ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

PHOTOINITIATED POLYMERIZATIONS BY ELECTRON TRANSFER REACTIONS

Ph. D. Thesis by
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Department : Polymer Science and Technology

Programme : Polymer Science and Technology

NOVEMBER 2010

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ELEKTRON TRANSFER REAKSİYONLARI İLE BAŞLATILMIŞ FOTOPOLİMERİZASYONLAR

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FOREWORD

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ABBREVIATIONS

MO : Molecular Orbital
IC : Internal Conversion
ISC : Intersystem Crossing
^{1}H NMR : Hydrogen Nuclear Magnetic Resonance Spectroscopy
FT-IR : Fourier Transform Infrared Spectrophotometer
UV : Ultra Violet
GPC : Gel Permeation Chromatography
TGA : Thermal Gravimetric Analysis
CH_2Cl_2 : Dichloromethane
$CDCl_3$: Deuterated Chloroform
CD_3CN : Deuterated Acetonitrile
THF : Tetrahydrofuran
CH_3CN : Acetonitrile
CHO : Cyclohexene Oxide
BVE : n-Butyl Vinyl Ether
NVC : *N*-Vinylcarbazole
MMA : Methyl Methacrylate
BA : Butyl Acrylate
S : Styrene
PS : Photosensitizer
PI : Photoinitiator
ISC : Inter System Crossing
COI : Coinitiator
TAS : Triaryl Sulphonium Salts
$EMP^+ PF_6^-$: *N*-ethoxy–2-methylpyridinium hexafluorophosphate
CTC : Charge Transfer Complex
$Ph_2^+PF_6^-$: Diphenyliodonium hezafluorophosphate
DDT : 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene
PDDT : Poly(dithienothiophene)
DBMP : 2,6-Di-*tert*-butyl-4-methylpyridine
DTDT : 4,7-di(2,3-dihydro-thieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole
DTDQ : 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl) quinoxaline
$PDA^+SbF_6^-$: *N*-Phenacyl-*N,N*-Dimethylanilinium Hexafluoroantimonate
$PPy^+SbF_6^-$: *N*-Phenacylpyridinium Hexafluoroantimonate
MBTMS : (4-Methoxybenzyl)trimethylsilane

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λ : Wavelength
$h\upsilon$: Radiation
c : Speed of light
v : Frequency
E : Energy
h : Planck's constant
mW : Miliwatt
nm : Nanometer
l : Light path length
c : Concentration
A : Absorbance
ε : Molar extinction coefficient
k : Rate constant
$\Phi_{R.}$: Quantum yield of radical formation
Φ_P : Quantum yield of photoinitiation
f_P : Initiation efficiency of photogenerated radicals
E_T : Triplet energy
F : Faraday constant
$E_{1/2}^{ox}$ $(D/D^{+\cdot})$: Oxidation potential of donor
$E_{1/2}^{red}$ $(A/A^{-\cdot})$: Reduction potential of acceptor
E_S : Singlet state energy of the sensitizer
ΔG : Gibbs Free Energy Change
ppm : Parts per million
K : Kelvin
^{o}C : Celsius
M_n : The number average molecular weight
M_w : The weight average molecular weight
M_w/M_n : The molecular weight distribution

PHOTOINITIATED POLYMERIZATIONS BY ELECTRON TRANSFER REACTIONS

SUMMARY

Recently, photoinitiated polymerization has received revitalized interest as it congregates a wide range of economic and ecological anticipations. It forms the basis of numerous applications in coatings, adhesives, inks, printing plates, optical waveguides and microelectronics due to its excellent advantages. It offers high rate of polymerization at ambient temperatures, low energy consumption, solvent-free polymerization, spatial and temporal control of initiation. 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. The majority of industrial applications of photoinitiated polymerizations for various techniques deal with free-radical systems. However, there are some drawbacks associated with this type polymerization such as the inhibition effect of oxygen and post-cure limitations which may affect the properties of the final product. Therefore, photinitiated cationic polymerization holds considerable promises in the future, particularly as a means of overcoming these limitations. Numerous cationic photoinitiators are known and their photochemistry has been studied in detail. Among them, the onium-type photoinitiators play an important role due to their thermal stability, solubility in most of the cationically polymerizable monomers, and competence in generating reactive species upon photolysis. 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. The spectral sensitivity of photoinitiated cationic polymerizations may be extended to the near UV and visible range by using appropriate free radical sources and aromatic sensitizers.

Conjugated polymers have attracted great interest due to their wide range of potential applications including light emitting diodes, batteries, electrochromic devices, sensors, electromagnetic shielding, and corrosion inhibition. Polythiophenes are one of the most extensively studied families of conjugated polymers because of their characteristic electronic and optical properties. Usually, polythiophenes are obtained by chemical or electrochemical polymerization processes, which provides films with different morphologies and consequently slightly different physical and chemical properties. Photopolymerization is considered to be useful candidate for the production of these materials in thin film forms and various strategies have been employed to polymerize thiophene and derivatives photochemically.

The present work describes the use of electron transfer reactions in photoinitiated polymerization systems. Electron transfer reactions were succeeded using highly

conjugated thiophene derivatives together with onium salts and phenacyl salts together with a benzylsilane compound.

The first part of the thesis states the use of highly conjugated thiophene derivatives for electron transfer photosensitization of onium salts (Figure 1). For this purpose, three different thiophene derivatives, namely 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT), 4,7-di(2,3-dihydro-thieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (DTDT) and 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl) quinoxaline (DTDQ) were used as photosensitizers. The excited state emission characteristics of the compounds were investigated by means of fluorescence and phosphorescence spectroscopic measurements. The cationic polymerization of typical monomers, such as cyclohexene oxide (CHO), *n*-butyl vinyl ether (BVE), styrene (S) and *N*-vinylcarbazole (NVC) was initiated at room temperature at appropriate wavelengths in the presence of diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$). A feasible mechanism, as correlated with optical absorption and fluorescence spectroscopic measurements, free energy changes (ΔG) and proton scavenging studies, involves formation of exciplex by the absorption of light in the first step. Subsequent electron transfer from excited sensitizers to iodonium ion yields radical cations of the thiophene derivatives. The resulting strong Brønsted acid derived from this process catalyzes the cationic polymerization of variety of monomers.

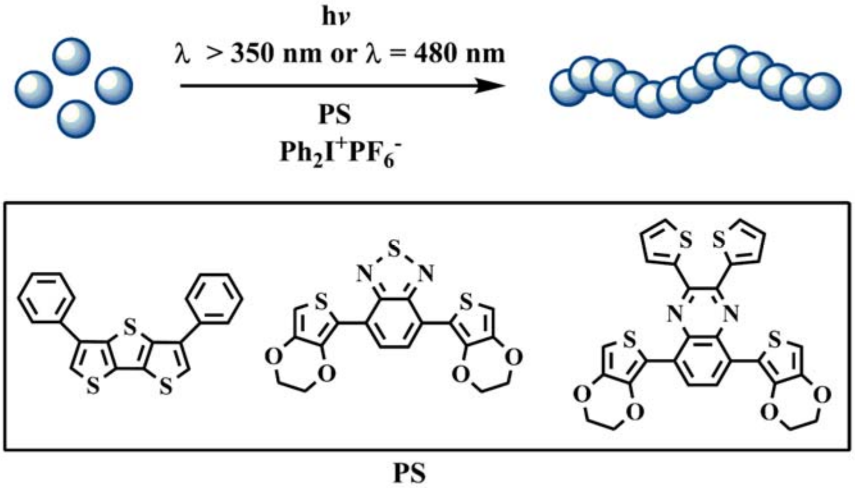


Figure 1 : Photosensitized cationic polymerization using highly conjugated thiopehene derivatives.

In the second part of the thesis, electron transfer photosensitization of onium salts by using DDT was further extended to the preparation of a conjugated thiophene polymer (Figure 2). By virtue of the thiophene type radical cation formation and the crucial role of these species in the electropolymerization, the electron transfer reactions between photoexcited thiophene derivatives and onium salts have the potential of forming polymeric molecules. Thus, step-growth polymerization of DDT was achieved by coupling reactions of radical cations accompanied by proton release. The polymerization was accompanied with darkening of the solution and a new absorption band at 740-800 nm appeared indicating extended conjugation due to polymer formation. The obtained polymer was characterized by spectral methods (^{1}H NMR and IR analysis), GPC and light scattering measurements. Thermal properties of PDDT was investigated by thermal gravimetric analysis (TGA).

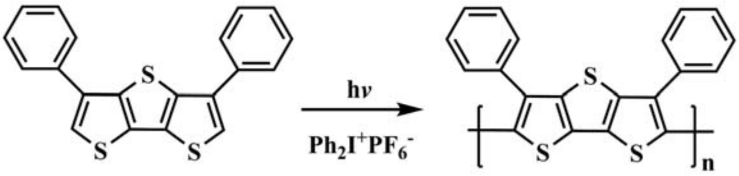


Figure 2 : Photoinduced step-growth polymerization of DDT in the presence of $Ph_2I^+PF_6^-$.

Finally, electron transfer reactions were used in photoinitiated free radical polymerization. A new free radical photoinitiating systmem consisting of phenacyl salts and a benzylsilane compound has been designed (Figure 3). For this purpose, *N*-phenacyl-*N,N*-dimethylanilinium hexafluoroantimonate ($PDA^+SbF_6^-$), *N*-phenacylpyridinium hexafluoroantimonate ($PPy^+SbF_6^-$) and (4-methoxybenzyl)trimethylsilane (MBTMS) were synthesized, and characterized by ^1H NMR and UV spectroscopy. Methyl methacrylate (MMA), butyl acrylate (BA) and styrene (S) were efficiently polymerized by using this initiating system. A mechanism involving formation of an aminium salt and subsequent electron transfer from aminium salt to MBTMS is proposed.

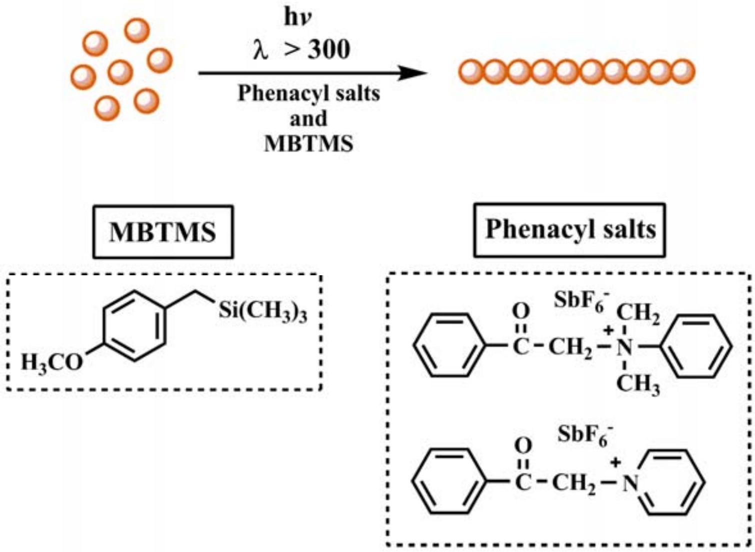


Figure 3 : Photoinitiated free radical polymerization by using phenacyl salts in the presence of a benzylsilane compound.

ELEKTRON TRANSFER REAKSİYONLARI İLE BAŞLATILMIŞ FOTOPOLİMERİZASYONLAR

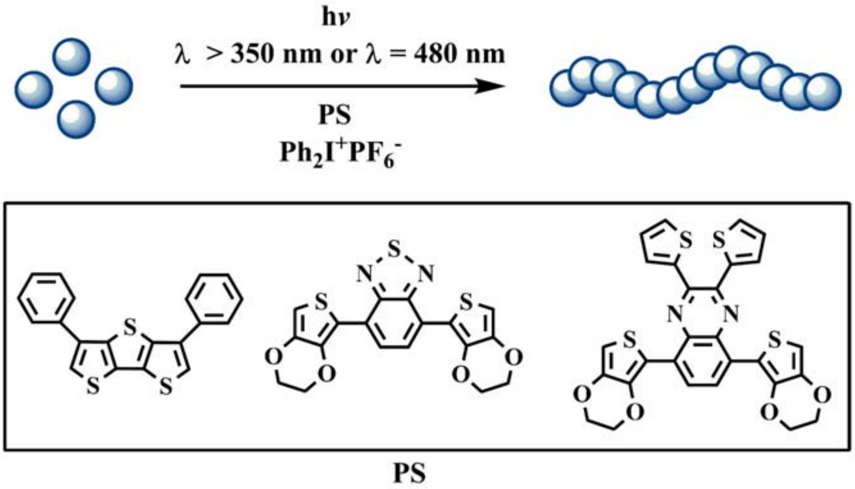
ÖZET

Son zamanlarda, fotobaşlatılmış polimerizasyon pek çok ekonomik ve ekolojik beklentiyi biraraya getirdiği için hayli ilgi çekmektedir. Fotobaşlatılmış polimerizasyon, sahip olduğu mükemmel avantajları dolayısı ile kaplama, mürekkep, baskı levhaları, optik frekans yönlendiricileri ve mikroelektronik gibi sayısız uygulamaların temelini oluşturmaktadır. Oda sıcaklığında yüksek polimerizasyon hızı, düşük enerji tüketimi, çözücüsüz ortamada polimerizasyon, uygulanacak yüzey alanı ve uygulama süresinin kontrol edilebilmesi gibi avantajlar sağlamaktadır. Fotopolimerizasyon radikalik, katyonik ve anyonik olarak başlatılabilse de çok sayıda fotobaşlatıcının ve yüksek reaktivitedeki monomerlerin bulunulabilirliği açısından serbest radikal ve katyonik sistemlere daha fazla ilgi duyulmaktadır. Genellikle endüstriyel uygulamalarda serbest radikal fotopolimerizasyon sistemleri kullanılmaktadır. Ancak, bu tip polimerizasyonların oksijenin yavaşlatma etkisi ve son ürünün özelliklerini etkileyebilen kürleşme sonrasındaki kısıtlamalar gibi bazı dezavantajları bulunmaktadır. Bu nedenle, fotobaşlatılmış katyonik polimerizasyon özellikle bu dezavantajların giderilmesi açısından gelecekte daha fazla yer alacağı düşünülmektedir. Bilinen pek çok katyonik fotobaşlatıcı mevcuttur ve fotokimyaları detaylı bir şekilde incelenmiştir. Bunlar arasında, onyum tipi fotobaşlatıcılar, ısısal kararlılıkları, katyonik olarak polimerleşebilen pek çok monomer içindeki çözünürlükleri ve fotoliz sonucunda reaktif türler oluşturma kabiliyetleri bakımından önemli bir role sahiptirler. Brønsted asitlerinin yanı sıra radikal türlerinin de meydana getiriliyor olmasından dolayı bu tuzlar serbest radikal fotobaşlatıcısı olarak ve eşzamanlı serbest radikal ve katyonik polimerizasyonlarında da kullanılabilmektedir. Fotobaşlatılmış katyonik polimerizasyonların spektral hassasiyetinin, uygun serbest radikal kaynakları ve aromatik uyarıcılar vasıtasıyla yakın UV ve görünür bölgeye genişletilmesi mümkündür.

Konjuge polimerler ışık yayan diyotlar, piller, elektrokromik aletler, sensörler, elektromanyetik koruma ve korozyonu önleme gibi çeşitli uygulamalarda kullanıldıkları için önem arzetmektedir. Politiyofenler, karakteristik elektronik ve optik özelliklerinden dolayı konjuge polimerler arasında en yaygın çalışılan türlerinden biridir. Genellikle, politiyofenler farklı morfolojilerde filmlerin oluşmasını ve bunun sonucunda kısmen farklı fiziksel ve kimyasal özelliklerin oluşmasını sağlayan kimyasal ve elektrokimyasal polimerizasyon prosesleri ile elde edilmektedir. Fotopolimerizasyon bu malzemelerin ince film halinde üretilebilmesi açısından kullanışlı bir aday olarak görülmektedir ve tiyofen ve türevlerinin fotokimyasal olarak polimerleştirilmesinde çeşitli stratejiler uygulanmıştır.

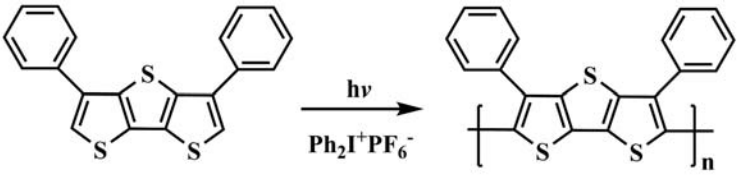
Bu çalışma elektron transfer reaksiyonlarının fotobaşlatılmış polimerizasyon sistemlerindeki kullanımını ele almaktadır. Elektron transfer reaksiyonları yüksek konjugasyona sahip tiyofen türevleri ile onyum tuzları varlığında ve fenaçil tuzları ile bir benzilsilan bileşiği varlığında gerçekleştirilmiştir.

Tezin ilk kısmı onyum tuzlarının elektron transfer fotouyarılmasında yüksek konjugasyona sahip tiyofen türevlerinin kullanımını anlatmaktadır (Şekil 1). Bu amaçla, üç farklı tiyofen türevi, 3,5-difenilditiyeno[3,2-*b*:2,3-*d*]tiyofen (DDT), 4,7-di(2,3-dihidro-tiyeno[3,4-*b*][1,4]dioksin-5-il)benzo[1,2,5]tiyadiazol (DTDT) ve 5,8-bis(2,3-dihidrotiyeno[3,4-*b*][1,4]dioksin-5-il)-2,3-di(tiyofen-2-il) kinoksalin (DTDQ) fotouyarıcı olarak kullanılmıştır. Bu bileşiklerin uyarulmış hal yayınım özellikleri floresans ve fosforesans spektroskopik ölçümleri vasıtasıyla incelenmiştir. Siklohekzen oksit (CHO), n-bütil vinil eter (BVE), stiren (S) ve *N*-vinilkarbazol (NVC) monomerlerinin katyonik polimerizasyonu oda sıcaklığında uygun dalgaboylarında difeniliyodonyum hekzaflorofosfat ($Ph_2I^+PF_6^-$) varlığında başlatılmıştır. Optik absorpsiyon ve floresans spektroskopik ölçümleri, serbest enerji değişimleri (ΔG) ve proton yakalama çalışmaları ile ilişkendirilen olası mekanizma, ilk aşamada ışığın absorplanmasıyla ekzipleks oluşumunu içermektedir. Sonraki adımda uyarılmış moleküllerden iyodonyum iyonuna elektron transfer edilmesiyle tiyofen türevlerinin radikal katyonları oluşmaktadır. Bu proses sonucunda meydana gelen güçlü Brønsted asidi çeşitli monomerlerin katyonik polimerizasyonunu katalize etmektedir.



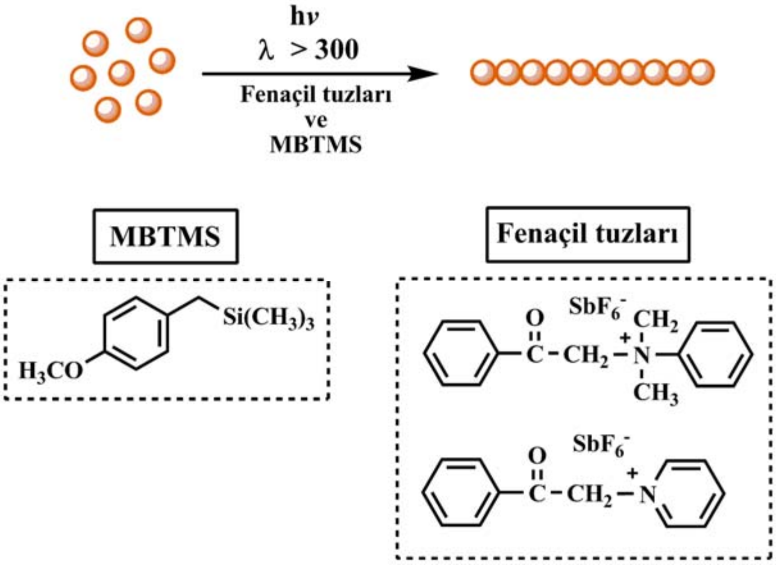
Şekil 1 : Yüksek konjugasyona sahip tiyofen türevleri kullanılarak gerçekleştirilen fotouyarılmış katyonik polimerizasyon.

Tezin ikinci kısmında, onyum tuzlarının DDT varlığındaki elektron transfer fotouyarılması daha da genişletilerek bir konjuge tiyofen polimeri sentezlenmeye çalışılmıştır (Şekil 2). Tiyofen tipi radikal katyon oluşumu ve bu türlerin elektropolimerizasyondaki önemi nedeniyle, fotouyarılmış tiyofen türevleri ve onyum tuzları arasında meydana gelen elektron transfer reaksiyonları polimerik molekülleri meydana getirmede potansiyel teşkil etmektedir. Bu nedenle, radikal katyonlarının proton vererek birleşmesi reaksiyonları sonucunda DDT'nin basamak polimerizasyonu gerçekleştirilmiştir. Polimerizasyonun gerçekleştiği çözeltinin koyulaşması ile gözlenmiş ve 740-800 nm arasında genişletilmiş konjugasyondan dolayı yeni bir absorpsiyon bandının ortaya çıkması polimerin oluşumunu doğrulamıştır. Elde edilen polimer, spektral yöntemlerle (^1H NMR ve IR analizleri), GPC ve ışık saçınım ölçümleriyle karakterize edilmiştir. PDDT'nin ısısal özellikleri termal gravimetik analizler (TGA) vasıtasıyla incelenmiştir.



Şekil 2 : DDT'nin $Ph_2I^+PF_6^-$ varlığında fotobaşlatılmış basamak polimerizasyonu.

Son olarak, elektron transfer reaksiyonları fotobaşlatılmış serbest radikal polimerizasyonunda kullanılmıştır. Fenaçil tuzlarını ve bir benzilsilan bileşiğini içeren yeni bir serbest radikal fotobaşlatıcı sistemi tasarlanmıştır (Şekil 3). Bu amaçla, *N*-fenaçil-*N,N*-dimetilanilinyum hekzafloroantimonat ($PDA^+SbF_6^-$), *N*-fenaçilpiridinyum hekzafloroantimonat ($PPy^+SbF_6^-$) ve (4-metoksibenzil)trimetilsilan (MBTMS) bileşikleri sentezlenerek, ^1H NMR ve UV spektroskopisi ile karakterize edilmiştir. Metil metakrilat (MMA), bütil akrilat (BA) ve stiren (S) monomerleri bu başlatıcı sistemi kullanılarak etkili bir şekilde polimerleştirilmiştir. Bir aminyum tuzu oluşumunu ve sonrasında aminyum tuzundan MBTMS bileşiğine elektron transferini içeren bir mekanizma önerilmiştir.



Şekil 3 : Bir benzilsilan bileşiği varlığında fenaçil tuzları kullanılarak gerçekleştirilen fotobaşlatılmış serbest radikal polimerizasyonu.

1. INTRODUCTION

Photoinitiated polymerization is a powerful industrial process widely used in various applications including printing inks, adhesives, surface coating, optical waveguides, microelectronics and printing plates [1-3]. The advantages of photoinitiated polymerization over conventional thermal polymerization lie in the high rate of polymerization at ambient temperatures, lower energy cost, and solvent-free formulation, thus elimination of air and water pollution [4, 5]. Much effort has been devoted to free radical systems mainly due to the availability of a wide range of photoinitiators and the great reactivity of acrylate-based monomers [1, 6]. Despite the most popular industrial applications are based on the photoinitiated free radical photopolymerization there are some drawbacks associated with this type polymerization such as the inhibition effect of oxygen and post-cure limitations which may affect the properties of the final product. Photoinitiated cationic polymerization has now found many applications due to the availability of highly photosensitive and efficient cationic photoinitiators, which can be designed to be responsive to various UV wavelengths. Moreover, UV initiated cationic polymerization holds considerable promises in the future, particularly as a means of overcoming volatile emission, toxicity and molecular oxygen inhibition limitations [7].

