ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

LONG WAVELENGTH PHOTOINITIATED FREE RADICAL POLYMERIZATION USING CONJUGATED THIOPHENE DERIVATIVES IN THE PRESENCE OF ONIUM SALTS

M. Sc. Thesis by
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Programme : Chemistry

JUNE 2011

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JUNE 2011

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KONJUGE TİYOFEN TÜREVLERİ KULLANILARAK UZUN DALGABOYUNDA FOTOBAŞLATILMIŞ SERBEST RADİKAL POLİMERİZASYONU

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FOREWORD

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Chemist

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ABBREVIATIONS

^{1}H NMR	**:** Hydrogen Nuclear Magnetic Resonance Spectroscopy
UV	**:** Ultra Violet
GPC	**:** Gel Permeation Chromatography
DSC	**:** Differential Scanning Calorimetry
ISC	**:** Intersystem Crossing
CH_2Cl_2	**:** Dichloromethane
$CDCl_3$	**:** Deuterated Chloroform
THF	**:** Tetrahydrofuran
NaOH	**:** Sodium Hydroxide
PI	**:** Photoinitiator
MMA	**:** Methyl Methacrylate
BA	**:** Butyl Acrylate
TMPTA	**:** Trimethylolpropane Triacrylate
DDT	: 3,5-diphenyldithieno[3,2-b:2′,3′-d]-thiophene

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LONG WAVELENGTH PHOTOINITIATED FREE RADICAL POLYMERIZATION USING CONJUGATED THIOPHENE DERIVATIVES IN THE PRESENCE OF ONIUM SALTS

SUMMARY

Photopolymerization is a technique that finds practical applications in a wide range of diverse fields such as coatings, inks, adhesives high-tech domains, optoelectronics, laser imaging, stereolithography, and nanotechnology. Photopolymerization processes present several important advantages compare to the corresponding thermal reactions. These advantages include low energy requirement, spatial and on and off control and fulfillment of green chemistry demands since polymerization processes may operate without solvent. Photopolymerizations are usually applied to all chain processes, namely free radical, cationic and anionic polymerizations, and also step-growth polycondensation. Although photoinitiated cationic polymerization has gained importance in recent years, the most of the curing applications are still based on the corresponding radical vinyl polymerization. Photoinitiated radical polymerization may be initiated by both cleavage (type I) and H-abstraction type (type II) initiators.

The use of photosensitizers is critical to the success of cationic photopolymerizations in many applications in which photopolymerizations are employed as it accelerates the rates of reactions and requires less energy as they provide polymerizations in longer wavelengths

Electron-rich polynuclear aromatic compounds such as anthracene, perylene, pyrene and phenothiazine, are suitable as photosensitizers as they give redox reactions with onium salts through exciplex to finally yield the initiating species for photo-induced cationic polymerizations.Because of the fact that besides Brønsted acids, radical species are also produced, these salts can also be used as photoinitiators for free radical, and concurrent free radical and cationic polymerizations.

In this thesis, possibility to initiate free radical polymerization via radical cation generation at conjugated thiophene derivative in the presence of onium salts was examined and succeeded. Effectivity of different type onium salts and various (meth) acrylic monomers also determined. The initiation mechanism was evaluated with controlled experiments and ^{1}H-NMR spectra. Lastly, photopolymeration efficiency was determined with photo-DSC analysis.

KONJUGE TİYOFEN TÜREVLERİ KULLANILARAK UZUN DALGABOYUNDA FOTOBAŞLATILMIŞ SERBEST RADİKAL POLİMERİZASYONU

ÖZET

Son yıllarda, fotobaşlatılmış polimerizasyon ekonomik ve çevresel avantajları sebebiyle en çok ilgi çeken araştırma konularından biri haline gelmiştir. Fotopolimerizasyon kaplama, mikroelektronik ve yapıştırıcı sektörü gibi birçok alanda yaygın olarak kullanılmaktadır. Son zamanlarda, fotobaşlatılmış katyonik polimerizasyon önem kazanmış olsa da hala birçok kürleme uygulaması radikalik vinil polimerizasyonuna dayanmaktadır. Fotobaşlatılmış radikal polimerizasyonu hem 1. Tip hem de 2. Tip fotobaşlatıcılar kullanılarak başlatılabilmektedir.

İyodonyum, sülfonyum ve alkoksi piridinyum gibi onyum tuzları ısısal stabiliteleri, katyonik olarak polimerleşebilen monomerlerin içindeki çözünürlükleri ve fotoliz sonucunda reaktif türler oluşturma kabiliyetleri nedeniyle katyonik polimerizasyon için kullanılan en önemli başlatıcılardandır. Brønsted asitlerinin yanı sıra radikalik türler de meydana getirebildikleri için bu tuzlar serbest radikal polimerizasyonunda da kullanılabilmektedir.

Onyum tuzları tek başlarına UV bölgede polimerizasyon başlatmalarına rağmen görünür bölgede veya görünür bölgeye yakın dalga boylarında işlevselliği yoktur. Bu yüzden, onyum tuzlarıyla beraber fotouyarıcılar kullanılmaktadır. Fotouyarıcılar genelllikle görünür bölgede polimerizasyon başlamasına yardımcı olmakta, bu özelliği ile fotopolimerizasyonun güneş ışığı altında bile başlayabilmesine imkan vermektedir. Dolayısı ile gereken enerji miktarını azaltmakta ve çevre dostu olarak nitelendirilmektedir.

Bu tezde, bilinen serbest radikal fotopolimerizasyon sistemlerine dahil olmayan bir fotobaşlatma sistemi incelenmiştir. Bu sistemde, konjuge bir tiyofen türevi olan 3,5-difenilditiyeno[3,2-b:2′,3′-d]-tiyofenin (DDT), bir onyum tuzu varlığında aydınlatılmasıyla elde edilen radikal katyon üzerinden ve onyum tuzunun parçalanması sonucu elde edilen radikalik ürünler üzerinden serbest radikal fotopolimerizasyonunun başlatılabileceği kanıtlanmıştır. Ayrıca bu sistemin polimerizasyon başlatma etkinliği incelenmiş ve başlatma mekanizması aydınlatılmıştır.

1. INTRODUCTION

Photopolymerization is a technique that finds practical applications in a wide range of diverse fields such as coatings, inks, adhesives high-tech domains, optoelectronics, laser imaging, stereolithography, and nanotechnology.[1-3] Although there is an increasing interest in the respective cationic mode,[4, 5] photoinitiated radical polymerization is in more advanced state due to its applicability to a wide range of formulations based on (meth)acrylates and the availability of photoinitiators having spectral sensitivity in a broad wavelength range.[6-9]

Photoinitiated radical polymerization may be initiated by both cleavage (type I) and H-abstraction type (type II) initiators.[7] Recently, an unconventional photoinitiating system not falling into these categories, namely photoinduced endoperoxide formation, was also proposed[10].

Onium salts containing aromatic groups such as diaryliodonium[11], triarylsulfonium[12] and alkoxy pyridinium[13] salts are efficient photoinitiators for the cationic polymerization of vinyl, epoxide, and other types of heterocyclic monomers due to their thermal stability, solubility in most of the cationically polymerizable monomers, and competence in generating reactive species upon photolysis[2, 14]. Because of the fact that besides Brønsted acids, radical species are also produced, these salts can also be used as photoinitiators for free radical, and concurrent free radical and cationic polymerizations[15, 16]. The performance of these photoinitiators particularly at long wavelengths can be improved by three main strategies: (i) oxidation of free radicals,[4, 17, 18] (ii) electron transfer between a photoexcited molecule and an onium salt,[2, 10, 19-27] and (iii) excitation of charge transfer complexes[12, 15, 27, 28] of certain onium salts. The spectral sensitivity of photoinitiated cationic polymerizations may be extended[28-35] to the near UV and visible range by using appropriate free radical sources and aromatic sensitizers.

DDT provides good sensitivity in the near UV region (350–400 nm). Several types of cationically polymerizable monofunctional monomers, such as cyclohexene oxide, n-

butyl vinyl ether, styrene and *N*-vinylcarbazole, and bifunctional monomers such as 3,4-epoxycyclohexyl-3′,4′-epoxycyclohexene carboxylate were readily polymerized in bulk or dichloromethane solutions upon irradiation at 350 nm in the presence of DDT and diphenyliodonium hexafluorophosphate. A mechanism based on electron transfer between excited DDT and iodonium ion was proposed (Scheme 1). A wide range of polynuclear aromatic compounds are known to undergo similar electron transfer reactions[29, 30, 33, 34, 36, 37]. Polymerizations were initiated either by DDT radical cations or the protons formed via hydrogen abstraction or coupling reactions.

