

LONG WAVELENGTH PHOTSENSITIZERS WITH BENZOTRIAZOLE AND
BENZIMIDAZOLE SKELETONS FOR CATIONIC POLYMERIZATION

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**LONG WAVELENGTH PHOTSENSITIZERS WITH
BENZOTRIAZOLE AND BENZIMIDAZOLE SKELETONS FOR CATIONIC
POLYMERIZATION**

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ABSTRACT

LONG WAVELENGTH PHOTSENSITIZERS WITH BENZOTRIAZOLE AND BENZIMIDAZOLE SKELETONS FOR CATIONIC POLYMERIZATION

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Benzimidazole and benzotriazole derivatives, 4-(2,3-Dihydrothieno[3,4-b][1,4]dioxin-5-yl)-7-(2,3-dihydrothieno[3,4b][1,4]dioxin-7-yl)-2-benzyl-1H-benzo[d]imidazole (BIm-Ed), 2-benzyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (BBTS), and 2-benzyl-4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2H-benzo[d][1,2,3]triazole (BBTES) were employed as photosensitizers for diaryliodonium salt photoinitiators in cationic photopolymerization of various epoxide and vinyl ether monomers. Diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) salt was used as the photoinitiator in this study. Extended conjugation and electron-rich moieties of the photosensitizers enabled the use of long wavelength UV and visible light emitting light sources in cationic photopolymerizations. Polymerizations were achieved at room temperature and monitored by optical pyrometry. Photopolymerization of a diepoxide monomer with ambient solar irradiation was examined.

Keywords: Benzimidazole; benzotriazole; photosensitizer; cationic polymerization; diaryliodonium salts; epoxides; photopolymerization.

ÖZ

YÜKSEK DALGA BOYUNDA SOĞURABİLEN BENZOTRİAZOL VE BENZİMİDAZOL TÜREVİ FOTOSENSİTİZERLER İLE KATYONİK POLİMERİZASYON

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Benzimidazol ve benzotriazol türevleri, 4-(2,3-dihidrotyono[3,4-b][1,4]dioksin-5-il)-7-(2,3 dihidrotyono[3,4b][1,4] dioksin-7-il)-2-benzil-1H-benzo[d]imidazol(BIm-Ed),2-benzil-4,7-di(tiyofen-2-il)-2H-benzo[d][1,2,3]triazol (BBTS) ve 2-benzil-4,7-bis(2,3-dihidrotyono[3,4-b][1,4]dioksin-5-il)-2H-benzo[d] [1,2,3]triazol (BBTES) sentezlenip çeşitli epoksi ve vinil eter monomerlerinin katyonik polimerizasyonunda diariliyodonyum tuzu fotobaşlatıcıları için fotosensitizer olarak kullanılmıştır. Bu çalışmada difenil iyodonyum hekzaflorofosfat ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) tuzu fotobaşlatıcı görevi görmüştür. Benzimidazol ve benzotriazol fotosensitizerlerin yüksek konjugasyona ve elektronca zengin gruplara sahip olması UV ve görünür bölgede katyonik fotopolimerizasyonun gerçekleşmesini sağlamıştır. Oda sıcaklığında gerçekleşen polimerizasyonlar optik pirometre cihazıyla incelenmiştir. Ayrıca diepoksi monomerinin güneş ışığıyla da fotopolimerizasyonu çalışılmıştır.

Anahtar kelimeler: Benzimidazol, benzotriazol, fotosensitizer, katyonik polimerizasyon, diaryliodonium tuzu, epoksi, fotopolimerizasyon.

To My Family

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LIST OF ABBREVIATIONS

BBTES	2-benzyl-4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2H-benzo[d][1,2,3] triazole
BBTS	2-benzyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3] triazole
BIm-Ed	2,4-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-7-(2,3-Dihydrothieno[3,4-b][1,4]dioxin-7-yl)-1H-benzo[d]imidazole.
CEVE	2-chloroethylvinylether
CHO	Cyclohexene oxide
DCM	Dichloromethane
EDOT	3,4-Ethylenedioxythiophene
ERL-4221E	3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate
LED	Light Emitting Diode
Ph₂I⁺PF₆⁻	Diphenyliodonium hexafluorophosphate
PI	Photoinitiator
PS	Photosensitizer
THF	Tetrahydrofuran
UV	Ultra Violet
VCHDO	Vinylcyclohexene Dioxide

CHAPTER 1

INTRODUCTION

1.1 Photopolymerization

Photopolymerization is considered as a groundbreaking innovation in recent years due to its rapidity, low energy requirement, low cost, room temperature treatment, non-polluting and solvent free formulations. Photopolymerization technique has been utilized in various applications such as coatings, adhesives, stereolithography, LEDs, circuit boards imaging etc. [1,2] In addition to these there are some other applications such as laser videodiscs, curing of acrylate dental fillings, [3] and 3D objects. [4]

Photopolymerization has also spreaded into biomaterials field. Some of the applications in this field are bones and tissue engineering, microchips, optical resins and recoding media, surface relief gratings, anisotropic materials, polymeric photo-optical control materials, clay and metal nanocomposites, photoresponsive polymers, liquid crystalline materials, interpenetrated networks, microlenses etc. [5]

Advantages of photopolymerization can easily be seen when it is compared to thermal polymerization. High temperatures are not required to perform photopolymerization whereas for thermal polymerization high temperatures are required. Photopolymerization technique is also useful for the monomers which can undergo polymerization only at low temperatures. Dental filling is a striking example for the advantages of photopolymerization since it cannot be carried out at high temperature. In addition to these, enzyme immobilization which is a biochemical application has to be carried out at low temperatures. These processes can be achieved by photopolymerization. [5]

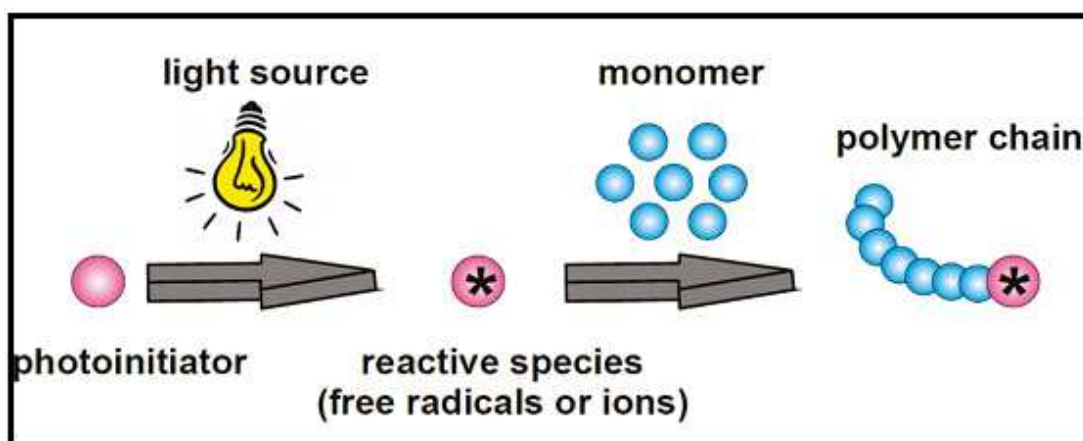


Figure 1.1 General Representation of Photoinitiated Polymerization. [5]

Photoinitiated polymerization is based on the excitation of the photoinitiator and/or photosensitizer by UV-Vis light irradiation. [6] By the absorption of light, photoinitiator becomes excited. Subsequently, hydrogen abstraction or electron transfer reaction may take place. Propagation readily occurs with the formation of reactive species. Then, termination process completes the photopolymerization. In this technique, polymerization is initiated by light and the resulting chain ends can be radicals [7] or cations [8] and in some cases it can be anions or weak bases. [9] If the chain end is radical polymerization type is radicalic polymerization. (Eq 1.1) If the chain end is cation, it is cationic polymerization (Eq 1.2) and if the chain end is anion, it is anionic polymerization.

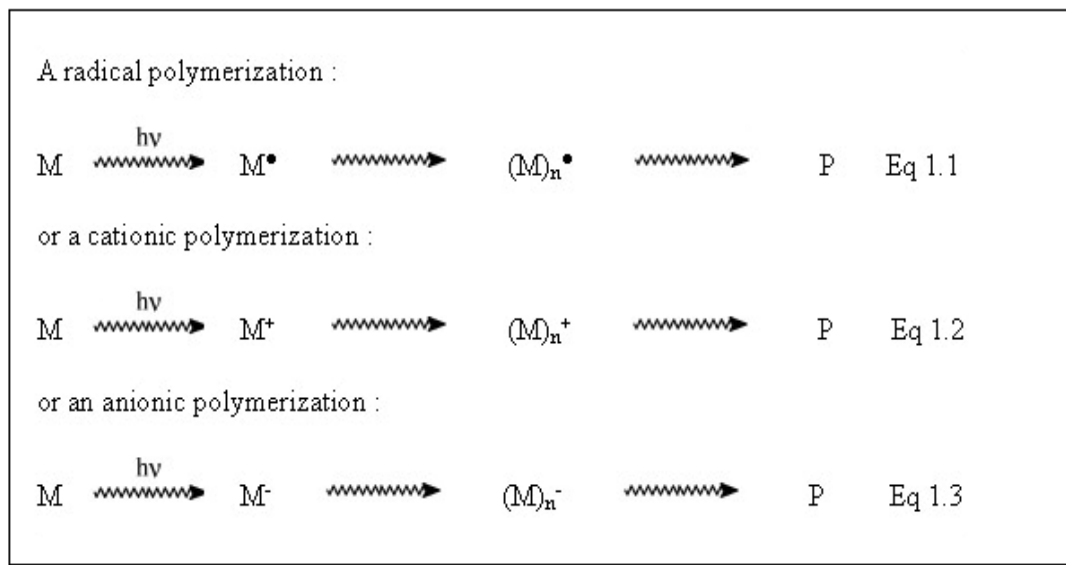


Figure 1.2 Types of Photopolymerization. [10]

Free radical and cationic photopolymerizations are very important due to their wide range of applications in industry.

1.2 Photoinitiated Free Radical Polymerization

Use of photoinitiated free radical polymerization has spreaded widely in industrial applications. It is mostly used in polymerizations of monomers having olefinic double bonds. Figure 1.3 gives the mechanism of photoinitiated free radical polymerization.

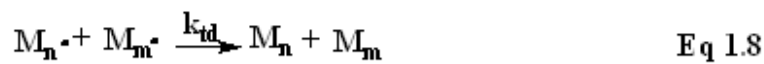


Figure 1. 3 Photoinitiated Free Radical Polymerization.

Photoinitiation step: This step consists of two reactions. First one is the production of radicals by homolytic dissociation of the initiator species. (Eq 1.4) k_d is the rate constant for the initiator dissociation. Following this reaction, addition of the radical to the monomer takes place to produce chain initiation species $M_1\cdot$ (Eq 1.5). k_i is the rate constant for the initiation step.

Propagation step: This step involves the attack of the monomer radical to another monomer resulting in growing polymer chain and k_p is the rate constant for propagation step. (Eq 1.6)

Termination step: Termination of the photoinitiated free radical polymerization occurs in two ways.

One of them is the reaction of monomers by coupling (Eq 1.7) and the other one is the reaction of monomers by disproportionation. (Eq 1.8) k_{tc} and k_{td} are rate constants for coupling and disproportionation reactions.

Photoinitiators employed in free radical polymerization have spectral sensitivity in near UV and Vis range. [11] There are two types of photoinitiators for photoinitiated free radical polymerization; cleavage (Type 1) and H abstraction (Type 2) initiators. [12, 13]

Type 1 photoinitiators are mostly aromatic carbonyl compounds. They undergo α -cleavage with the absorption of the light yielding free radicals. In Figure 1.4 photoinitiation mechanism of the benzoin is given as an example for this type of photoinitiators.

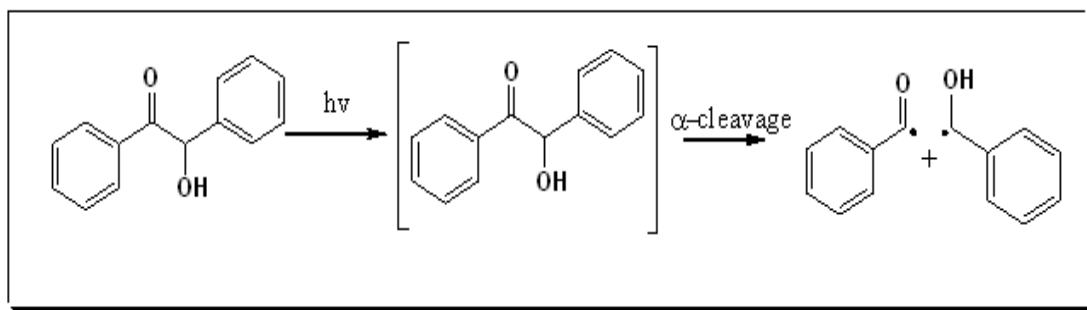


Figure 1.4 Photolytic α -Cleavage of Benzoin.

Benzoin and derivatives are mostly used photoinitiators due to their several advantages such as high quantum yield and reactivity of the free radicals. Commonly, benzoin derivatives are used in polymerization of styrene monomers. Aromatic ketones such as benzophenone, thioxanthenes, and quionones etc. are the basic Type 2 photoinitiators. Figure 1.5 shows the photoinitiation mechanism of benzophenone:

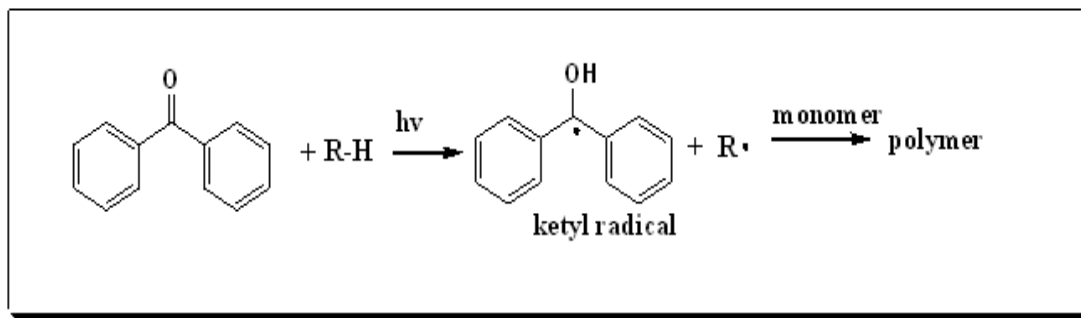


Figure 1.5 Type II Photoinitiation Mechanism with Benzophenone and Hydrogen Donors.

When these two types of photoinitiators are compared, it can be concluded that generation of free radicals from the photolysis of Type 2 photoinitiators is slower than that of Type 1 photoinitiators. Also, curing rate of Type 2 is again slower than that of Type 1 due to the bimolecular reaction of Type 2.

Monomers used in free radical polymerization possess unsaturated C=C bonds. Unsaturated monomers are prone to free radical polymerization because free radicals are neutral and they do not need to have electron donating or withdrawing groups. Acrylate and methacrylate monomers are most widely used in photoinitiated free radical polymerization. Having high reaction rates enables these monomers to be involved in film and coating industry.