Many cationic photoinitiators are known and their photochemistry has been studied in detail. Among them, the onium-type photoinitiators such as iodonium, sulfonium and alkoxypyridinium salts play an important role due to their thermal stability, solubility in most of the cationically polymerizable monomers, and efficiency in generating reactive species upon photolysis [8, 9]. Moreover, they possess high photolysis quantum yields and are efficient photoinitiators of cationic polymerization when irradiation is carried out using light in the short- to mid-wavelength UV regions (230-300 nm).

A common strategy employed for improving the performance of onium salts particularly at long wavelengths, is based on the activation of these photoinitiators, by light sensitive additives, which do not directly initiate the polymerization. One can adapt the initiating system to different wavelength of irradiation by three ways; (i) oxidation of free radicals by onium salts (also called as free radical promoted cationic polymerization) [10-12], (ii) electron transfer between photoexcited sensitizer and onium salt [13-15], and (iii) electron transfer in photoexcited charge transfer complexes of certain onium salts [16-18].

The free radical oxidation process is limited to the photoinitiators capable of forming electron-donating radicals. For instance, except structurally specially designed, long wavelength absorbing aclyphosphine oxide photoinitiators do not generate oxidizable radicals. Charge transfer complex activation is achieved only with alkoxy pyridinium type onium salts. Thus, electron-transfer photosensitization by using electron-rich polynuclear aromatic compounds such as anthracene, perylene, pyrene and phenothiazine appears to be an alternative efficient pathway to shift the absorption sensitivity to longer wavelengths [19]. Despite the many potential applications, these photosensitizers also have several serious disadvantages that limit their use. For example, they are generally expensive, toxic, and poorly soluble in most reactive monomers and polymer systems. Moreover, they are easily lost from thin film coatings during polymerization and have high vapor pressure at room temperatures. As a result, there is a continuing need for long-wavelength-active photosensitizers in order to overcome these limitations.

Conjugated polymers, which consist alternating single and double bonds in their polymer backbone, have attracted great interest due to their wide range of potential applications including light emitting diodes, batteries, electrochromic devices, sensors, electromagnetic shielding, and corrosion inhibition [20]. They are described as extended conjugated systems containing delocalized π-electrons arising from their alternating structure of single and double bonds along polymer chains. Among these polymers, polythiophenes have a special place due to their electronic and optical properties and they are usually obtained by chemical or electrochemical polymerization processes. Photopolymerization can be referred as a potential candidate for the preparation of these materials in thin film forms. Several strategies have been employed to polymerize thiophene and derivatives photochemically [21-25].

In this thesis, three different strategies were described for the use of electron transfer reactions in photoinitiated polymerization systems. Highly conjugated thiophene derivatives were used for electron transfer photosensitization of onium salts in order to overcome the progressing need in this area [26, 27]. This strategy was also extended to the synthesis of conjugated thiophene polymers [28]. Finally, a two component free radical photoinitiating system by combination of cleavage and electron transfer reactions was described.

2. THEORETICAL PART

2.1 Absorption of Light and Photophysical Processes

2.1.1 Light

Humankind has had a long and complicated journey towards understanding the true nature of light. The ancients stressed the importance of light for life. Pythagoras, Empedocles (490–430 BC) and Plato (427–347 BC) were among the Greek philosophers who believed that vision is initiated in the eyes in the process of reaching out to 'touch' or 'feel'something and, in return, one can see. As a follower of Plato, Euclid of Alexandria still harboured the notion that light originated in the eyes but added that light travels in straight lines called rays. He provided a geometrical basis for the phenomena of sight. Aristotle (384–322 BC) did not believe in his teacher, Plato's tactile theory. He argued that the process of seeing occurs when particles are emitted from the object. For him, the eyes are passive rather than actively linked with sunlight, as proposed by Plato. Whilst the Aristotelian account of light is more convincing than Plato's, it fails to explain how a particle can enter the eyes. An important breakthrough in our understanding of the nature of light occurred through the work of the Arab mathematician and physicist, Ibn Al-Haytham (AD 965–1039). He faulted the tactile theory of light on the grounds that an extremely bright object can injure the eyes and said that light comes to the surface of the eye from the light of the visible object. A notable feature of Al-Haytham's approach is the use of the scientific method, unlike the philosophical approach of the ancient Greeks [29].

The classical theories of light began to emerge in the late 17th century with the work of the English scientist Isaac Newton (1624–1727). Newton hypothesized that light consisted of vast quantities of invisible particles thrown off from a luminous source. Ten years later Christian Huygens, a Dutch physicist, formulated the first clear statement of the wave theory—that light consisted of waves emanating from a luminous surface. But because Huygens could not explain all observable behaviors of light with his theory, and because Newton's authority as a scientist was so great, Newton's corpuscular theory of light was widely accepted. Unfortunately, this retarded the development of the wave theory for the next one hundred years. Proponents of both the particle and wave theories believed that light required a medium through which it would travel, and since light travels across space in which there is no matter, then the whole of space must be filled with this medium, called "ether." Huygens conceived of the ether as an elastic solid through which the waves were transmitted from the luminous source. We now know that "ether" is not necessary: light requires no medium through which to travel. Both Huygens and Newton were partially correct about the nature of light—light exhibits the characteristics of waves when traveling, and the characteristics of particles when interacting with a surface—and the wave-particle duality of light is now commonly accepted [29].

According to wave model, light behaves as a wave. Light waves are also called electromagnetic waves because they are made up of both electric (E) and magnetic (B) fields. Electromagnetic fields oscillate perpendicular to the direction of wave travel, and perpendicular to each other (Figure 2.1) [30]. Light waves are known as transverse waves as they oscillate in the direction traverse to the direction of wave travel.

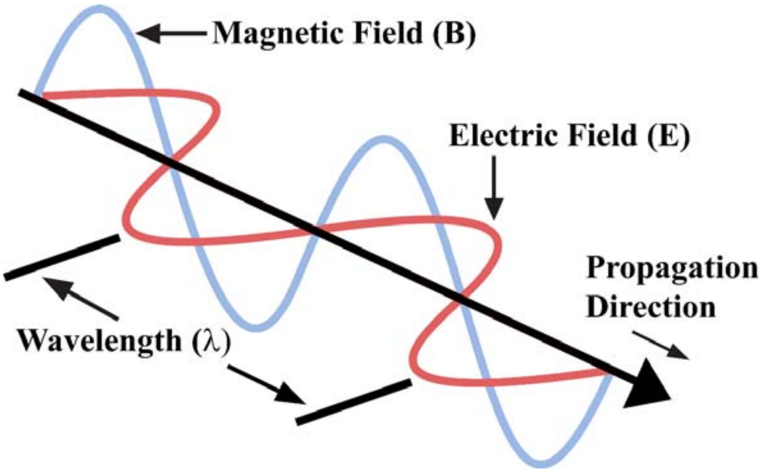


Figure 2.1 : Electromagnetic wave.

Waves have two important characteristics, wavelength and frequency. Wavelength is described as the distance between corresponding points of two consecutive waves or the distance from crest to crest, and it is designated by Greek letter lambda (λ). The fequency (ν) of electromagnetic wave is the number of waves passing from a given point in one second. Since all wavelengths travel at the speed of light, the relationship among speed c, frequency (ν), and wavelength (λ), can be stated as follows:

$$c = \lambda \cdot \nu \qquad \textbf{(2.1)}$$

According to particle model, light is composed of photons, very small packets of energy. The frequency of the wave is proportional to the particle's energy. Because photons are emitted and absorbed by charged particles, they act as transporters of energy [30]. The energy per photon can be calculated from the Planck–Einstein equation:

$$E = h \cdot \nu \qquad \textbf{(2.2)}$$

where E is the energy, h is Planck's constant, and ν is frequency.

2.1.2 Electromagnetic spectrum

The electromagnetic spectrum is a continuum of all electromagnetic waves arranged according to frequency and wavelength. The sun, earth, and other bodies radiate electromagnetic energy of varying wavelengths. Electromagnetic energy passes through space at the speed of light in the form of sinusoidal waves.

Light is a particular type of electromagnetic radiation that can be seen and sensed by the human eye, but this energy exists at a wide range of wavelengths [31]. The micron is the basic unit for measuring the wavelength of electomagnetic waves. The spectrum of waves is divided into sections based on wavelength (Figure 2.2). The shortest waves are gamma rays, which have wavelengths of 10^{-6} microns or less. The longest waves are radio waves, which have wavelengths of many kilometers. The range of visible consists of the narrow portion of the spectrum, from 0.4 microns (blue) to 0.7 microns (red).

Ultraviolet (UV) light is electromagnetic radiation with a wavelength shorter than that of visible light, but longer than x-rays, in the range 10 nm to 400 nm. It is so named because the spectrum consists of electromagnetic waves with frequencies higher than those that humans identify as the colour violet. The UV spectrum is divided into Vacuum UV (40-190 nm), Far UV (190-220 nm), UVC (220-290 nm), UVB (290-320), and UVA (320-400 nm). The sun is the primary natural source of UV radiation.

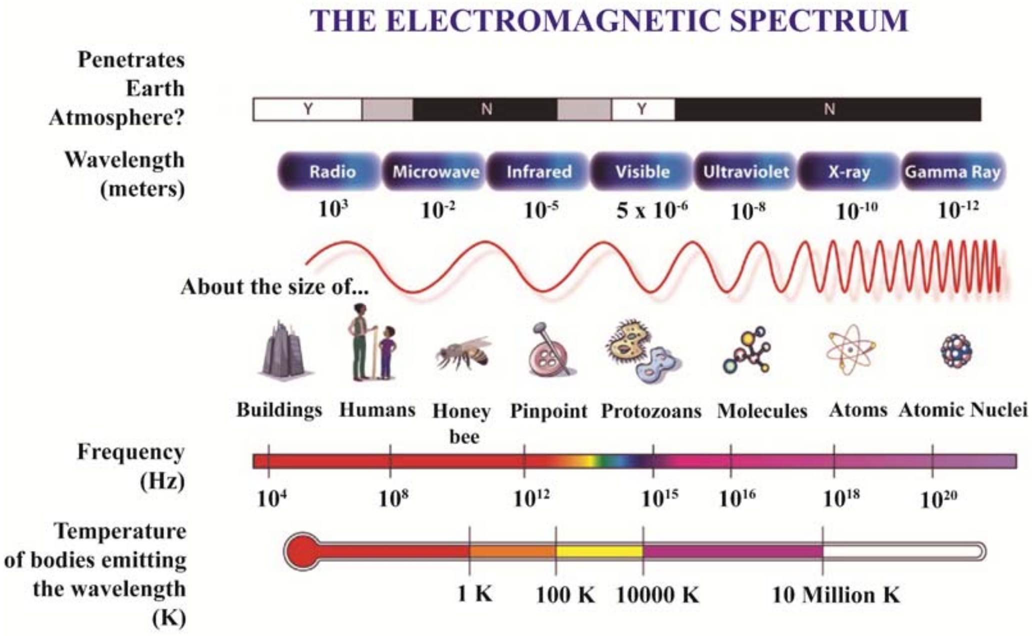


Figure 2.2 : Electromagnetic spectrum.

2.1.3 The Beer-Lambert law

Experimentally, the absorption of light is recorded as a function of the wavelength or the wave number $\nu = \lambda^{-1}$ by measuring the change in the intensity of a light beam passing through a sample of unit path length (1 cm) [32].

For a homogeneous, isotropic medium containing an absorbing compound at concentration c ($\mathrm{mol \cdot L^{-1}}$), the light absorption is described by equation (2.3), the Beer-Lambert law:

$$A = \log (I_0/I) = \varepsilon \cdot c \cdot l \tag{2.3}$$

where I_0 and I are the light intensities of the beams entering and leaving the absorbing medium, respectively. ε is the molar (decadic) absorption coefficient (commonly expressed in $\mathrm{L \cdot mol^{-1} \cdot cm^{-1}}$), c is the concentration (in $\mathrm{mol\ L^{-1}}$) of absorbing species and l is the absorption path length (thickness of the absorbing medium) (in cm) [33].

For a given substance, the molar absorption coefficient varies with the wavelength of the light used. A plot of ε (or log ε) against wavelength (or wavenumber) is called the absorption spectrum of the substance. The principal use of absorption spectra from the photochemist's point of view is that they provide information as to what wavelength (λ_{max}) a compound has at its maximum value of the molar absorption coefficient (ε_{max}). Thus, irradiation of the compound at λ_{max} allows optimum photoexcitation of the compound to be carried out [34].

2.1.4 The Molecular orbital model

Changes in the electronic structure of a molecule can be visualized with the aid of the molecular orbital (MO) model [32, 35]. Molecular orbitals are thought to be formed by the linear combination of the valence shell orbitals of the atoms linked together in the molecule. The combination of two single orbitals of two adjacent atoms results in two molecular orbitals, one of lower and the other of higher energy than before combination. The low-energy orbital, denoted as the bonding orbital, is occupied by a pair of electrons of antiparallel spin. The high energy molecular orbital is called an antibonding orbital. It is unoccupied in the ground state, but may be occupied by an electron upon electronic excitation of the molecule.

There are different kinds of molecular orbitals: bonding σ and π orbitals, nonbonding n orbitals, and antibonding σ^* and π^* orbitals. σ and σ^* orbitals are completely symmetrical about the internuclear axis, whereas π and π^* orbitals are antisymmetric about a plane including the internuclear axis. n orbitals, which are located on heteroatoms such as oxygen, nitrogen, or phosphorus, are nonbonding and are of almost the same energy as in the case of the isolated atom. A pair of electrons occupying an n orbital is regarded as a lone pair on the atom.

The simple MO model is based on several hypotheses. For example, σ and π orbitals are assumed not to interact. Moreover, molecules are described by localized orbitals each covering two nuclei only. Delocalized orbitals involving more than two nuclei are thought to exist only in the case of π-bonding in conjugated systems. When a molecule in its ground state absorbs a photon, an electron occupying a σ, π or n orbital is promoted to a higher-energy σ^* or π^* orbital. In principle, the following transitions are possible: $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and $n \rightarrow \sigma^*$ [32]. As can be seen in Figure 2.3, the orbital energy increases in the series of $\sigma < \pi < n < \pi^* < \sigma^*$.

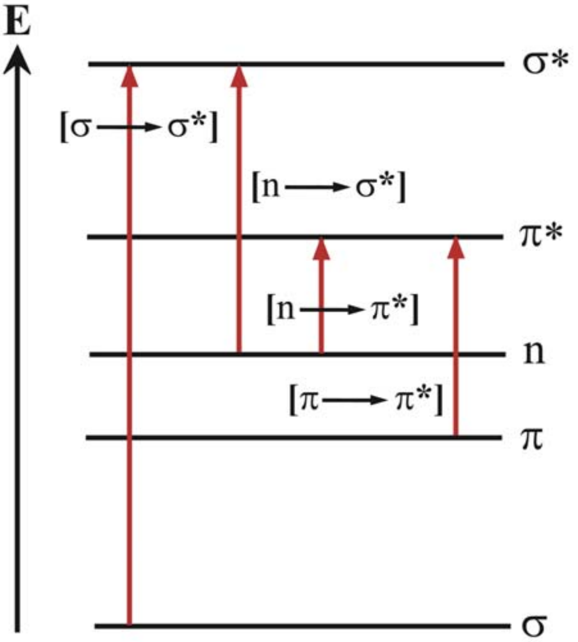


Figure 2.3 : Molecular orbitals and electronic transitions induced by the absorption of a photon.

According to the differences in the orbital energies, the electron transitions indicated in Figure 2.3 correspond to light absorption in different wavelength regions. This is illustrated in Table 2.1.

Therefore, under conveniently available conditions ($\lambda > 200$ nm), photon absorption initiates transitions of n or π electrons rather than those of σ electrons.

Table 2.1 : The correspondence of electron transition and optical absorption.

Electron transition	**Absorption region (nm)**	**Extinction coefficient ($L\cdot mol^{-1}\cdot cm^{-1}$)**
$\sigma\rightarrow\sigma^*$	100-200	10^3
$n\rightarrow\sigma^*$	150-250	10^2-10^3
$\pi\rightarrow\pi^*$	-	10^2-10^4
Isolated π-bonds	180-250	-
Conjugated π-bonds	220-IR	-
$n\rightarrow\pi^*$	-	1-400
Isolated groups	220-320	-
Conjugated segments	250-IR	-

Molecular orbitals can be classified as occupied (doubly), singly occupied, and unoccupied [32]. The acronyms HOMO and LUMO denote the frontier orbitals, i.e. the Highest Occupied and the Lowest Unoccupied Molecular Orbital, respectively. SOMO denotes the Single Occupied Molecular Orbital (see Fig. 2.4).

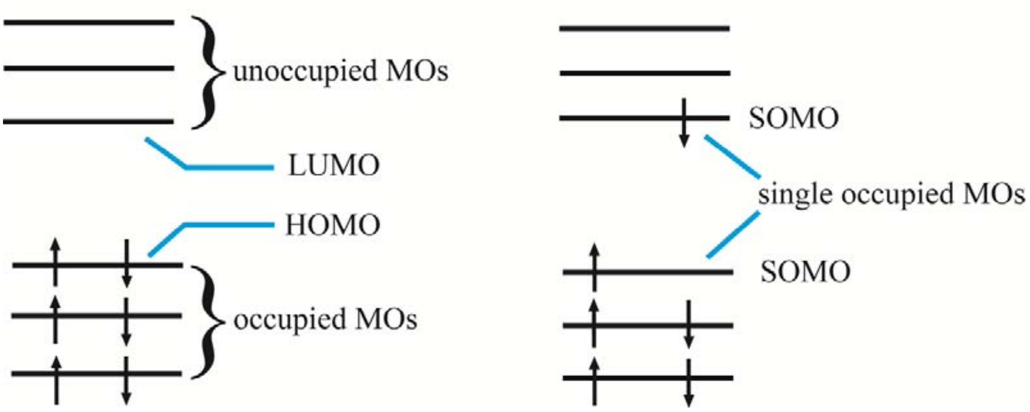


Figure 2.4 : Classification of molecular orbitals with respect to electron occupancy.

2.1.5 The Jablonski diagram

The Jablonski diagram (Figure 2.5) is used for visualizing the possible photophysical processes for an excited molecule in solution: photon absorption, internal conversion, fluorescence, intersystem crossing, phosphorescence, delayed fluorescence and triplet–triplet transitions [33]. The singlet electronic states are denoted S_0 (fundamental electronic state), S_1, S_2, . . . and the triplet states, T_1, T_2, ... Vibrational levels are associated with each electronic state. It is important to note that absorption is very fast ($\approx 10^{-15}$ s) with respect to all other processes.

The vertical arrows corresponding to absorption start from the 0 (lowest) vibrational energy level of S_0 because the majority of molecules are in this level at room temperature. Absorption of a photon can bring a molecule to one of the vibrational levels of S_1; S_2; . . .

2.1.5.1 Internal conversion (IC)

Internal conversion (IC) is a non-radiative transition between two electronic states of the same spin multiplicity. In solution, this process is followed by a vibrational relaxation towards the lowest vibrational level of the final electronic state. The excess vibrational energy can be indeed transferred to the solvent during collisions of the excited molecule with the surrounding solvent molecules.

When a molecule is excited to an energy level higher than the lowest vibrational level of the first electronic state, vibrational relaxation (and internal conversion if the singlet excited state is higher than S_1) leads the excited molecule towards the 0 vibrational level of the S_1 singlet state with a time-scale of 10^{-13}–10^{-11} s.

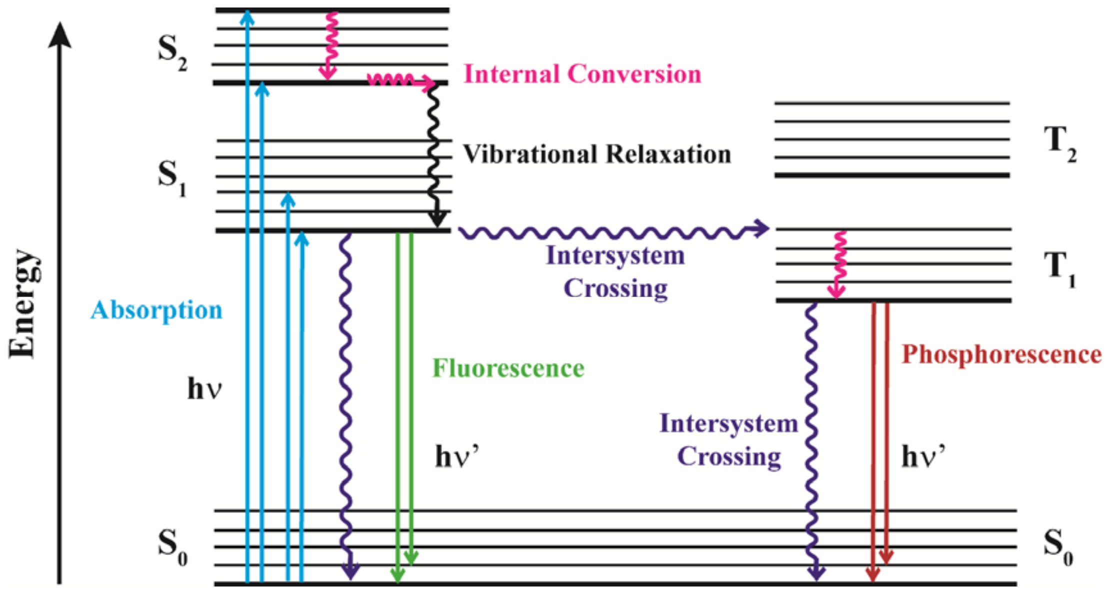


Figure 2.5 : The Jablonski diagram.

From S_1, internal conversion to S_0 is possible but is less efficient than conversion from S_2 to S_1, because of the much larger energy gap between S_1 and S_0. Therefore, internal conversion from S_1 to S_0 can compete with emission of photons (fluorescence) and intersystem crossing to the triplet state from which emission of photons (phosphorescence) can possibly be observed.

2.1.5.2 Fluorescence

Emission of photons accompanying the $S_1 \rightarrow S_0$ relaxation is called fluorescence. It should be emphasized that, apart from a few exceptions, fluorescence emission occurs from S_1 and therefore its characteristics (except polarization) do not depend on the excitation wavelength (provided of course that only one species exists in the ground state).

The 0–0 transition is usually the same for absorption and fluorescence. However, the fluorescence spectrum is located at higher wavelengths (lower energy) than the absorption spectrum because of the energy loss in the excited state due to vibrational relaxation (Figure 2.5). According to the Stokes Rule (an empirical observation pre dating the Jablonski diagram), the wavelength of a fluorescence emission should always be higher than that of absorption. However, in most cases, the absorption spectrum partly overlaps the fluorescence spectrum, i.e. a fraction of light is emitted at shorter wavelengths than the absorbed light. Such an observation seems to be, at first sight, in contradiction to the principle of energy conservation.

However, such an ‘energy defect’ is compensated for (as stated by Einstein for the first time) by the fact that at room temperature, a small fraction of molecules is in a vibrational level higher than level 0 in the ground state as well as in the excited state. At low temperature, this departure from the Stokes Law should disappear. In general, the differences between the vibrational levels are similar in the ground and excited states, so that the fluorescence spectrum often resembles the first absorption band (‘mirror image’ rule). The gap (expressed in wavenumbers) between the maximum of the first absorption band and the maximum of fluorescence is called the Stokes shift.