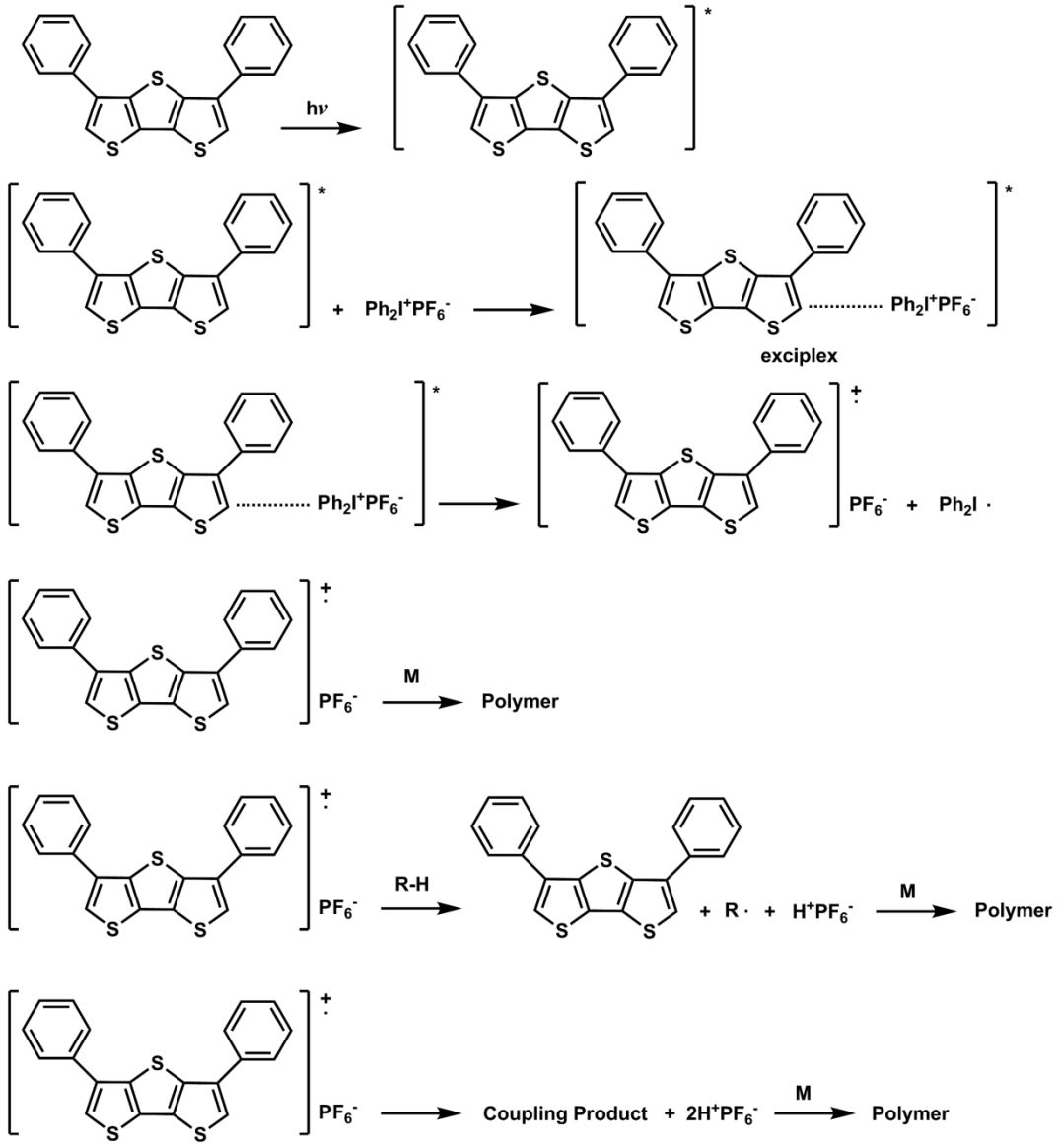


Figure 1.1 : Photoinitiated cationic polymerization by using 3,5 diphenyldithieno [3,2-*b*:2′,3′-*d*]-thiophene (DDT) and diphenyliodonium salt

By virtue of the thiophene-type radical cation formation and the involvement of the thiophene radical in coupling reactions in the electropolymerization, the described photoinduced process has the potential to initiate also free radical polymerization. It seemed, therefore, appropriate to expand the electron transfer reactions between photoexcited thiophene derivatives and onium salts to free radical polymerizing systems. This thesis reports on the photoinitiated free radical polymerization at long wavelengths using highly conjugated thiophene derivative, DDT in the presence of onium salts.

2. TEORETICAL PART

2.1 Photopolymerization

Photopolymerizations that proceed under the influence of visible light have many current as well as potential future applications. For example, photocurable multifunctional methacrylates have revolutionized the field of dental restoratives and composites. In addition to that, photopolymerization finds great interest by other application areas like photoresists, printing plates, highly pigmented coatings, integrated circuits, laser-induced 3D curing, holographic recordings, and nanoscale micromechanics. Many studies involving various photopolymerization processes have been continuously conducted in biomaterials [38] for bones and tissue engineering, microchips, optical resins and recording media, surface relief gratings, anisotropic materials, polymeric photo-optical control materials, clay and metal nanocomposites, photoresponsive polymers, liquid crystalline materials, interpenetrated networks, microlenses, multilayers, surface modification, block and graft copolymerization, two-photon polymerization, spatially controlled polymerizations, topochemical polymerization, solid-state polymerization, living/ controlled polymerization, interfacial polymerization, mechanistically different concurrent polymerizations, pulsed laser polymerization, polymerizations in microheterogenous media, and so forth. Interest has also grown in identifying the reactive species involved in the polymerization process by laser flash photolysis,

time-resolved fluorescence and phosphorescence, and electron spin resonance spectroscopy as well as monitoring the polymerization itself by different methods including real time IR spectroscopy, in-line NIR reflection spectroscopy, differential scanning calorimetry, in situ dielectric analysis, and recently developed optical pyrometry[39].Photopolymerization processes present several important advantages compared to the corresponding thermal reactions[4, 40]. These advantages include low energy requirement, spatial and on and off control and fullfilment of green chemistry demands since polymerization processes may operate without solvent.

Photopolymerization is typically a process that transforms a monomer into polymer by a chain reaction initiated by reactive species (free radicals or ions), which are generated from photosensitive compounds, namely photoinitiators and/or photosensitizers, by ultra violet-visible (UV-Vis) light irradiation[41]. The wavelength or range of wavelengths of the initiating source is determined by the reactive system including the monomer(s), the initiator(s), and any photosensitizers, pigments or dyes that may be present. An active center is produced when the initiator absorbs light and undergoes some type of decomposition, hydrogen abstraction, or electron transfer reactions. Upon generation of active centers, photopolymerizations propagate and terminate in the same manner as traditional (i.e. thermal) polymerizations. Although photopolymerization can be initiated radically, cationically and anionically, much effort has been devoted to free radical and cationic systems mainly due to the availability of a wide range of photoinitiators and the great reactivity of monomers.

2.1.1 Photoinitiated free radical polymerization

Photoinitiated free radical polymerization basicly contains three steps; namely photoinitiation, propagation, and termination (Figure 2.1). In this process, light has role at the first step that includes absorption and generating free radicals. Propagation and termination steps are totally thermal process and light does not affect these steps.

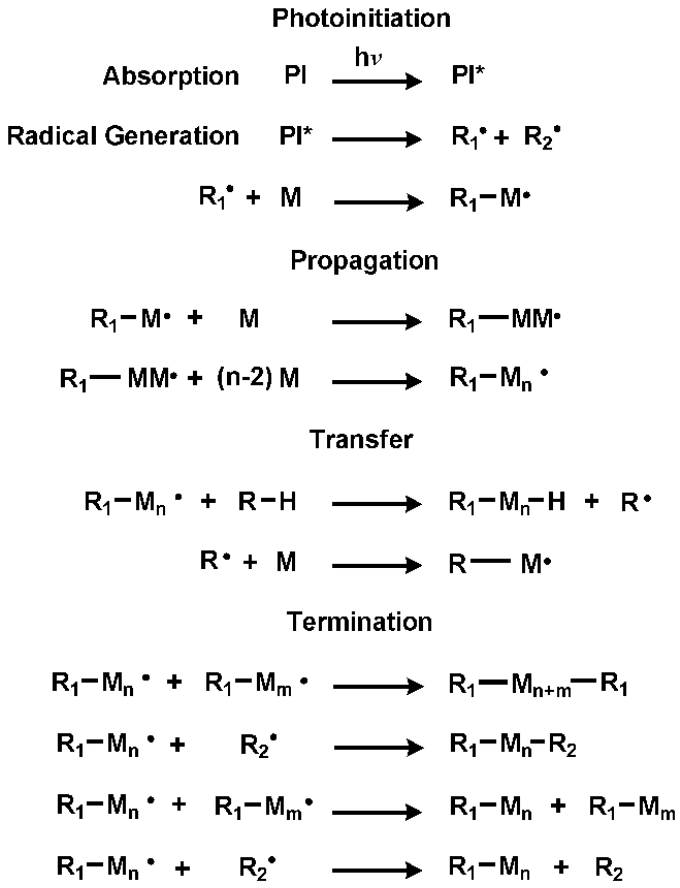


Figure 2.1 : General photopolymerization mechanism

Photoinitiation includes absorption of light by a photosensitive compound or transfer of electronic excitation energy from a light absorbing sensitizer to the photosensitive compound. Homolytic bond cleavege results in the formation of a radical that reacts with one monomer unit. Repeated addition of monomer units to the chain radical produces the polymer backbone (propagation).