1.3 Photoinitiated Cationic Polymerization

Although photoinitiated free radical polymerization dominates in majority of industrial applications, photoinitiated cationic polymerization has gained significant interest in recent years. This can be explained by the advantages of cationic photopolymerization over free radical photopolymerization. [14, 15]

Free radical polymerization is limited to monomers having olefinic double bonds whereas epoxide and vinyl monomers can also be polymerized by photoinitiated cationic polymerization. In addition, these monomers have low volatility, low toxicity, and good rheological properties. [16] Free radical photopolymerization has molecular oxygen inhibition problem. Initiating and propagating radicals are quenched by O₂ yielding highly unstable peroxy radicals, which cannot take place in further polymerization reactions. (Figure 1.6) [17, 18, 19, 20, 21] On the other hand, photoinitiated cationic polymerization does not have this type of inhibition problem. Thus, polymerization can be achieved in the presence of air.

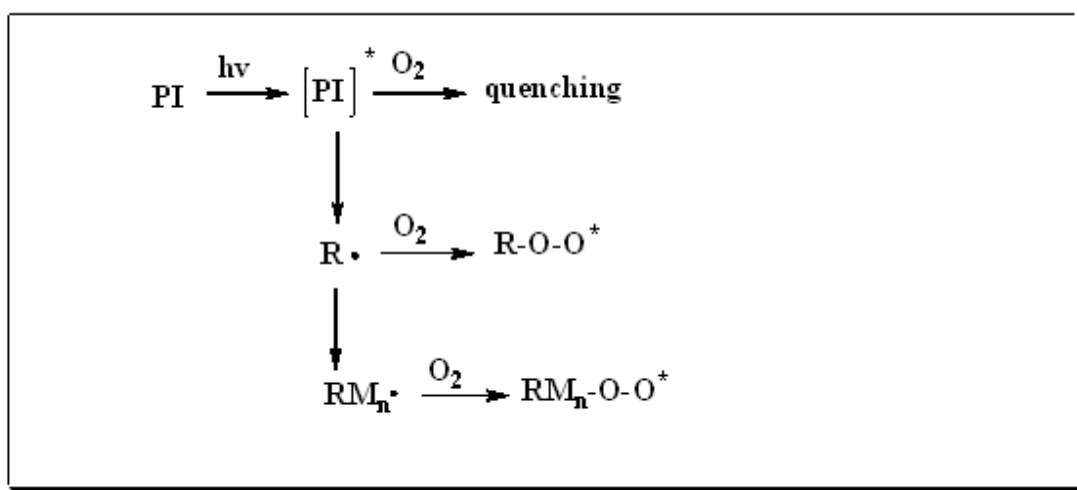


Figure 1.6 Inhibition of Photoinitiated Polymerization Reaction by Oxygen.

Another problem is shrinkage which negatively effects applications that require accurate shape and size during free radical polymerization of acrylates and methacrylates. However, this problem is less pronounced for epoxy monomers which are prone to photoinitiated cationic polymerization. [5] Termination lifetime is also an important difference between these polymerization types. Free radicals have very short active center life times. On the other hand, cationic active center lifetime is longer because time needed for the consumption of active centers is very long in cationic polymerization. [22] Therefore, cationic photopolymerization is preferred

for various applications in industry. [1] Photoinitiated cationic polymerization is mostly used in stereolithography, LED imaging, circuit boards imaging, curing of dental fillings, photoresists, laser induced fabrication of 3D objects, etc. [23, 24, 25, 26, 4, 27]

1.4 Photoinitiators

Photoinitiated cationic polymerization has received great interest as a new UV curing system due to development of photosensitive onium salts. Crivello and Lam showed the initiation mechanism with onium salt photolysis. [28] Since cationic initiators caused gelation, cationic polymerization was impossible to be used in practical applications until the discovery of onium salts. Since onium salts are highly efficient and photosensitive initiators, they provide very rapid polymerization in many applications. The most commonly used cationic initiators are diaryliodonium salts [29] and triarylsulfonium salts [30] because they are thermally stable, soluble in most of the cationically polymerizable monomers, and efficient in producing reactive species when they are irradiated. [31] These salts have high performance in photoinitiated cationic polymerization by using the short to mid-wavelength UV light. [32]

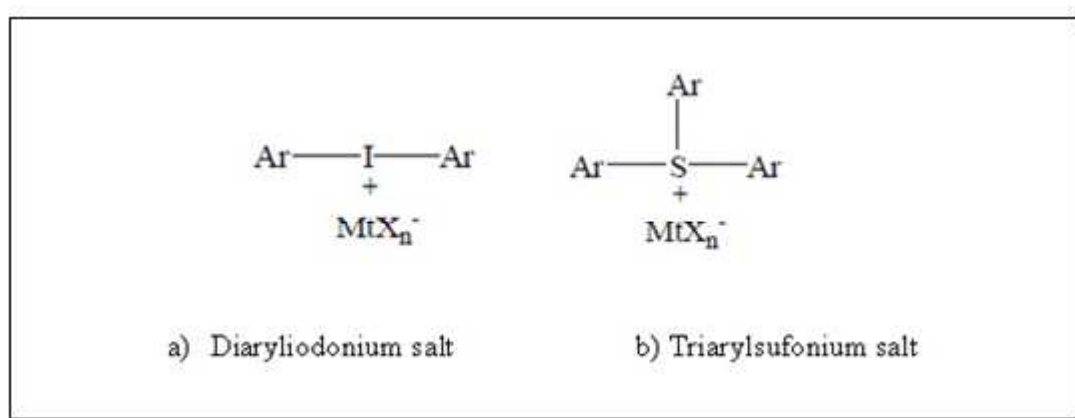
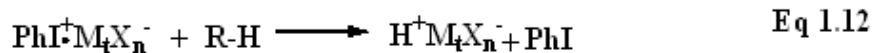
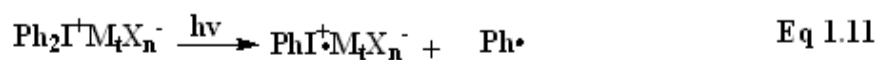


Figure 1.7 Diaryliodonium and Triarylsulfonium salts.

Efficiency of photoinitiators depends on cationic and anionic moieties of the molecules. UV absorption characteristics, ability to be photosensitized, quantum yield, and thermal stability of the photoinitiator are mostly based on cationic portion of the molecule. Upon irradiation by UV light, onium salt produces Brønsted acid which initiates the polymerization. Acid formation strength of the photoinitiator depends on the anionic portion of the molecule. Nucleophilicity of the anion affects the rate of polymerization. Nucleophilicity of the counter ion effects the performance of the initiator in the photoinitiated cationic polymerization. Counter ion of the photoinitiator must have low nucleophilicity for the progress of the polymerization. [33]

Diaryliodonium and triarylsulfonium salts undergo photoinduced decomposition yielding reactive intermediates such as cations, radicals and radical-cationic species. Photolysis of diaryliodonium salts occurs either by homolytic or heterolytic cleavage of the halogen-aryl bond. (Eq 1.11) Resulting species react with a hydrogen donor solvent or monomer leading to the formation of a Brønsted acid, H^+ , which initiates the polymerization. It immediately attacks to monomer and further nucleophilic attack by other monomers takes place resulting in the growth of the polymer chain. (Eq 1.13) In addition, the electron donating substituents on the aromatic structures contribute to absorption at longer wavelengths and increase in polymerization rates.

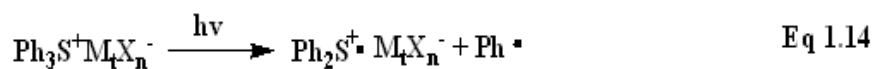


M_tX_n^- : PF_6^- , SbF_6^- , AsF_6^- , etc.

R-H: Solvent or monomer

Figure 1.8 Cationic Photoinitiation with Diaryliodonium Salt.

Similar mechanism is valid for the photoinitiation with triarylsulfonium salt. Again, with the irradiation, triarylsulfonium salt undergoes heterolytic or homolytic cleavage yielding active species. (Eq 1.14) They react with monomer or solvent releasing Brønsted acid, H^+ , which initiates the polymerization as in the photoinitiation with diaryliodonium salt mechanism. (Eq 1.17)



M_tX_n^- : PF_6^- , SbF_6^- , AsF_6^- , etc.

R-H : Solvent or monomer

Figure 1.9 Cationic Photoinitiation with Triarylsulfonium Salt.

Triarylsulfonium salts can initiate polymerization either by irradiation or thermal treatment. [34] They are also efficient for both free radical and cationic polymerizations, which makes them important for coatings and adhesion applications. Despite these properties, their solubility problem in monomers which are cationically polymerizable make them useless in cationic polymerization. However, this problem can be avoided by the modification of structure with different alkyl groups to improve solubility.

1.5 Photosensitization of Cationic Photoinitiators

Diaryliodonium and triarylsulfonium salts show considerable performance in UV-initiated cationic polymerizations using light in the short to mid wavelength UV regions (230-300nm), however, they are not active in the long wavelength UV and visible region. Thus, their use in applications requiring long wavelength light emitting sources is limited. This drawback can be circumvented using an activator

that broadens the spectral sensitivity of the onium salt photoinitiators. These activators are photosensitizers and they can initiate polymerization in the near-UV or visible wavelengths of light. Photosensitization of the photoinitiators can be done in two ways: Free radical promoted photosensitization [35,36], or electron transfer photosensitization. [37,38] Figure 1.10 shows the free radical promoted photosensitization of diaryliodonium salt.

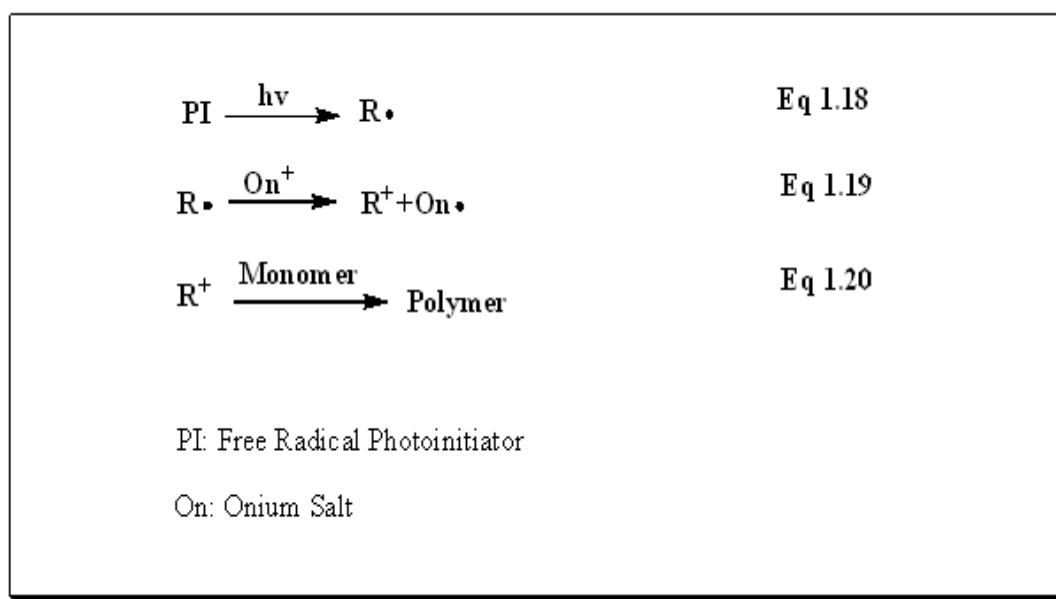


Figure 1.10 Free Radical Promoted Photosensitization.

In this type of photosensitization, decomposition of the free radical photoinitiator takes place upon irradiation (Eq 1.18). Following this decomposition, electron transfer occurs from free radical and to onium salt (Eq 1.19), and the resulting carbocation initiates the polymerization reacting with the monomer (Eq 1.20). Since diaryliodonium salts have lower oxidation potentials compared to triarylsulfonium salts, this type of photosensitization works better for diaryliodonium salts. The technique may provide significant efficiency for photosensitization of arylonium salts if the free radical absorbs at long wavelengths.

Another way of photosensitization is electron transfer photosensitization. As shown in Figure 1.11, the photosensitizer is excited by irradiation (Eq 1.21). Then, exciplex formation occurs between onium salt and excited photosensitizer (Eq 1.22). According to Rodrigues and Neumann ‘electron-transfer can occur by the photoinduced excitation of a ground state complex formed between the onium salt and the photosensitizer’.[39,40] This is followed by the electron transfer from the photosensitizer to the photoinitiator yielding the corresponding cation-radical of the photosensitizer and the highly unstable diaryliodonium free radical (Eq 1.23). This unstable free radical decomposes rapidly (Eq 1.24) preventing back electron transfer and making the overall process irreversible. Resulting photosensitizer radical cation can initiate polymerization through various species such as a Brønsted acid that is formed by the protonation of the metal anion (Eq 1.25). However, exciplex formation between the photosensitizer and the onium salt may not always take place. Therefore, being electron rich and having strong absorption in the UV-Vis region are important for photosensitizers. [41]

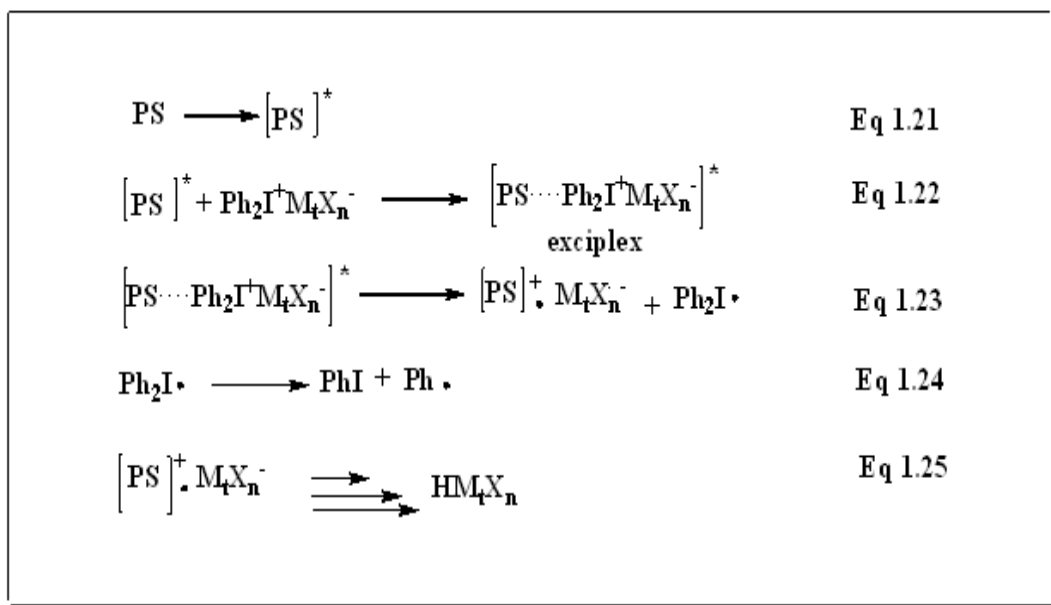


Figure 1.11 Electron-transfer Photosensitization.