It should be noted that emission of a photon is as fast as absorption of a photon ($\approx 10^{-15}$ s). However, excited molecules stay in the S_1 state for a certain time (a few tens of picoseconds to a few hundreds of nanoseconds, depending on the type of molecule and the medium) before emitting a photon or undergoing other deexcitation processes (internal conversion, intersystem crossing). Thus, after excitation of a population of molecules by a very short pulse of light, the fluorescence intensity decreases exponentially with a characteristic time, reflecting the average lifetime of the molecules in the S_1 excited state. Such an intensity decay is formally comparable with a radioactive decay that is also exponential, with a characteristic time, called the radioactive period, reflecting the average lifetime of a radioelement before disintegration.

The emission of fluorescence photons just described is a spontaneous process. Under certain conditions, stimulated emission can occur (e.g. dye lasers).

2.1.5.3 Intersystem crossing (ISC)

Intersystem crossing is a non-radiative transition between two isoenergetic vibrational levels belonging to electronic states of different multiplicities. For example, an excited molecule in the 0 vibrational level of the S_1 state can move to the isoenergetic vibrational level of the T_n triplet state; then vibrational relaxation brings it into the lowest vibrational level of T_1. Intersystem crossing may be fast enough (10^{-7}–10^{-9} s) to compete with other pathways of de-excitation from S_1 (fluorescence and internal conversion $S_1 \rightarrow S_0$).

Crossing between states of different multiplicity is in principle forbidden, but spin–orbit coupling (i.e. coupling between the orbital magnetic moment and the spin magnetic moment) can be large enough to make it possible. The probability of intersystem crossing depends on the singlet and triplet states involved. If the transition $S_0 \rightarrow S_1$ is of $n \rightarrow \pi^*$ type for instance, intersystem crossing is often efficient. It should also be noted that the presence of heavy atoms (i.e. whose atomic number is large, for example Br, Pb) increases spin–orbit coupling and thus favors intersystem crossing.

2.1.5.4 Phosphorescence

Because internal conversion and vibrational relaxation are very fast, phosphorescence corresponds to a transition from the thermally equilibrated lowest triplet state T_1 into the ground state S_0 and the phosphorescence spectrum is approximately a mirror image of the $S_0 \rightarrow T$, absorption spectrum, which is spin forbidden and therefore difficult to observe because of the low intensity. Generally, the T_1 state is energetically below the S_1 state, and phosphorescence occurs at longer wavelengths than fluorescence.

In solution at room temperature, non-radiative de-excitation from the triplet state T_1, is predominant over radiative de-excitation called phosphorescence. In fact, the transition $T_1 \rightarrow S_0$ is forbidden (but it can be observed because of spin–orbit coupling), and the radiative rate constant is thus very low. During such a slow process, the numerous collisions with solvent molecules favor intersystem crossing and vibrational relaxation in S_0.

On the contrary, at low temperatures and/or in a rigid medium, phosphorescence can be observed. The lifetime of the triplet state may, under these conditions, be long enough to observe phosphorescence on a time-scale up to seconds, even minutes or more.

The phosphorescence spectrum is located at wavelengths higher than the fluorescence spectrum because the energy of the lowest vibrational level of the triplet state T_1 is lower than that of the singlet state S_1.

2.1.5.5 Delayed fluorescence

Thermally activated delayed fluorescence

Reverse intersystem crossing $T_1 \rightarrow S_1$ can occur when the energy difference between S_1 and T_1 is small and when the lifetime of T_1 is long enough. This results in emission with the same spectral distribution as normal fluorescence but with a much longer decay time constant because the molecules stay in the triplet state before emitting from S_1. This fluorescence emission is thermally activated; consequently, its efficiency increases with increasing tempera-ture. It is also called delayed fluorescence of E-type because it was observed for the first time with eosin. It does not normally occur in aromatic hydrocarbons because of the relatively large difference in energy between S_1 and T_1. In contrast, delayed fluorescence is very efficient in fullerenes.

Triplet–triplet annihilation

In concentrated solutions, a collision between two molecules in the T_1 state can provide enough energy to allow one of them to return to the S_1 state. Such a triplet–triplet annihilation thus leads to a delayed fluorescence emission (also called delayed fluorescence of P-type because it was observed for the first time with pyrene). The decay time constant of the delayed fluorescence process is half the lifetime of the triplet state in dilute solution, and the intensity has a characteristic quadratic dependence with excitation light intensity.

2.1.5.6 Triplet-triplet transitions

Once a molecule is excited and reaches triplet state T_1, it can absorb another photon at a different wavelength because triplet–triplet transitions are spin allowed. These transitions can be observed provided that the population of molecules in the triplet state is large enough, which can be achieved by illumination with an intense pulse of light.

2.1.6 Fluorescence quenching

The intensity of fluorescence can be decreased by a wide variety of processes. Such decreases in intensity are called quenching [36]. Quenching can occur by different mechanisms. Collisional (dynamic) quenching occurs when the excited state fluorophore is deactivated upon contact with some other molecule in solution, which is called the quencher. In this case, the fluorophore is returned to the ground state during a diffusive encounter with the quencher. The molecules are not chemically altered in the process. For collisional quenching, the decrease in intensity is described by the well-known Stern-Volmer equation [30, 36]:

$$\frac{F_0}{F} = \frac{I_0}{I} = 1 + K[\mathrm{Q}] = 1 + k_q\tau_0[\mathrm{Q}] \tag{2.4}$$

In this expression K is the Stern-Volmer quenching constant, k_q is the bimolecular quenching constant, τ_0 is the unquenched lifetime, and [Q] is the quencher concentration. I_0 and I are the steady-state fluorescence intensities in the absence and in the presence of quencher, respectively. Generally, the ratio I_0/I is plotted against the quencher concentration (Stern-Volmer plot). If the variation is found to be linear, the slope gives the Stern-Volmer constant. Then, k_q can be calculated if the excited state lifetime in the absence of quencher is known.

A wide variety of molecules can act as collisional quenchers. Examples include oxygen, halogens, amines, and electron deficient molecules like acrylamide. The mechanism of quenching varies with fluorophore-quencher pair. Quenching by halogens and heavy atoms occurs due to spin-orbit coupling and intersystem crossing to the triplet state.

Besides collisional quenching, fluorescence quenching can occur by several other processes. Fluorophores can form nonfluorescent complexes with quenchers. This process is referred as static quenching since it occurs in the ground state and does not rely on diffusion or molecular collisions. Quenching can also occur by a variety of trivial, i.e., nonmolecular mechanisms, such as attenuation of the incident light by the fluorophore itself or other absorbing species.

2.2 Photopolymerization

In recent years, photoinitiated polymerization has received revitalized interest as it congregates a wide range of economic and ecological anticipations. For more than 30 years, photopolymerization has been the basis of numerous conventional applications in coatings, adhesives, inks, printing plates, optical waveguides, and microelectronics [1, 3, 37-39]. Some other less traditional but interesting applications, including production of laser videodiscs, curing of acrylate dental fillings [40], and fabrication of 3D objects [41] are also available. Many studies involving various photopolymerization processes have been continuously conducted in biomaterials [42] for 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, 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 [5].

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 [43]. 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 which may be present. An active center is produced when the initiator absorbs light and undergoes some type of decomposition, hydrogen abstraction, or electron transfer reaction. 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.

2.2.1 Photoinitiated free radical polymerization

Photoinitiated free radical polymerization is one of the most widely employed route in industrial applications because of its applicability to a wide range of formulations based on acrylates, unsaturated polyesters, and polyurethanes and the availability of photoinitiators having spectral sensitivity in the near-UV or visible range.

$$\left.\begin{array}{lll} PI \xrightarrow{h\nu} PI\cdot & & \text{Absorption} \\ PI\cdot \longrightarrow R_1\cdot + R_2\cdot & & \text{Radical Generation} \\ R_1\cdot + M \longrightarrow R_1{-}M\cdot & & \end{array}\right\} \text{Photoinitiation} \qquad \textbf{(2.5a)}$$

$$\left.\begin{array}{l} R_1{-}M\cdot + M \longrightarrow R_1{-}MM\cdot \\ R_1{-}MM\cdot + (n\text{-}2)M \longrightarrow R_1{-}M_n\cdot \end{array}\right\} \text{Propagation} \qquad \textbf{(2.5b)}$$

$$\left.\begin{array}{l} R_1{-}M_n\cdot + R{-}H \longrightarrow R_1{-}M_n{-}H + R\cdot \\ R\cdot + M \longrightarrow R{-}M\cdot \end{array}\right\} \text{Transfer} \qquad \textbf{(2.5c)}$$

$$\left.\begin{array}{l} R_1{-}M_n\cdot + R_1{-}M_m\cdot \longrightarrow R_1{-}M_{n+m}{-}R_1 \\ R_1{-}M_n\cdot + R_2\cdot \longrightarrow R_1{-}M_n{-}R_2 \\ R_1{-}M_n\cdot + R_1{-}M_m\cdot \longrightarrow R_1{-}M_n + R_1{-}M_m \\ R_1{-}M_n\cdot + R_2\cdot \longrightarrow R_1{-}M_n + R_2 \end{array}\right\} \text{Termination} \qquad \textbf{(2.5d)}$$

It consists of four distinct steps:

i) photoinitiation step involves absorption of light by a photosensitive compound or transfer of electronic excitation energy from a light absorbing sensitizer to the photosensitive compound. Homolytic bond rupture leads to the formation of a radical that reacts with one monomer unit.

ii) propagation step involves repeated addition of monomer units to the chain radical produces the polymer backbone.

iii) chain transfer step involves termination of growing chains by hydrogen abstraction from various species (e.g., from solvent) and formation of new radicals capable of initiating other chain reactions.

iv) termination step involves termination of chain radicals by disproportionation or recombination reactions. Termination can also occur by recombination or disproportionation with any other radical including primary radicals produced by the photoreaction.

The role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating radicals. The reaction of these radicals with monomer, propagation, transfer and termination are purely thermal processes; they are not affected by light.

In most cases of photoinduced polymerization, initiators are used to generate radicals. Photoinitiators are generally divided into two classes, *Type I* and *Type II*, according to the process by which initiating radicals are formed.

2.2.1.1 *Type I* photoinitiators (unimolecular photoinitiator system)

Photoinitiators termed unimolecular are so designated because the initiation system involves only one molecular species interacting with the light and producing free-radical active centers. These substances undergo a homolytic bond cleavage upon absorption of light (reaction 2.6). The fragmentation that leads to the formation of radicals is, from the point of view of chemical kinetics, a unimolecular reaction (equation 2.7).

$$PI \xrightarrow{h\nu} PI^* \xrightarrow{k} R_1\cdot + R_2\cdot \tag{2.6}$$

$$\frac{d[R_1^\bullet]}{dt} = \frac{d[R_2^\bullet]}{dt} = k[PI^*] \tag{2.7}$$

The number of initiating radicals formed upon absorption of one photon is termed as quantum yield of radical formation ($\Phi_{R\bullet}$) (equation 2.8).

$$\Phi_{R\cdot} = \frac{\text{Number of initiating radicals formed}}{\text{Number of photons absorbed by the photoinitiator}} \tag{2.8}$$

Theoretically, cleavage type photoinitiators should have a $\Phi_{R\cdot}$ value of two since two radicals are formed by the photochemical reaction. The values observed, however, are much lower because of various deactivation routes of the photoexcited initiator other than radical generation. These routes include physical deactivation such as fluorescence or non-radiative decay and energy transfer from the excited state to other, ground state molecules, a process referred to as quenching. The reactivity of photogenerated radicals with polymerizable monomers is also to be taken into consideration. In most initiating systems, only one in two radicals formed adds to monomer thus initiating polymerization. The other radical usually undergoes either combination or disproportionation. The initiation efficiency of photogenerated radicals (f_P) can be calculated by the following formula:

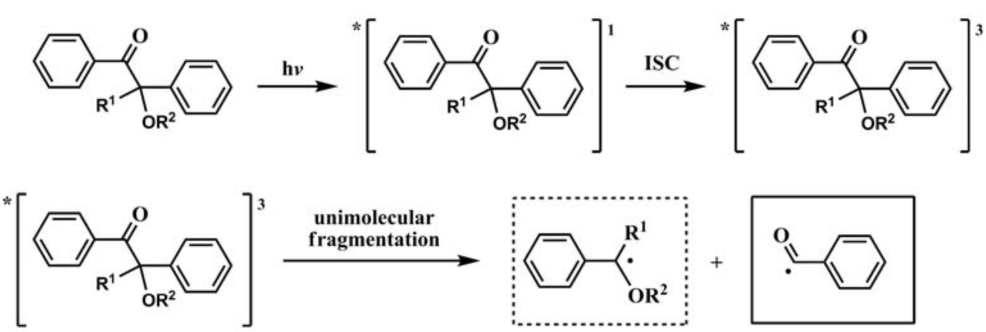
$$f_P = \frac{\text{Number of chain radicals formed}}{\text{Number of primary radicals formed}} \tag{2.9}$$

The overall photoinitiation efficiency is expressed by the quantum yield of photoinitiation (Φ_P) according to the following equation:

$$\Phi_P = \Phi_{R\cdot} \text{ x } f_P \tag{2.10}$$

Regarding the energy necessary, it has to be said that the excitation energy of the photoinitiator has to be higher than the dissociation energy of the bond to be ruptured. The bond dissociation energy, on the other hand, has to be high enough in order to ensure long term storage stability.

Initiating radicals, formed by direct photofragmentation process (α or less common β cleavage) of *Type I* photoinitiators upon absorption of light, are capable of inducing polymerization. As illustrated in reaction 2.11, the photoinitiator forms an excited singlet state, which then undergoes rapid intersystem crossing to form a triplet state. In the triplet state, two radicals (benzoyl and benzyl radicals) are generated by α-cleavage fragmentation. The benzoyl radical is the major initiating species, while, in some cases, the benzyl radical may also contribute to the initiation.



(2.11)

R^1 = H, alkyl, substituted alkyl
R^2 = H, alkyl, substituted alkyl

The majority of *Type I* photoinitiators are aromatic carbonyl compounds with appropriate substituents. Benzoin ether derivatives, benzil ketals, hydroxylalkylphenones, α-aminoketones and acylphosphine oxides are the most efficient ones (Table 2.2) [44-47].

2.2.1.2 *Type II* photoinitiators (bimolecular photoinitiator systems)

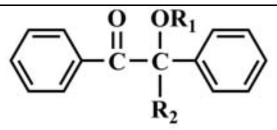
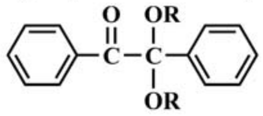
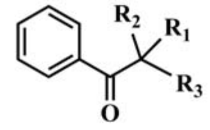
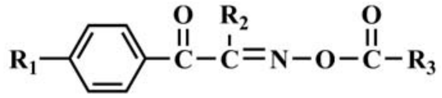
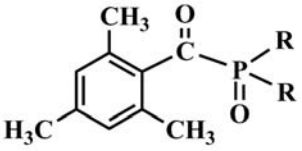
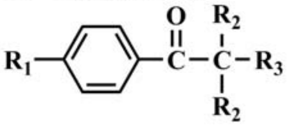
The excited states of certain compounds do not undergo *Type I* reactions because their excitation energy is not high enough for fragmentation (i.e., their excitation energy is lower than the bond dissociation energy). The excited molecule can, however, react with another component of the polymerization mixture (co-initiator (COI)) to produce initiating radicals (reaction 2.12). In this case, radical generation follows second-order kinetics (equation 2.13).

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{PI}^* + \mathrm{COI} \xrightarrow{k} \mathrm{R}_1\cdot + \mathrm{R}_2\cdot \tag{2.12}$$

$$\frac{d[R_1^{\bullet}]}{dt} = \frac{d[R_2^{\bullet}]}{dt} = k[PI^*]\,[COI] \tag{2.13}$$

Typical *Type II* photoinitiators include aromatic carbonyls such as benzophenone and derivatives [48-51], thioxanthone and derivatives [52-56], benzyl [49], quinines [49], and organic dyes [57-62], whereas alcohols, ethers, amines, and thiols are used as hydrogen donors. Recently, thiol and carboxylic acid derivatives of thioxanthones have been reported to initiate photopolymerization without co-initiators as they contain functional groups with H-donating nature [63-65].

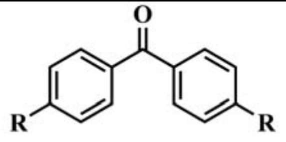
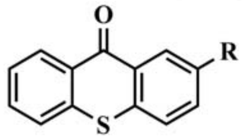
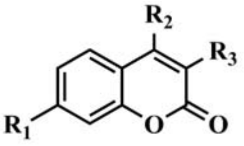
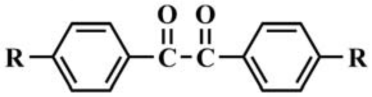
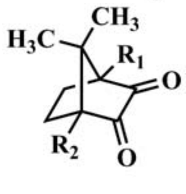
Table 2.2 : Structures of typical *Type I* radical photoinitiators.

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, OCH_3	380
Aminoalkyl phenones	 R_1 = SCH_3, morpholine R_2 = CH_3, CH_2Ph, C_2H_5 R_3 = $N(CH_3)_3$, morpholine	320

Alternative approach concerns the attachment of both chromophoric and hydrogen donating groups into polymer chains [66-80]. This way, the odor and toxicity problems observed with the conventional photoinitiators and amine hydrogen donors were overcome. A novel thioxanthone based photoinitiator have also been developed possesssing anthracene group that does not require an additional hydrogen donor for radical formation and initiates the polymerization of both acrylate and styrene monomers in the presence of air [81]. In addition, TX-A possesses excellent optical absorption properties in the near-UV spectral region, ensuring efficient light absorption. Quite recently, thioxanthone-fluorene carboxylic acid (TX-FLCOOH) and its sodium salt (TX-FLCOONa) were synthesized as efficient photoinitiators in visible light [82]. In fact, photoinitiators with higher wavelength absorption characteristics are desired as they cost lower energy and are defined to be “green”.

Typical photoinitiators for *Type II* system are listed in Table 2.3.

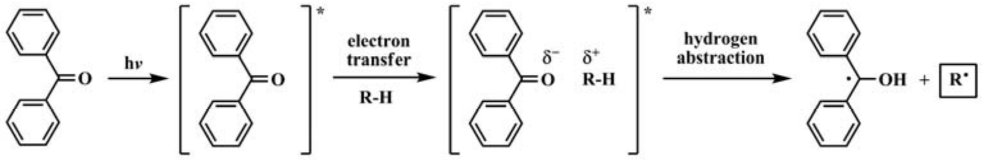
Table 2.3 : Structures of typical *Type II* photoinitiators.

Photoinitiator	**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
Camphorquinones	 **R_1 = CH_3, H** **R_2 = H, CH_3**	470

Radical generation by Type II initiating systems has two distinct pathways:

Hydrogen abstraction from a suitable hydrogen donor

Bimolecular hydrogen abstraction is limited to diaryl ketones [83]. The free radical generation process is the H-abstraction reaction of triplet photoinitiator from hydrogen donors (R-H) such as amines and alcohols. The radical derived from the donor can initiate the polymerization, whereas ketyl radicals stemming from aromatic carbonyl compound are usually not reactive toward vinyl monomers because of bulkiness, the delocalization of the unpaired electrons, or both. The overall process is depicted in the example of benzophenone in reaction 2.14.



(2.14)

R = amines, alcohols, ethers, thiols

Photoinduced electron transfer reactions and subsequent fragmentation

Photoinduced electron transfer is a more general process, which is not limited to a certain class of compounds and is more important as an initiation reaction comprising the majority of bimolecular photoinitiating systems. The photoexcited compounds (sensitizer) can act as either an electron donor with the coinitiator as an electron acceptor or vice-versa. The radical ions obtained after the photoinduced electron transfer can generally undergo fragmentation to yield initiating radicals (2.15-2.17).

$$\mathrm{PS} \xrightarrow{h\nu} \mathrm{PS}^{*} \tag{2.15}$$

$$\mathrm{PS}^{*} + \mathrm{A} \longrightarrow \mathrm{PS}^{\cdot +} + \mathrm{A}^{\cdot -} \longrightarrow \mathrm{R}_1\cdot + \mathrm{R}_2\cdot \tag{2.16}$$

$$\mathrm{PS}^{*} + \mathrm{D} \longrightarrow \mathrm{PS}^{\cdot -} + \mathrm{D}^{\cdot +} \longrightarrow \mathrm{R}_1\cdot + \mathrm{R}_2\cdot \tag{2.17}$$

The electron transfer is thermodynamically allowed, if Gibbs Energy Change (ΔG) calculated by the Rehm-Weller equation (2.18) is negative [84].

$$\Delta G = F\,[E_{1/2}^{ox}\,(D/D^{+\cdot}) - E_{1/2}^{red}\,(A/A^{-\cdot})] - E_S + \Delta E_c \tag{2.18}$$

where
F = Faraday constant
$E_{1/2}^{ox}\,(D/D^{+\cdot})$, $E_{1/2}^{red}\,(A/A^{-\cdot})$ = redox potentials of the donor and acceptor
E_S = excitation state of the reactive state of the sensitizer; $E_S = h\nu$
ΔG = Coulombic stabilization energy

Electron transfer is often observed for aromatic ketone/amine pairs and always with dye/coinitiator systems. Dyes comprise a large fraction of visible light photoinitiators because their excited electronic states are more easily attained. Co-initiators, such as tertiary amines, iodonium salts, triazines, or hexaarylbisimidazoles, are required since dye photochemistry entails either a photo-reduction or photo-oxidation mechanism. Numerous dye families are available for selection of an appropriate visible initiation wavelength; examples of a thiazine dye (with an absorption peak around 675 nm), acridine dyes (with absorption peaks around 475nm), xanthene dyes (500–550 nm), fluorone dyes (450–550 nm), coumarin dyes (350–450 nm), cyanine dyes (400–750 nm), and carbazole dyes (400 nm) [85-88]. The oxidation or reduction of the dye is dependent on the co-initiator; for example, methylene blue can be photo-reduced by accepting an electron from an amine or photo-oxidized by transferring an electron to benzyltrimethyl stannane [86]. Either mechanism will result in the formation of a free-radical active center capable of initiating a growing polymer chain.

2.2.1.3 Monomers

Unsaturated monomers, which contain a carbon–carbon double bond (C=C), are used extensively in free radical photopolymerizations. The free-radical active center reacts with the monomer by opening the C=C bond and adding the molecule to the growing polymer chain. Most unsaturated monomers are able to undergo radical polymerization because free-radical species are neutral and do not require electron-donating or electron-withdrawing substituents to delocalize the charge on the propagating center, as is the case with ionic polymerizations. Commercial consideration in formulation development is therefore given to the final properties of the polymer system, as well as the reactivity of the monomer. Acrylate and methacrylate monomers are by far most widely used in free-radical photopolymerization processes. These monomers have very high reaction rates, with acrylates having an even faster reaction rate than their methacrylate counterparts [89]. This makes them especially amenable for high speed processing needed in the films and coatings industry.