Chain transfer also takes place, that is, growing chains abstracts an hydrogen from various species and generates new radicals that has capabilty to initiates new chains..

Finally, active species are consumed by disproportionation or recombination reactions. Termination can also occur by recombination or disproportionation with any other radical including primary radicals produced by the photoreaction.

2.1.2 Absorption of light

Photochemistry is concerned with chemical reactions induced by optical radiation [42-44]. The radiation is most often ultraviolet (200–400 nm) or visible (400–800 nm) light but is sometimes infrared (800–2500 nm) light.

The absorption of a photon of light excites the electrons of a molecule. The stability of bond of compound is reduced by electronic excitation, under this circumstance, lead to its dissociation.

Chromophoric groups defined as having functional group which show high absorbency. For example, phenyl rings or carbonyl groups take place in this groups. The energy causing excitation, E, is described by $E=hc/\lambda$ where h is Planck's constant, c is the speed of light, and , λ is the wavelength of the exciting light. Light absorption is described by $A= \varepsilon x C x l$, where ε is the molar absorptivity (extinction coefficient), C is the concentration of the species, and *l* is the light path length.

2.1.3 Initiators for free radical photopolymerization

Most of photoinduced reactions are carried out by using photoinitiators in order to generate radicals. A photoinitiator is a molecule that absorbs energy of radiation, and consequently initiates polymerization. Photoinitiators are generally divided into two classes according to the process by which initiating radicals are formed. Type I photoinitiators and Type II Photoinitiators.

Type I Photoinitiators: Unimolecular Photoinitiators

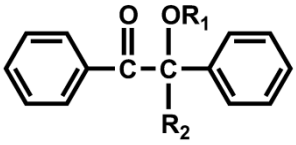
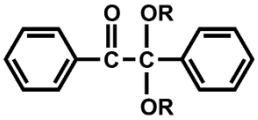
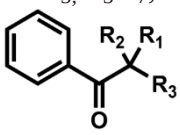
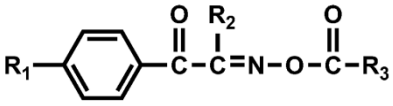
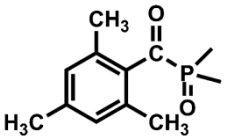
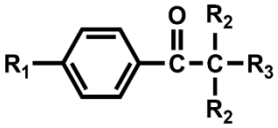
Compounds which generate free radicals via unimolecular bond cleavage upon irradiation as shown in Eq. 2.1 are named "*Type I* photoinitiators". This process is termed homolytic cleavage or direct fragmentation. The fragmentation that leads to the formation of radicals is, from the point of view of chemical kinetics, a unimolecular reaction.

$$PI \xrightarrow{h\nu} PI^* \xrightarrow[\text{fragmentation}]{\text{unimolecular reaction}} \underset{\text{free radicals}}{R_1^\bullet + R_2^\bullet} \qquad (2.1)$$

There are many photoinitiators which are classified as most efficient *Type I* photoinitiators, and are termed as benzoin ether derivatives, benzil ketals,

hydroxylalkylphenones, α-aminoketones and acylphosphine oxides. Examples of them are given in the Table 2.1 [45-48].

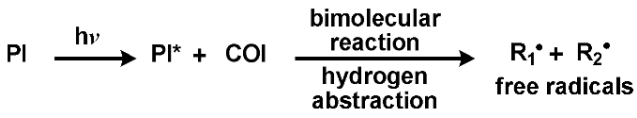
Table 2.1: Main *Type I* photoinitiators for free radical polymerization

Photoinitiators	***Structure***	λ_{max} ***(nm)***
Benzoin ethers	 R_1 = H, alkyl R_2 = H, substituted alkyl	323
Benzil ketals	 R = CH_3, C_3H_7, CH_2	365
Acetophenones	 R_1 = OCH_3, OC_2H_5 R_2 = OCH_3, H R_3 = C_6H_5, OH	340
Benzyl oximes	 R_1 = H, SC_6H_5 R_2 = CH_3, C_6H_{13} R_3 = C_6H_5, OC_2H_5	335
Acylphosphine oxides	 R = C_6H_5 or OCH_3	380
Aminoalkyl phenones	 R_1 = SCH_3, morpholine R_2 = CH_3, CH_2Ph or C_2H_5 R_3 = $N(CH_3)_3$, morpholine	320

Type II Photoinitiators: Bimolecular Photoinitiators

When certain compounds absorb light leading to excited state molecules, they do not undergo *Type I* reactions because their excitation energy is not high enough for fragmentation (i.e., their excitation energy is lower than the bond dissociation energy). The photoinitiator that absorbs the light and a co-initiator that serves as a hydrogen or electron donor. The excited state photoinitiator interacts with the

coinitiator (COI), to generate initiating radicals in a bimolecular reaction as shown in Eq. 2.2, the initiating system is termed a "*Type II* Photoinitiator".



(2.2)

In *Type II* systems, radicals are generated by two distinct pathways: hydrogen abstraction and photo-induced electron transfer process.

Hydrogen abstraction

Photoinitiators that proceed via a hydrogen abstraction mechanism are exemplified by combination of benzophenone and a hydrogen donor (Figure 2.2) When R-H is an amine with transferable hydrogen, benzophenone undergoes an electron transfer followed by a hydrogen abstraction to produce an initiating species and semipinacol radical. The semipinacol radical does not efficiently initiate polymerization and typically react with other radicals in the system as a terminating species causing a reduction in the polymerization rate.

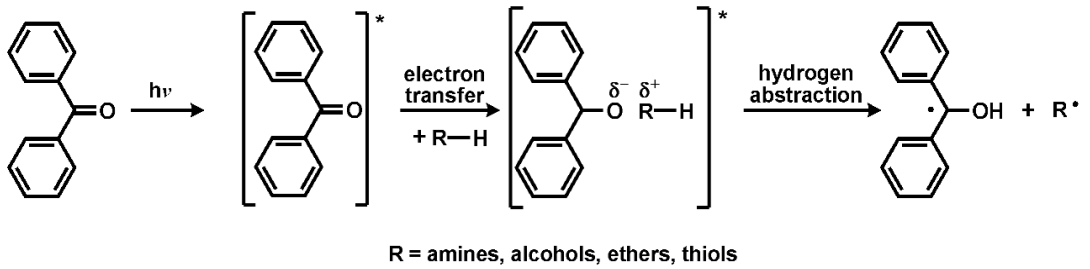
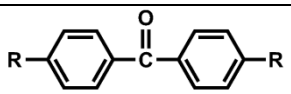
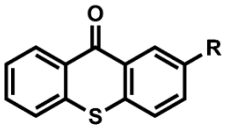
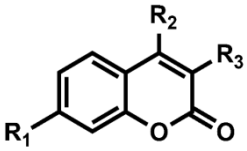
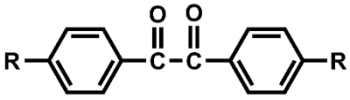


Figure 2.2 : Photo-induced free radical formation upon irradiation of benzophenone in the presence of hydrogen donor

Table 2.2: *Type II* free radical photoinitiators

Photoinitiators	Structure	λ_{max} (nm)
Benzophenones	 R = H, OH, $N(C_2H_5)_2$, C_6H_5	335
Thioxanthones	 R = H, Cl, isopropyl	390
Coumarins	 R_1 = $N(C_2H_5)_2$, $N(CH_3)_2$ R_2 = CH_3, cyclopentane R_3 = benzothiazole, H	370
Benzils	 R = H, CH_3	340

Type II photoinitiators including benzophenones, thioxanthones, benzyls, and ketocoumarins are listed in Table 2.2

Upon photolysis of aromatic ketones, such as benzophenone and thioxanthones, in the presence of hydrogen donors, such as alcohols or amines, formation of a radical produced from the carbonyl compound (ketyl type radical) and another radical derived from the hydrogen donor occurs. The photopolymerization of vinyl monomers is usually initiated by the radical produced from the hydrogen donor. The ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electron.