1.6 Photosensitizers

Most onium salts absorb light at short wavelength of the UV region and do not absorb broad band of the spectrum (Figure 1.12). For this reason when a broadband light source is used, some of the energy emitted by the source is wasted. A photosensitizer enables onium salt (photoinitiator) to absorb light at wavelengths which they normally do not absorb. Broadening the spectral range, the photoinitiator captures the higher fraction of the light and this leads to accelerating the polymerization and monomer conversion. Increasing the curing rate brings about some advantages such as increasing productivity and decreasing photoinitiator concentrations, which reduces the cost. Furthermore, photosensitizer provides a wide range of photopolymerization applications, which can be carried out by solar energy. For instance, ‘ building panels, roofs, and water delivery and sewerage systems’ are some of these applications. [42]

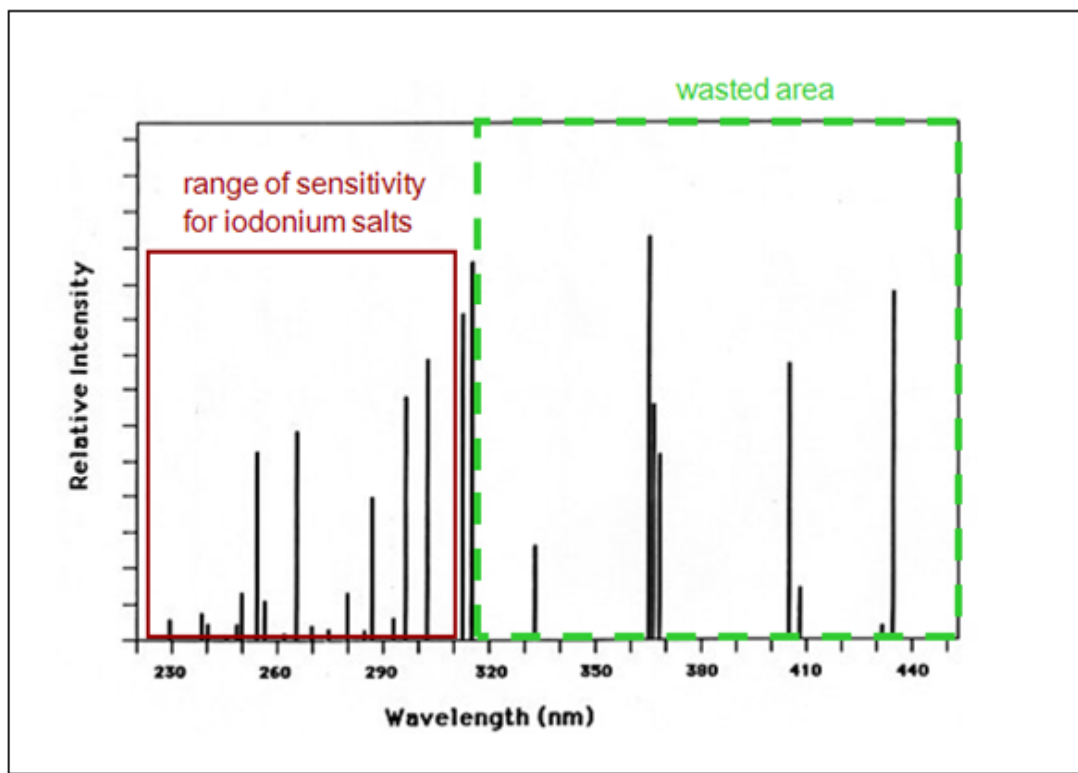


Figure 1.12 Spectral distribution for Medium Pressure Hg Arc Lamps.

Polynuclear aromatic hydrocarbons were used as photosensitizers such as anthracene [43], pyrene [44], perylene [45], phenothiazine [40], etc. which are electron rich molecules and have strong absorption in the UV-Vis region. Although they are efficient in electron-transfer photosensitization of diaryliodonium salts, they have some serious drawbacks such as limited spectral range and poor solubility in monomers. The most serious one is their toxicity. Besides, they can be easily evaporated or sublimed from liquid monomer samples during the process. This problem is based on their high vapor pressure at room temperature. [42]

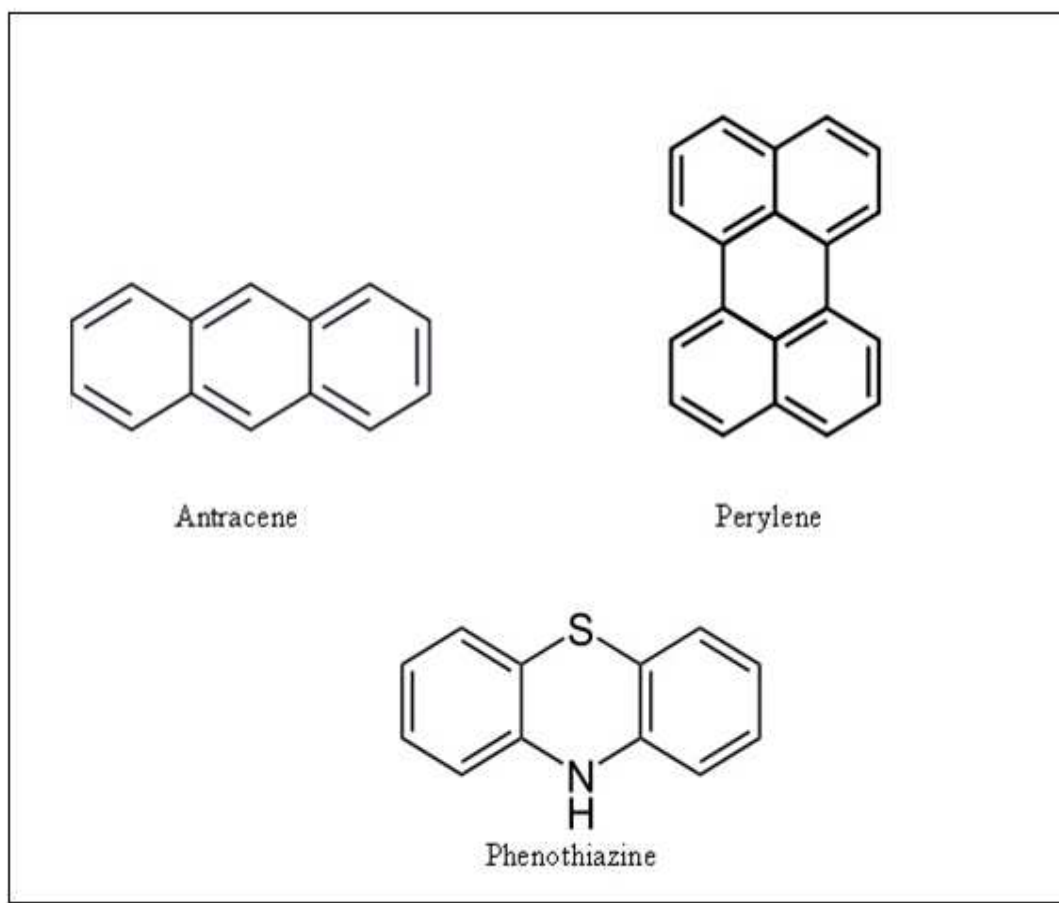


Figure 1.13 Polynuclear aromatic hydrocarbons.

Accordingly, several studies have been done in order to develop more efficient photosensitizers with higher spectral sensitivity. Coumarin [46], dithienothiophene derivatives [47], fluoflavin dyes, [48] and quinoxaline [2] are examples of such long wavelength photosensitizers. In addition to these, curcumin is a natural photosensitizer which is extracted from Indian Turmeric. Crivello and Bulut achieved cationic photopolymerization of various monomers by using curcumin as a photosensitizer. [41]

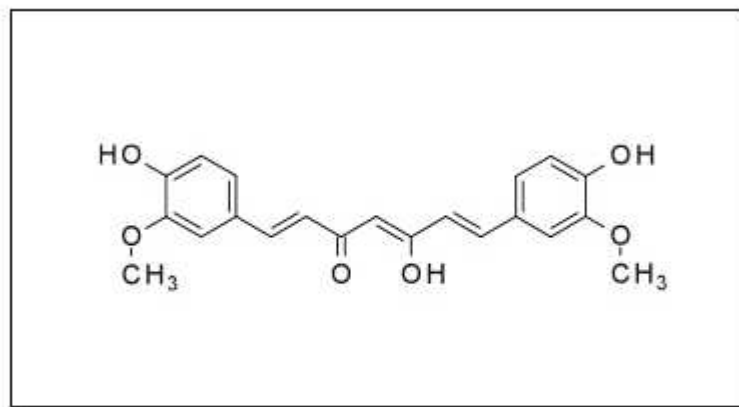


Figure 1.14 Curcumin

In this study, benzimidazole and benzotriazole derivatives were used as photosensitizers. Since these molecules are highly conjugated and have strong absorptions in the UV-Vis region, they are promising for being efficient photosensitizers in photoinitiated cationic polymerizations.

1.6.1 Benzimidazole Derivative

Benzimidazole (BIm) is an aromatic compound composed of benzene and imidazole ring. Conducting polymers can be obtained by the polymerization of benzimidazole due to the presence of conjugated π -bonds in its structure. (Figure 1.15)

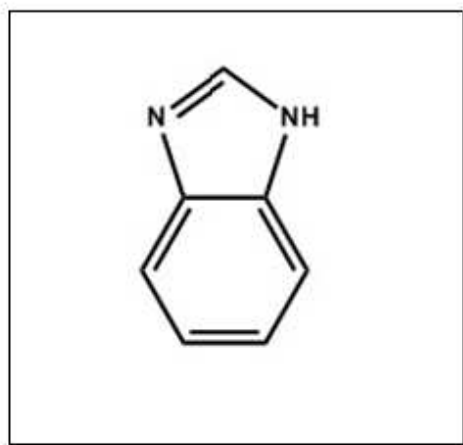


Figure 1.15 Benzimidazole (BIm)

Moreover, it is a biologically important compound that is found in Vitamin B12 and shows antitumor, antibacterial, and virucidal properties. [49,50] Also, chemically polymerized benzimidazole has thermal stability and high resistance at elevated temperatures. [51] Therefore, they have been used in biological applications and aerospace field. [52,53,54]

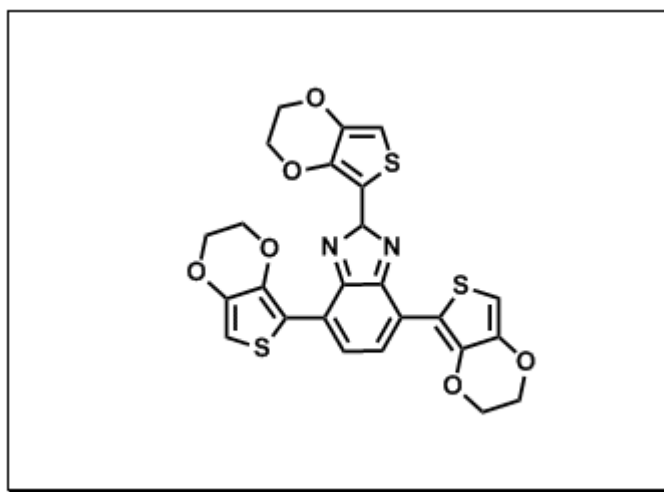


Figure 1.16 2,4-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-7-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)-1H-benzo[d]imidazole (BIm-Ed).

BIm-Ed was synthesized by Toppare Research Group. It is electrochemically polymerized and electrochromic studies were done. [55] In this study, it is employed as a photosensitizer for photoinitiated cationic polymerization of vinyl ether and epoxide monomers. Modification of benzimidazole with ethylenedioxythiophene (EDOT) leads to a highly conjugated compound which has low oxidation potential and strong absorption in UV-Vis region. Additionally, it is soluble in various organic solvents. Due to the aforementioned properties, BIm-Ed is expected to be an efficient photosensitizer for diaryliodonium salts.

1.6.2 Benzotriazole Derivatives

‘Benzotriazole is an organic compound consisting benzene and triazole ring, which can exist in the following tautomeric forms.’ [56]

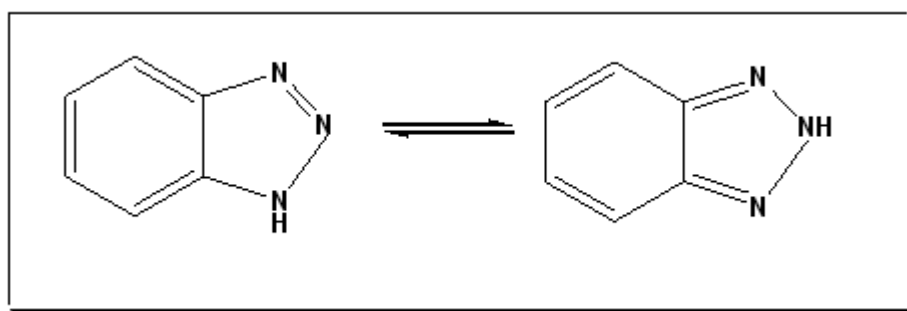


Figure 1.17 Benzotriazole.

It can either act as a weak acid or a weak base. Moreover, benzotriazole can also make a bonding with copper surface through lone pairs of electrons on the nitrogen. This property enables benzotriazole to be used for preventing the corrosion of the copper and its alloys in aqueous media. [57,58]

Benzotriazole molecules are employed as monomers for the synthesis of conducting polymers to be used in electrochromic materials [59,60] and solar cells [61,62] by

Toppare research group. In this study, use of two benzotriazole derivatives BBTES and BBTS as photosensitizers for diaryliodonium salts has been described. These molecules were synthesized by Toppare research group and electrochemically polymerized. [63,64] Being highly conjugated, having strong absorptions in the UV-Vis region, low oxidation potentials, and solubility in polar or nonpolar monomers make these substituted benzotriazoles promising for being efficient photosensitizers in photoinitiated cationic polymerizations.

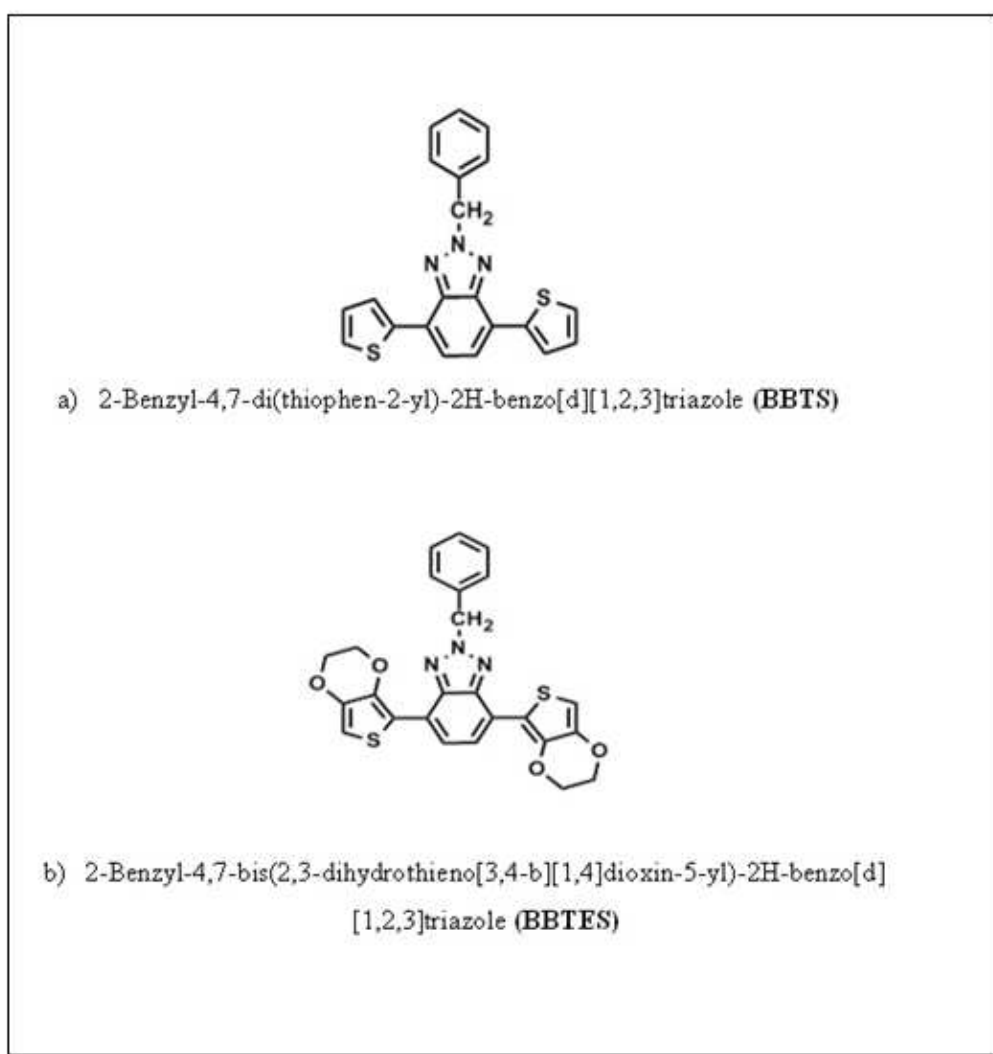


Figure 1.18 Benzotriazole derivatives, BBTS (a) and BBTES (b).