Multiacrylates increase the mechanical strength and solvent resistance of the ultimate polymer by forming cross-linked networks rather than linear polymer chains, whereas monoacrylates reduce the viscosity of the prepolymer mixture for ease of processing [2, 89]. One of the drawbacks of acrylate and methacrylate systems is their relatively large polymerization shrinkage. Shrinkage is caused by the formation of covalent bonds between monomer molecules. When a covalent bond is formed between two monomer molecules, the distance between them is approximately half as much as that between two molecules experiencing van der Waal's forces in solution. This shrinkage causes stresses in the polymer parts, which can affect their ultimate performance, especially in applications such as stereo lithography, dentistry, and coatings. One way to overcome this disadvantage is to develop oligomeric acrylates. These oligomers contain 1 to 12 repeat units formed through step-growth polymerization; the ends are then capped with two or more (meth) acrylate functional groups.

Diallyldiglycolcarbonate has been used for many years in optical components such as lenses [90]. Acrylamide is used in stereo lithography and to prepare holographic materials [91-93]. N-vinylpyrrolidinone is copolymerized with acrylates and methacrylates for cosmetic and biomedical applications [94]. Norbornene is copolymerized with thiols for optical fiber coatings [95].

2.2.2 Photoinitiated cationic polymerization

Although the most popular industrial applications are based on the photo-initiated free radical polymerization, there are some drawbacks associated with this type of polymerization, such as the inhibition effect of oxygen and post-cure limitations, which may affect the properties of the final product. Several advantages of the photoinitiated cationic polymerization over the photoinitiated free radical polymerization have been reported [4, 96, 97]. Cationic photopolymerization overcomes volatile emissions, limitations due to molecular oxygen inhibition, toxicity, and problems associated to high viscosity. Furthermore, once initiated, cationically polymerizable monomers such as vinyl ethers and epoxides undergo dark-polymerization in which they slowly polymerize without radiation [43].

There are two possible pathways for the initiation of photoinduced cationic polymerization; direct photolysis and indirect photolysis.

2.2.2.1 Direct photolysis

In direct photolysis, initiating species are generated upon irradiation of a photosensitive compound, namely photoinitiator (PI), at appropriate wavelengths. PI absorbs incident light and undergoes decomposition leading to production of initiating species. Active species, radical cation ($R^{+\cdot}$) and/or protonic acid react with cationic polymerizable monomers (M), and yield polymer (2.19-2.21). Most photoinitiators, used in cationic photopolymerization mainly absorbs light between 225 to 350 nm. For practical applications, however, they are expected to absorb light at quite longer wavelengths. Several attempts have been described to overcome this problem.

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{H}^{+} + \mathrm{R}^{\cdot +} + \text{other products} \qquad \textbf{(2.19)}$$

$$\mathrm{R}^{\cdot +} + \mathrm{M} \longrightarrow \text{polymer} \qquad \textbf{(2.20)}$$

$$\mathrm{H}^{+} + \mathrm{M} \longrightarrow \text{polymer} \qquad \textbf{(2.21)}$$

Photoinduced cationic polymerization can be initiated by a number of agents including Lewis and Brønsted acids, carbonium ions and onium salts. A key feature of cationic polymerization is the use of acids possessing anions of very low nucleophilicity, which do not terminate the polymerization process. Therefore, most cationic photoinitiators are based on salts of non-nucleophilic anions such as BF_4^-, PF_6^-, AsF_6^- and SbF_6^-. Generally, molecular weights and percentage conversion increase in the order of $BF_4^- < PF_6^- < AsF_6^- < SbF_6^-$.

Cationic photoinitiators are generally divided into two classes, ionic and non-ionic photoinitiators. These classes consist of structurally related compounds which undergo similar photochemical reactions.

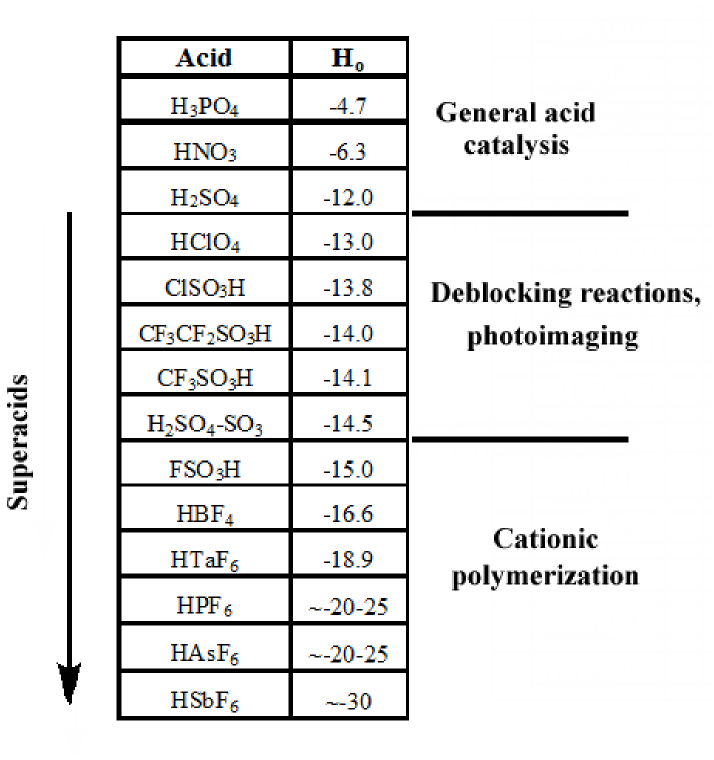
1) Ionic cationic photoinitiators: Onium salts and organometallic salts

2) Non-ionic cationic photoinitiators: Organosilanes, latent sulphonic acids and miscellaneous non-ionic compounds

Among these photoinitiators, onium salts will be discussed as the present thesis involves the use of them in the experimental section.

Onium salts

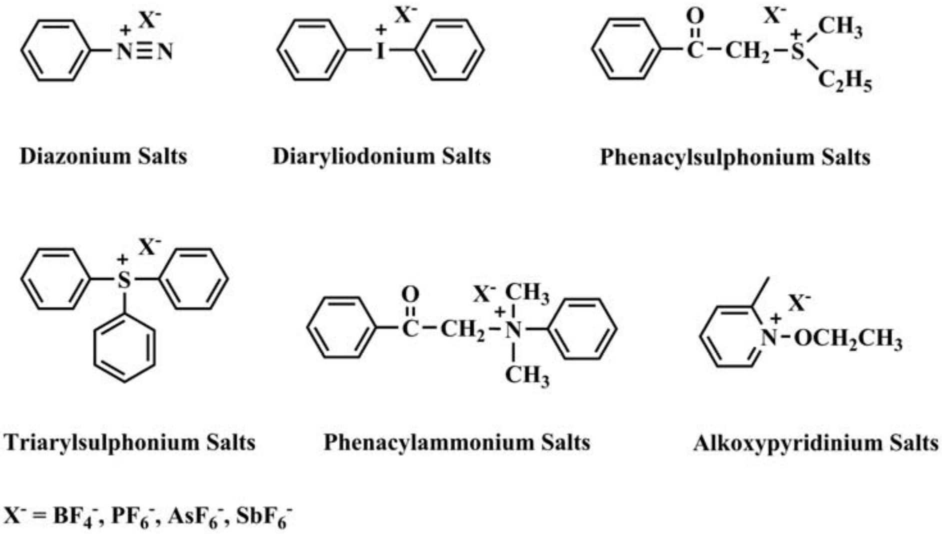
Onium salts are the most widely used cationic photoinitiators. They contain chromophopric groups as the light sensitive body with heteroatoms as cationic centers in the structure. As counterions, mostly inorganic metal complex anions are used [8]. Each of these componenets has specific function and can 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 2.6) [98, 99].



Acid	H_0
H_3PO_4	-4.7
HNO_3	-6.3
H_2SO_4	-12.0
$HClO_4$	-13.0
$ClSO_3H$	-13.8
$CF_3CF_2SO_3H$	-14.0
CF_3SO_3H	-14.1
H_2SO_4-SO_3	-14.5
FSO_3H	-15.0
HBF_4	-16.6
$HTaF_6$	-18.9
HPF_6	~-20-25
$HAsF_6$	~-20-25
$HSbF_6$	~-30

Figure 2.6 : 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 [100-103]. Different types of onium salts are shown in Figure 2.7.



$X^- = BF_4^-, PF_6^-, AsF_6^-, SbF_6^-$

Figure 2.7 : Types of onium salt photoinitiators.

So far, the most frequently used onium salts are diaryliodonium [9, 104], triarylsulfonium [105, 106], alkoxypyridinium [107, 108] and phenacyl [109-117] salts with non-nucleophillic counter ion that mainly absorb the light in the region between 225 and 350 nm for photoinitiated cationic polymerization.

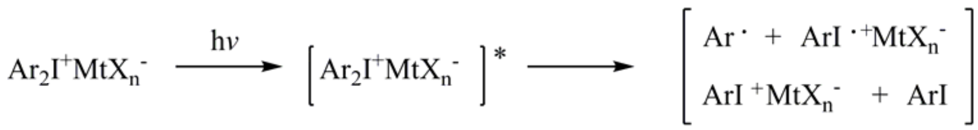
Diaryliodonium salts

Diaryliodonium salts are the most frequently used halonium salts as they are easy to obtain and quite reactive [104, 118, 119]. 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.

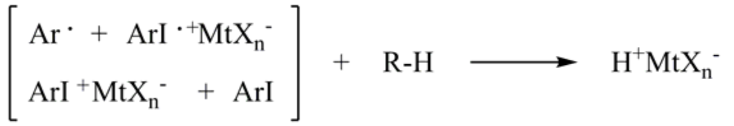
Photolysis of diaryliodonium salts take place either through homolytic or heterolytic cleavage of the halogen-aryl bond to form species which react with a hydrogen donor compound to yield a Brønsted acid that initiates polymerization (reactions 2.22-2.24).

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.



$$\mathrm{Ar_2I^+MtX_n^-} \xrightarrow{h\nu} \left[\mathrm{Ar_2I^+MtX_n^-}\right]^* \longrightarrow \left[\begin{array}{l} \mathrm{Ar^{\cdot} + ArI^{\cdot +}MtX_n^-} \\ \mathrm{ArI^{+}MtX_n^- + ArI} \end{array}\right]$$

(2.22)



$$\left[\begin{array}{l} \mathrm{Ar^{\cdot} + ArI^{\cdot +}MtX_n^-} \\ \mathrm{ArI^{+}MtX_n^- + ArI} \end{array}\right] + \mathrm{R\text{-}H} \longrightarrow \mathrm{H^+MtX_n^-}$$

(2.23)

$$\mathrm{H^+MtX_n^-} + \mathrm{M} \longrightarrow \mathrm{M^+MtX_n^-} \overset{\mathrm{M}}{\underset{\longrightarrow}{\overset{\longrightarrow}{\longrightarrow}}} \mathrm{Polymer}$$

(2.24)

R-H : solvent or monomer

$\mathrm{MtX_n^-}$: $\mathrm{PF_6^-}$, $\mathrm{SbF_6^-}$, $\mathrm{AsF_6^-}$, etc.

Triarylsulphonium salts

Triaryl sulphonium salts (TAS) are generally produced by the method of Pitt: [120] 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 [121].

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 2.25-2.29).

$$\mathrm{Ar_3S^+MtX_n^-} \xrightarrow{h\nu} \mathrm{Ar_2S^{\cdot +}MtX_n^-} + \mathrm{Ar^{\cdot}} \tag{2.25}$$

$$\mathrm{Ar_2S^{\cdot +}MtX_n^-} + \mathrm{R\text{-}H} \longrightarrow \mathrm{Ar_2HS^+MtX_n^-} + \mathrm{R^{\cdot}} \tag{2.26}$$

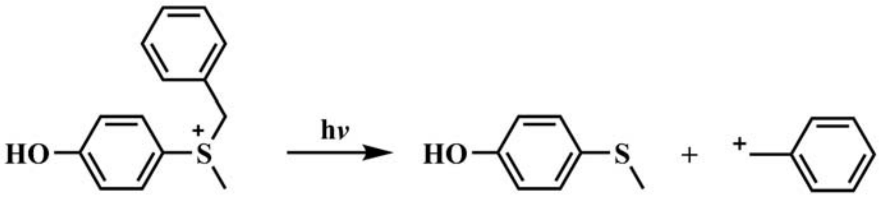
$$\mathrm{Ar_2HS^+MtX_n^-} \longrightarrow \mathrm{Ar_2S} + \mathrm{H^+MtX_n^-} \tag{2.27}$$

$$\mathrm{Ar_3S^+MtX_n^-} \xrightarrow{h\nu} \mathrm{Ar_2S} + \mathrm{Ar^+MtX_n^-} \tag{2.28}$$

$$\mathrm{Ar^+MtX_n^-} + \mathrm{R\text{-}H} \longrightarrow \mathrm{Ar\text{-}R} + \mathrm{H^+MtX_n^-} \tag{2.29}$$

R-H : solvent or monomer
$\mathrm{MtX_n^-}$: $\mathrm{PF_6^-}$, $\mathrm{SbF_6^-}$, $\mathrm{AsF_6^-}$, 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 (2.30).



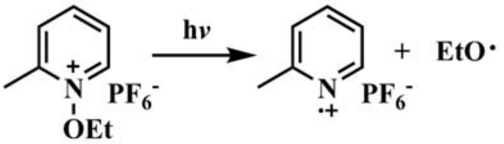
(2.30)

Recently, novel sulfonium type initiators, which can initiate polymerization either upon irradiation or thermal treatment have been developed [122]. 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 [123-125]. 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.

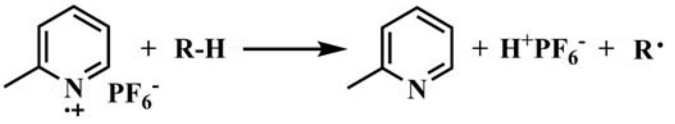
N-Alkoxy pyridinium salts

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 [107]. Quinolinium salts can also be prepared from the corresponding *N*-oxides [126]. 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 [107].

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.

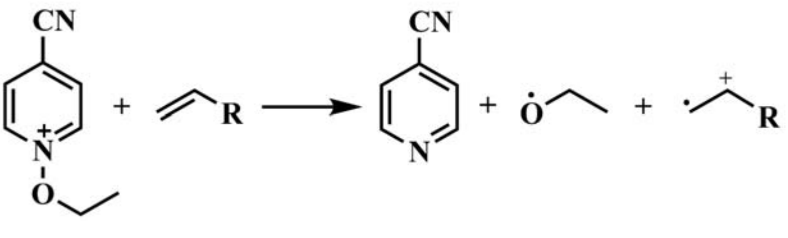


(2.31)



(2.32)

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 (2.33).



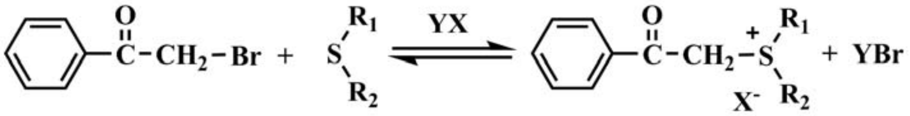
(2.33)

Phenacyl salts

Onium salts, namely sulfonium, phosphonium, ammonium, and pyridinium salts containing phenacyl group are photoinitiators appropriate for the polymerization of monomers such as oxiranes and vinyl ethers, which are not polymerizable by a free-radical mechanism [114]. The initiation is accomplished by direct or indirect (sensitized) photolysis of the salts.

Commonly, phenacyl-based onium salts are synthesized by the reaction of phenacyl halides with the corresponding heteroatom nucleophiles followed by anion exchange with potassium or sodium salts with non-nucleophlic counteranions such as, SbF_6^-, PF_6^-, AsF_6^-, etc. Bromides were used as the halides to afford the salts with the improved yields.

A new simplified method for the synthesis of phenacylsulfonium salts was reported by Crivello and Kong [109]. The method involves a one-pot reaction of phenacyl bromides or their aryl counter parts with the appropriate dialkyl sulfides in the presence of an alkali metal salt with desired anion (reaction 2.34).



(2.34)

This simple one-pot reaction was also used for the synthesis of the other phenacyl onium salts. Accordingly, phenacyl bromide was reacted with *N,N*-dimethyl aniline, triphenylphosphine, and pyridine to yield the respective salts [116]. In this approach, the precipitation of insoluble NaBr or KBr depending on the initial salt strongly shifts the two simultaneous equilibrium reactions toward the desired final product.

The light-absorbing chromophore in phenacyl-type onium salts is the phenyl ketone group. Therefore, most of the primary reactions occur through the excitation of this group. However, depending on the heteroatom in the salt structure, the photodecomposition may differ. In the case of phenacylsulfonium, the photolysis in the absence of monomers is essentially reversible and, the ylides rapidly react with the protonic acid to afford the starting salt.

The detailed mechanistic studies revealed that intramolecular hydrogen abstraction of photoexcited salt from the carbon atoms neighboring sulfur atom is followed by internal electron transfer. Subsequent deprotonation gives a sulfur ylide and a protonic acid, which in the presence of monomer initiates the polymerization as illustrated in Figure 2.8.

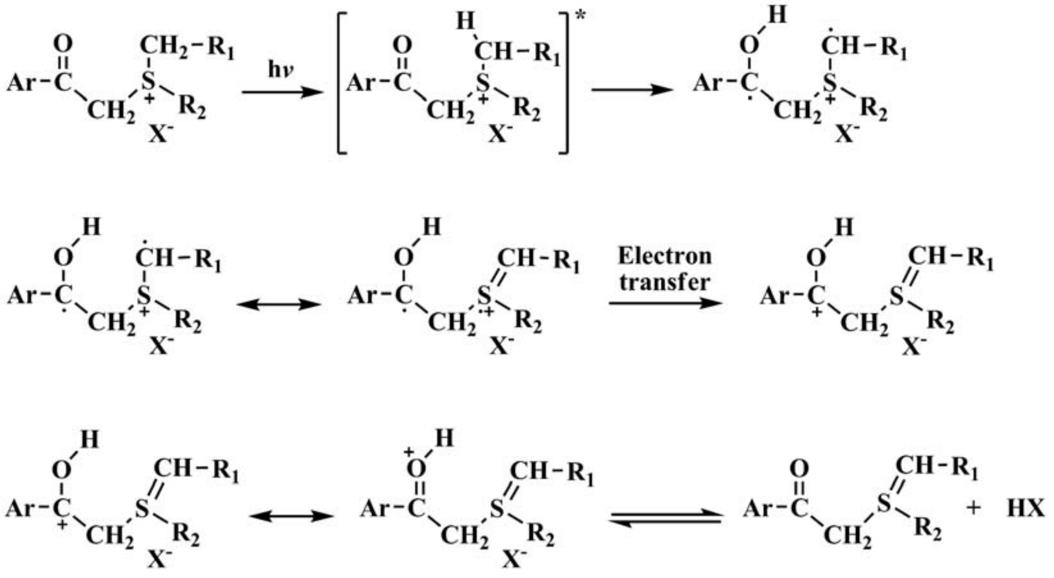


Figure 2.8 : Photoinitiated cationic polymerization mechanism by using phenacyl sulphonium salts.

Interestingly, phenacyl-type onium salts other than sulfonium salts undergo irreversible photolysis leading to fragmentation of the photoinitiator (Figure 2.9) [111, 127]. Electronically excited salt may undergo heterolytic cleavage (b) resulting in the formation of phenacylium cations. It is also feasible that homolytic cleavage (a) followed by the intermolecular electron transfer (a′) essentially yields the same species.

Photoinitiated free-radical and zwitterionic polymerizations by using phenacyl-type salts are also possible [116]. Although phenacyl onium salts that contain counter anions with low nucleophilicity, are efficient and convenient compounds to generate Lewis bases photochemically, they suffer from the drawback of the termination of the anionic species by the photofragments formed from these compounds. The phenacylium cations stabilized with non-nucleophilic counteranions can react with the initiating and propagating centers. For this reason, for potential application of these salts as photoinitiators for anionic polymerization it is necessary to equip them with counteranions with higher nucleophilicity.

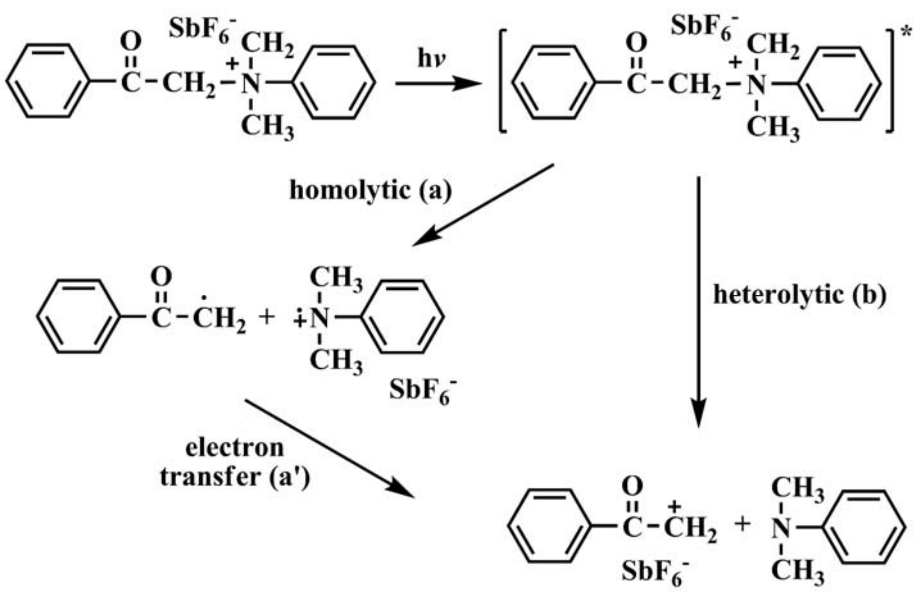
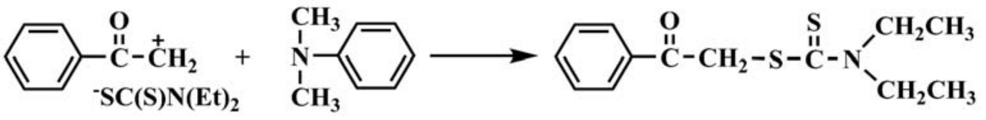


Figure 2.9 : Photolysis of phenacyl anilinium salt.

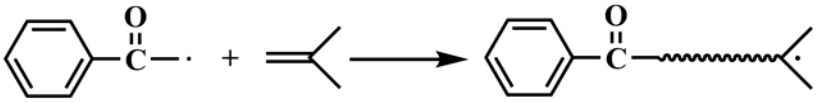
Electronically excited salt undergoes heterolytic cleavage resulting in the formation of phenacylium cations and an alternative pathway in which homolytic cleavage followed by electron transfer essentially yields the same species. Notably, phenacylium cation is converted to covalently bonded inert compound as a result of the combination of the cation with thiocarbamate anion and free Lewis base, dimethylaniline is liberated in reaction 2.35.



(2.35)

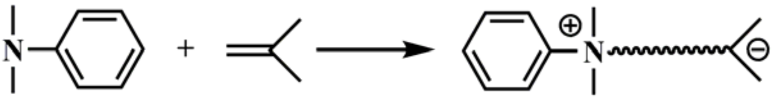
If the polymerization mechanism involves only free radical species, the polymerization would be completely inhibited by a radical scavenger. Accordingly, if the polymerization is initiated via a zwitterionic mechanism, sample containing protonation agent would yield no polymer. It is therefore most probable that both radical and zwitterionic mechanisms are responsible for the initiation. Phenacyl radicals induce freeradical polymerization while dimethylaniline initiates zwitterionic polymerization according to the following reactions 2.36 and 2.37.