2.1.4 Sensitization via exciplexes

The use of photosensitizers is critical to the success of cationic photopolymerizations in many applications in which photopolymerizations are employed as it accelerates the rates of reactions and requires less energy as they provide polymerizations in longer wavelengths [2, 20, 24, 31, 49-52].

Electron-rich polynuclear aromatic compounds such as anthracene, perylene, pyrene and phenothiazine, are suitable as photosensitizers as they give redox reactions with onium salts through exciplex to finally yield the initiating species for photo-induced cationic polymerizations [53]. The mechanism of a polymerization followed via exciplex formation through the excited sensitizer with the ground state onium salt is illustrated by reactions 2.3 :

$$PS \xrightarrow{h\nu} [PS]^*$$

$$[PS]^* + Ar_2I^+MtX_n^- \longrightarrow \underset{\text{exciplex}}{[PS....Ar_2I^+MtX_n^-]^*}$$

$$[PS....Ar_2I^+MtX_n^-]^* \longrightarrow [PS]^{+\cdot}MtX_n^- + Ar_2I\cdot$$

$$Ar_2I\cdot \longrightarrow ArI + Ar\cdot$$

$$[PS]^{+\cdot}MtX_n^- \xrightarrow{\text{Monomer}} \text{Polymer}$$

$$[PS]^{+\cdot}MtX_n^- + R\text{-}H \longrightarrow PS + R\cdot + H^+MtX_n^- \xrightarrow{\text{Monomer}} \text{Polymer}$$

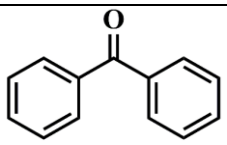
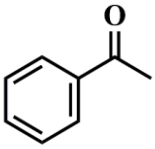
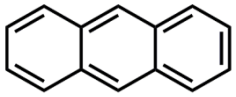
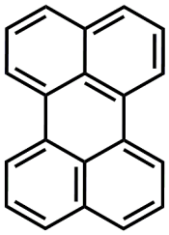
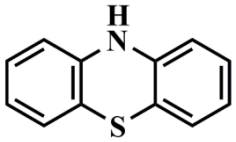
$$[PS]^{+\cdot}MtX_n^- \longrightarrow \text{Coupling Product} + 2H^+MtX_n^- \xrightarrow{\text{Monomer}} \text{Polymer}$$

Figure 2.3 : The mechanism of a polymerization followed via exciplex formation through the excited sensitizer with the ground state onium salt

First, photosensitizer absorbs the light to give the corresponding excited species [PS]*. An excited state complex (exciplex) is formed as an intermediate between onium salt and excited photosensitizer. In the following step, one-electron is transferred from the sensitizer to the onium salt. Unstable diaryliodine radical decomposes rapidly and makes the process irreversible by preventing back electron transfer. The radical cations would be capable of initiating cationic polymerization since direct initiation by the species formed from polynuclear aromatic compounds is

a well known process and, because of the non-nucleophilicity of PF_6^- ions, cationic chain propagation would not be prevented.

Table 2.3: Structures, oxidation potentials, triplet or singlet excitation energies and absorption characteristics of some common photosensitizers

Photosensitizer	$E_{1/2}^{ox}$ (PS) (V)	E^* (PS) (kJ·mol^{-1})	λ_{max} (nm) (ε_{max} (mol^{-1}·cm^{-1}))
 Benzophenone	2.7	290 (E_T)	252 (17600) 333 (148) 342 (140)
 Acetophenone	2.9	308 (E_T)	242 (12600) 279 (1050) 318 (60)
 Anthracene	1.1	319 (E_S)	252 (220000) 356 (8500) 374 (8500)
 Perylene	0.9	277 (E_S)	252 (53000) 435 (39500)
 Phenothiazine	0.6	239 (E_T)	254 (61000) 318 (4680)

In recent works, use of electron rich compounds as a free radical photopolymerization initiator has examined. Neckers et al. described free radical photopolymerization initiating ability of gold nanoparticle tailored with conjugated thiophene derivative.[54] This work shows possibility of initiation free radical polymerization via radical cation generated at conjugated systems. In the light of this

knowledge, possibility of initiatiating free radical polymerization via radical cation generated at exciplex state is examined. As far as we know this is first example of this type initiation systems.

2.1.5 Onium salts

Onium salts are the most widely used cationic photoinitiators. They contain chromophopric groups as the light sensitive body with heteroatoms as cationic centers in the structure. As counterions, mostly inorganic metal complex anions are used [42]. Each of these components has specific function and can be varied independently depending on the purposed application. The cation of an onium salt is the light absorbing portion of the compound and its structure determines the wavelength sensitivity and quantum yield of the initiator. In addition, the character of the cation also has an influence on the excited state chemistry and whether or not the onium salt can undergo photosensitization with a photosensitizer. The character of the anion can be widely varied to tune the strength of the acid that is generated. It is known that there is a correlation between the Hammett acid strength (H_o) of various acids and their effective use in several reactions (Figure 2.4) [55, 56].

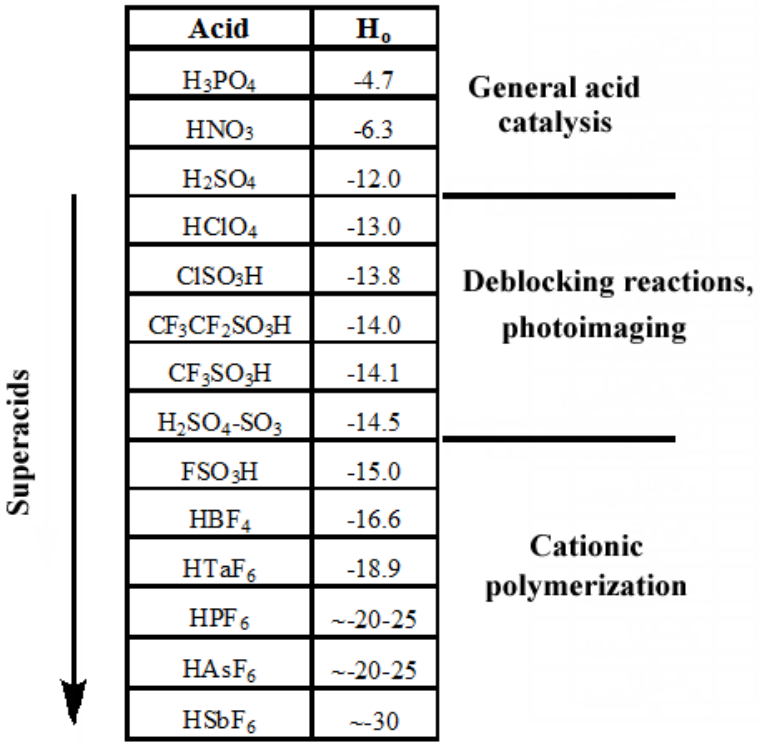


Figure 2.4 : Relationship between Hammett acid strength (Ho) and the catalysis of various types of reactions

In recent years, onium salts with highly nucleophilic counterions such as Cl^-, Br^- and I^- have also been used in conjuction with Lewis acids. Different types of onium salts are shown in Figure 2.5.

