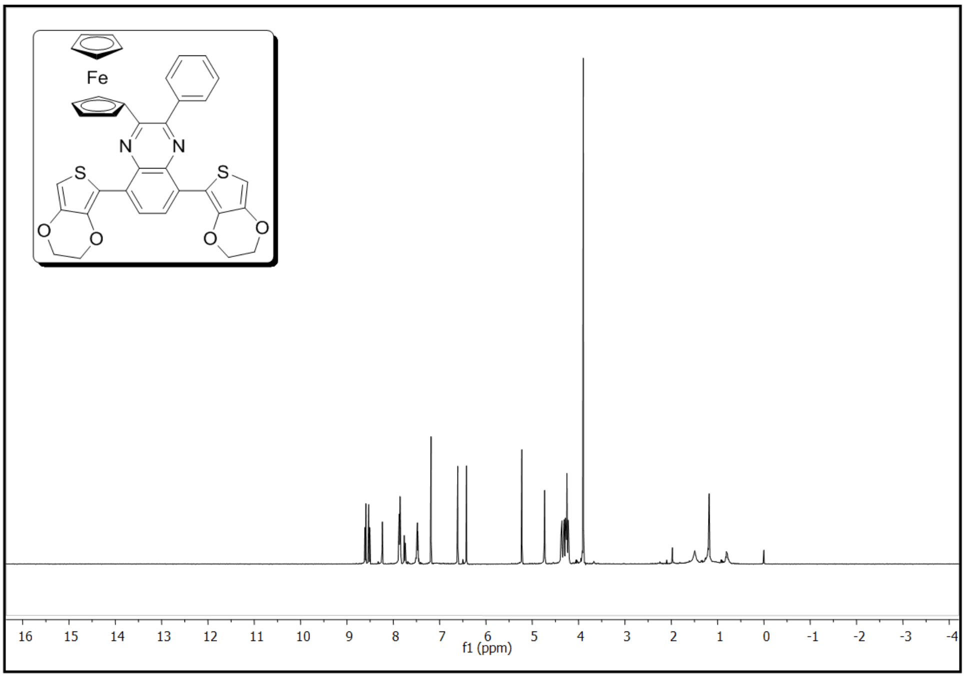

Figure A.3: ^{1}H-NMR spectrum of 5, 8-bis (2, 3-dihydrothieno [3, 4-b][1,4]dioxin-5-yl)-2-(phenyll)-3-ferrocenylquinoxaline (PS2)

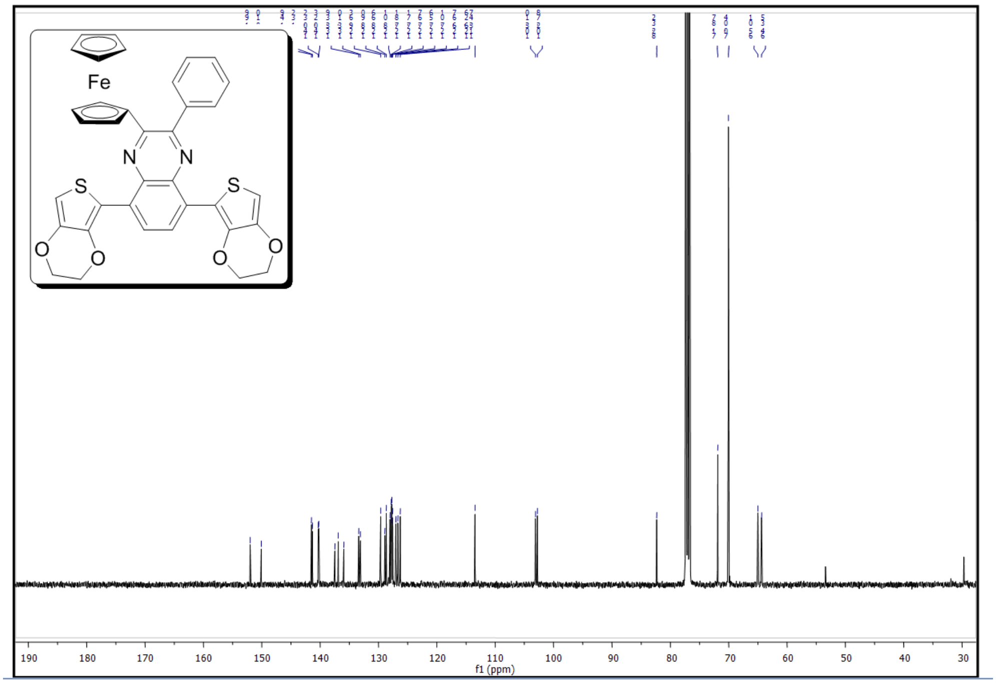

Figure A.4: ^{13}C-NMR spectrum of 5, 8-bis (2, 3-dihydrothieno [3, 4-b][1,4]dioxin-5-yl)-2-(phenyll)-3-ferrocenylquinoxaline (PS2)