Free radical polymerization



(2.36)

Zwitterionic polymerization



(2.37)

2.2.2.2 Indirect photolysis

Without absorption of the incident photon energy, photochemical processes cannot occur. Medium- and high-pressure mercury lamps that are frequently used as light sources provide emissions at 313 and 366 nm. If daylight is to be used for curing a coating formula, light absorption at wavelengths longer than 400 nm is highly desired. Rather than introducing electron-donating substituents to the structure as mentioned before, some electron-rich compounds such as trimethoxybenzene or hexamethylbenzene can be added to polymerization mixture to form charge transfer complexes (CTCs) with initiators in the electronic ground state that have absorptions at longer wavelengths. Moreover, some special additives can be used in conjunction with photoinitiators to carry out polymerization at longer wavelengths. Notably, in general, the additives are the light absorbing species here. Provided the systems thus obtained do initiate cationic polymerizations, the initiation can be explained through one of the following mechanisms:

Sensitization by Classical Energy Transfer

This mechanism involves the electronic excitation of the ground state of the sensitizer, a molecule possessing a suitable absorption spectrum, to its excited state. Energy may be transferred from the excited sensitizer (S*) to the onium salt (I) by either resonance excitation or exchange energy transfer (2.38-2.39). Depending on the two components involved, the energy transfer may proceed either in the excited singlet or in the triplet state.

$$S \longrightarrow S^* \tag{2.38}$$

$$S^* + I \longrightarrow S + I^* \tag{2.39}$$

In consequence of the transfer process, the sensitizer returns to its ground state and excited onium salt species (I*) are formed. The further reactions may also differ from those, taking place when the onium salt is excited by direct absorption of light. This conclusion has been drawn on the bases of product analyses [128-130]. An obvious explanation for this difference is the spin multiplicity: in the below discussed sensitized excitations triplet states of the onium salts are populated. In contrast to this, through direct irradiation of the onium salt, electrons are excited primary to the singlet state. A sufficient energy transfer requires the excitation energy of the sensitizer E*(S) to be at least as large as the excitation energy of the photoinitiator E*(I). The photopolymerization with most onium salts can be sensitized by commonly used photosensitizers, such as acetophenone or naphthalene. However, in many cases this reaction does not proceed via energy transfer, since most onium salts are capable of oxidizing these sensitizers in an exciplex formed between sensitizer and onium salt.

Diphenyl iodonium salts are shown to take action of energy transfer with suitable additives like *m*-trifluoromethyl acetophenone [131]. However, energy transfer using TAS salts are shown to be impossible because of unfavorable thermodynamic conditions. Energy transfer sensitization did not turn out to be technically useful, although being a possible pathway in starting the decomposition of onium salts. The reason is that the high triplet energies required allow only the use of sensitizers absorbing at wavelengths below 350 nm. Other multicomponent initiating systems (vide infra) show a more practical spectral response.

Free Radical Promoted Cationic Polymerization

Many radicals can be oxidized by onium salts leading to generation of cations which are considered as initiating species for cationic polymerization. Two types of free radical induced initiation are available: oxidation of radicals and addition fragmentation reactions.

Among these reactions, oxidation of radicals is the most flexible route, since free radical photoinitiators with a wide range of absorption characteristics are available.

Many photochemically formed radicals can be oxidized by onium salts. The cations thus generated are used as initiating species for cationic polymerization according to the following reactions [10, 11]:

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{R}^{\cdot} \qquad \textbf{(2.40)}$$

$$\mathrm{R}^{\cdot} \xrightarrow{\mathrm{On}^{+}} \mathrm{R}^{+} + \mathrm{On}^{\cdot} \qquad \textbf{(2.41)}$$

$$\mathrm{R}^{+} + \mathrm{M} \longrightarrow \mathrm{Polymer} \qquad \textbf{(2.42)}$$

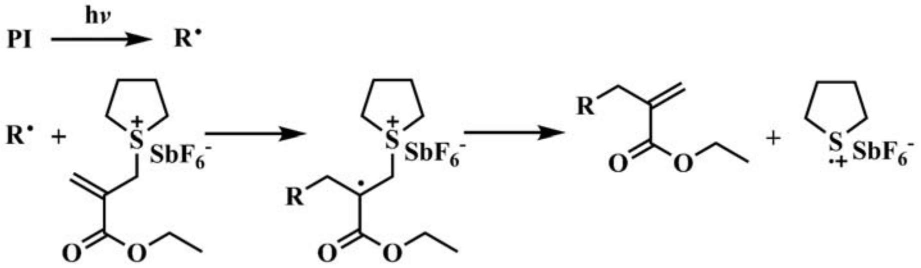
The cations thus generated are used as initiating species for cationic polymerization. This so-called free radical promoted cationic polymerization is an elegant and fairly flexible type of sensitized cationic polymerization. Free radicals may be produced not only by photochemically but also thermally or by irradiating the system with high-energy rays. The photochemical generation of radicals can be applied even at low temperatures. Being photolyzed with high quantum yields, benzoin derivatives are so far the most effective photoinitiators for the free radical promoted cationic polymerization [108]. The other suitable free radical promoters include benzyl ketals [108], benzaldehyde [132], acylphosphine oxides [133, 134], azo compounds [108], benzophenone and certain dyes in conjunction with hydrogen donors [135], manganese decacarbonyl in the presence of alkyl halides [136], substituted vinyl halides [137], polysilanes [138, 139] and acylgermane based photoinitiators [140]. Recently, Crivello reported efficient three component visible sensitive photoinitiator systems for cationic ring opening polymerization of epoxides and related monomers [141, 142]. The photoinitiator systems consists of camphorquinone or titanium-complex free radical photoinitiator in combination with a benzyl alcohol to generate free radicals by the absorption of visible light. The electron transfer reactions of resulting radicals with iodonium salt present in the system essentially leads to the formation of Brønsted acid capable of catalyzing the ring-opening polymerization of epoxy substrates. Although a broad range of spectral flexibility can be achieved, the free radical oxidation is limited to the photoinitiators capable of forming electron donor radicals. For instance, except structurally specially designed, long wavelength absorbing acylphosphine oxide photoinitiators do not generate oxidizable radicals.

The use of addition fragmentation reactions in photoinduced cationic polymerization is another distinguished approach and it has been subject of recent investigations

[143-153]. Addition fragmentation reactions are indeed a very versatile method to adjust the spectral response of the polymerization mixture with the aid of free radical photoinitiators, since they are not based on easily oxidizable radicals. The allylic salts have so far been applied for addition fragmentation type initiations.

The advantage of allylic salts that can undergo addition fragmentation reactions derives from the fact that virtually all sorts of thermal and light-sensitive radical initiators may be utilized for cationic polymerization, which enables an adaptation to most initiation conditions. In contrast to radical promoted cationic polymerization based on the oxidation of radicals, one is not limited to oxidizable radicals.

The mechanism of the addition fragmentation type initiation is depicted on the example of ethyl-α-(tetrahydrothiophenium methyl) acrylate hexafluoroantimonate (ETM$^+$SbF$_6^-$) (2.39-2.40) [143].



(2.43)

(2.44)

The first step consists in the photogeneration of free radicals (reaction 2.43). Virtually any photolabile compound undergoing homolytic bond cleavage may be used as a radical source. The radicals add to the double bond of the allylonium salt thus producing a radical in β-position to the heteroatom of the onium salt cation. Consequently, the molecule undergoes fragmentation yielding initiating cations (reaction 2.44).

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 [154-161].

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 [162]. The mechanism of a polymerization followed via exciplex formation through the excited sensitizer with the ground state onium salt is illustrated by reactions 2.45a-g.

$$\mathrm{PS} \xrightarrow{h\nu} [\mathrm{PS}]^* \qquad \textbf{(2.45a)}$$

$$[\mathrm{PS}]^* + \mathrm{Ar_2I^+MtX_n^-} \longrightarrow \underset{\text{exciplex}}{[\,\mathrm{PS....Ar_2I^+MtX_n^-}\,]^*} \qquad \textbf{(2.45b)}$$

$$[\,\mathrm{PS....Ar_2I^+MtX_n^-}\,]^* \longrightarrow [\mathrm{PS}]^{+\cdot}\mathrm{MtX_n^-} + \mathrm{Ar_2I}\cdot \qquad \textbf{(2.45c)}$$

$$\mathrm{Ar_2I}\cdot \longrightarrow \mathrm{ArI} + \mathrm{Ar}\cdot \qquad \textbf{(2.45d)}$$

$$[\mathrm{PS}]^{+\cdot}\mathrm{MtX_n^-} \xrightarrow{\text{Monomer}} \text{Polymer} \qquad \textbf{(2.45e)}$$

$$[\mathrm{PS}]^{+\cdot}\mathrm{MtX_n^-} + \mathrm{R\text{-}H} \longrightarrow \mathrm{PS} + \mathrm{R}\cdot + \mathrm{H^+MtX_n^-} \xrightarrow{\text{Monomer}} \text{Polymer} \qquad \textbf{(2.45f)}$$

$$[\mathrm{PS}]^{+\cdot}\mathrm{MtX_n^-} \longrightarrow \text{Coupling Product} + 2\mathrm{H^+MtX_n^-} \xrightarrow{\text{Monomer}} \text{Polymer} \qquad \textbf{(2.45g)}$$

First, photosensitizer absorbs the light to give the corresponding excited species [PS]* (2.45a). An excited state complex (exciplex) is formed as an intermediate between onium salt and excited photosensitizer (2.45b). In the following step, one-electron is transferred from the sensitizer to the onium salt (2.45c). Unstable diaryliodine radical decomposes rapidly and makes the process irreversible by preventing back electron transfer (2.45d). The radical cations formed by reaction 2.45c would be capable of initiating cationic polymerization (2.45e) 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. Principally, polymerization could also be initiated by the Brønsted acids formed via hydrogen abstraction (reaction 2.45f) or coupling reactions (reaction 2.45g).

A good photosensitizer, therefore, is not only a molecule that readily absorbs light energy, but also one that readily transfers it to another molecule. Some compounds are capable of forming such transfer complexes in the ground state, but many more form exiplexes in the excited state. Others can form complexes between a compound in the ground state and another one in the excited state. Such complexes are called excimers or excited dimers. The difference between the excited state of a dimer and an exiplex is that the dimmers possess binding energy in the ground state, while exiplexes lack any binding energy in the ground state [163].

According to the Rehm-Weller equation [84] (2.46) electron transfer from the excited sensitizer to onium salt is feasible if the change in free energy (ΔG) is negative. Based on the oxidation potential ($E_{1/2}^{ox}$) and active excitation energy (E^*) of the photosensitizer (PS) and the reduction potential ($E_{1/2}^{red}$) of the initiator (PI), the free energy change (ΔG) for the photoinduced electron transfer process is estimated. The calculation of ΔG is applied in order to predict whether or not an oxidation would take place.

$$\Delta G = F[E_{1/2}^{ox}\,(\mathrm{PS}) - E_{1/2}^{red}\,(\mathrm{PI})] - E^*\,(\mathrm{PS}) \qquad \textbf{(2.46)}$$

The oxidation potentials and absorption characteristics of sensitizers used most frequently in conjunction with onium salts are summarized in Table 2.4.

Despite the many potential applications, photosensitizers also have several serious drawbacks that limit their use. For example, they are generally expensive, toxic, and poorly soluble in most reactive monomers and polymer systems. Moreover, they are easily lost from thin film coatings during polymerization and have high vapor pressure at room temperatures. Therefore, there is a progressing need for long-wavelength-active photosensitizers in order to overcome these limitations.

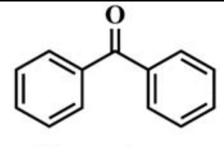
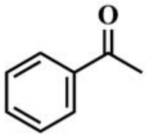
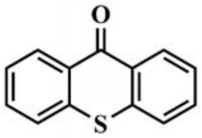
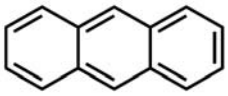
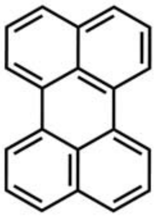
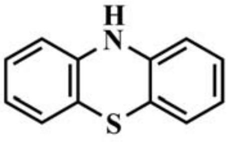
One way to obtain non-toxic polymers through sensitization is to copolymerize compounds, which can behave either as a photosensitizer or as a monomer with different monomers. Another way is to polymerize these monomeric photosensitizers and afterwards subject them to sensitize the polymerization of convenient monomers. In both ways non-toxic and odorless polymers can be obtained after polymerization [164-167].

Ground state charge-transfer complexes (CTCs)

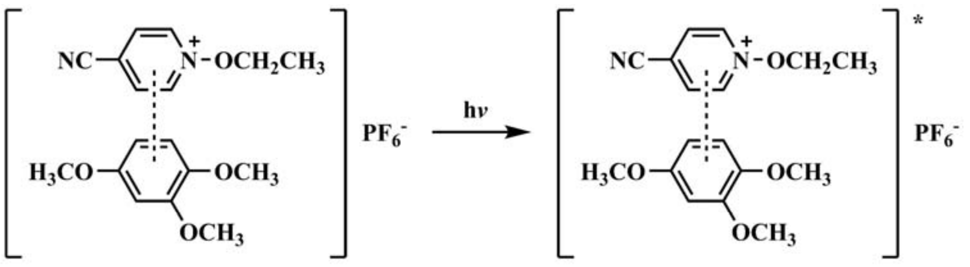
Although it is not considered to be a general method for the indirect initiation, certain salts can undergo decomposition upon irradiation in their appropriate charge transfer complexes (CTC). For example, pyridinium salts are capable of forming ground state CTCs with electron-rich donors such as methyl- and methoxysubstituted benzene [16]. Notably, these complexes absorb at relatively high wavelengths, where the components are virtually transparent. For example, the complex formed between *N*-

ethoxy-4-cyano pyridinium hexafluorophosphate and 1,2,4-trimethoxybenzene possesses an absorption maximum at 420 nm.

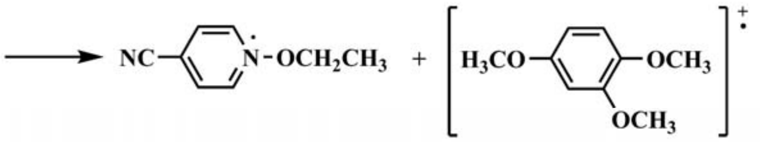
Table 2.4 : Structures, oxidation potentials, triplet or singlet excitation energies and absorption characteristics of some common photosensitizers.

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)
 **Thioxanthone**	1.7	277 (E_T)	219 (15200) 255 (44200) 298 (3510)
 **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)

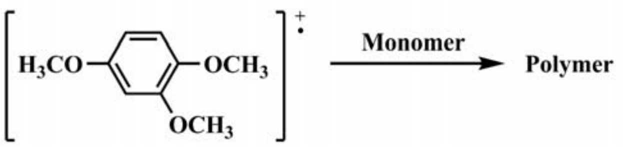
The following mechanism shows the action of a CTC as photoinitiator (reactions 2.47-2.49). Since polymerization takes place even in the presence of a proton scavenger like 2,6-di-*tert*-butylpyridine an initiation through Brønsted acid formation can totally be excluded.



(2.47)



(2.48)



(2.49)

2.2.2.3 Monomers

The types of general monomers which may undergo photo-initiated cationic polymerization are vinyl and alkoxy vinyl monomers, heterocyclic monomers involving sulphur, oxygen, nitrogen atoms in their rings. Cationically polymerizable monomers and their corresponding polymers [168] are summarized in Figure 2.10. In UV-curing applications, difunctional epoxide and alkyl vinyl ether monomers are usually employed.

Although wide variety of monomers is available, demands from many industrial applications promote design of new monomers with high polymerization rate and improved features. For this reason, several works in recent decades have been conducted to development of new monomers, especially epoxides, with high reactivity. Furthermore, some works have been subjected to synthesis of monomers carrying functional groups allowing for design of the special polymer since nature of the monomers affects the physical and mechanical properties of the resulted polymer.

Newly developed monomers containing a wide variety of functional groups may lead to a high monomer conversion, acceleration in polymerization as well as production of polymers with improved properties.

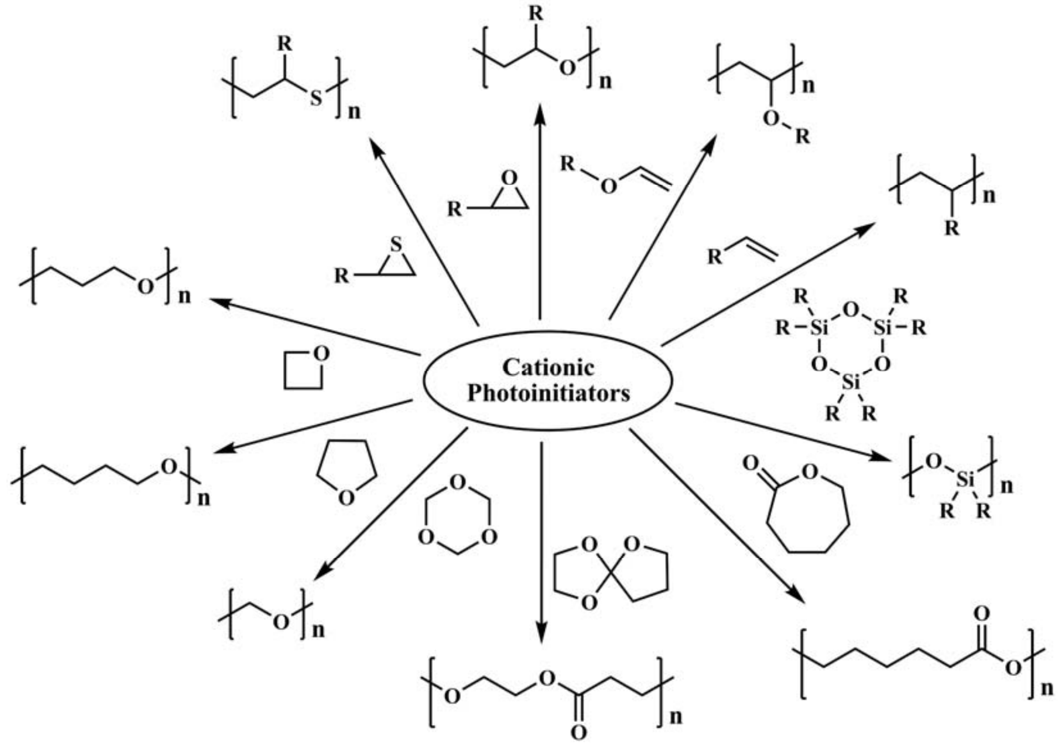
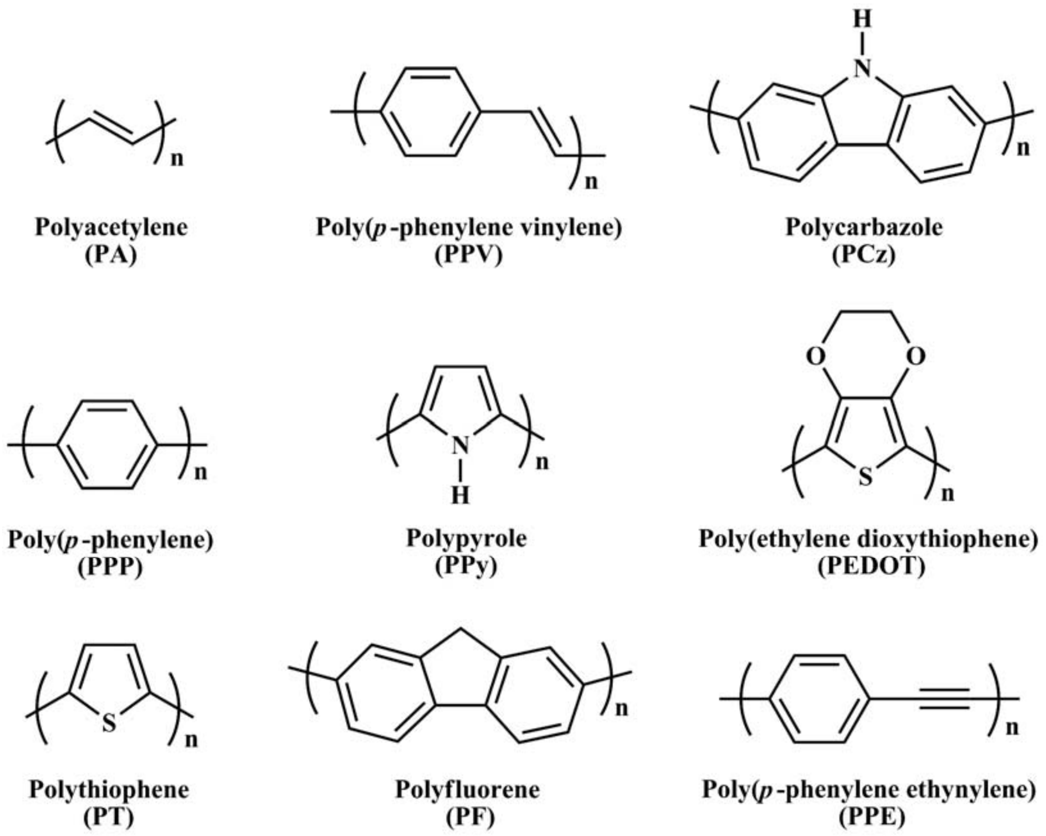


Figure 2.10 : Photoinitiated cationic polymerization of various monomers.

2.3 Conjugated Polymers

Conjugated polymers have attracted great interest [20] due to their wide range of potential applications including light emitting diodes [169], batteries [170], electrochromic devices [171], sensors [172], electromagnetic shielding [173], and corrosion inhibition [174]. In 1977, MacDiarmid, Shirakawa, and Heeger demonstrated that chemical doping of polyacetylene with oxidizing agents (e.g., I_2, $FeCl_3$, and AsF_5) results in increased electronic conductivity by several orders of magnitude [175-177]. They were awarded the 2000 Nobel Prize in Chemistry for this work. Since then, electronically conducting and semiconducting materials based on conjugated polymers have become the subject of multidisciplinary research.

Conjugated polymers possess excellent properties such as non-linear optical behaviour, electronic conductivity, photoluminescence, electroluminescence, thermochromism, electrochromism, and exceptional mechanical properties [20, 178-182]. Typical conjugated polymers include polyacetylene (PA), poly(*p*-phenylene) (PPP), polythiophene (PT), poly(*p*-phenylene vinylene) (PPV), polypyrole (PPy), polyfluorene (PF), polycarbazole (PCz), poly(ethylene dioxythiophene) (PEDOT) and poly(*p*-phenylene ethynylene) (PPE) (Figure 2.11).



Polyacetylene (PA)

Poly(*p*-phenylene vinylene) (PPV)

Polycarbazole (PCz)

Poly(*p*-phenylene) (PPP)

Polypyrole (PPy)

Poly(ethylene dioxythiophene) (PEDOT)

Polythiophene (PT)

Polyfluorene (PF)

Poly(*p*-phenylene ethynylene) (PPE)

Figure 2.11 : Structures of typical conjugated polymers.

2.3.1 Structure of conjugated polymers

Conjugated polymers are organic macromolecules, which consist alternating single and double bonds in their polymer backbone. They are described as extended conjugated systems containing delocalized π-electrons arising from their alternating structure of single and double bonds along polymer chains [20]. The unique electric and optical properties of conjugated polymers are attributed to the overlap of p-orbitals and delocalized π-electrons. For example, strong absorption of light in the visible region is one of the special features of molecules containing conjugated repeating units, which is due to the lower energy required by the π-electrons to promote them to the excited state, since they are less tightly bound to the carbon nuclei. The degeneration of the molecular orbital of double bonds gives a HOMO band and a LUMO band, as an analogue to the valence band and the conduction band in inorganic semiconductors. The energy difference between these two bands is called the band gap.

Figure 2.12 shows the band structures of insulators, semiconductors and conductors.