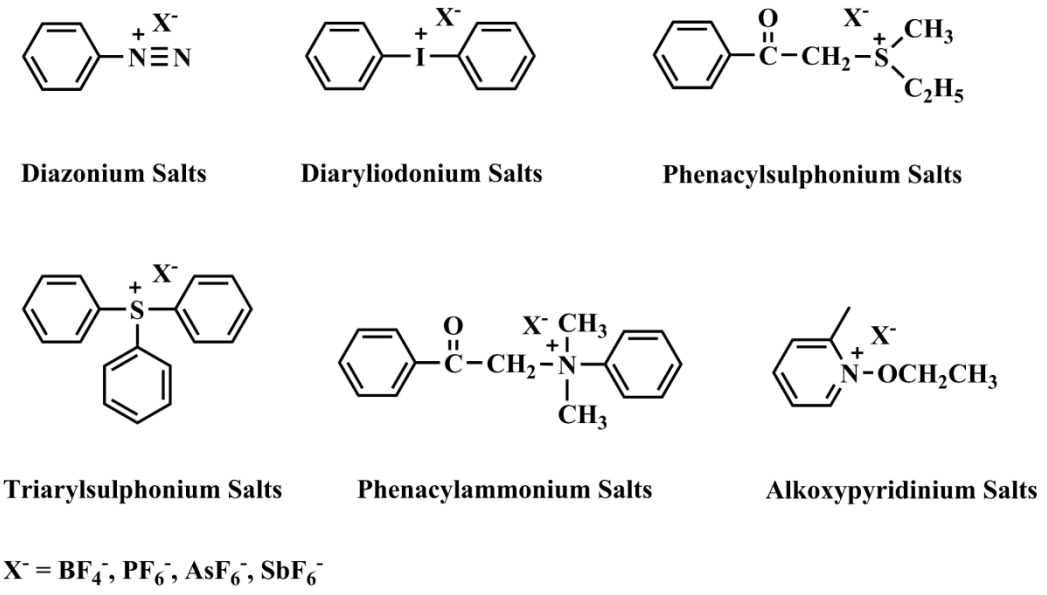


Figure 2.5 : Types of onium salt photoinitiators

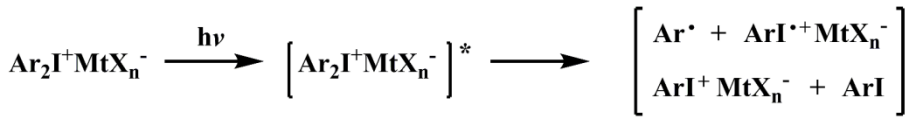
So far, the most frequently used onium salts are diaryliodonium [11, 57], triarylsulfonium [58, 59], alkoxypyridinium [13, 35] and phenacyl [14, 60-67] salts with non-nucleophillic counter ion that mainly absorb the light in the region between 225 and 350 nm for photoinitiated cationic polymerization.

Diaryliodonium salts

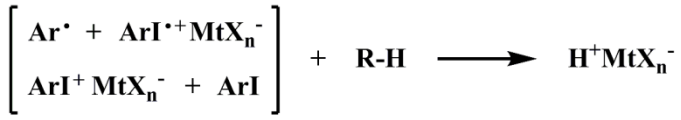
Diaryliodonium salts are the most frequently used halonium salts as they are easy to obtain and quite reactive [11, 68, 69]. The nucleophillic halogen counter-ion must be replaced by a non-nucleophillic anion in order to prevent the termination of cationic polymerization.

As they generally have low spectral sensitivity, an electrophillic substitution reaction can be applied on the aromatic rings to posses electron donating species which can move absorption bands to lower energies. Alternatively, some special additives can be used to carry out polymerization at longer wavelengths.

Photolysis of diaryliodonium salts take place either through homolytic or heterolytic cleavage of the halogen-aryl bond to form species which react with a hydrogen donor compound to yield a Brønsted acid that initiates polymerization (reactions 2.3-2.5).



(2.3)



(2.4)

(2.5)

R-H : solvent or monomer

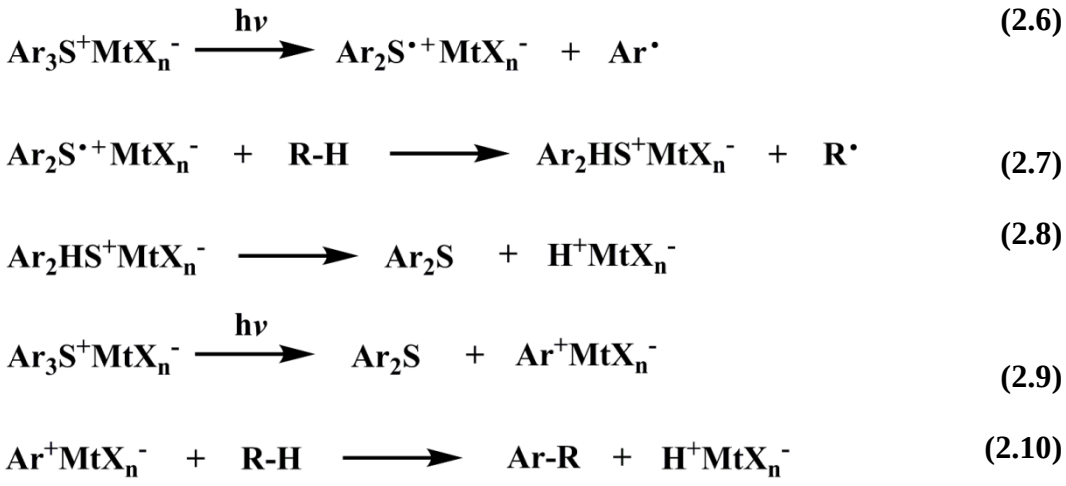
MtX_n^- : PF_6^-, SbF_6^-, AsF_6^-, etc.

Notably, the electron donating substituents on the aromatic structures not only shifts absorption bands to longer wavelengths, but also favors photolysis of diaryliodonium salts to afford higher polymerization rates.

Triarylsulphonium salts

Triaryl sulphonium salts (TAS) are generally produced by the method of Pitt: [70] a Friedel–Crafts condensation of aromatic hydrocarbons with sulphur dichloride, followed by chlorination and further condensation. Various alkylaryl sulphonium salts may be synthesized by an alkylation of mercaptobenzene [71].

The photolysis mechanism is similar with the diaryliodonium salts. When irradiated in appropriate wavelengths, TAS's undergo either a homolytic or a heterolytic cleavage followed by a proton release after some additional steps which are summarized in (reactions 2.6-2.10).



(2.6)

(2.7)

(2.8)

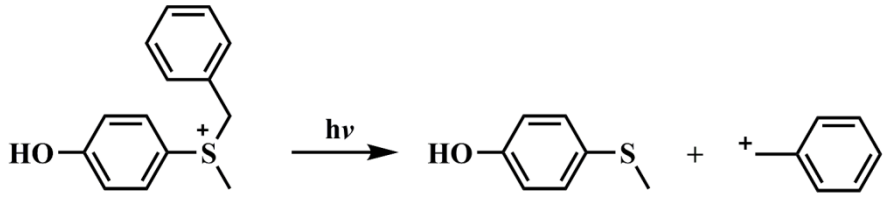
(2.9)

(2.10)

R-H : solvent or monomer

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

In some special cases, a Brønsted acid does not need to be the only initiating species. If heterolytical cleavage of one of the alkyl groups results with a stable carbocation, polymerization can possibly be initiated by this intermediate structure (2.11).



(2.11)

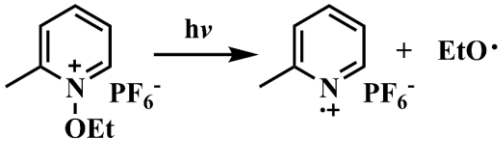
Recently, novel sulfonium type initiators, which can initiate polymerization either upon irradiation or thermal treatment have been developed [72]. In addition, these photoinitiators are shown to be functional for both cationic and radical polymerization. This dual activity is particularly important in hybrid curing systems for coatings and adhesions. Dialkyl-4-hydroxyphenylsulphonium salts with absorption maxima in the middle UV region have also been reported [73-75]. Being poorly soluble in common monomers used in photocationic curing, these sulfonium compounds attract little attention. However, derivating the structure with possessing different alkyl groups, improved solubility characteristics can be achieved.

N-Alkoxy pyridinium salts

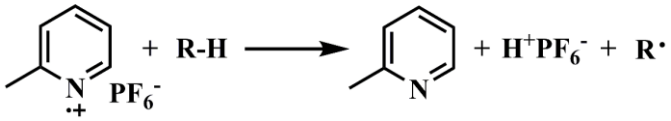
N-Alkoxy Pyridinium salts are obtained with relatively high yields by a reaction of pyridine *N*-oxides with a triethyloxonium salt in methylene chloride or chloroform

[13]. Quinolinium salts can also be prepared from the corresponding *N*-oxides [76]. In both cases, an anion exchange is not necessary since the triethyl oxonium salt is available with non-nucleophilic counter anions. The spectral response of these salts is in 260-310 nm range [13].

When irradiated in suitable wavelengths, these salts readily initiate polymerization of appropriate monomers according to the following mechanism as exemplified for the case of *N*-ethoxy–2-methylpyridinium hexafluorophosphate ($EMP^+ PF_6^-$) in reactions 2.31 and 2.32.

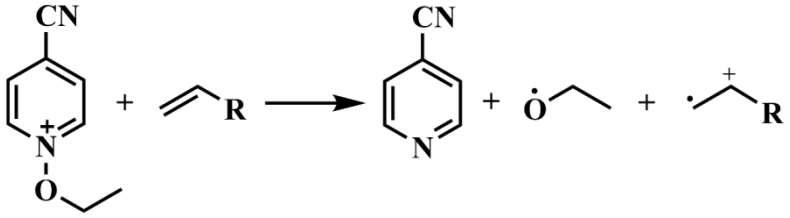


(2.12)



(2.13)

Notably, some reactive monomers like isobutylvinylether and *N*-vinylcarbazol are observed to polymerize even in dark when used in conjuction with *N*-ethoxy-4 cyanopyridinium (EPP) and *N*-ethoxyisoquinolinium (EIQ) salts. An electron transfer from the monomer to these initiators can be proposed as an explanation for the observed reactivity in the absence of light (2.14).