1.7 Monomers in Photoinitiated Cationic Polymerization

Types of monomers that undergo photoinitiated cationic polymerization are mostly vinyl ethers [65], epoxide [66], and 1-propenyl ether monomers. [67] Development of cationically polymerizable monomers has become an important issue with increasing use of photoinitiated cationic polymerization in many industrial applications.

Polymers resulted from photoinitiated cationic polymerization of epoxide monomers has very low shrinkage, good adhesion, and high resistance against chemicals. Therefore, they are used in high-performance protective and decorative coatings for metals, plastics, wood and in pressure-sensitive adhesives. [68] Curing rate is very important for these applications. One of the factors that affect the curing rate is the reactivity of the monomer. Polymerization of epoxide monomers is mostly due to the structure of the monomer. [69] For example, cycloaliphatic epoxy monomers having the epoxycyclohexane moiety are more reactive when compared to aliphatic or glycidyl ether counterparts due to the higher ring strain cycloaliphatic monomers have.

Vinyl ethers are very reactive monomers which are known to be readily polymerized by photoinitiated cationic polymerization with the help of suitable onium salt photoinitiators. [70] Importance of vinyl polymers for the industrial applications is based on their photoconductive properties. Various vinyl polymers were used as organic photoconductors. [71]

1.8 Fluorescence

According to Stokes' Law, lower energy, longer wavelength light is emitted when high energy, short wavelength light is directed onto a sample. Absorbing the light, molecule becomes excited and it can return to its ground state. A rapid return results in fluorescence and slow return results in phosphorescence. The Jablonski

Diagram (Figure 1.19) shows a number of possible ways that excited molecule can go back to its ground state.

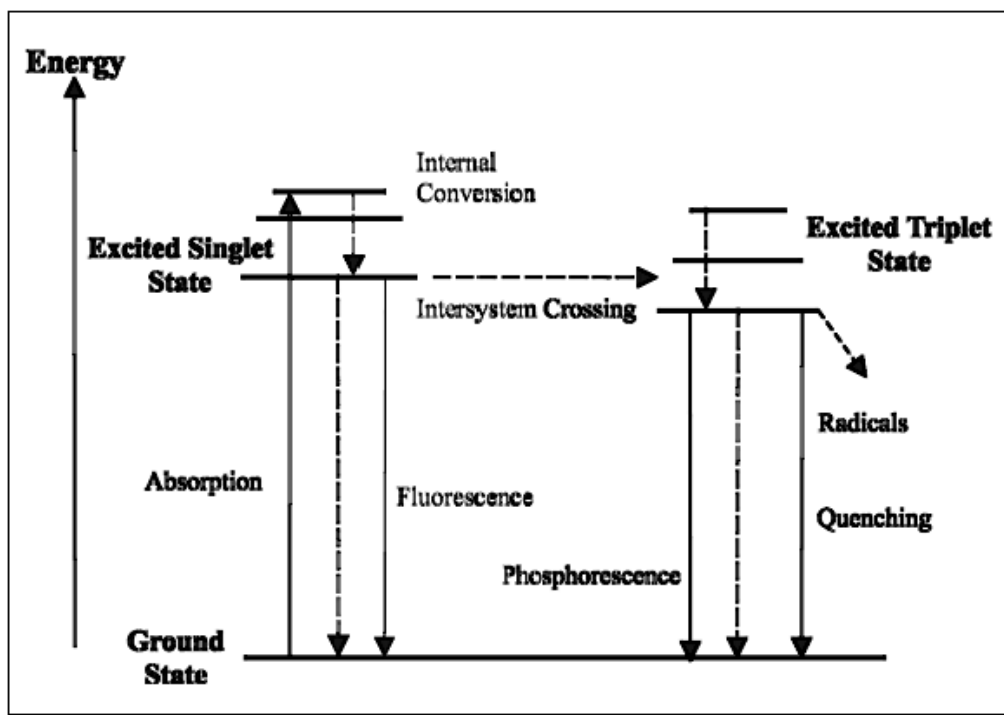


Figure 1.19 Jablonski Diagram.

1.9 Aim of This Work

In this study, photoinitiated cationic polymerization of vinyl ether and epoxide monomers were achieved using benzotriazole and benzimidazole derivatives as photosensitizers for diaryliodonium salt photoinitiators. Polymerization was performed upon irradiation with UV-Vis light. Additionally, photoinitiated cationic polymerization of monomers was achieved using solar irradiation. Effect of photosensitizers on polymerization efficiency was investigated. Reactivities of photoinitiators and monomers were also discussed. Importance of photoinitiated

cationic polymerization of vinyl ether and epoxide monomers in applications which are very rapid and room temperature treatments was highlighted.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

All the chemicals included in this study were used without any further purification. All polymerization reactions were carried out at room temperature. The photosensitizers BIm-Ed (2,4-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-7-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)-1H-benzo[d]imidazole), [55] BBTS (2-Benzyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole), [63] and BBTES (2-Benzyl-4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2Hbenzo[d][1,2,3]triazole) were synthesized by Toppare Research Group using the method described in the literature. [64] Cyclohexene oxide (CHO), Vinylcyclohexene dioxide (VCHDO), 2-chloroethylvinylether (CEVE), (3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate)(ERL-4221E), diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$), and dichloromethane (DCM) were purchased from the Aldrich Chemical Co. (Milwaukee, WI). The corona-treated poly(propylene) films were kindly provided as gifts from Superfilm Co. Gaziantep, Turkey. UV spectra of the photosensitizers were recorded on a Varian Cary 5000 Spectrometer. Optical Pyrometry instrument was used in order to determine the photoinitiated cationic polymerization.

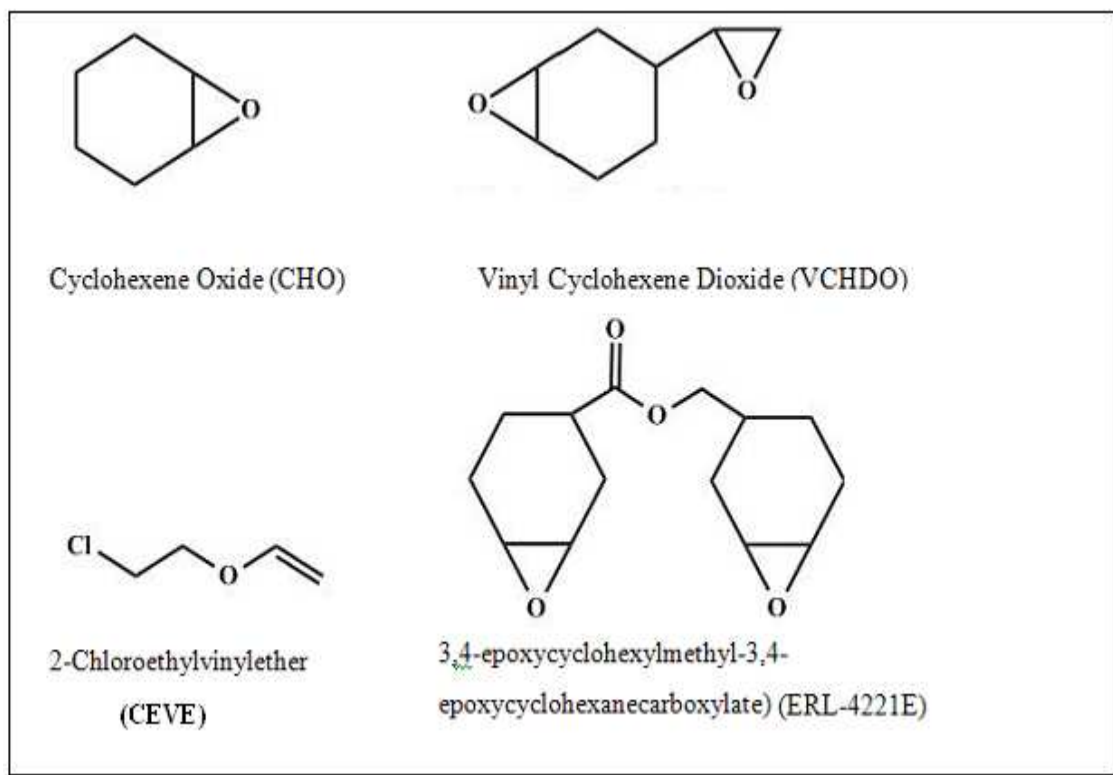


Figure 2.1 Vinyl and Epoxide monomers.

2.2 Methods

2.2.1 Synthesis of Photosensitizers

2.2.1.1 Synthesis of BIm-Ed (2,4-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-7-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)-1H-benzo[d]imidazole

Starting from benzothiadiazole, bromination by HBr and reduction by NaBH₄ reactions take place. Then, resulting 3,6-Dibromobenzene-1,2-diamine reacts with tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)stannane in the presence of THF at 100 °C yielding (2,4-Bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-7-(2,3-dihydrothieno[3,4-b][1,4]dioxin-7-yl)-1H-benzo[d]imidazole (BIm-Ed). [55]

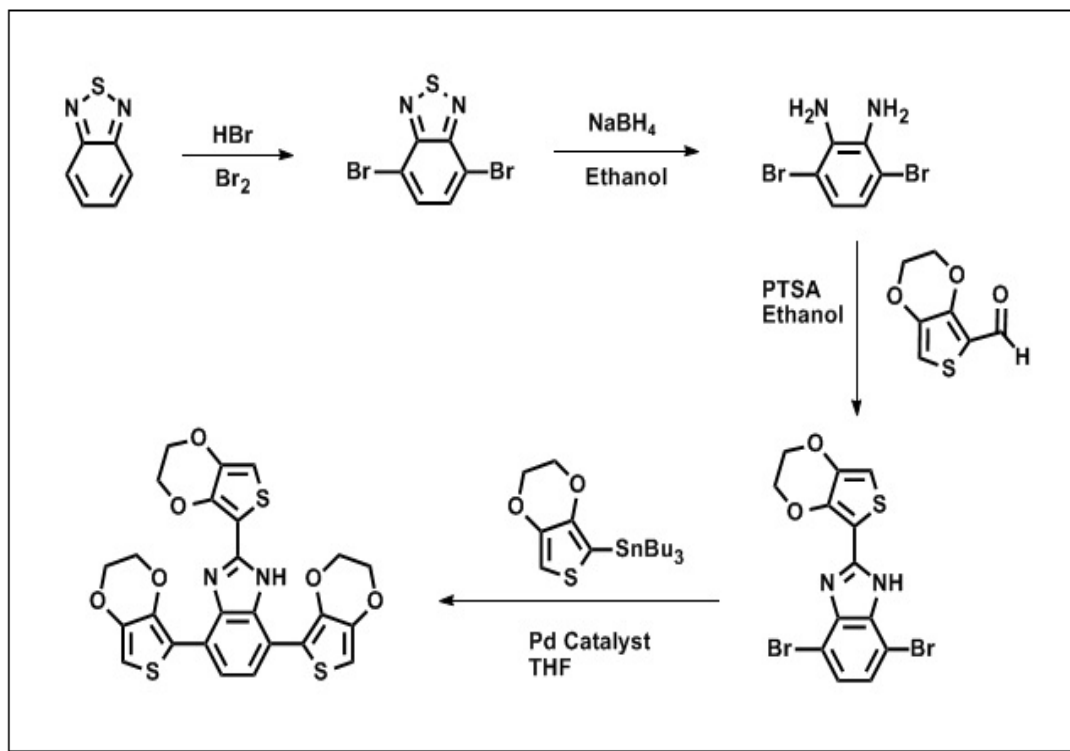


Figure 2.2 Synthesis route for BIm-Ed.

2.2.1.2 Synthesis of BBTS (2-Benzyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole)

Starting with benzothiadiazole, bromination by HBr and reduction by NaBH₄ reactions take place. Subsequently, 3,6-Dibromobenzene-1,2-diamine undergoes reaction with NaNO₂. Then, benzylbromide is added to dibromobenzotriazole and potassium tertbutoxide dissolved in ethanol. Resulting 2-Benzyl-4,7-dibromo-1H benzo[d][1,2,3]triazole reacts with tributyl(thiophen-2-yl)stannane. Reaction takes place in the presence of dry THF. Dichlorobis (triphenylphosphine)-palladium (II) is added at room temperature under an argon atmosphere. Finally, 2-Benzyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (BBTS) is obtained after purifications. [63]

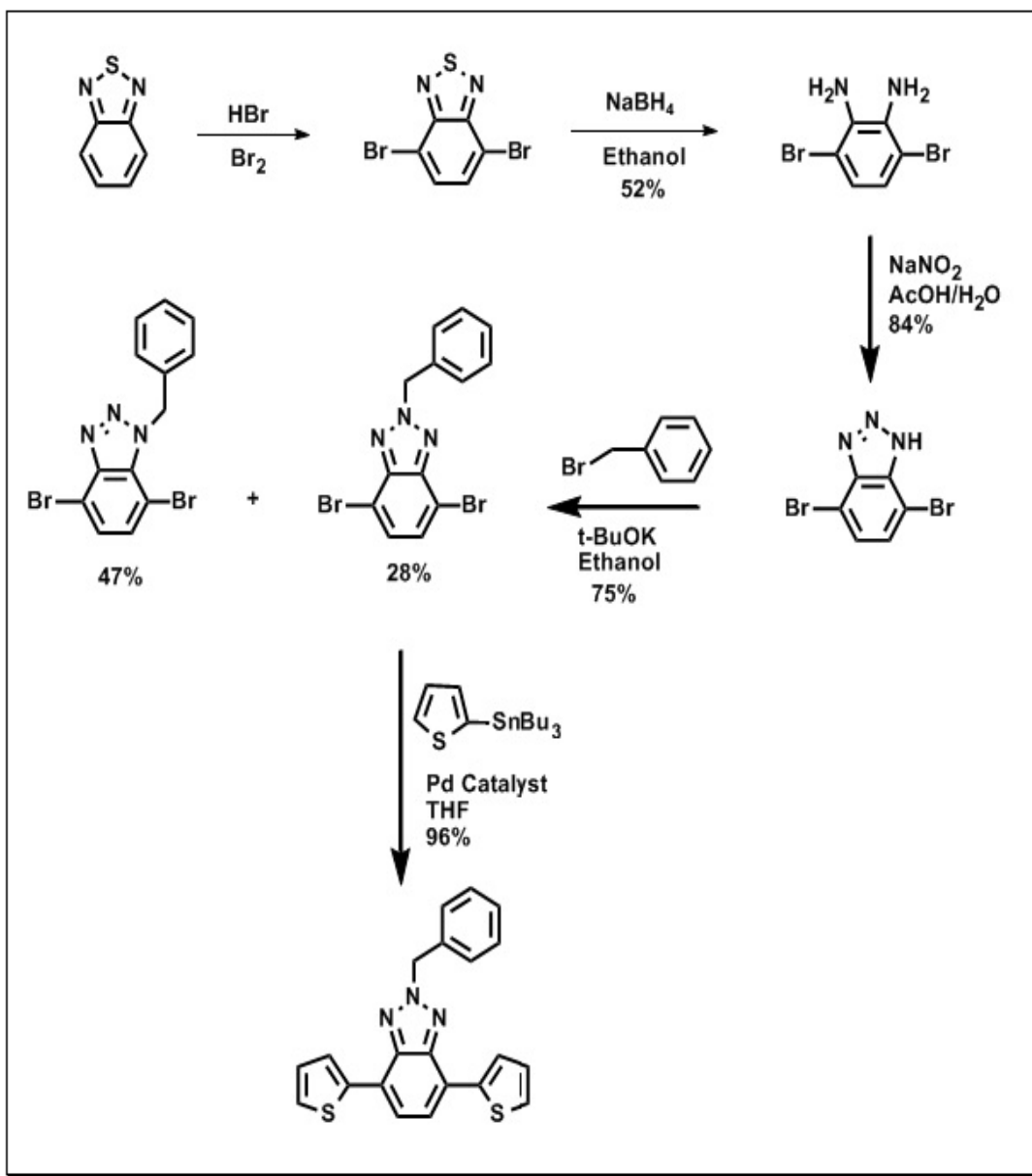


Figure 2.3 Synthesis route for BBTS.