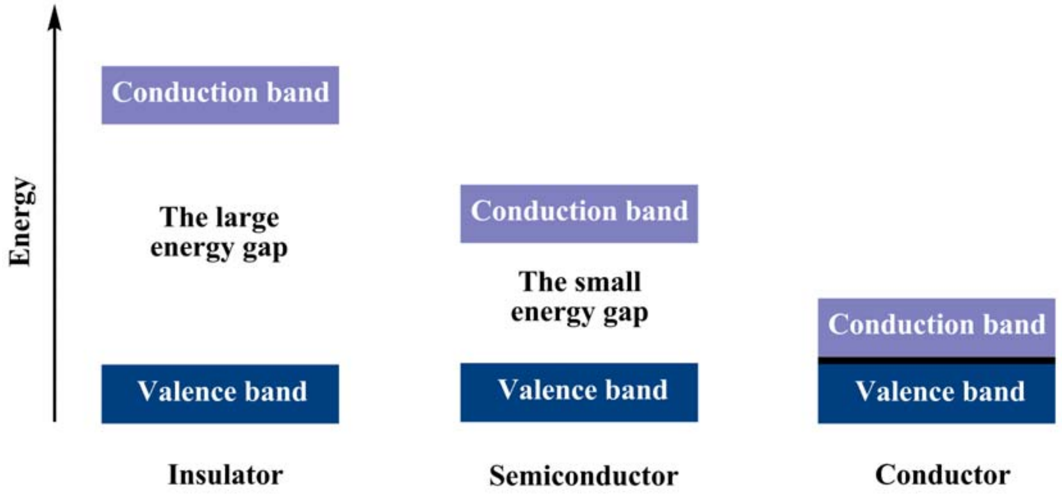


Figure 2.12 : Band structures of insulator, semiconductor and conductor.

Conductors (metals) are materials that possess partially filled bands, and this characteristic is the key factor leading to the conductive nature of this class of materials. Semiconductors, on the other hand, have filled (valence bands) and unfilled (conduction bands) bands that are separated by a range of forbidden energies (known as the 'band gap'). The conduction band can be populated, at the expense of the valance band, by exciting electrons (thermally and/or photochemically) across this band gap. Insulators possess a band structure similar to semiconductors except here the band gap is much larger and inaccessible under the environmental conditions employed.

Conjugated polymers are considered as insulators or sometimes as semiconductors in their neutral state. Charge injection (doping) into a conjugated polymeric system leads to wide varieties of semiconductors and conductors. Doping introduces charge carriers into the polymer, thus every repeating unit can essentially be an active redox site. Therefore, conjugated polymers can be doped with an oxidant (p-type) or with a reductant (n-type). In the oxidative doping two new states are produced within the energy gap between the valence and the conduction bands, and the presence of these bands gives rise to new low-energy transitions in the doped material. On the other hand, in the reductive doping electrons are injected into the conduction band and these electrons serve as the charge carriers. Upon doping the charge carriers are allowed to move along the shared intramolecular π bonds. The charge carrier delocalization along the polymer backbone increases the effective conjugation length of the polymer and extends into a three dimensional system through inter-chain charge transfer. After doping, the electrical conductivity through mobility of either holes or electrons increases dramatically and the doped conjugated polymers behave as conductors.

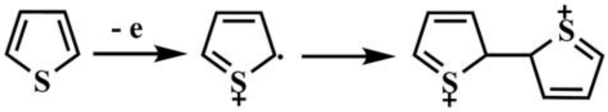
2.3.2 Synthesis of conjugated polymers

Various conjugated polymers are usually prepared by chemical or electrochemical processes [20, 183, 184], which provide films with different morphologies, and consequently slightly different physical and chemical properties.

The most common procedures used for the preparation of conjugated polymers are electrochemical polymerization, chemical oxidative coupling polymerization, organometallic coupling processes and photochemical polymerization.

2.3.2.1 Electrochemical polymerization

Electrochemical preparation of conjugated polymers was firstly described by Diaz in 1981 [185]. The polymerization proceeds via coupling of two radical cations, formed by oxidation of the monomer, to produce a dihydrodimer dication which leads to a dimer after loss of two protons and rearomatization (reactions 2.50-2.51) [178].



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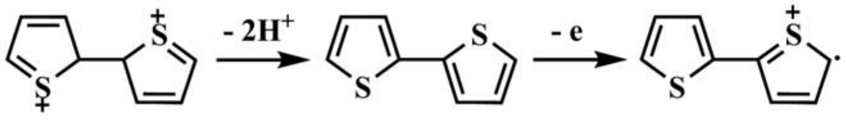


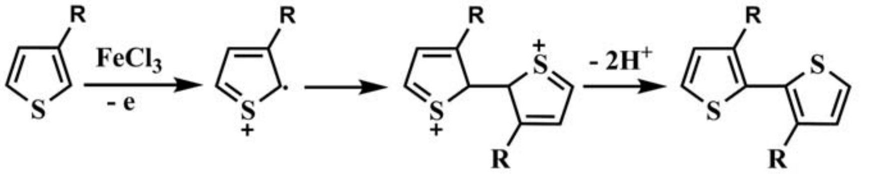
(2.51)

In this coupling process the formation of the dihydro dimer is the key driving force. The dimer has lower oxidation potential than the monomer and, consequently it is readily oxidized to lead to further couplings.

Electrochemical polymerization involves short reaction times, small amounts of monomers, and yields polymers in their oxidized state in the form of electrode supported, stable films, which possess favorable opto-electronic properties. However, the polymer obtained by electrochemical polymerization possesses a regioirregular structure [186-188]. This method is useful for the preparation of conducting polymer films for electronic devices such as electro-analytical sensors composed of a receptor for a particular compound anchored on a conducting polymer film. On the other hand, electropolymerization is not regarded as a method suitable for the large-scale production of conducting polymers [183].

2.3.2.2 Chemical oxidative coupling polymerization

The oxidative chemical polymerization can be carried out with different oxidizing agents. The most commonly used oxidants for the synthesis of conjugated polymers are Lewis acid catalysts such as $FeCl_3$, $MoCl_3$ and $RuCl_3$. This method was developed by Yoshino and co-workers to synthesize poly(9,9-dialkylfluorene)s (PAFs) and poly(3-alkylthiophene)s (PATs) [189, 190]. In this method the monomer is dissolved in chloroform or other appropriate solvents and oxidatively polymerized with $FeCl_3$. Ferric chloride oxidizes the 3-alkylthiophene monomer to produce radical cations in the 2 and 5- positions of the thiophene which then couple to form a polymer. The cycle of three consecutive steps (*e.g.*, loss of electron, coupling of radical cations, and deprotonation) is repeated to yield regiorandom-PATs with relatively high molecular weights and broad polydispersities. Polymers obtained by the oxidative polymerization exhibit a regiorandom structure (reactions 2.52-2.53).



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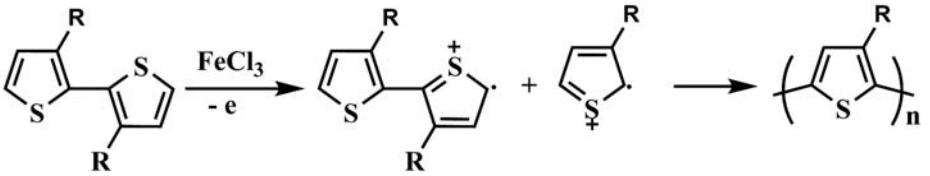


(2.53)

2.3.2.3 Organometallic coupling

Nickel, palladium, zinc, boron and tin-catalyzed cross-coupling of an organometallic compound with organohalides is a well known method. Suzuki, Yamamoto, Kumada and Heck coupling reactions are frequently used to prepare conjugated polymers.

Suzuki coupling

Suzuki coupling (Suzuki-Miyaura coupling), first published in 1979 by Suzuki, is an organic reaction of an aryl- or vinyl-boronic acid with an aryl- or vinyl-halide catalyzed by palladium(0) complex [191-194].

Recent catalyst and method developments have broadened the possible applications enormously, so that the scope of the reaction is not restricted to aryls, but also includes alkyls, alkenyls, and alkynyls. The reaction relies on a palladium catalyst such as tetrakis(triphenylphosphine)palladium(0) to effect part of the transformation. The palladium catalyst is 4-coordinate, and usually involves phosphine ligands. Potassium trifluoroborates and organoboranes or boronate esters may be used in place of boronic acids. Some pseudohalides such as triflates may also be used as coupling partners.

The mechanism of the Suzuki reaction viewed from the perspective of the palladium catalyst, is shown in Figure 2.13. The first step is the oxidative addition of palladium to the halide **(2)** to form the organo-palladium species **(3)**. Reaction with base gives intermediate **(4)**, which via transmetallation with the boronate complex **(6)** forms the organopalladium species **(8)**. Reductive elimination of the desired product **(9)** restores the original palladium catalyst **(1)**.

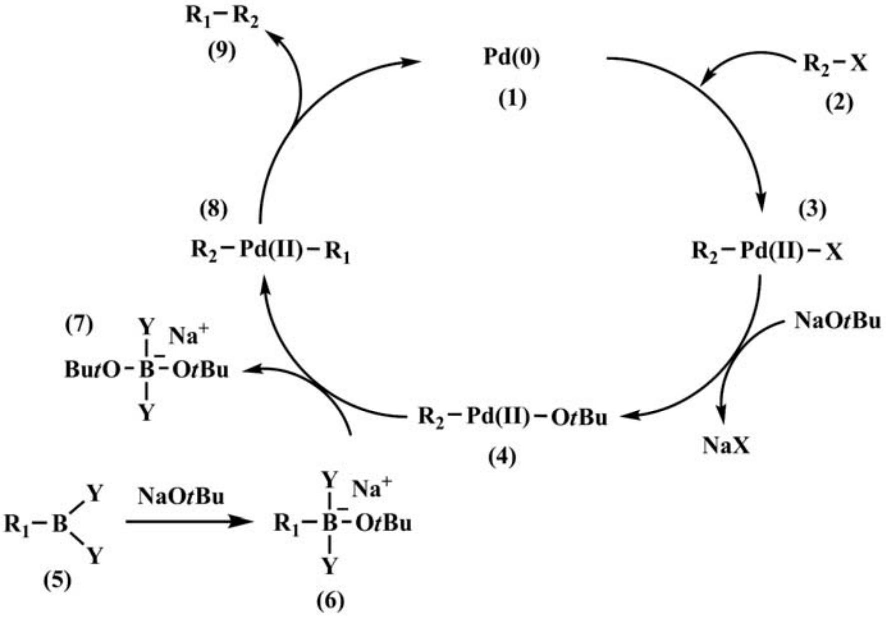


Figure 2.13 : The mechanism of Suzuki coupling reaction.

The versatility of the reaction originates from the mild reaction conditions and accessibility of the reagents. Moreover, it is not influenced by the presence of water, is highly tolerant to a wide variety of functional groups and proceeds region- and stereoselectivity. Non-toxicity and easy removal of the inorganic by-products makes the reaction attractive for laboratories and industrial applications [195].

The catalyst tetrakis(triphenylphosphine)palladium is the most common, but also otherhomogeneous catalysts as well as immobilized or heterogeneous palladiumcompounds have been used.

Yamamoto coupling

Yamamoto coupling, which was developed by using the polycondensation of dihaloaromatic compounds, is a convenient and efficient approach for the synthesis of conjugated polymers [196]. The polymerization is considered to proceed through oxidative addition, disproportionation and reductive elimination steps by using nickel(0) complexes (reactions) (Figure 2.14) [197].

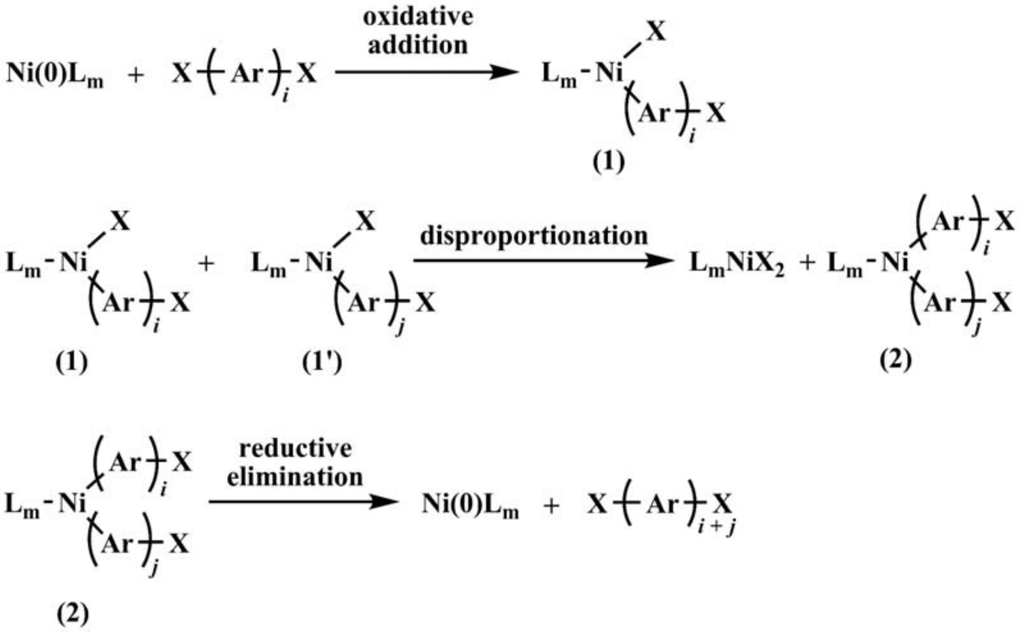


Figure 2.14 : The mechanism of Yamamoto coupling reaction.

The first step is oxidative addition of C-X to Ni(0)L_m. The second step is disproportionation. In the final step, diorganonickel (II) complexes NiR_2L_m undergo reductive coupling (or reductive elimination) reactions to give R-R. The coordination of molecules, such as aromatic compounds, leading to the backdonation from the central metal facilitates the reductive elimination of R-R. It is possible to isolate the complexes **(1)** and **(2)** as well as a complex of the type L_m(XNi-Ar-Ni(X)L_m when the Ni-C bond is highly stabilized [198].

A relatively large amount of Ni(0) complex (stoichiometric amount) is used in this reaction, since the Ni(0) complex works as a reagent instead of a catalyst. The Ni(0) complex reagent is oxidized and then reduced during the reaction, but does not return to the Ni(0) state, so it loses the reactivity after the reaction. In addition, the Ni(0) complex is extremely sensitive to ambient air and moisture, so the reaction has to be prepared under a strictly inert atmosphere.

The molecular weight of the conjugated polymers prepared by Yamamoto coupling seems to be dependant on the solubility and crystallinity of the polymers [198]. There is a trend that crystalline polymers have a lower molecular weight whereas less crystalline species (especially those with an alkyl chain) propagate to form a higher molecular weight polymer.

Kumada coupling

Kumada Coupling (Corriu-Kumada) coupling is the first Pd or Ni catalyzed cross coupling reaction between an alkyl or aryl Grignard reagent and an aryl or vinyl halocarbon [199]. The coupling of Grignard reagents with alkyl, vinyl or aryl halides under Ni-catalysis provides an economic transformation, but the reaction is limited to halide partners that do not react with organomagnesium compounds.

The main steps in the mechanism for Ni(0) or Pd(0) catalysts are oxidative addition of the organohalide, transmetallation of the Grignard, and reductive elimination, as illustrated in Figure 2.15. The advantage of this reaction is the direct coupling of Grignard reagents, which avoids additional reaction steps such as the conversion of Grignard reagents to zinc compounds for the starting materials in the Negishi Coupling.

Heck coupling

Heck coupling is an efficient approach used for coupling of aryl or alkenyl halides with an alkene or terminal alkyne [200]. Reaction steps involve oxidative addition, insertion and β-hydride elimination (reactions 2.54-2.56). The product is an alkene.

As the by-product a stong acid is liberated, a base must be present in the reaction mixture for scavenging. The success of the reaction is dependent on each step involved. Electron withdrawing groups attached to halides increase the rate of oxidative addition. With Pd(II) salts, it is believed that they are transformed to Pd(0) by redox processes. The insertion is stereospecific and syn.

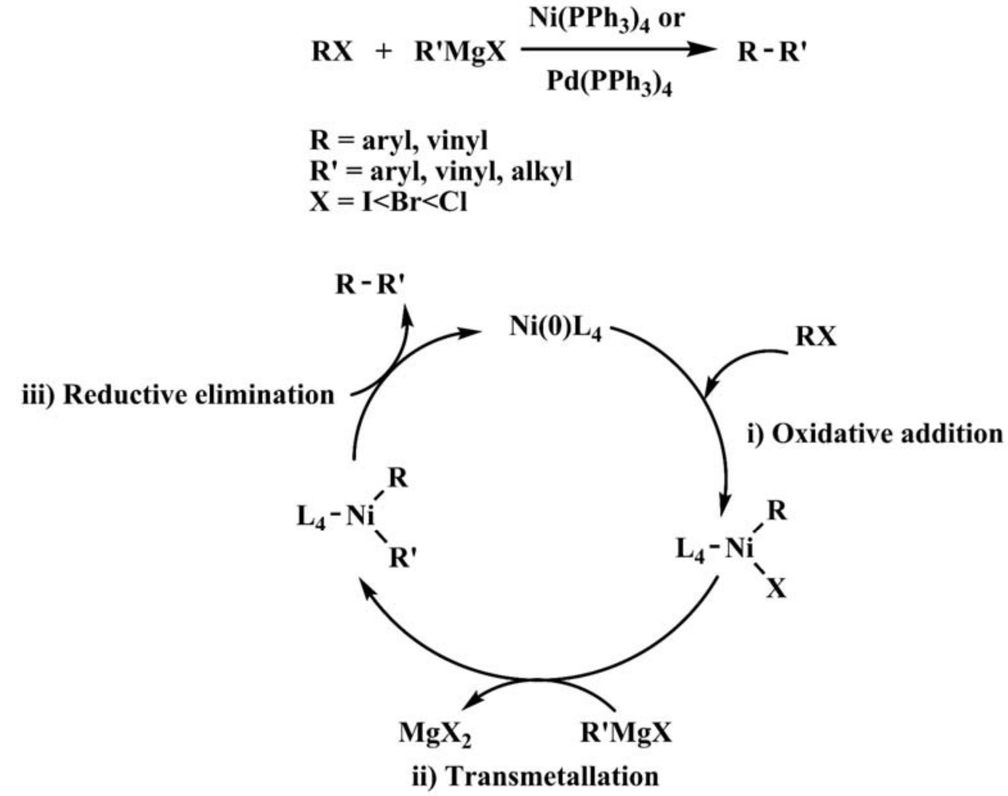
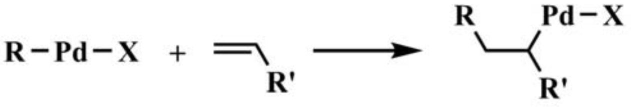
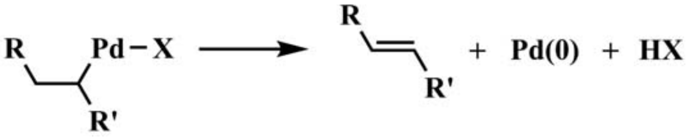


Figure 2.15 : The mechanism of Kumada coupling reaction.

$$R-X \;+\; Pd(0) \longrightarrow R-Pd-X$$ **oxidative addition** **(2.54)**



insertion **(2.55)**

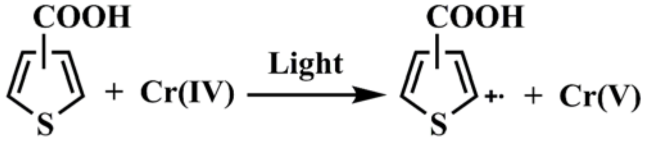


β-hydride elimination **(2.56)**

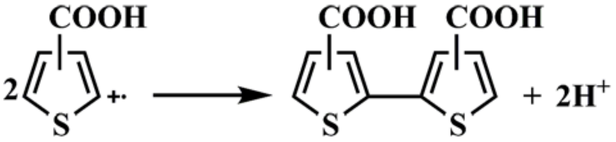
With alkenes bearing electron withdrawing groups, the rate of insertion increases. Sterical hindrance of alkene is also important at insertion step. β-hydride elimination is also syn, but in the case of acyclic alkenes, due to the free rotation, a stable trans alkene is obtained. Generally, polar solvents are used for the reaction. By intramolecular Heck reactions, ring systems are obtained with good efficiencies and free of limitations such as sterical hindrances, and also syn stereochemistry of both insertion and elimination steps are kept.

2.3.2.4 Photochemical polymerization

Photopolymerization is considered to be useful candidate for the production of these materials in thin film forms. Various strategies have been employed to polymerize thiophene and derivatives photochemically [21-25, 201]. For example, Davis and co-workers [21] photopolymerized acetic acid derivative of thiophene in aqueous solution catalyzed by potassium dichromate. It was suggested that the polymerization proceeds via charge transfer reaction of complex between thiophene derivative and Cr(V) in the excited state (2.57-2.58).



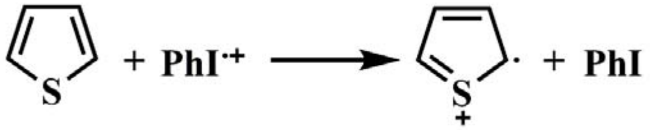
(2.57)



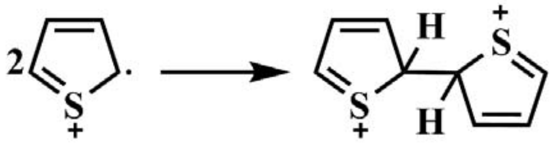
(2.58)

Another successful approach that has been employed is the photolysis of dithienothiophene derivatives and oligothiophenes in the presence of electron acceptors such as dinitrobenzene and carbon tetrachloride [22-24]. In this case, the polymerization intermediate radical cation of the monomer was efficiently generated by the photoinduced electron transfer from the excited thiophene derivative to the electron acceptor. Recently, thiophene eas polymerized photochemically by using onium salts such as diaryliodonium and triarylsulfonium salts [25, 201]. Although these salts are known to be photoinitiators for UV induced cationic polymerizations [168], they were also found to be effective in facilitating the polymerization of thiophene. Detailed investigations involving laser flash photolysis and EPR studies revealed that the polymerization mechanism involves electron transfer from photochemically generated phenyliodinium radical cations to thiophene (2.59-2.62).

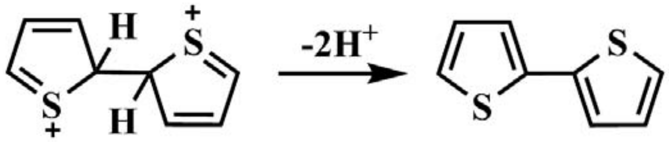
$$Ph_2I^+PF_6^- \xrightarrow{h\nu} PhI^{\cdot+}PF_6^- + Ph^{\cdot} \qquad (2.59)$$



(2.60)



(2.61)



(2.62)

2.3.3 Polythiophenes

Polythiophenes are of great interest due to their relatively small band gaps, environmental stability, and good processibility [178]. One major disadvantage of these compounds is their low solubility in most organic solvents, which may be attributed to strong intermolecular π-π interactions. Moreover, there are also some other special features such as fast nonlinear optical (NLO) response, excellent crystallinity, and better mechanical properties, which polythiophenes usually does not afford. These features could be achieved by structural modification approaches such as attachment of pendant side chains to polythiophene backbone, annulations of thiophene ring, introduction of conjugated spacers, synthesis of regioregular polythiophene derivatives, synthesis of thiophene based copolymers and thiophene based metallopolymers [178].