(2.14)

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Methyl methacrylate (MMA, 99%, Aldrich):

It was used as received.

Butyl acrylate (BA, ≥99%, Aldrich):

It was used as received.

Methyl acrylate (MA, 99%, Aldrich):

It was used as received.

Trimethylolpropane triacrylate (TMPTA, 99%, Sigma-Aldrich) :

Trimethylolpropane triacrylate was used as recieved.

3.1.2 Solvents

Dichloromethane (99.8, J.T. Baker):

It was extracted first with sulfuric acid, then with 5% NaOH solutions. After washing with water, CH_2Cl_2 was dried over anhydrous $CaCl_2$ and CaH_2 and finally distilled with a fractionation column.

Methanol (Technical):

It was used for the precipitation of polymers without further purification.

Ethanol (Riedel-de Haën):

It was used for the crystallization of a monomer without further purification.

Tetrahydrofuran (THF, 99.8%, J.T.Baker):

(a) It was used as eluent for chromatography as received (High Performance Liquid Chromatography Grade).

(b) For use in the chemical reactions, it was dried and distilled over benzophenone/sodium.

Acetone (99%, Carlo Erba):

It was used without further purification.

3.1.3 Other chemicals

Diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$, 98%, Alfa Aesar):

It was used at received.

2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO, 99%, Aldrich):

It was used at received.

Sulfuric acid (H_2SO_4, 95-97%, Fluka) : Sulfuric acid was used as recieved.

Triphenylsulfonium hexafluorophosphate ($Ph3S^+PF_6^-$)[77] :
it was prepared according to the previously described procedure.

N-ethoxy-2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$)[4, 78]:
it was prepared according to the previously described procedure.

3.2 Equipments

3.2.1 Photoreactor

A Polilight PL400 Forensic Plus light source emitting light at 350 nm was used.

3.2.2 ^{1}H Nuclear magnetic resonance spectroscopy (^{1}H-NMR)

^{1}H-NMR spectra of 5–10 % (w/w) solutions in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer.

3.2.3 UV-Visible spectrophotometer

UV-Visible spectra were recorded on a Shimadzu UV-1601 UV-visible spectrophotometer.

3.2.4 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV

detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL GPC columns ($G2000H_{HR}$, $G3000H_{HR}$ and $G4000H_{HR}$), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were 456–42,800, 1050–107,000, and 10,200–2,890,000, respectively. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 30°C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Molecular weights were calculated with the aid of polystyrene standards.

3.2.5 Photocalorimetry (Photo-DSC)

The photo-differential scanning calorimetry (Photo-DSC) measurements were carried out by means of a modified Perkin-Elmer Diamond DSC equipped with a Polilight PL400 Universal Forensic Light Source at 350 nm. A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 67 mW cm^{-2} by a UV radiometer covering broad UV range. The mass of the samples was 3 mg and the measurements were carried out in an isothermal mode at 30 °C under a nitrogen flow of 20 mL min^{-1}. The reaction heat liberated in the polymerization was directly proportional to the number of acyrlate double bonds reacted in the system. By integrating the area under the exothermic peak, the conversion of the acrylate or methacrylate groups (C) or the extent of the reaction was determined according to eq 1:

$$C = \Delta H_t / \Delta H_0^{\text{theory}} \quad \textbf{(3.1)}$$

where ΔH_t is the reaction heat evolved at time t and ΔH_0^{theory} is the theoretical heat for complete conversion. ΔH_0^{theory} = 86 kJ mol^{-1} for an acrylic double bond.[5] The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by eq 3,2:

$$R_p = dC/dt = (dH/dt)/\Delta H_0^{theory} \quad \textbf{(3.2)}$$

3.3 Preparation Methods

3,5-Diphenyldithieno[3,2-b:2',3'-d]thiophene (DDT) was kindly synthesized by Ipek Oksen from Ozturk group. Its synthesis procedure is given below.

3.3.1 Synthesis of 3,5-diphenyldithieno[3,2-*b*:2',3'-*d*]thiophene (DDT).

Dithieno[3,2-*b*;2',3'-*d*]thiophene, having phenyl groups (at 3- and 5-positions for further delocalization) was synthesized, employing a recently developed 1,8-diketone ring closure reaction. This method opens up a way to form dithienothiophenes via a one-pot two ringclosure reaction of α-dithioketones at the 3- and 4-positions of the thiophene ring. The synthesis of the target molecule required four steps starting with tetrabromination of thiophene with Br2, which gave 95% of tetrabromothiophene. Selective removal of the bromines at the 2- and 5-positions was carried out using Zn to yield 85% of 3,4-dibromothiophene, to which α-thioketones at the 3- and 4-positions were introduced via a one-pot, three step reaction; (i) lithiation with *n*BuLi at -78 °C, (ii) addition of sulfur and (iii) introduction of α-thioketones by adding α-bromoketones to the mixture. The yield of the product was found as 55%. The crucial dual ring closure was achieved by treatment of the diketone with P4S10 in boiling anhydrous toluene, which took nearly 3 h to complete. Yield of 43% was obtained for the final compound (Figure 3.1) [17,18]. (mp 130-132 °C). Anal. Calcd for $C_{20}H_{12}S_3$: C 68.96, H 3.44 found: C 68.99, H 3.38; FABMS *m/e* 348 (M+); 1H NMR (200 MHz, $CDCl_3$) δ 7.81 (d, J = 7.4 Hz, 4H, Ph), 7.42 (m, 8H, Ph+thiophene); ^{13}C NMR (50.32 MHz, CDCl3) δ 135.9, 134.5, 131.3, 129.0, 128.4, 127.5, 126.6, 121.3.

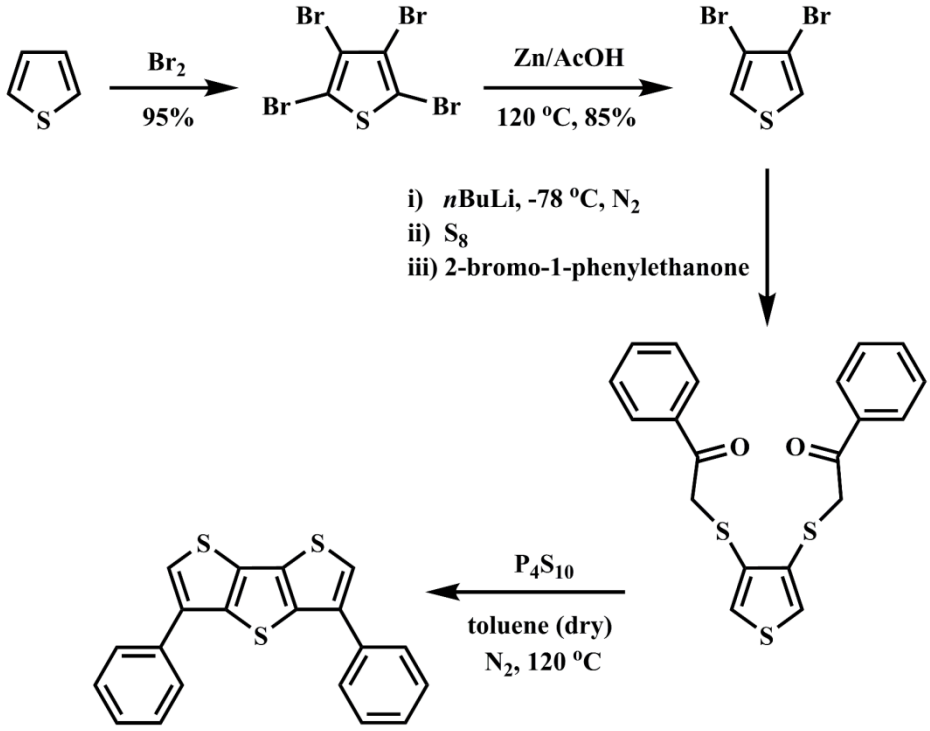


Figure 3.1: Synthesis of DDT

3.3.2 General procedure for photopolymerization

Photopolymerizations were carried out under nitrogen atmosphere. Prior to irridation, the appropriate solutions of monomers containing given amounts of DDT, onium salts, and CH_2Cl_2 were placed in pyrex tubes and irradiated at λ= 350 nm. The viscous polymer solutions formed during the irradiation were poured into methanol. The precipitated polymers were then filtered off and dried in vacuo.

4. RESULTS AND DISCUSSION

3,5-Diphenyldithieno[3,2-b:2′,3′-d]thiophene (DDT) aborbs the light at 350-450 nm wavelength region where the onium salts are transparent and photoexcited DDT is rapidly quenched by onium salts (Figure 4.1).