2.2.1.3 Synthesis of BBTES (2-Benzyl-4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2H-benzo[d][1,2,3]triazole)

Similar to the synthesis of BBTS, after the bromination and reduction steps dibromobenzotriazole reacts with benzylbromide yielding both symmetrical and asymmetrical isomers in the presence of potassium tertbutoxide. This asymmetrical monomer is coupled with tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane in dry THF. Then, dichlorobis(triphenylphosphine)-palladium (II) is added at room temperature under an argon atmosphere. BBTES is obtained after reflux and removal of solvent. [64]

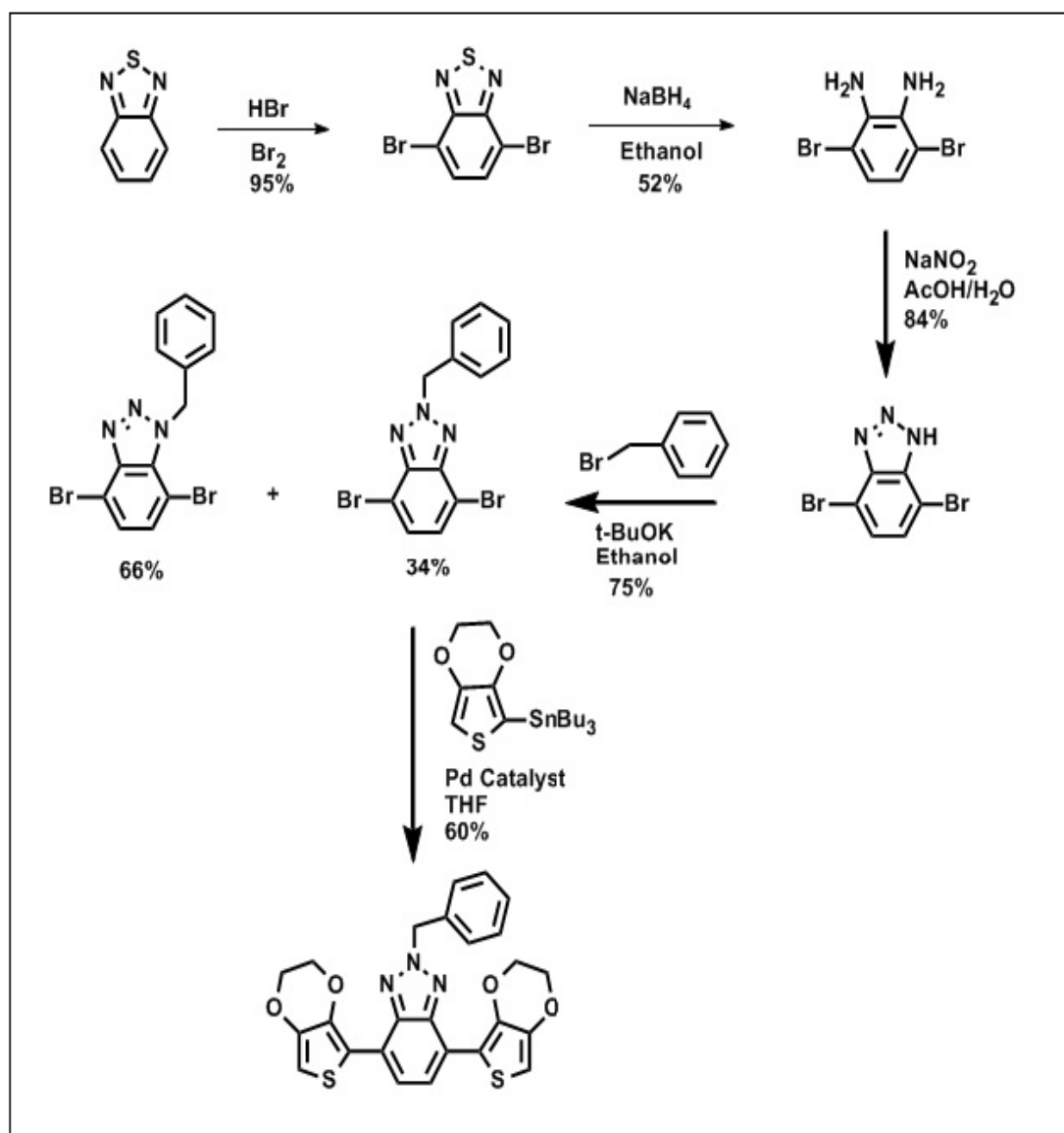


Figure 2.4 Synthesis route for BBTES.

2.2.2. Fluorescence Quenching Studies

Fluorescence quenching means decrease in intensity of a species due to the interaction with other species in the solution. In this study, fluorescence quenchings of photosensitizers were observed resulting from interaction with diaryliodonium salts. The Varian Cary Eclipse Fluorescence Spectrometer was employed to carry out the fluorescence quenching studies for BIm-Ed, BBTES and BBTS. The fluorescence emission band at 350 nm was monitored. Solutions of each photosensitizer with a concentration of 1×10^{-4} M and with varying concentrations of $\text{Ph}_2\text{I}^+\text{PF}_6^-$ in dichloromethane were exposed to excitation wavelength of 362 nm for BIm-Ed, 408 nm for BBTES and 386 nm for BBTS.

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

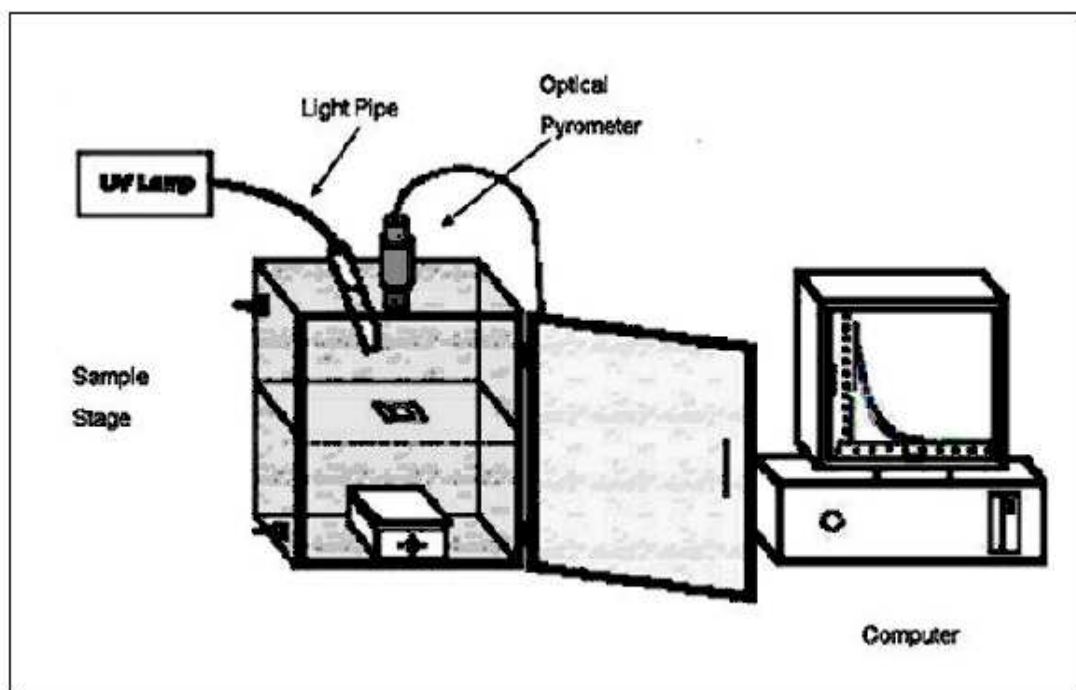


Figure 2.5 Optical Pyrometry.

Optical pyrometry was used for determining the efficiency of photopolymerizations by monitoring the temperature change in the samples. Method and apparatus of OP were described in an earlier communication. [72] Homogeneous solutions of monomer, diaryliodonium salt photoinitiator with and without the photosensitizers were prepared and placed between two thin films of oriented and corona-treated poly(propylene). Then, they were placed in plastic slide frames (2 cm x 2 cm) and put in the sample holder. The 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 only between 300 and 750 nm, blocking the transmission in the infrared region. All optical pyrometer experiments in this investigation were carried out at ambient temperature (25-28°C). With the onset of UV irradiation, temperature data were collected at a rate of 1 measurement per second and recorded to personal computer for analysis. Three kinetic runs were performed for every polymerization with and without photosensitizers and the graphs were plotted using average values of these runs.

2.2.3. Solar Irradiation Induced Polymerization

In this study, photoinitiated cationic polymerization of epoxy cyclohexylmethyl 3', 4'-epoxycyclohexanecarboxylate (ERL-4221E) was achieved via solar irradiation with the help of photosensitizers. A glass slide was coated with a solution of ERL-4221E with 1.0 mol % diaryliodonium salt photoinitiator and 0.1 mol % photosensitizer. Then, sample was exposed to direct solar irradiation in METU, Ankara on July 31, 2010 at 15:00 where the ambient temperature was 34°C. This study was performed for each photosensitizer.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Photoinduced Electron Transfer Photosensitization

In photoinduced electron transfer photosensitization, an electron is transferred from the photosensitizer to the photoinitiator, as shown in eq. 2. The free energy change of this transfer reaction can be estimated based on the well-known Rehm-Weller equation. [73]

$$\Delta G = (E_{\text{sens}}^{\text{ox}} - E_{\text{onium}}^{\text{red}}) - E_{\text{sens}}^* \quad \text{Eq 3.1}$$

where $E_{\text{onium}}^{\text{red}}$ is the reduction potential of the onium salt, $E_{\text{sens}}^{\text{ox}}$ is the oxidation potential of the photosensitizer, and E_{sens}^* is its excited-state energy. As can be inferred from the equation, the lower the oxidation potential of the photosensitizer, electron transfer between photosensitizer and diaryliodonium salt is facilitated as the overall free energy change will have a more negative value.

3.1.1 Benzimidazole Derivative (BIm-Ed)

Benzimidazole is an electron rich aromatic compound with a conjugated bicyclic skeleton. Modification of benzimidazole with ethylenedioxythiophene (EDOT) further increases the conjugation, hence, the electron density. Accordingly, this electron rich molecule has a low oxidation potential, reported as 0.80 V, and strong absorption bands in UV-Vis region between 300 and 440 nm. (Figure 3.1)

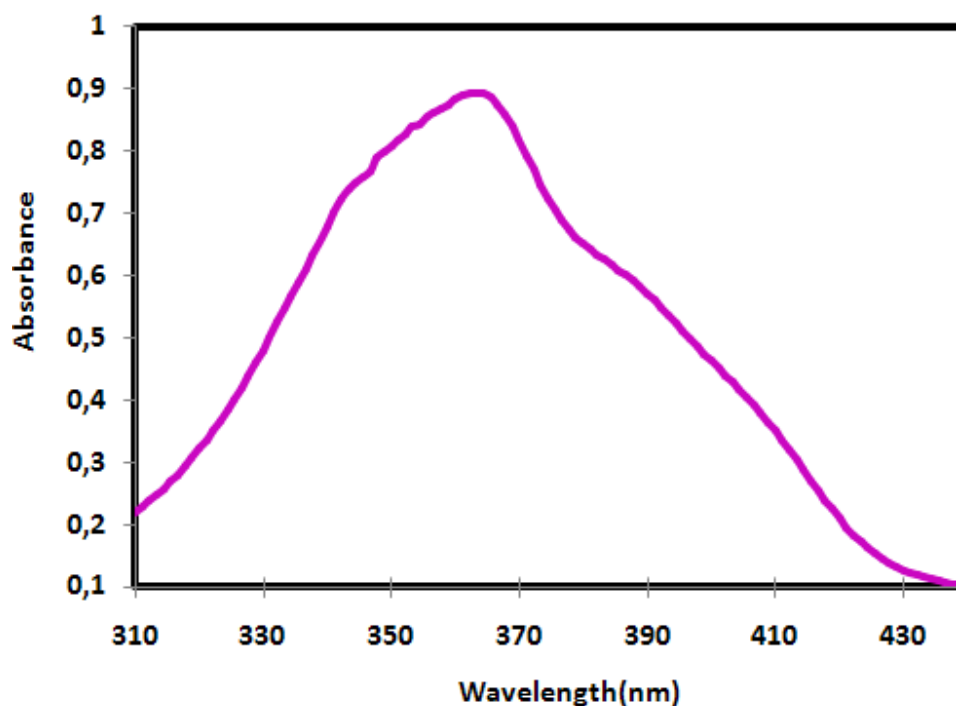


Figure 3.1 UV-Vis spectrum of 1×10^{-4} mol L⁻¹ BIm-Ed in CH₂Cl₂.

3.1.2 Benzotriazole Derivatives (BBTES and BBTS)

Benzotriazole is a non-toxic, highly stable, and inexpensive compound. Easy introduction of various substituents into this fully conjugated molecule makes it attractive as a precursor in the synthesis of long wavelength absorbing chromophores. In this study, the conjugation in benzotriazole backbone is extended by the substitution of electron rich ethylenedioxythiophene (EDOT) or thiophene units. Accordingly, these electron rich units lower the oxidation potentials of the photosensitizers, reported as 0.92 V BBTES and 1.33 V for BBTS in earlier studies. [63,64]

Lower oxidation potential of BBTES compared to BBTS can be explained by the higher electron density of the ethylenedioxythiophenyl substituent than that of the

thiophenyl unit. Moreover, the extended conjugation and high electron density impart enhanced spectral sensitivity to the photosensitizer molecules and absorption at long wavelength UV and visible regions. As anticipated, BBTES and BBTS have strong absorption bands between 330 nm and 460 nm (Figure 3.2) making it possible to use visible light emitting light sources in cationic polymerizations.