Structural modification of polythiophenes has a great importance, since they possess so many unique properties for possible wide range of applications. There are two important reasons for functionalization of polythiophenes: i) improving electrical properties in order to obtain low band gap polythiophene derivatives with good conductivity and ii) improving physical properties in order to obtain processable polythiophene derivatives with long term stability [202].

During the past two decades, tremendous efforts were put into searching for low band gap polythiophene derivatives due to their practical advantages over other higher band gap materials. Easy doping with possible intrinsic metallic conductivity, improved photoconductivities for solar cell application, large nonlinear optical coefficients, and possible transparent materials in doped states are the reasons for the significance of low band-gap conducting polymers [202].

Polymers based on dithienothiophenes have lower band gaps compared to polythiophene analogues, due to their additional fused ring. These polymers were first synthesized electrochemically [203, 204], and later it was found that they are very attractive polymers with high doping levels, high columbic efficiencies and excellent cycling abilities for battery applications [205]. Various photochemical strategies have also been employed to synthesize polydithienothiophenes [21-24].

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Styrene (St, 99%, Aldrich):

It was passed through a basic alumina column to remove the inhibitor before use.

Cyclohexene oxide (CHO, 98%, Aldrich):

It was distilled over CaH_2 under reduced pressure before use.

n-Butyl vinyl ether (BVE, >97%, Fluka):

It was distilled over CaH_2 under reduced pressure before use.

N-Vinylcarbazole (NVC, 98%, Aldrich):

It was crystallized from ethanol before use.

Methyl methacrylate (MMA, 99%, Aldrich):

It was passed through a basic alumina column to remove the inhibitor before use.

Butyl acrylate (BA, ≥99%, Aldrich):

It was passed through a basic alumina column to remove the inhibitor before use.

3,4-Epoxycyclohexyl-3',4'-epoxycyclohexene carboxylate (EEC, Ciba Specialty Chemicals, CY-179):

It was used as received.

1,3-Bis(3,4-epoxycyclohexylethyl)tetramethyl disiloxane (EPOX, Ivoclar):

It was used as received.

3.1.2 Solvents

Dichloromethane (J.T. Baker):

It was dried with calcium chloride and distilled over P_2O_5. It was stored over molecular sieves for use as a solvent in the photopolymerization experiments.

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.

Toluene (99.9%, Sigma-Aldrich):

It was dried with calcium chloride and distilled over sodium wire.

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.

n-Hexane (95%, Aldrich):

It was used without further purification.

Diethyl ether (J.T. Baker):

It was dried with calcium chloride and distilled over sodium wire.

Acetonitrile (98%, Aldrich):

It was used without further purification.

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 without further purification.

Anthracene (99%, Acros):

It was used without further purification.

Sodium hydroxide (NaOH, Riedel-de Haën):

It was used as received.

Calcium chloride ($CaCl_2$*, J. T. Baker):*

It was used as received.

Calcium hydride (CaH_2*, Acros):*

It was used as received.

Thiophene (Aldrich):

It was distilled under reduced presure before use.

n-Butyl lithium (nBuLi, Acros):

It was used as received.

Bromine (Br_2*, Acros):*

It was used as received.

2-Bromo-1-phenylethanone (Aldrich):

It was used without further purification.

Phosphorus pentasulfide (P_4S_{10}*, Aldrich):*

It was used without further purification.

3,4-(Ethylenedioxy)thiophene (Bayer):

It was used without further purification.

Tributylstannyl chloride (Aldrich):

It was used as received.

o-Phenylenediamine (Acros):

It was used without further purification.

Triethylamine (Acros):

It was used as received.

Thionyl chloride ($\geq$ 99 %, Aldrich):

It was used as received.

Magnesium sulfate ($MgSO_4$, 97 %, Acros):

It was used as received.

Hydrogen bromide (HBr, $\geq$ 99 %, Aldrich):

It was used as received.

Sodium bisulfite ($NaHSO_3$, Acros):

It was used as received.

Sodium borohydride ($NaBH_4$, Aldrich):

It was used as received.

Bis(triphenylphosphine)palladium(II) dichloride ($PdCl_2(PPh_3)_2$, Aldrich):

It was used as received.

2,2′-thenil (Aldrich, 98%):

It was used without further purification.

2,6-Di-tert-butyl-4-methylpyridine (DBMP, 98%, Aldrich):

It was used as received.

Sodium hexafluoroantimonate ($NaSbF_6$, 98%, Acros):

It was used as received.

2-Bromoacetophenone (98%, Acros):

It was used as received.

Pyridine (99.5%, Acros):

It was used as received.

Magensium (99.9+%, turnings, Acros):

It was used as received.

Chlorotrimethylsilane (98%, Acros):

It was used as received.

3.2 Equipment

3.2.1 Photoreactor

A Rayonet type photoreactor equipped with 16 Philips 8W / O6 lamps emitting light nominally at 350 nm was used.

3.2.2 Light sources

(a) AMCO monochromatic light source

An AMCO monochromatic light source equipped with an Osram XBO 75 W xenon lamp was used.

(b) Bluephase light source

A Bluephase light source emmiting light at 430-490 nm was used.

(c) Polilight PL400 Forensic Plus

A Polilight light source emmitting light at 350, 415, 430, 450, LP530, 490, 505, 515, 530, 550, 560, LP560, 570, 590, 620, 650, white, half white and bank was used.

3.2.3 Nuclear magnetic resonance spectroscopy (NMR)

(a) ^1H NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument.

(b) ^{1}H NMR and ^{13}C NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using Bruker Spectrospin Avance DPX-400 (400 MHz) spectrometer.

3.2.4 Infrared spectrophotometer (FT-IR)

FT-IR spectra were recorded on a Perkin Elmer FTIR Spectrum One B spectrometer.

3.2.5 UV-Visible spectrophotometer

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

3.2.6 Gel permeation chromatography (GPC)

(a) Gel permeation chromatography (GPC) analyses were performed with a set up consisting of a Waters 410 Differential Refractometer, a Waters 515 HPLC Pump and an apparatus equipped with three Waters ultrastyragel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate 0.3 mL/min. Molecular weights were calculated on the basis of a calibration curve recorded with mono disperse polystyrene standards.

(b) 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 456–42800, 1050–107000, and 10200–2890000, 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.

(c) The GPC set-up (TD-GPC) with an Agilent 1200 model isocratic pump, four Waters Styragel columns (guard, HR 5E, HR 4, HR 3, and HR 2), and a Viscotek TDA 302 triple detector (RI, dual laser light scattering (LS) ($\lambda = 670$ nm, 90° and 7°) and a differential pressure viscometer was conducted to measure the absolute molecular weights in THF with a flow rate of 0.5 mL/min at 35 °C. All three detectors were calibrated with a PS standard having narrow molecular weight distribution (M_n = 115,000 g/mol, M_w/M_n = 1.02, [η] = 0.519 dL/g at 35 °C in THF, dn/dc = 0.185 mL/g) provided by Viscotek company. Data were collected by using Omni-Sec version 4.5 software from Viscotek Company.

3.2.7 Thermal gravimetric analyzer (TGA)

Thermal gravimetric analysis were performed on Perkin–Elmer Diamond TA/TGA with a heating rate of 10 ºC min under nitrogen flow.

3.2.8 Fluorescence spectrophotometer

Fluorescence and phosphorescence measurements were performed on a Jobin Yvon-Horiba Fluoromax-P spectrophotometer.

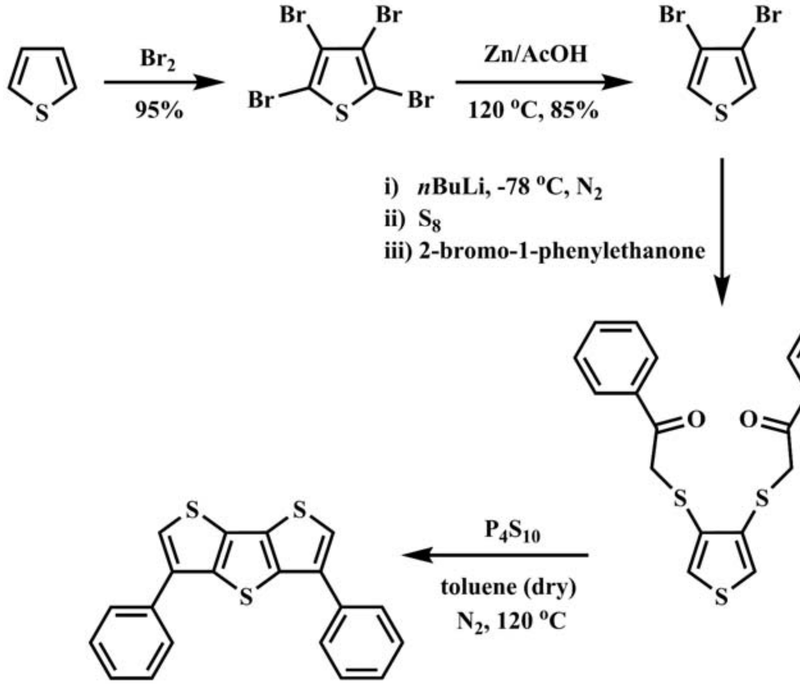
3.3 Preparation Methods

3,5-Diphenyldithieno[3,2-b:2′,3′-d]thiophene (DDT) was kindly synthesized by Ali S. Gundogan 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 Br_2, 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 P_4S_{10} in boiling anhydrous toluene, which took nearly 3 h to complete. Yield of 43% was obtained for the final compound (Scheme 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, $CDCl_3$) δ 135.9, 134.5, 131.3, 129.0, 128.4, 127.5, 126.6, 121.3.



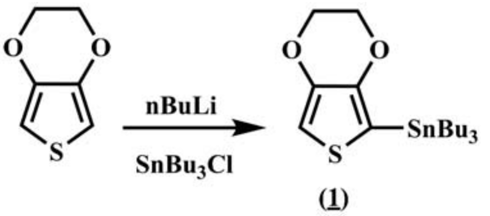
(3.1)

5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DTDQ) and 4,7-di(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-benzo[1,2,5]thiadiazole (DTDT) were kindly synthesized by Asuman Durmus and Gorkem E. Gunbas from Toppare group. Their synthesis procedures are given below.

3.3.2 Synthesis of tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (1)

A 2.0 g (14 mmol) sample of 3,4-(ethylenedioxy)thiophene in 150 mL of dry THF was treated dropwise with 10 mL (16.2 mmol) of 1.6 M *n*-butyl lithium at −78 °C under argon. After the solution was stirred for 0.5 h and warmed to −40 °C, 5.95 g (18.8 mmol) of tributylstannyl chloride was added to the solution, and the new solution was warmed to room temperature. The solvent was removed by rotary evaporation after the solution was stirred for 8 h. The residue was dissolved in hexanes and filtered. The filtrate was dried in vacuum to afford 6.0 g of (**1**) as a yellow liquid. The compound was used for the next reaction as obtained, with no further purifications. ^{1}H NMR (250 MHz, $CDCl_3$): δ ppm 6.56 (s, 1H); 4.16 (s, 4H); 1.61-1.49 (m, 6H); 1.39-1.22 (m, 6H); 1.09 (t, 9H); 0.90 (q, 6H). ^{13}C NMR (125

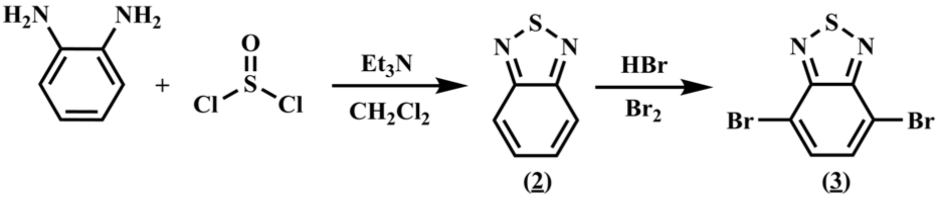
MHz, $CDCl_3$)): δ ppm 147.88, 142.65, 109.08, 105.99, 64.86, 64.80, 29.08, 27.40, 13.79, 10.71. MS: $(M + H)^+$ found 431, calcd for $C_{18}H_{32}O_2SSn$ 430.11.



(3.2)

3.3.3 Synthesis of 4,7-dibromobenzo[1,2,5]thiadiazole (3)

4,7-Dibromobenzo[1,2,5]thiadiazole (**3**) was synthesized as described previously [29]. It was synthesized by a two-step procedure. First, benzothiadiazole (**2**) was synthesized and in the second step, it was converted to 4,7-dibromobenzo[1,2,5]thiadiazole (**3**) according to the procedures given below:



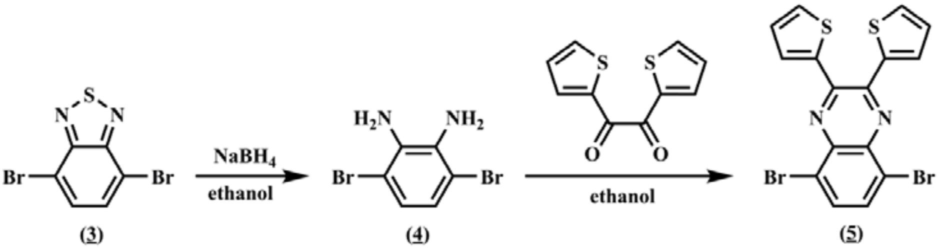
(3.3)

To a 1000 mL flask were added commercial *o*-phenylenediamine (10.00 g, 92.47 mmol), 300 mL of CH_2Cl_2 and triethylamine (37.44 g, 369.98 mmol). The solution was stirred until total dissolution of the diamine. Thionyl chloride was added dropwise very slowly and the mixture refluxed for 4 h. The solvent was removed in a rotatory evaporator and 700 mL of water added. Concentrated HCl was added to a final pH of 2. The desired compound was purified by direct steam distillation following addition of water to the mixture. The steam distilled mixture was extracted three times with 200 mL of CH_2Cl_2, dried over $MgSO_4$ and filtered. The solvent was removed, affording pure compound (**2**) in 93% yield (11.71 g, 85.99 mmol). (mp 43.6–44.4 °C). ^1H NMR ($CDCl_3$): δ ppm 7.99 (dd, 2H, *J*= 3.3, 4.6 Hz); 7.57 (dd, 2H, *J*= 3.1, 6.8 Hz). ^{13}C NMR ($CDCl_3$): δ ppm 154.6; 129.1; 122.4. FT-IR (KBr, cm^{-1}): 1659, 1433, 1264, 1104, 747.

To a 500 mL two-necked round bottom flask were added benzothiadiazole (**2**) (10.00 g, 73.44 mmol) and 150 mL of HBr (47%). A solution containing Br_2 (35.21 g, 220.32 mmol) in 100 mL of HBr was added dropwise very slowly (slow addition is essential!). If necessary, an additional 100 mL of HBr can be added to the solution. After total addition of the Br_2, the solution was refluxed for 6 h. Precipitation of an orange solid was noted. The mixture was allowed to cool to room temperature and sufficient saturated solution of $NaHSO_3$ added to consume completely any excess Br_2. The mixture was filtered under vacuum and washed exhaustively with water. The solid was then washed once with cold Et_2O and dried under vacuum for ca. 20 h, affording the desired dibrominated product **(3)** in 95% yield (20.51 g, 69.77 mmol). (mp 187–188 °C). ^1H NMR ($CDCl_3$/DMSO-*d*$_6$—two drops): δ ppm 7.73 (s, 2H). ^{13}C NMR ($CDCl_3$/DMSO- *d*$_6$—two drops): δ ppm 152.6; 132.1; 113.6.

3.3.4 Synthesis of 5,8-dibromo-2,3-di(thiophen-2-yl)quinoxaline (5)

5,8-Dibromo-2,3-di(thiophen-2-yl)quinoxaline was synthesized as described previously [29]. It was synthesized by a two-step procedure. First, 3,6-dibromo-1,2-phenylenediamine **(4)** was synthesized. In the second step, it was converted to 5,8-dibromo-2,3-di(thiophen-2-yl)quinoxaline **(5)** by the condensation reaction of **(4)** and 2,2′-thenil according to the procedure given below:



(3.4)

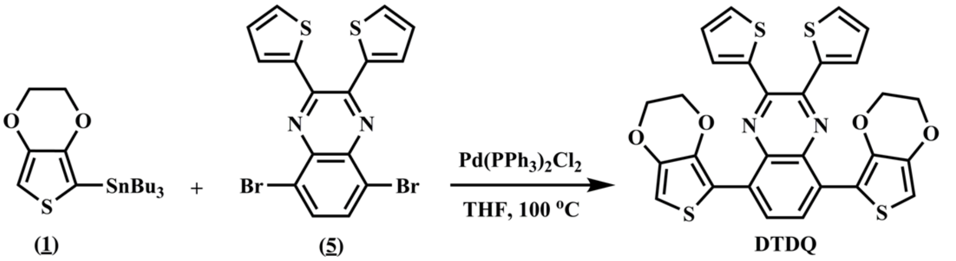
To a suspension of **(3)** (5.0 g, 17 mmol) in ethanol (170 ml), $NaBH_4$ (11.4 g, 300 mmol) was added portionwise at 0 °C, and the mixture was stirred for 20 h at r.t. After evaporation in vacuo, H_2O (100 ml) was added, and the mixture was extracted with Et_2O. The organic phase was washed with saturated aqueous NaCl solution and dried (Na_2SO_4). Evaporation in vacuo gave **(4)** (3.9 g, 87%). White solid. (mp 94–95 °C). ^1H NMR (400 MHz, $CDCl_3$): δ ppm 3.91 (s, 4 H), 6.81 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 151.4, 131.1, 117.6.

A solution of **(4)** (1.0 g, 3.8 mmol) and 2,2′-thenil (0.84 g, 3.8 mmol) in ethanol (40 ml) was heated to reflux for 1 h, then cooled to 0 °C. The formed precipitate was isolated by filtration and washed with ethanol to afford **(5)** (1.16 g, 70%). White solid. (mp 221–222 °C). ^1H NMR (400 MHz, $CDCl_3$): δ ppm 7.01 (t, 2H), 7.41 (d, 2

H), 7.49 (d, 2 H), 7.76 (s, 2 H). ^{13}C NMR (100 MHz, CDCl3): δ ppm 127.81, 131.56, 132.86, 132.98, 134.73, 136.79, 141.67 and 145.83.

3.3.5 Synthesis of 5,8-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DTDQ)

5,8-Dibromo-2,3-di(thiophen-2-yl)quinoxaline (**5**) (200 mg, 0.440 mmol) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (948 mg, 2.2 mmol) were dissolved in dry tetrahydrofuran (THF, 80 mL), the solution was purged with argon for 30 min, and $PdCl_2(PPh_3)_2$ (60 mg, 0.85 mmol) was added at room temperature under argon atmosphere. The mixture was stirred at 100 °C under argon atmosphere for 15 h, cooled, and concentrated on the rotary evaporator. The residue was subjected to column chromatography (CH_2Cl_2/Hexane: 3/1) to afford an orange solid (148 mg, yield 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (m, 4 H), 4.28 (m, 4H), 6.5 (s, 2 H), 6.95 (t, J = 3.97 Hz 2 H), 7.40 (d, J = 3.57 Hz, 2 H) 7.44 (d, J = 4.8, 2 H), 8.46 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.35, 63.94, 102.05, 112.04, 126.34, 127.34, 127.48, 128.21, 128.80, 135.56, 139.27, 140.38, 140.68, 142.89. MS: *m*/*e* 574 (M+).

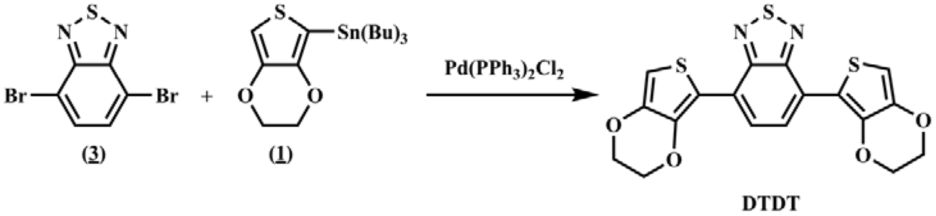


(3.5)

3.3.6 Synthesis of 4,7-di(2,3-dihydro-thieno[3,4-b][1,4]dioxin-5-yl)-benzo[1,2,5]thiadiazole (DTDT)

4,7-dibromobenzo[1,2,5]thiadiazole (**3**) (382 mg, 1.3 mmol) and tributyl-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (**1**) (4192.5 mg, 9.75 mmol) were dissolved in dry THF (100 ml), the solution was purged with argon for 15 min. and $PdCl_2(PPh_3)_2$ (178 mg, 0.254 mmol) was added at room temperature under argon atmosphere. The mixture was stirred at 100 °C under argon atmosphere for 15 hours, cooled, and concentrated on the rotary evaporator. The residue was washed consequently with brine, water, and hexanes and subjected to column chromatography (CH_2Cl_2/Hexane: 3/1) to afford dark red solid (59% yield). (m.p. >

260 ◦C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.19-4.49 (m, 8H, *ethylene*); 6.56 (s, 2H, *EDOT*), 8.39 (s, 2H, *H6*); ^{13}C APT NMR (400 MHz, CDCl$_3$): 64.35, 64.99, 101.95, 113.69, 123.65, 126.61, 140.24, 140.63, 152.32. EI/MS (70 eV): m/z 416 (100) [M$^+$], 332 (21), 319 (55). HRMS (ESI) Calculated for $C_{28}H_{13}N_2O_4S_3$ (M+H$^+$): *m/z* 417.004. Found: *m/z* 417.0032.



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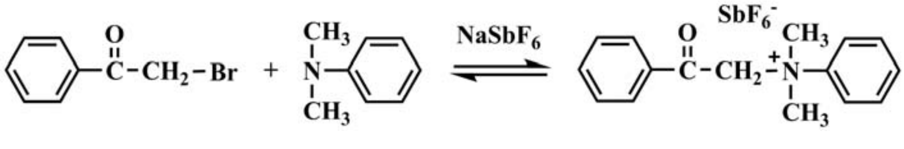
3.3.7 Synthesis of *N*-phenacyl-*N,N*-dimethylanilinium hexafluoroantimonate (PDA$^+$SbF$_6^-$)

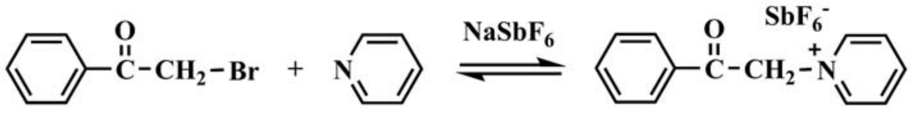
Into a 100 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 1.5 g (7.54 × 10^{-3} mol) 2-bromoacetophenone, 0.914 g (7.54 × 10^{-3} mol) *N,N*-dimethylaniline, 1.951 g (7.54 × 10^{-3} mol) NaSbF$_6$ and 50 mL of acetone. The reaction mixture was brought to reflux and held at this temperature for 15 min. The dark pink solution was filtered to remove NaBr, which was formed during the reaction. Then the solvent was removed on a rotary evaporator, leaving *N*-phenacyl-*N,N*-dimethylanilinium hexafluoroantimonate (PDA$^+$SbF$_6^-$) as a tan solid. The product was recrystallized twice from ethanol solution. The salt was washed with water and dried at vacuum, mp. 122°C, yield 50%. ^{1}H NMR (250 MHz, DMSO): δ 8-7.5 (m, 10H), 6.10 (s, 2H), 3.75 (s, 6H). UV: λ_{max} = 255 nm, ε_{255} = 21615 mol^{-1}·cm^{-1}.