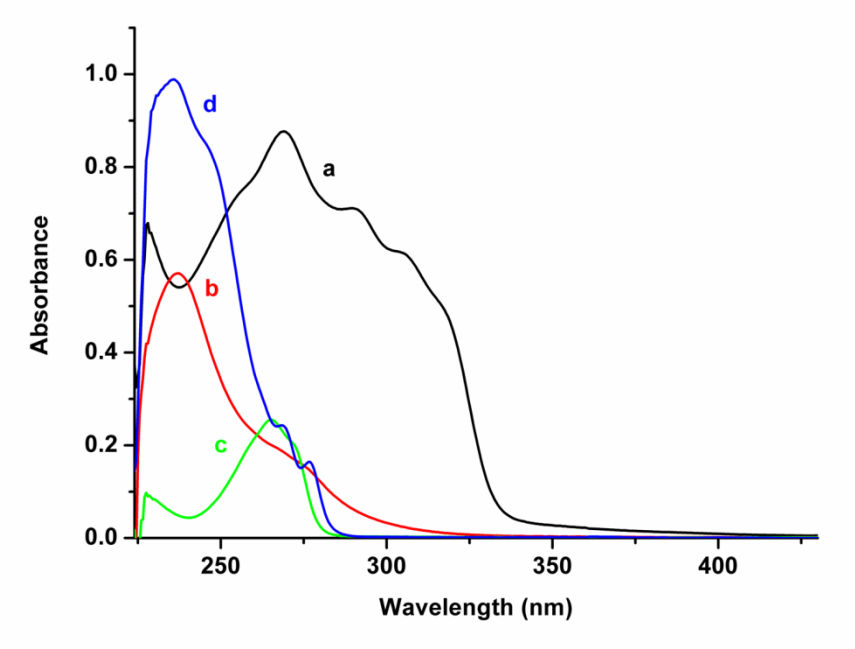


Figure 4.1 : UV spectra of (a) DDT (5×10^{-5} mol L^{-1}), (b) $Ph_2I^+PF_6^-$ (5×10^{-5} mol L^{-1}), (c) $EMP^+PF_6^-$ (5×10^{-5} mol L^{-1}) and (d) $Ph_3S^+PF_6^-$ (5×10^{-5} mol L^{-1}) in CH_2Cl_2

Thus, photoinitiated polymerization of several (meth)acrylate monomers was performed at 350 nm by using DDT in the presence of diphenyliodonium salt. Polymerizations were conducted in dichloromethane solutions since onium salts are not soluble in the monomers employed. Typical results are presented in Table 4.1.

Table 4.1 : Photoinitiated radical polymerization of various monomers in the presence of 3,5-diphenyldithieno[3,2-*b*:2',3'-*d*]thiophene (DDT) and $Ph_2I^+PF_6^-$ at room temperature (λ=350 nm, light intensity = 67 mW cm^{-2})

Run	Monomer (mol $L^{-1}\times10^3$)	PS[d] (mol L^{-1})	Onium salt (mol L^{-1})	Time (min)	Conv. (%)	$M_n\times10^{-4}$	M_w/M_n
1	MA(9.3)	2.5×10^{-4}	5×10^{-4}	5	10.1	32.4	1.87
2	MA(9.3)	5×10^{-4}	1×10^{-3}	5	14.0	25.3	1.45
3	MA(9.3)[a]	5×10^{-4}	1×10^{-3}	5	-	-	-
4	MA(9.3)[b]	5×10^{-4}	1×10^{-3}	5	-	-	-
5	MA(9.3)[c]	5×10^{-4}	1×10^{-3}	5	23	26.1	1.92
6	MA(9.3)	-	1×10^{-3}	5	-	-	-
7	BA(5.8)	5×10^{-4}	1×10^{-3}	20	17.6	17.96	2.03
8	BA(5.8)	-	1×10^{-3}	20	-	-	-
9	MMA(7.8)	5×10^{-4}	1×10^{-3}	20	2.7	2.8	1.54
10	MMA(7.8)	-	1×10^{-3}	20	-	-	-

[a] The experiment was performed in the presence of a radical scavenger TEMPO (2.5 × 10–3 mol·L–1). [b] Oxygen saturated. [c] Benzophenone/ N,N-dimethylaniline system was used instead of DDT/$Ph_2I^+PF_6^-$, [d] Photosensitizer

They give clear indication for the sensitization effect of the thiophene compound for the polymerization as no polymerization occured in the absence of DDT since iodonium salt is transparent at the irradiation wavelength. However, at very high iodonium concentrations some but little polymerization is occured due to the pronounced tail absorption of the salt. As can also be seen that among the monomers tested, methyl acrylate (MA) seemed to undergo polymerization more readily due to the less sterical hindrance and higher propagation rate constant. The polymerization was totally inhibited by the addition of 2, 2, 6, 6- tetramethyl-1- piperidinyloxy (TEMPO) as the radical scavanger indicating that the free radical mechanism is responsible for the initiation. Possible effect of oxygen in the polymerization was

also examined. Expectedly, the polymerization was totally inhibited when air was present in the system (Table 1, Run 4). For comparison, MA was polymerized using benzophenone/ N,N dimethylaniline as conventionally used photoinitiator for various applications. As can be seen, benzophenone initiates polymerization more efficiently then the described system. However, our system provides flexibility to apply to both radical and cationic formulations without any additional component.

Table 4.2 Photoinitiated radical polymerization of methyl acrylate (MA) in the presence of DDT and several onium salts at room temperature. (λ= 350 nm, light intensity= 67 mW·cm^{-2})

Onium Salt	Time (min)	Conversion (%)	Mn (g·mol^{-1})	Mw/Mn	ΔGS[b] (kcal·mol^{-1})
$Ph_2I^+ PF_6^-$	5	14.0	253300	1.45	–57.8
$Ph_3S^+PF_6^-$	30	9.4	546800	3.50	–34.7
$EMP^+PF_6^-$	30	5.7	422800	2.95	–46.3

[a] For diphenyliodonium salt E_{red} = –0.20 V vs. SCE[20], for triphenylsulfonium salt E_{red} = –1.20 V vs. SCE[20] and for N-ethoxy-2-methylpyridinium salt E_{red} = –0.70 V vs. SCE[31], [b] Free Energy Changes

Table 4.2 gives data for a series of polymerization of MA utilizing DDT and different onium salts. Although all onium salts are effective in initiating the polymerization, diphenyliodonium salt seemed to be the most efficient oxidizing agent in the process. Expectedly, the other onium salts, sulfonium and Nalkoxy pyridinium salts exhibit lower efficiency due to their less favorable redox potentials compared to the iodonium salt.

According to the Rehm-Weller equation (eq 4.1) electron transfer from the excited sensitizer to onium salt is feasible if the change in free energy (G) is negative. Based on the oxidation potential (Eox) and active excitation energy (E*) of the photosensitizer (PS) and the reduction potential (Ered) of the initiator (PI), the free energy change (G) for the photoinduced electron transfer process was estimated.[31]

$$\Delta G = E\text{ox(PS)} - E\text{red(PI)} - E^*\text{(PS)} \qquad \textbf{(4.1)}$$

Table 2 also summarizes the GS and GT values of the free energy changes for the electron transfer from the singlet and triplet excited states, respectively, of DDT to the ground-state cationic salts. Eox for DDT determined by cyclic voltametry is 0.88 V[79], whereas the singlet excitation energy ES* and triplet excitation energy E_T* have been found to be 82.6 kcal mol^{-1} and 63.7 kcal mol^{-1} , respectively. Scheme 2 shows the mechanism for free radical polymerization of MA based on electron transfer concerning the reaction of excited DDT with onium salt on the example of iodonium salt. As in the case of corresponding cationic polymerization (see Scheme 1), initially DDT radical cations are formed. Polymerization is expected to occur at the α position of thiophene first by reaction of DDT radical cations with MA and then deprotonation.