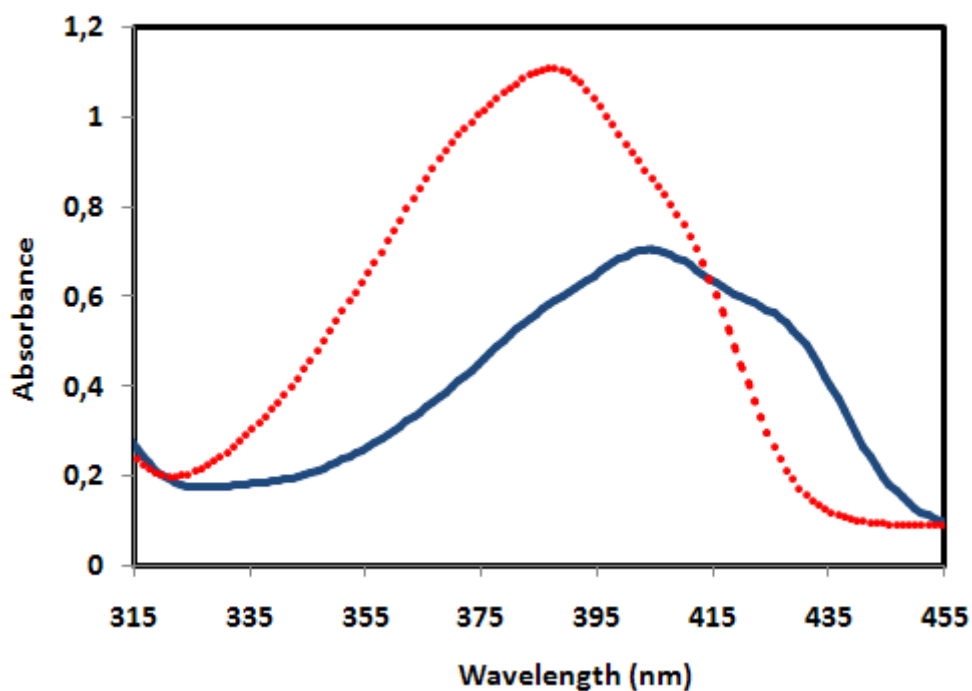


Figure 3.2 UV-Vis spectrum of 1×10^{-4} mol L⁻¹ BBTS (—) and BBTES (---) in CH₂Cl₂.

3.2 Fluorescence Quenching Study

For the low concentrations, the quenching of fluorescence by an electron acceptor molecule in solution follows the Stern-Volmer relationship. [74]

$$I_0/I = 1 + k_Q [Q] \quad \text{Eq 3.2}$$

where I_0 is the intensity of fluorescence without quencher, I is the intensity of fluorescence at the quencher concentration $[Q]$, and k_Q is called the quenching constant. Fluorescence quenching studies for the photosensitizers in the presence of the photoinitiator were performed in order to justify the electron transfer between photosensitizer and photoinitiator that showed in the mechanism in (Figure 1.11)

3.2.1 Fluorescence Quenching of Benzimidazole Derivative (BIm-Ed)

A typical Stern-Volmer plot is displayed in Figure 3.3 where fluorescence intensity of the photosensitizer BIm-Ed decreases as the photoinitiator $\text{Ph}_2\text{I}^+\text{PF}_6^-$ concentration increases. The linear correlation shows that electron transfer from photosensitizer to photoinitiator demonstrated in eq. 1.23 (Figure 1.11) was actually taking place. It was also confirmed that the presence of the photoinitiator was mandatory as no polymerization was observed when photoinitiator was omitted in the formulations.

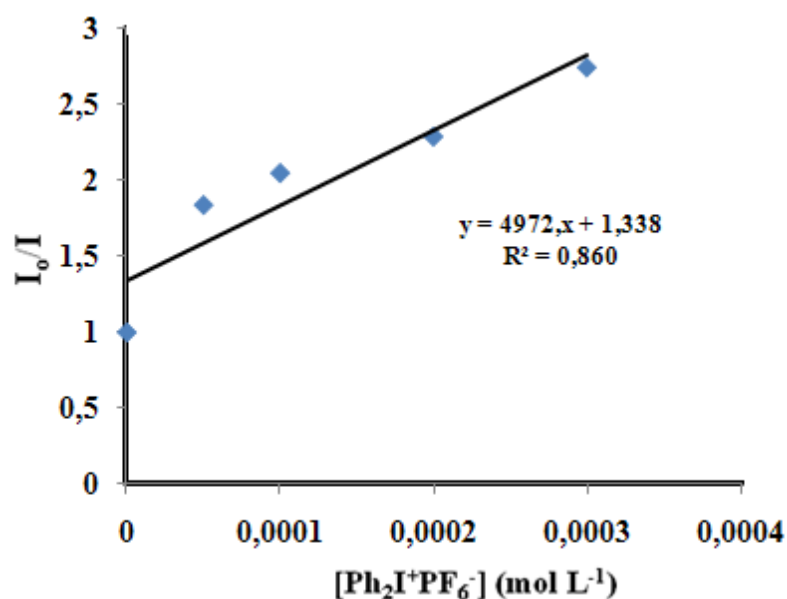


Figure 3.3 Stern-Volmer plot of the quenching of BIm-Ed (1×10^{-4} M) by diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) in dichloromethane. (excitation wavelength 362 nm for BIm-Ed).

3.2.2 Fluorescence Quenching of Benzimidazole Derivative (BBTES and BBTS)

The same study was done for determining the fluorescence quenching of the photosensitizers BBTES and BBTS in the presence of photoinitiator diaryliodonium salt as a quencher. It can easily be seen in Figure 3.4 that the fluorescence intensity of the photosensitizers decreases with increasing photoinitiator concentration. This linear correlation confirms that the electron transfer from the photosensitizer to the photoinitiator has occurred.

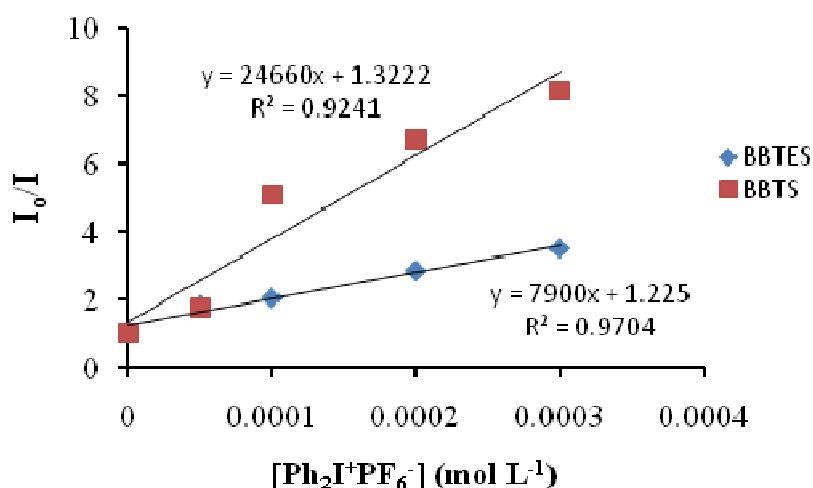


Figure 3.4 Stern-Volmer plot of the quenching of BBTS (\square) (1×10^{-4} M) and BBTES (\diamond) (1×10^{-4} M) by diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) in dichloromethane. (excitation wavelength 408 nm for BBTES and 386 nm for BBTS).

3.3 Optical Pyrometry Study

Solutions containing the monomer, photoinitiator, and photosensitizer were prepared and polymerized under UV irradiation. Both photosensitizers were completely soluble in various cationically polymerizable monomers. The progress of the polymerizations was monitored by Optical Pyrometry (OP). This method enables the investigation of the molecules as potential photosensitizers in a very short time.

3.3.1 Photosensitizer Concentration Optimization Studies

In this study polymerization of CHO was carried out in absence of photosensitizer BBTES and in the presence of different concentrations of BBTES. By this way, optimum photosensitizer concentration was determined for the progress of

polymerization. In the absence of photosensitizer, there was very little or no polymerization while very rapid polymerization took place with the aid of the photosensitizer. Most efficient polymerization was carried out with 0.1 % mol BBTES concentration. Figure 3.5 shows that there is no linear relation between the efficiency of the polymerization and the concentration of the photosensitizer. When the concentration of the photosensitizer is raised to 0.25%, efficiency of the polymerization decreases due to the screening effects. The optimum concentration of BBTES was detected as 0.1 mol %.

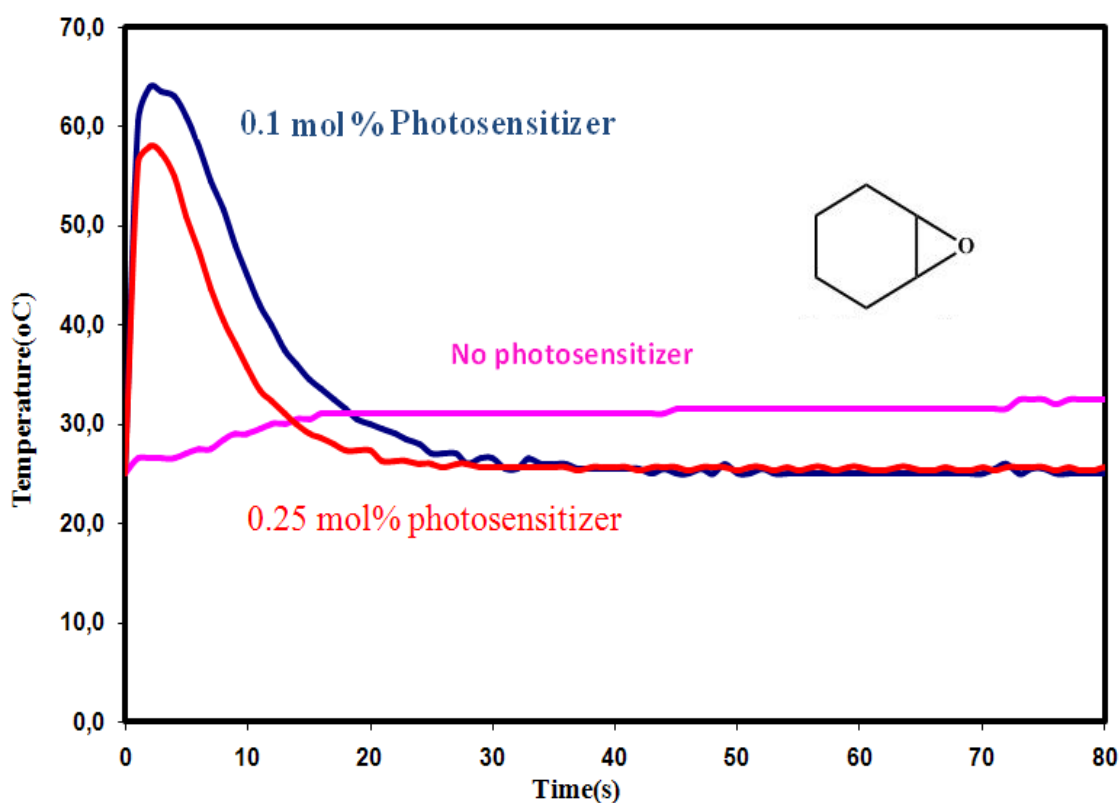


Figure 3.5 OP study of the photopolymerization of cyclohexene oxide with 1.0 mol % photoinitiator in the absence of a photosensitizer and in the presence of 0.1mol% and 0.25 mol% photosensitizer BBTES. (light intensity 12.7 mW cm^{-2})

3.3.2 OP Study of Benzimidazole Derivative (BIm-Ed)

As can be seen in the Figure 3.6, a sharp increase in the temperature indicates that very rapid polymerization of ERL-4221E took place in the presence of photosensitizer BIm-Ed. The purple line which belongs to solution without photosensitizer shows that there is no or very little polymerization without photosensitizer. ERL-4221E is a difunctional epoxide monomer which is widely used in coating and adhesive applications and it undergoes very rapid polymerization with the help of the photosensitizer BIm-Ed.

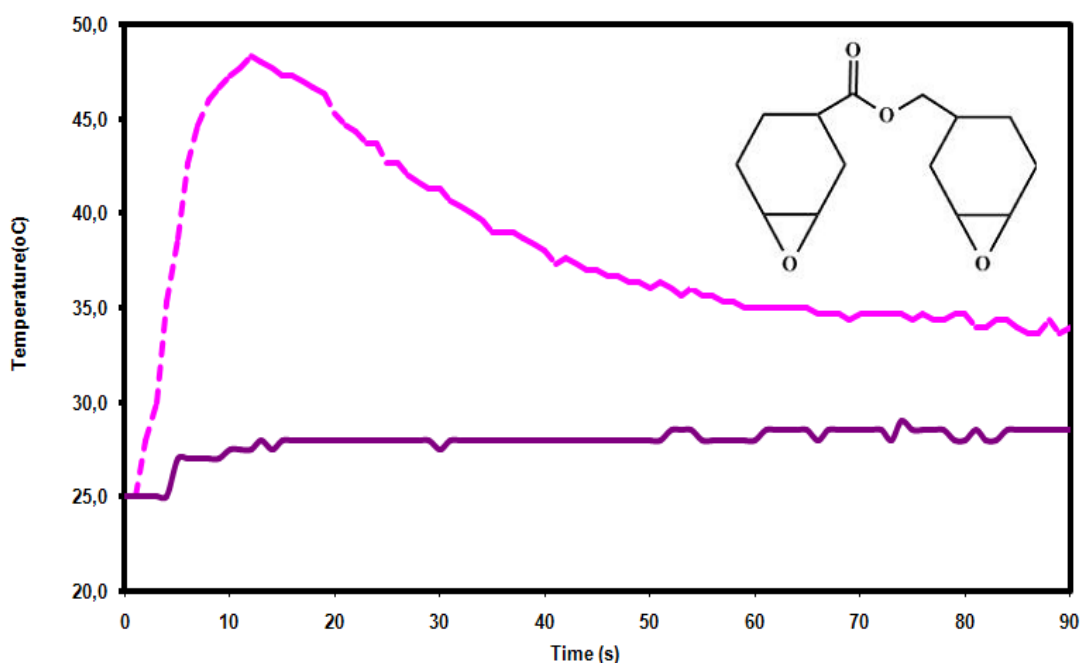


Figure 3.6 Cationic photopolymerization of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ERL-4221E) with 1.0 mol% $\text{Ph}_2\text{I}^+\text{PF}_6^-$ in the absence of a photosensitizer (—) and in the presence of 0.1 mol% BIm-Ed photosensitizer(---). (light intensity 12.7 mW cm^{-2})

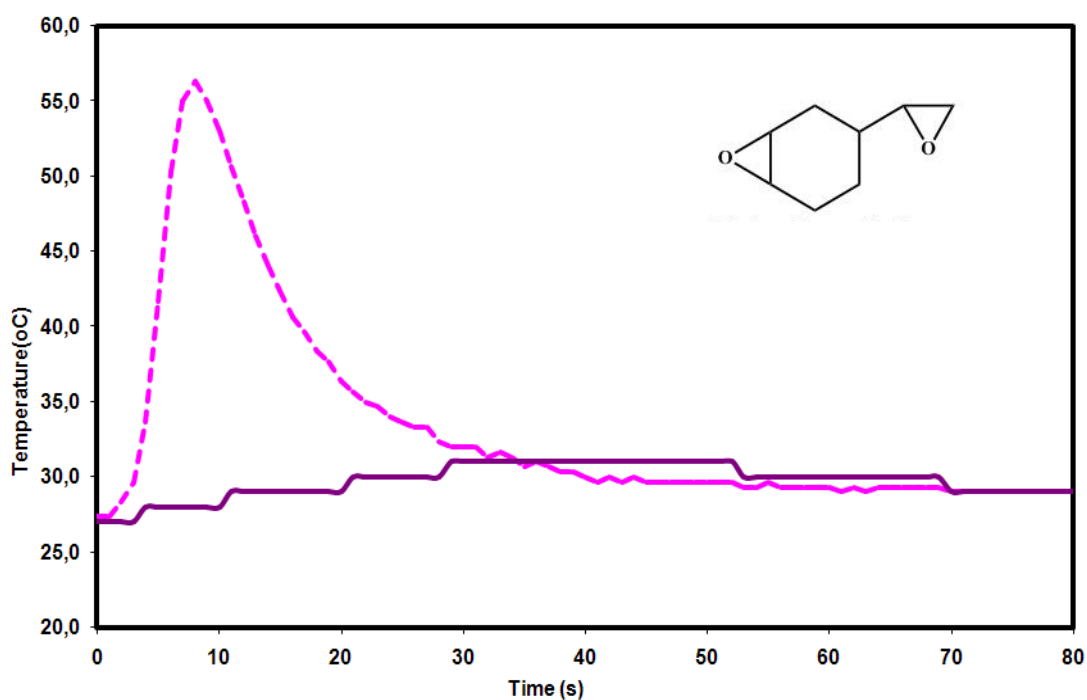


Figure 3.7 Cationic photopolymerization of vinylcyclohexene dioxide (VCHDO) with 1.0 mol% $\text{Ph}_2\text{I}^+\text{PF}_6^-$ in the absence of a photosensitizer (—) and in the presence of 0.1 mol% BIm-Ed photosensitizer (---). (light intensity 12.7 mW cm^{-2})

The polymerization of vinylcyclohexene dioxide (VCHDO), a difunctional epoxide monomer, took place within a very short time in the presence of BIm-Ed. This quick process is very critical for industrial applications and it can be achieved by benzimidazole photosensitizer. On the other hand, polymerization of VCHDO is very slow without photosensitizer.