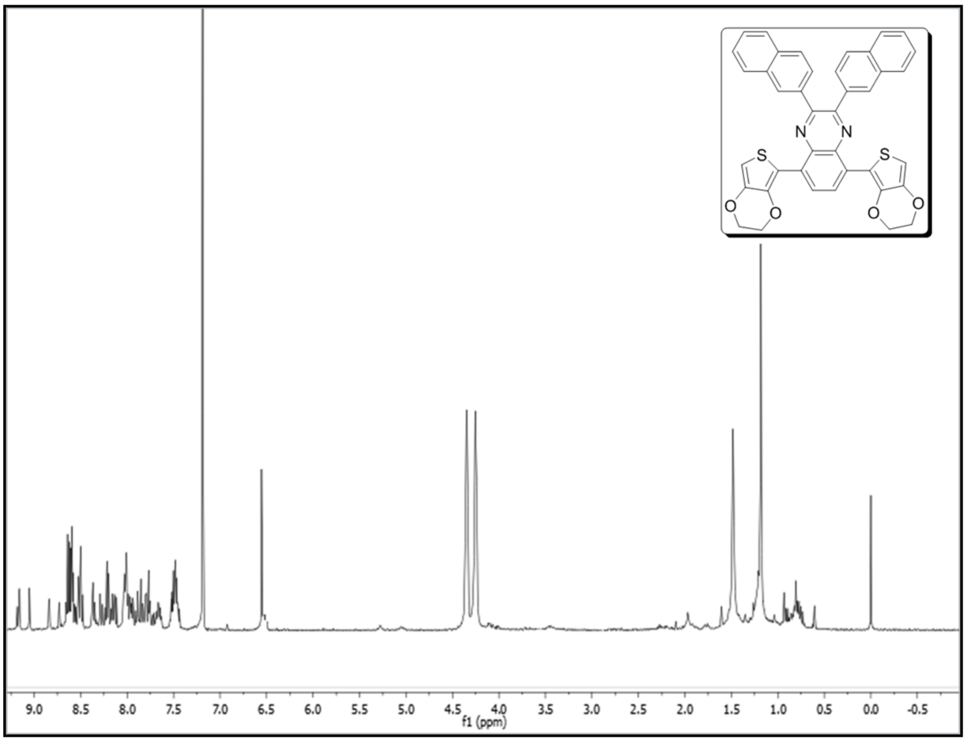

Figure A.5: ^{1}H-NMR spectrum of 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di (naphthalen-2-yl)quinoxaline (PS3)

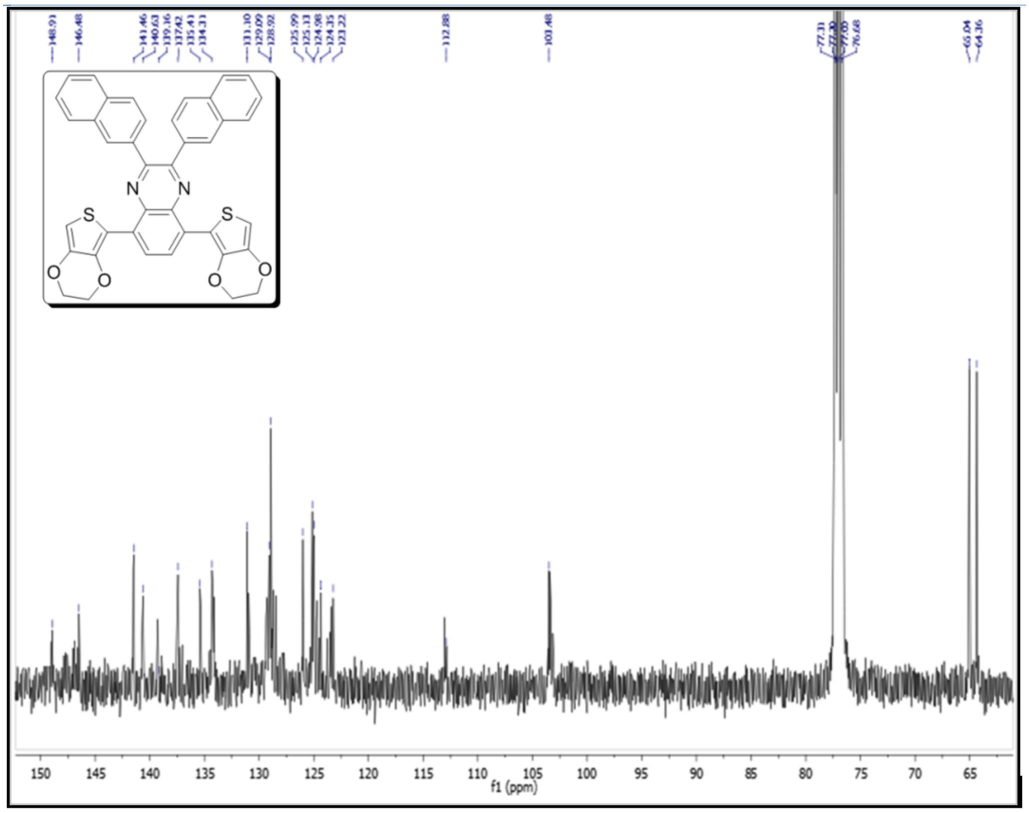

Figure A.6: ^{13}C-NMR spectrum of 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di (naphthalen-2-yl) quinoxaline (PS3)