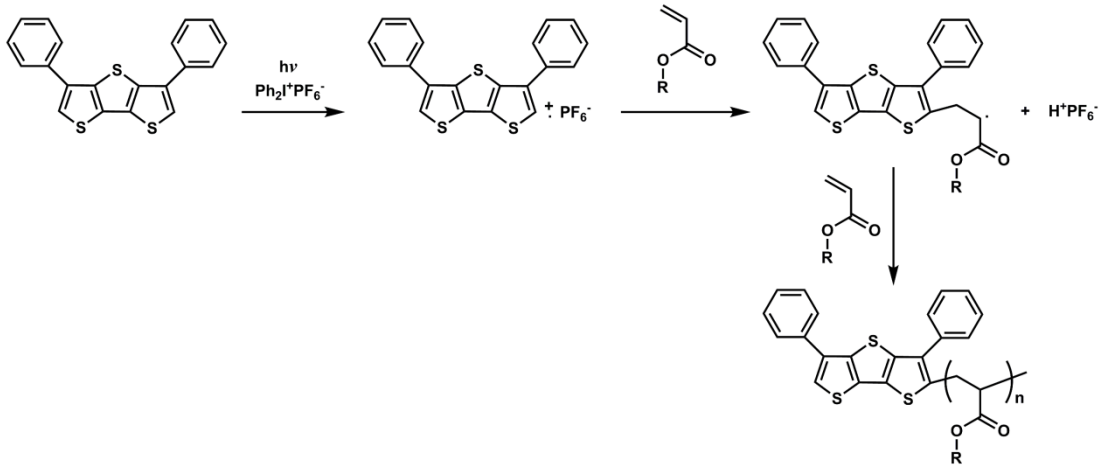


Figure 4.2 : Photoinitiated free radical polymerization of acrylates by using 3,5 diphenyldithieno[3,2-*b*:2',3'-*d*] thiophene and diphenyliodonium salt

Similar mechanism was accounted for the photoinitiated free radical polymerization through thiophene radical cations formed on gold nanoparticles. Neckers and coworkers[54] elegantly showed that the charge-separated states of the gold nanoparticles attached to bithiophene group generated upon exposure to UV light are active intermediates that can cause polymerization of an acrylic monomer. In addition to the efficient photoinitiation, the process leads to the uniform distribution of gold nanoparticles in the polymer matrix and polymer nanocomposite with a unique texture was obtained by one step photochemical process.

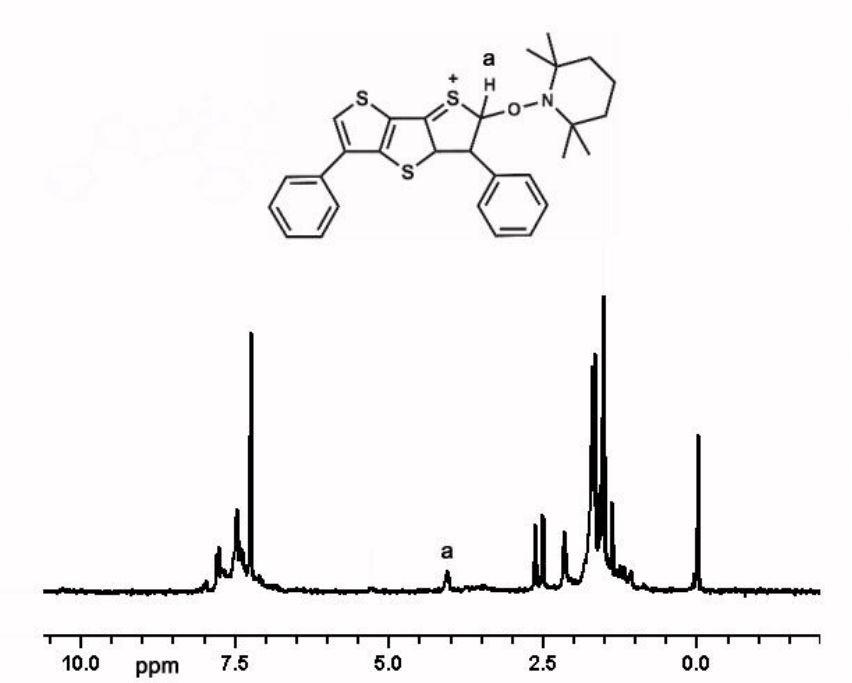


Figure 4.3 : ^{1}H NMR spectrum of the product formed from the photolysis of DDT and iodonium salt in the presence of TEMPO in $CDCl_3$

To investigate further if the thiophene based radical cations are the reactive intermadiates playing a crusial role in the polymerization process and to determine the initiating radicals, the experiments using an excess of a stable radical, such as TEMPO in the absence of an added monomer was performed. Indeed, the ^{1}H NMR spectrum of the product (Figure 4.3) formed from the photolysis of DDT and iodonium salt in the presence of TEMPO in methylene chloride present a weak resonances of the aromatic proton at 4.1 ppm indicative of the thiophene radical cation coupling product of the following structure (figure 4.4).

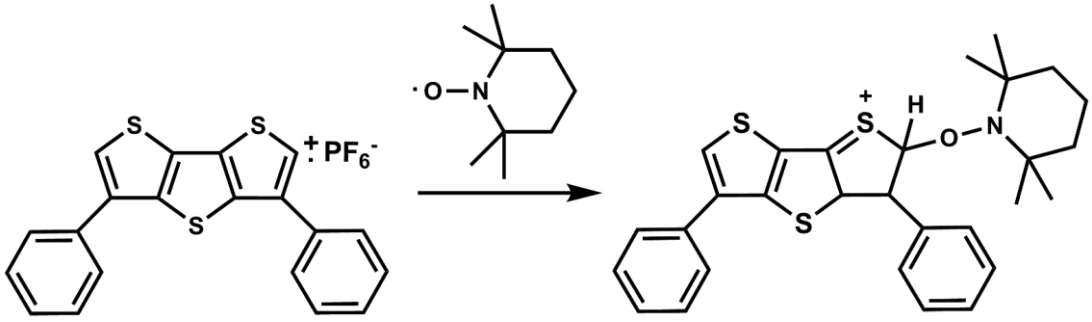


Figure 4.4 : Structure of the coupling product formed from the photolysis of DDT and diphenyliodonium salt in the presence of TEMPO

The efficiency of the photoinitiating system in the photocuring of formulations containing multifunctional monomers such as trimethylolpropane triacrylate (TMPTA) was also studied. In Figure 4.5, Photo-DSC profiles referring to the polymerization of TMPTA in the presence and absence of DDT under 350 nm are shown. Figure 4.6 displays plots of the conversion versus irradiation time derived from Figure 4.5. It can be seen that rapid polymerization takes place with DDT in conjunction with diphenyliodonium salt.

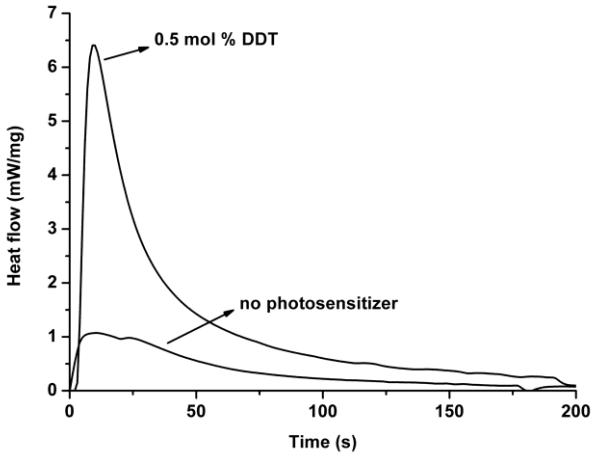


Figure 4.5 : Heat flow vs. time for the polymerization of TMPTA initiated by 1 mol % $Ph_2I^+PF_6^-$ in the absence and presence of 0.5 mol % DDT at 30°C (350 nm, light intensity= 67 $mW \cdot cm^{-2}$)

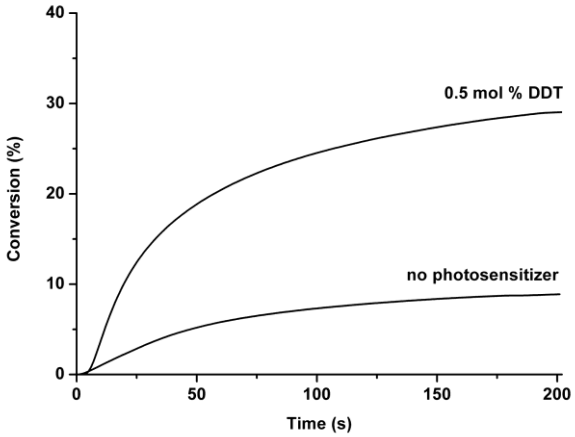


Figure 4.6 : Conversion vs. time for the polymerization of TMPTA initiated by 1 mol % $Ph_2I^+PF_6^-$ in the absence and presence of 0.5 mol % DDT at 30°C (350 nm, light intensity= 67 $mW \cdot cm^{-2}$)

5. CONCLUSION

In this thesis, we have shown the use of thiophene derivatives as free radical polymerization initiator. Preliminary experimental results fully support the idea that suitable thiophene derivatives in combination with oxidizing cations may be used to promote not only cationic polymerization but also free radical polymerization of (meth)acrylates. Mechanistic details remain to be evaluated, an important feature is the generation of radical cations by electron transfer from the excited state of the thiophene derivative to the onium salt; leading to formation of radical species with obvious implications to UV curing applications at near UV and visible region.

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