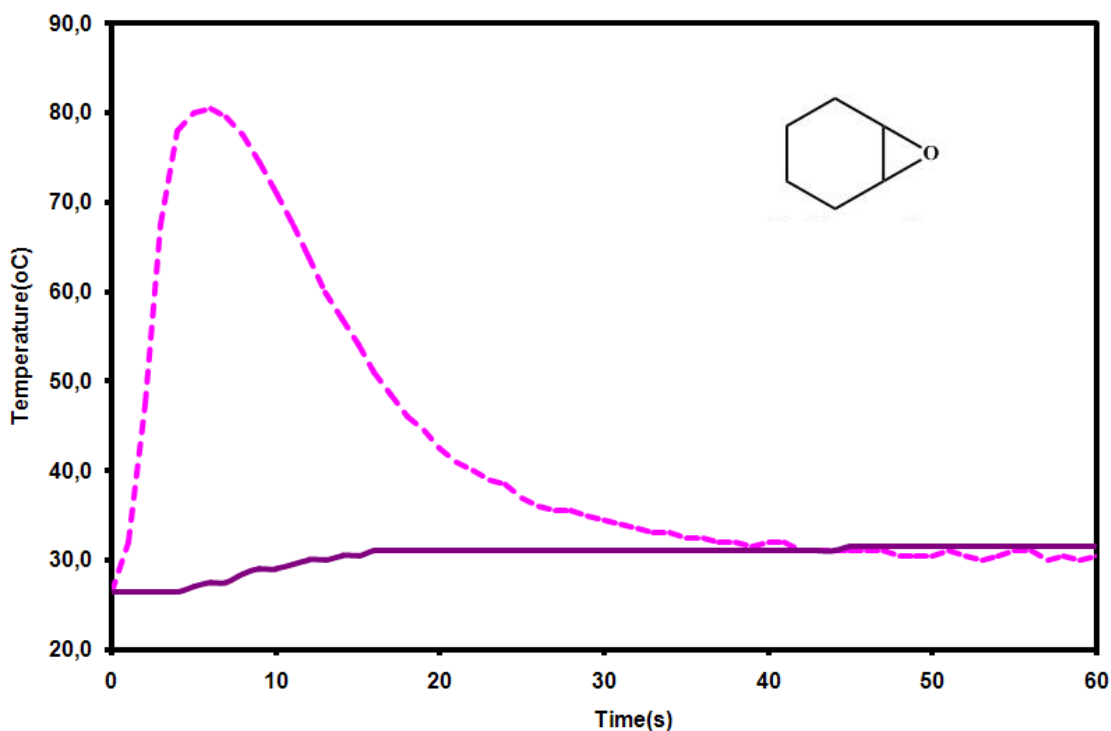


Figure 3.8 Cationic photopolymerization of cyclohexene oxide (CHO) with 1.0 mol% $\text{Ph}_2\text{I}^+\text{PF}_6^-$ in the absence of a photosensitizer (—) and in the presence of 0.1 mol% BIm-Ed photosensitizer (---). (light intensity 12.7 mW cm^{-2})

Polymerization of cyclohexene oxide proceeded immediately and also there was no induction period when photosensitizer was present. However, when the photosensitizer was absent there was very little increase in the temperature which demonstrates very little polymerization.

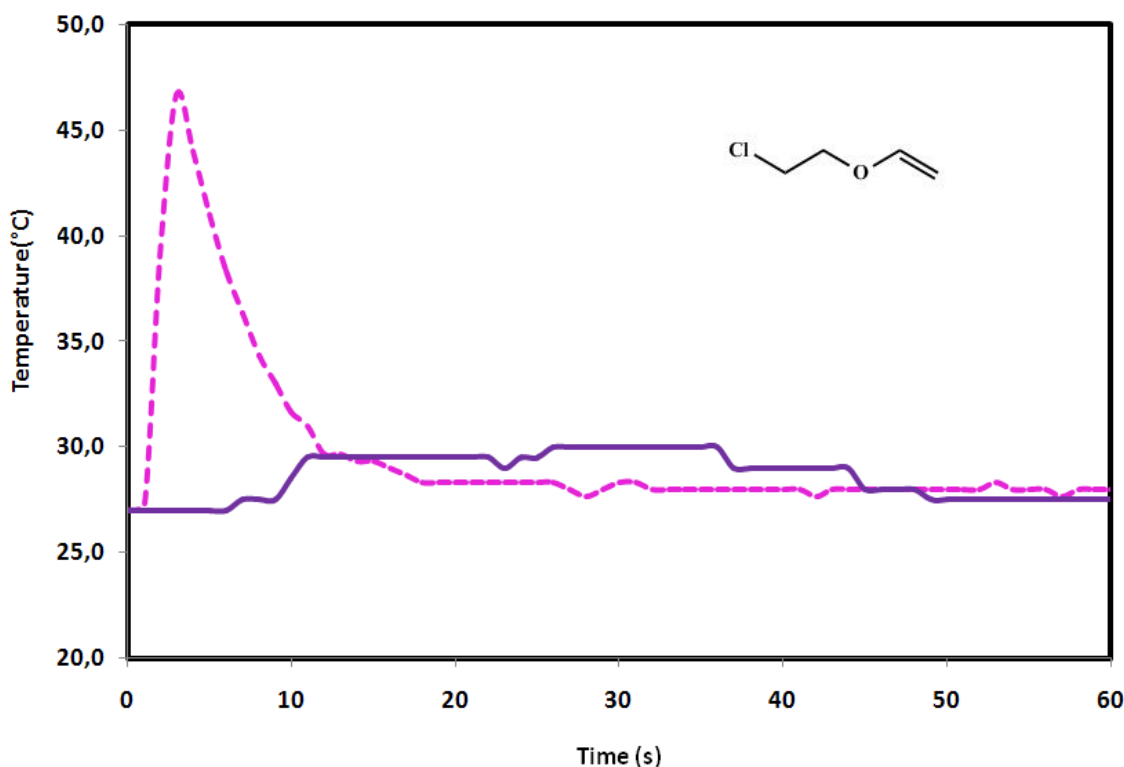


Figure 3.9 Cationic photopolymerization of 2-chloroethylvinylether (CEVE) with 1.0 mol% $\text{Ph}_2\text{I}^+\text{PF}_6^-$ in the absence of a photosensitizer (—) and in the presence of 0.1 mol% BIm-Ed photosensitizer (---). (light intensity 12.7 mW cm^{-2})

In the absence of BIm-Ed, photopolymerization took off after a very long induction period. When BIm-Ed was used, immediate polymerization of CEVE took place rapidly with the start of irradiation. Additionally, polymerization was completed in a very short time such as ten seconds.

3.3.3 OP Study of Benzotriazole Derivatives (BBTES and BBTS)

Figure 3.10 shows the progress of the polymerizations of the difunctional monomer ERL-4221E in the presence of photosensitizers BBTES and BBTS. When the photosensitizer was absent polymerization of ERL-4221E could not be achieved. On

the contrary, polymerization was initiated within the first seconds with the contribution of photosensitizers. When these two photosensitizers are compared to each other, as the Figure 3.10 depicts, BBTES is more efficient than BBTS in photosensitized polymerization of ERL-4221E.

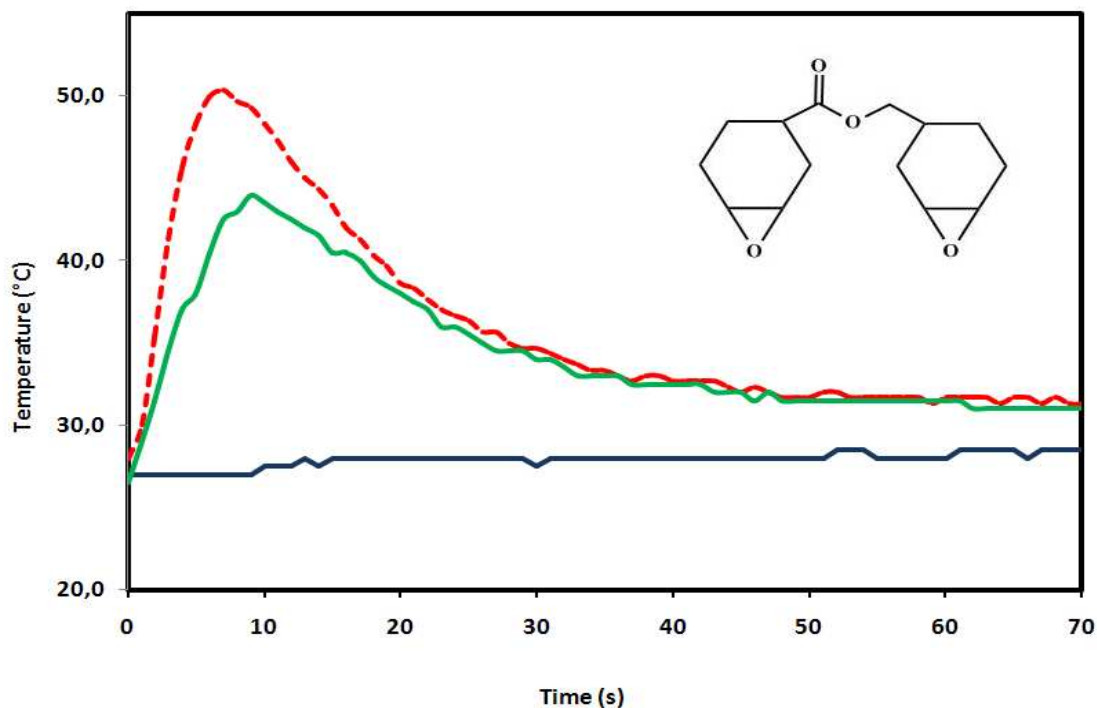


Figure 3.10 Cationic photopolymerization of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (ERL-4221E) with 1.0 mol% $\text{Ph}_2\text{I}^+\text{PF}_6^-$ in the absence of a photosensitizer (—) in the presence of 0.1 mol% BBTES photosensitizer (---) and 0.1 mol% BBTS photosensitizer (—). (light intensity 12.7 mW cm^{-2})

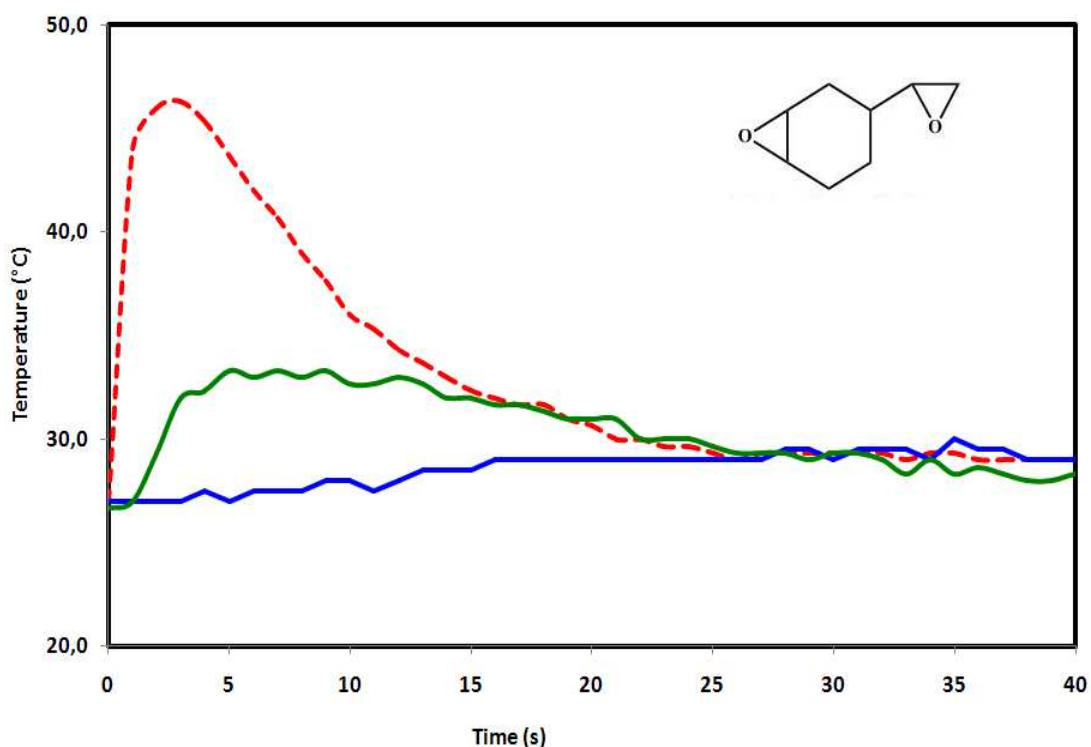


Figure 3. 11 Cationic photopolymerization of Vinylcyclohexene dioxide (VCHDO) with 1.0 mol% $\text{Ph}_2\text{I}^+\text{PF}_6^-$ in the absence of a photosensitizer(—), in the presence of 0.1 mol% BBTES photosensitizer (---) and 0.1 mol% BBTS photosensitizer (—).
(light intensity 12.7 mW cm^{-2})

Initiation of polymerization of VCHDO was so quick that there was no induction period in the presence of BBTES. With BBTS, polymerization started again in a very short time but not as rapid as the one with BBTES. Also, time required for the completion of the polymerization was very short. It took about twenty seconds to complete the polymerization either with BBTES or BBTS.

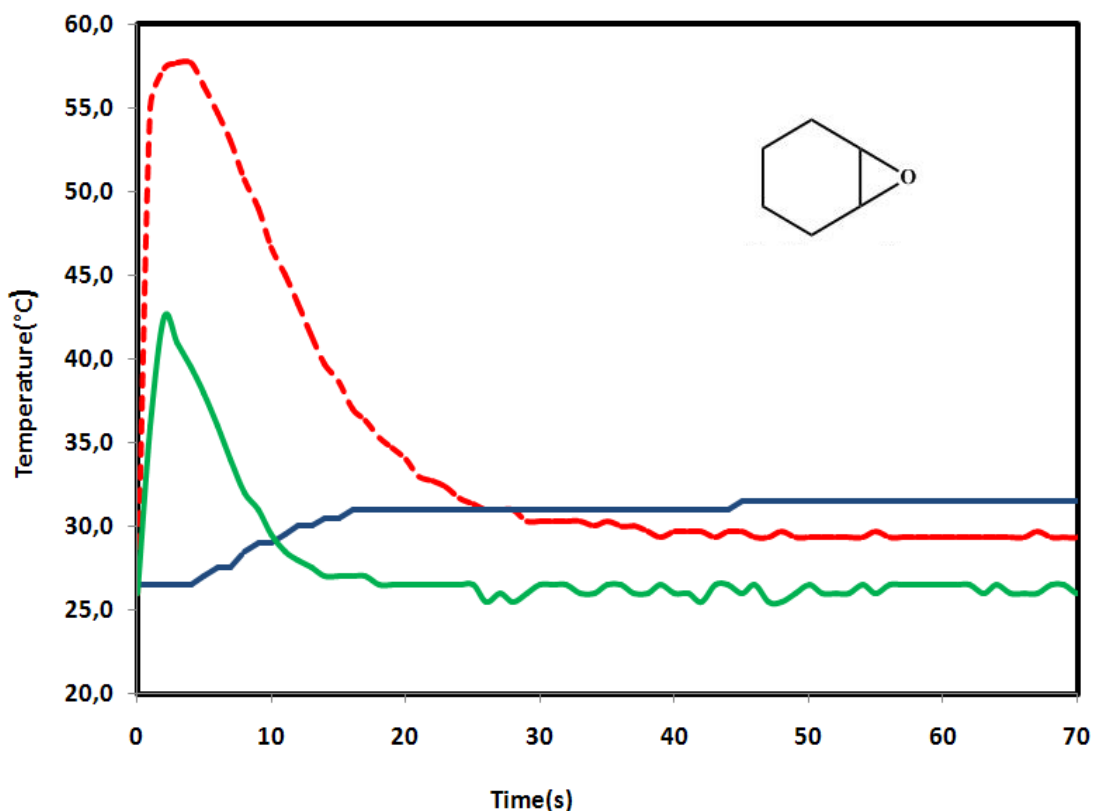


Figure 3. 12 Cationic photopolymerization of Cyclohexene oxide (CHO) with 1.0 mol% $\text{Ph}_2\text{I}^+\text{PF}_6^-$ in the absence of a photosensitizer (—), in the presence of 0.1 mol% BBTES photosensitizer (---) and 0.1 mol% BBTS photosensitizer (—). (light intensity 12.7 mW cm^{-2})

Polymerization of cyclohexene oxide started in the first seconds in the presence of BBTES or BBTS. Temperature was raised up to 60 °C with BBTES whereas it was raised up to 45 °C. This difference may be resulted from higher efficiency of BBTES. When there was no photosensitizer, very little polymerization took place.

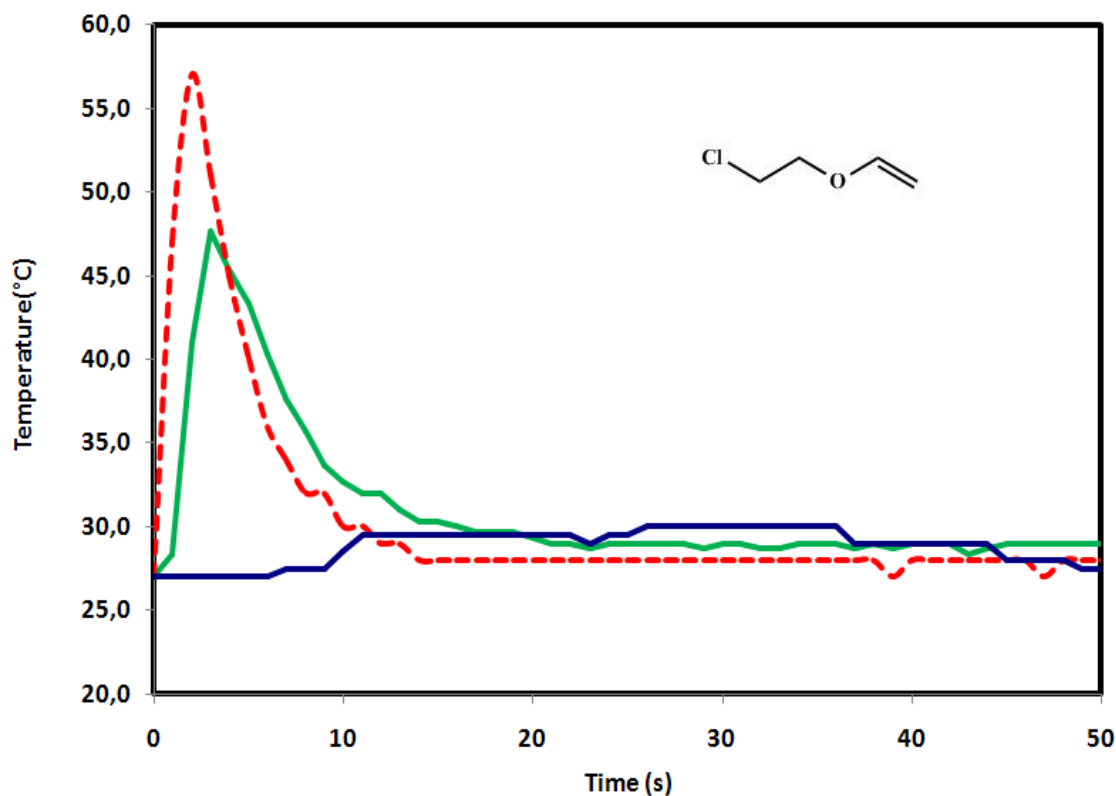


Figure 3.13 Cationic photopolymerization of 2-chloroethylvinylether (CEVE) with 1.0 mol % $\text{Ph}_2\text{I}^+\text{PF}_6^-$ in the absence of a photosensitizer (—), in the presence of 0.1 mol % BBTES photosensitizer (---) and 0.1 mol% BBTS photosensitizer (—). (light intensity 12.7 mW cm^{-2})

Photopolymerization of the vinylether monomer (CEVE) was achieved in the control system, however, the induction period diminished with the use of BBTS or vanished in the presence of BBTES.

In all cases, higher temperatures and shorter induction periods are observed with BBTES compared to BBTS, which indicates a more efficient process with BBTES than that of BBTS containing systems, and can be attributed to higher electron density and lower oxidation potential of BBTES than BBTS as formerly discussed.

3.4 Solar Irradiation Studies

Since these photosensitizers are effective in the visible region we also examined their efficiencies in the photopolymerization of ERL-4221E using solar irradiation. As a result rapid photopolymerizations of ERL-4221E were achieved by solar irradiation with the help of photosensitizers.

3.4.1 Solar Irradiation Study of Benzimidazole Derivative (BIm-Ed)

Solution of monomer, photoinitiator and photosensitizer was prepared as described in the experimental part. When the sample was exposed to solar irradiation first color change was observed in the second minute and very pale brown sample started to change into brown. At the end of seven minutes it turned into dark brown and it was fully cured. Since the process is irreversible color of the sample did not turn to its original color. (Figure 3.14)

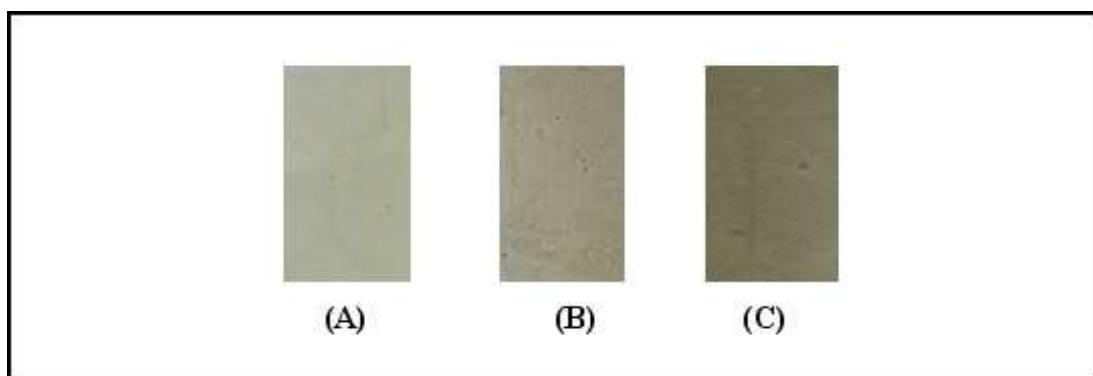


Figure 3.14 ERL4221E / $\text{Ph}_2\text{I}^+\text{PF}_6^-$ / BIm-Ed mixture (A) upon exposure to solar irradiation, (B) after 2 minutes and (C) after 7 minutes of irradiation.

3.4.2 Solar Irradiation Study of Benzotriazole Derivatives (BBTES and BBTS)

Samples containing either BBTES or BBTS were prepared and exposed to direct solar irradiation as described in experimental section. BBTES containing solution with a yellow color changed into yellow-green in a minute and after 2 minutes it was green and completely tack-free. (Figure 3.15).

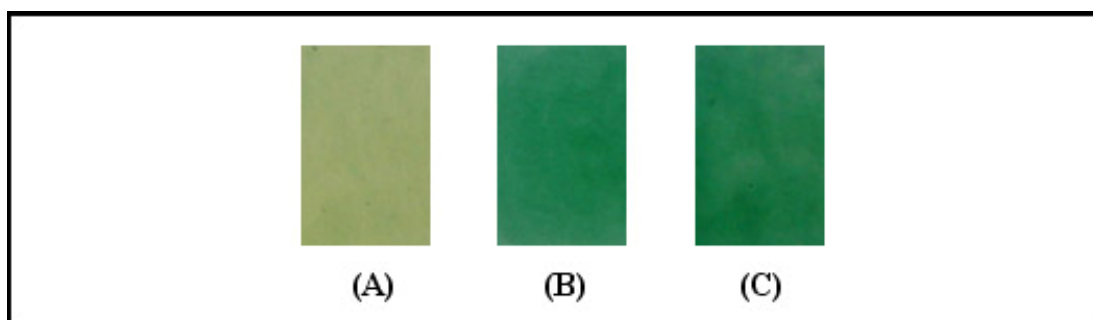


Figure 3.15 ERL4221E / $\text{Ph}_2\text{I}^+\text{PF}_6^-$ / BBTES mixture (A) upon exposure to solar irradiation, (B) after 1 minute and (C) after 2 minutes of irradiation.

BBTS containing solution turned to pale brownish green from dark yellow in 1 minute, and it took 5 minutes to turn into dark green and fully cured (Figure 3.16). After the completion of the polymerization the sample did not turn to its original color since the process is irreversible.

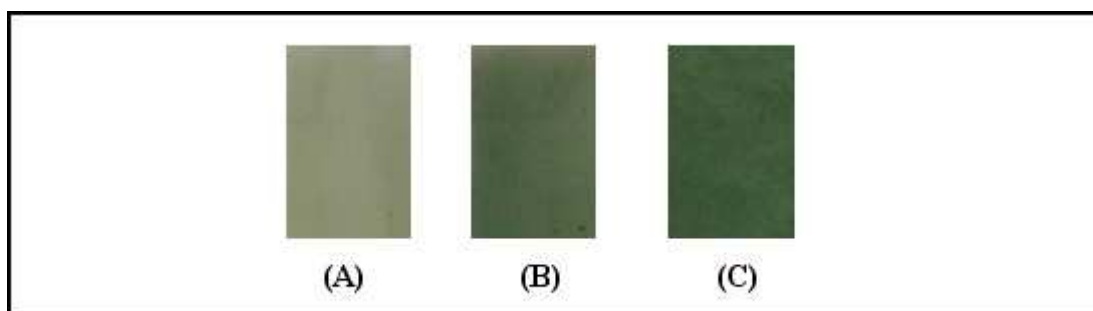


Figure 3.16 ERL4221E / $\text{Ph}_2\text{I}^+\text{PF}_6^-$ / BBTS mixture (A) before exposure to solar irradiation, (B) after 1 minute and (C) after 5 minutes of irradiation.

CHAPTER 4

CONCLUSION

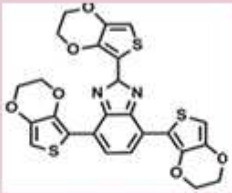
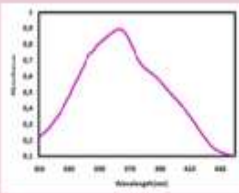
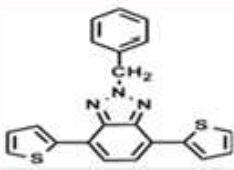
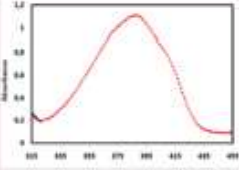
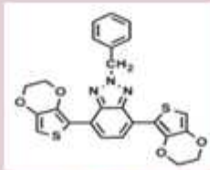
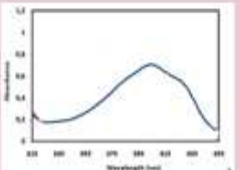
Photosensitizers	λ max	Ox.Potential	OP results	Solar irradiation times
 BIm-Ed	 362nm	0.80 V	efficient	7 min
 BBTS	 386 nm	1.33 V	efficient	5 min
 BBTES	 408 nm	0.92 V	More efficient than BIm-Ed and BBTS	2 min

Figure 4.1 Comparison of photosensitizers.

In this study, we have examined the efficiency of a benzimidazole and two benzotriazole derivatives as photosensitizers for diaryliodonium salt in photoinitiated cationic polymerization using UV light and solar irradiation. The benzimidazole derivative bearing EDOT groups has showed high performance as a photosensitizer.

It has strong absorption in the long UV-Vis region, low oxidation potential due to highly conjugated structure and good solubility in vinyl and epoxide monomers. Benzotriazole derivatives bearing benzyl units as well as thiophene or EDOT donor groups were also employed as photosensitizers for diaryliodonium salts using long wavelength UV light. Photosensitizer molecules had extended spectral sensitivity, low oxidation potential, and excellent solubility in a variety of monomers. Polymerizations were initiated immediately in the presence of the photosensitizers. Moreover, completion of polymerizations took very short time. The molecules were also employed as photosensitizers under solar irradiation yielding fully cured polymers. As figure 4.1 shows when the performance of the two benzotriazole derivatives compared; BBTES is more efficient than BBTS due to its electron rich EDOT groups. Also BBTES has lower oxidation potential and better absorption which makes the process easier and more efficient. Although BIm-Ed has lower oxidation potential and three EDOT groups it is less efficient than BBTES. This difference may be explained with the better absorption of BBTES in long UV-Vis region. Moreover, according to the solar irradiation studies polymerization of BBTES was completed in 2 minutes while polymerizations of BBTS and BIm-Ed were completed in 5 minutes and 7 minutes respectively. In conclusion, both benzimidazole and benzotriazole derivatives are very efficient photosensitizers for diaryliodonium salt in the cationic photopolymerizations of vinyl ether and epoxide monomers by using UV and sun light.

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