(3.7)

3.3.8 Synthesis of *N*-phenacylpyridinium hexafluoroantimonate (PPy$^+$SbF$_6^-$)

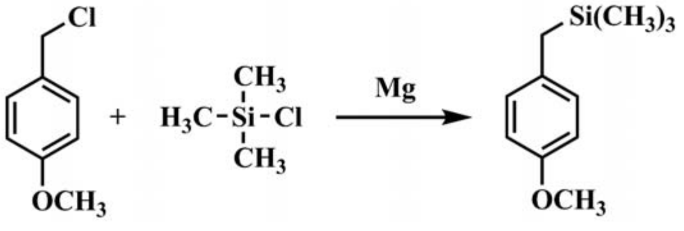
Into a 50 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser were placed 0.5 g (2.5 × 10^{-3} mol) 2-bromoacetophenone, 0.2 mL (2.5 × 10^{-3} mol) pyridine and 25 mL of acetonitrile. The reaction mixture was stirred and held at room temperature for 5 h. White solid particles were obtained at the end. Then, acetonitrile was evaporated and the residue was dissolved in water. The aqueous solution was washed with petroleum ether. Finally, 0.65 g (2.5×10^{-3} mol) $NaSbF_6$ was added to aqueous part in one portion. White precipitates were obtained and dried at vacuum, mp. 195°C, yield 45%. ^1H NMR (250 MHz, CD_3CN): δ 9.2-7.6 (m, 10H, C_6H_5), 6.46 (s, 2H, N^+-CH_2). UV: λ_{max} = 248, 438 nm, ε_{248} = 12680, ε_{248} = 7263 $mol^{-1} \cdot cm^{-1}$.



(3.8)

3.3.9 Synthesis of (4-methoxybenzyl)trimethylsilane (MBTMS)

Into a flame-dried 250 mL three-neck, round bottom flask equipped with a magnetic stirrer, a reflux condenser, N_2 inlet and 50 mL addition funnel were placed 1.94 g (8×10^{-2} mol) dry magnesium turnings, 60 mL dry tetrahydrofuran (THF) and 10.12 mL (8×10^{-2} mol) chlorotrimethylsilane. 4-Methoxybenzyl chloride (10 mL, 7.4×10^{-2} mol) in dry THF (40 mL) was added slowly, at a rate to maintain gentle reflux. After addition was complete, the mixture was heated under reflux for 2 h, cooled, and poured into 100 mL of cold water. Pentane (90 mL) was added, and pentane layer was washed three times with cold water (50 mL) and once with saturated NaCl solution (50 mL). The resulting solution was dried with $MgSO_4$ and then rotary evaporated to yield the crude product, bp. 73-78°C, yield 85%. ^1H NMR (250 MHz, $CDCl_3$): δ 7.0-6.7 (m, 4H), 3.78 (s, 3H), 2.0 (s, 2H), 0.0 (s, 9H).



(3.9)

3.3.10 General procedure for photosensitized cationic polymerization

Monomer either in bulk form or in solution with dichloromethane (CH_2Cl_2), photosensitizer (DDT, DTDT, DTDQ or), and co-initiator ($Ph_2I^+PF_6^-$) were put into a Pyrex tube, degassed with nitrogen, and irradiated at room temperature in a photoreactor (Rayonet) equipped with 16 lamps and emitting light nominally at 350 nm. A cupric sulfate aqueous solution was used as the photofilter in order to avoid the absorption of onium salt. At the end of irradiation, the content of the tube was dissolved in CH_2Cl_2 followed by precipitation in 10-fold excess methanol. Finally, the solid polymer was collected by filtration and dried overnight at reduced pressure. Conversions were determined gravimetrically.

3.3.11 General procedure for photoinitiated free radical polymerization by combination of cleavage and electron tarnsfer reactions

Monomer in solution with acetonitrile (CH_3CN), phenacyl salt ($PDA^+SbF_6^-$ or $PPy^+SbF_6^-$) and (4-methoxybenzyl)trimethylsilane (MBTMS) were put into a pyrex tube, degassed with nitrogen, and irradiated at room temperature in a photoreactor (Rayonet) equipped with 16 lamps and emitting light at $\lambda > 300$ nm. At the end of irradiation, the content of the tube was precipitated in 10-fold excess methanol. Finally, the solid polymer was collected by filtration and dried overnight at reduced pressure. Conversions were determined gravimetrically.

3.3.12 Fluorescence quenching studies

The fluorescence quenching studies were performed with solutions containing a constant concentration of DDT, DTDT or DTDQ (1×10^{-5} mol·L^{-1}) and varying amounts of $Ph_2^+PF_6^-$. 2-Methyltetrahydrofuran was used as solvent. The variation of the fluorescence emission intensity was investigated by the increasing concentration of $Ph_2^+PF_6^-$.

3.3.13 Photopolymerization of DDT

Photopolymerization was carried out under nitrogen atmosphere. Prior to irradiation, the appropriate solution of dithienothiophene (0.040 g, 1.15×10^{-4} mol) containing predetermined amounts of onium salt (0.098 g, 2.30×10^{-4} mol) and dichloromethane as the solvent (5 mL) were placed in a pyrex tube and irradiated in a Rayonet merry-go-round type photoreactor equipped with 16 lamps emitting light nominally at $\lambda = 350$ nm and a cooling system. At the end of irradiation, the dark solution was poured into methanol. The precipitate was isolated by filtration and dried for 24 hours in vacuum oven at 25°C ($M_{n,GPC} = 1147$, $M_w/M_n = 1.76$).

4. RESULTS AND DISCUSSION

The main objective of this thesis is to describe the use of electron transfer reactions in photoinitiated polymerization systems. The first strategy followed throughout the thesis was electron transfer photosensitization by using highly conjugated thiophene derivatives. Afterwards this strategy was extended to the synthesis of conjugated thiophene polymers. In the final strategy, a novel free radical photoinitiating system by combination of cleavage and electron transfer reactions was suggested.

4.1 Electron Transfer Sensitization by Using Highly Conjugated Thiophene Derivatives for Onium Salt Photoinitiated Cationic Polymerization

The long wavelength initiating systems for cationic polymerization received drastically increased attention in the past several years. The existing strategies are based on the activation of the most prominent cationic photoinitiators, namely onium salts, by light sensitive additives, which do not directly initiate the polymerization. Electron transfer photosensitization by using electron-rich polynuclear aromatic compounds such as anthracene, perylene, pyrene and phenothiazine appears to be an alternative efficient pathway to shift the absorption sensitivity to longer wavelengths. As it will be shown below, highly conjugated thiophene derivatives in conjunction with iodonium salt can also be used as new and efficient visible light cationic photoinitor systems.

4.1.1 Electron transfer photosensitization using 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT)

As it is shown in Figure 4.1, 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) possesses three fused thiophene rings, the orientations of which vary depending on the location of the sulphur atom of the peripheral thiophene. As DDT is rich in sulfur, with three S atoms, it is an electron rich compound, which makes it a good electron donor.

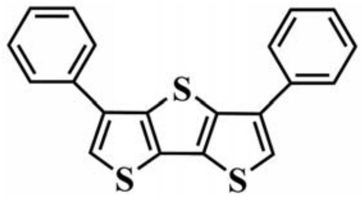


Figure 4.1 : Structure of 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT).

In the ground state, DDT strongly absorbs light between 350 and 450 nm where onium salts are transparent (Figure 4.2). Moreover, it has the advantage of being highly soluble in various monomers and solvents.

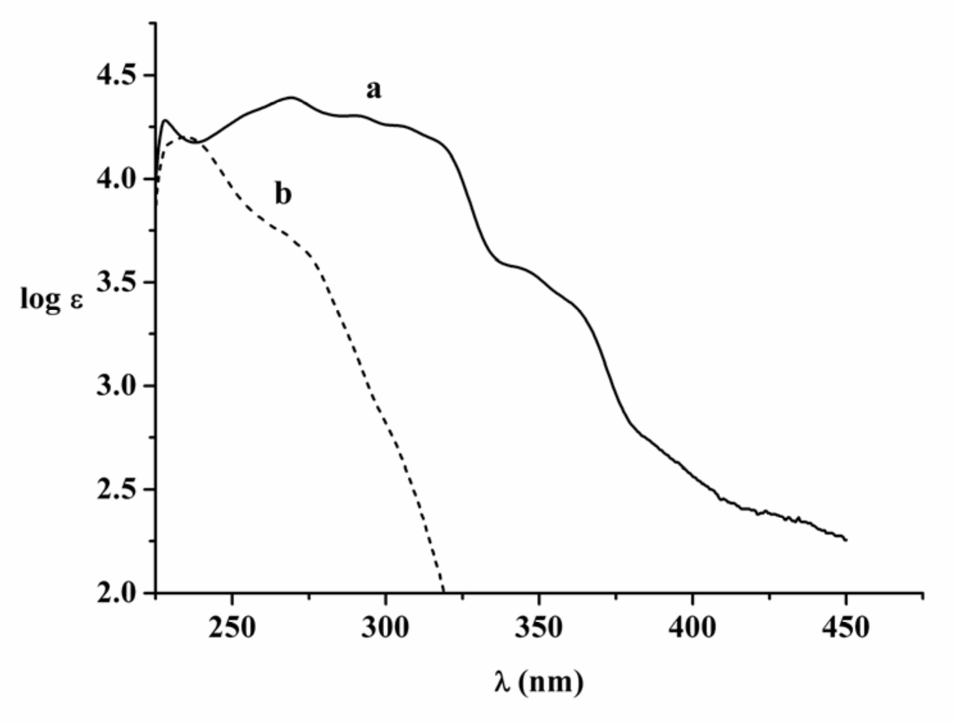


Figure 4.2 : Optical absorption spectra of DDT (a) and $Ph_2I^+PF_6^-$ (b) in CH_2Cl_2.

For the potential use of DDT as a photosensitizer, the excited state emission characteristics were investigated by means of fluorescence and phosphorescence spectroscopic measurements. Figure 4.3 depicts the normalized fluorescence excitation and emission spectra of DDT in CH_2Cl_2 at room temperature. It is clear that a nearly mirror-image like relation exists between absorption and emission of dithienothiophene compound.

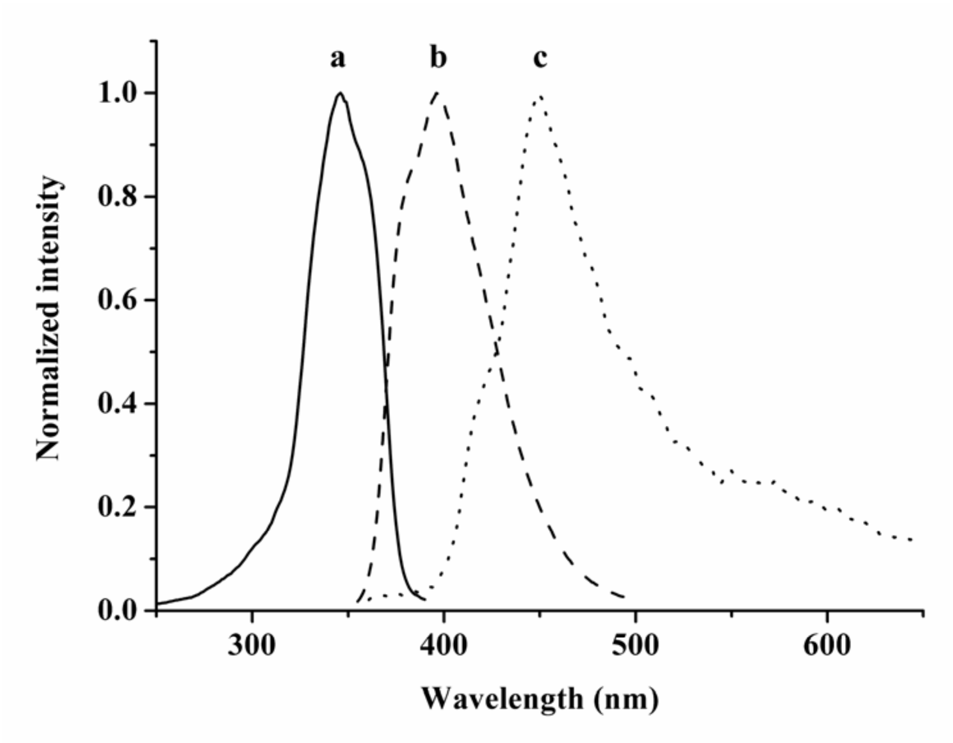


Figure 4.3 : Normalized excitation (a) and emission (b) fluorescence spectra of DDT in CH_2Cl_2 at room temperature and emission phosphorescence spectra (c) at 77 K.

It was found that in the presence of diphenyl iodonium salt, the fluorescence of DDT is markedly quenched. In Figure 4.4, a typical Stern-Volmer plot is shown for the fluorescence quenching of DDT as a function of the concentration of the diphenyliodonium salt. The linear correlation shown in the plot is strong confirming evidence for the reaction of excited state of DDT with the iodonium salt.

The polymerization of cyclohexene oxide (CHO), *n*-butyl vinyl ether (BVE), styrene (S) and *N*-vinyl carbazole (NVC) were examined. Typical results are presented in Table 4.1. As can be seen, all monomers were readily polymerized upon irradiation at room temperature at $\lambda > 350$ nm either in bulk or CH_2Cl_2 solutions with DDT in the presence of iodonium salt. For comparison, polymerization sensitized with a typical polynuclear aromatic hydrocarbon, anthracene was also included (Table 4.1, Run 4). It should be noted that the two components of the initiating system are indispensable for the polymerization to occur; either no polymer or negligible amount of polymer is formed in the absence of DDT or iodonium salt at the irradiation wavelength. Notably, vinyl monomers with strong electron donating groups, BVE and NVC polymerized much more readily.

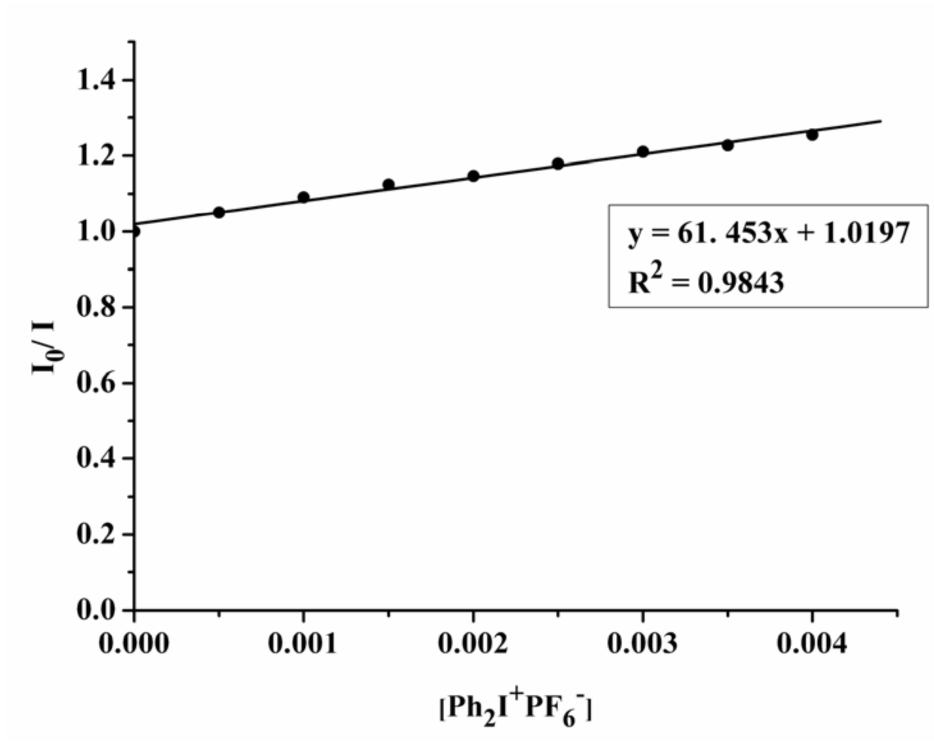


Figure 4.4 : Stern-Volmer plot of the quenching of DDT (1×10^{-5} mol·L^{-1}) by $Ph_2I^+PF_6^-$ in CH_2Cl_2 (excitation wavelength = 350 nm). I_0 = fluorescence intensity of DDT, I = fluorescence intensity in thepresence of $Ph_2I^+PF_6^-$.

Table 4.1 : Photoinitiated[a] cationic polymerization of various monomers in the presence of DDT and $Ph_2I^+PF_6^-$ at room temperature for 30 min at λ >350 nm.

Run	M[b] (mol·L^{-1})	[PS][b] (mol·L^{-1})	[On][b] (mol·L^{-1})	Conversion (%)	M_n[f]	M_w/M_n[f]
1	CHO(9.88)	1×10^{-2}	1×10^{-2}	58	4450	1.97
2	CHO(9.88)	-	1×10^{-2}	<1	-	-
3	CHO(9.88)	1×10^{-2}	-	<1	-	-
4	CHO(9.88)	1×10^{-2}	1×10^{-2}	53[e]	3450	2.56
5	BVE(3.84)[c]	0.5×10^{-2}	0.5×10^{-2}	66	14510	1.87
6	S (4.35)[c]	0.5×10^{-2}	0.5×10^{-2}	5	3700	2.26
7[e]	NVC(1.03)[c]	0.5×10^{-2}	0.5×10^{-2}	98	1970	2.47

[a] An interference filter (aqueous cupric sulfate solution) was used in all experiments.

[b] M: monomer, PS: photosensitizer, On: onium salt, CHO: cyclohexene oxide, BVE: n-butyl vinyl ether, St: styrene, NVC: *N*-vinyl carbazole

[c] In CH_2Cl_2 solution.

[d] Anthrecene is used instead of DDT.

[e] Small portions of high molecular weight (Mn= 98000, PDI= 1.8) polymer was obtained.

[f] Determined from GPC measurements.

Even more convincing evidence for the sensitizing effect of DDT on cationic polymerization induced by iodonium salt was obtained from the cross-linking monomer 1,2-epoxyethyl-3,4-epoxycyclohexane (EEC). Photopolymerizations of the bis-epoxide containing 5×10^{-3} M $Ph_2I^+PF_6^-$ were carried out. In the absence of DDT control experiments failed to produce a gel. In contrast, addition of 5×10^{-3} M DDT produced complete gelation after irradiation for 24 min at λ >350 nm at room temperature. Interestingly, anthracene did not function to promote the polymerization under identical experimental conditions.

According to the Rehm-Weller equation (4.1) (Coulombic energy neglected) electron transfer from the excited sensitizer to onium salt is feasible if the change in free energy (ΔG) is negative. Based on the oxidation potential (E_{ox}) and active excitation energy (E^*) of the photosensitizer (PS) and the reduction potential (E_{red}) of the initiator (PI), the free energy change (ΔG) for the photoinduced electron transfer process was estimated [84].

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

Table 4.2 summarizes the ΔG_S and ΔG_T values of the free energy changes for the electron transfer from the singlet and triplet excited states, respectively, of the photosensitizer to the ground-state iodonium salt. E_{ox} for DDT was previously determined by cyclic voltammetry and found to be 0.88 V [206]. The singlet excitation energy E_S^* and triplet excitation energy E_T^* have been calculated by using the Planck–Einstein equation (4.2):

$$E = \frac{h\,\text{c}}{\lambda} \qquad \textbf{(4.2)}$$

where h is Planck's constant (6.62×10^{-34} J·s), c is speed of light (3×10^8 m·s^{-1}), and λ is 346 (the maximum wavelength of excitation fluorescence spectrum) and 449 nm (the maximum wavelength of emission phosphorescence spectrum) for E_S^* and E_T^*, respectively.

Table 4.2 : Free energy changes (ΔG_S or ΔG_T) for the electron transfer from either singlet or triplet excited states of DDT to the initiator.

E_{red} [a] (V) vs. SCE	E_S^* (kcal·mol^{-1})	E_T^* (kcal·mol^{-1})	ΔG_S (kcal·mol^{-1})	ΔG_T (kcal·mol^{-1})
-0.20	82.6	63.7	-57.8	-38.8

[a] Referance [161]

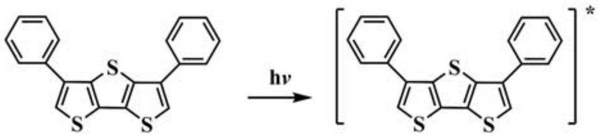
Although the electron transfer in both the singlet and triplet excited states of the dithienothiophene derivative is thermodynamically favorable, relatively low conversion of styrene polymerization indicates that triplet state also involves in the electron transfer process. Styrene is known to be strong triplet quencher and reacts with triplet excited states with a high rate constant [3].

A mechanism based on electron transfer concerning the reaction of excited DDT with iodonium ion is described in reactions 4.3a-f. DDT radical cations formed by reaction 4.3c would be capable of initiating cationic polymerization and, because of the non-nucleophilicity of PF_6^- ions, cationic chain propagation would not be prevented. Principally, polymerization could also be initiated by the protons formed via hydrogen abstraction (4.3e) or coupling reactions (4.3f). It was previously presented evidences for such reactions of thiophene radical cations with the aid of laser flash photolysis studies [25, 201].

It is clear that DDT is an efficient electron-transfer photosensitizer for iodonium salt and, cyclic ethers and vinyl monomers can efficiently be polymerized at wavelengths of λ> 350 nm with the aid of dithienothiophene compound.

4.1.2 Electron transfer photosensitization using 4,7-di(2,3-dihydro-thieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (DTDT) and 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl) quinoxaline (DTDQ)

Figure 4.5 shows the structures of DTDT and DTDQ. These highly conjugated compounds are the building blocks of first green colour electrochromic polymers with exceptional switching properties and remarkable stability. The polymers, obtained from the corresponding monomers, DTDT and DTDQ by electropolymerization, exhibited two simultaneous absorption bands in the red and blue regions of the visible spectrum where these bands should be controlled with the same applied potential. The approach is based on the incorporation of both electron donor, 3,4-ethylenedioxythiophene (EDOT) and acceptor, thiadiazole and quinoxaline groups, for DTDT and DTDQ, respectively into monomer and consequently polymer structure.



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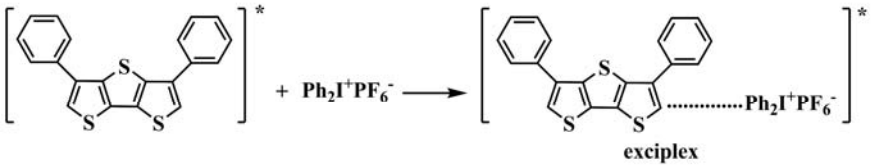

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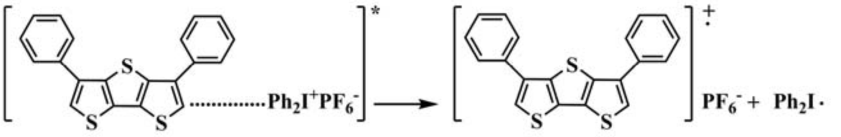

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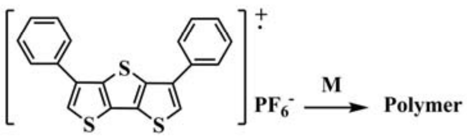

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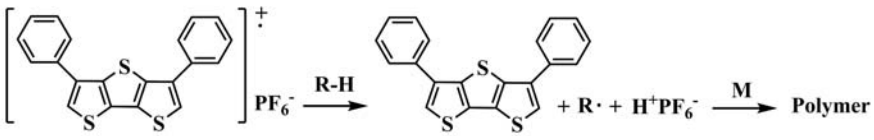

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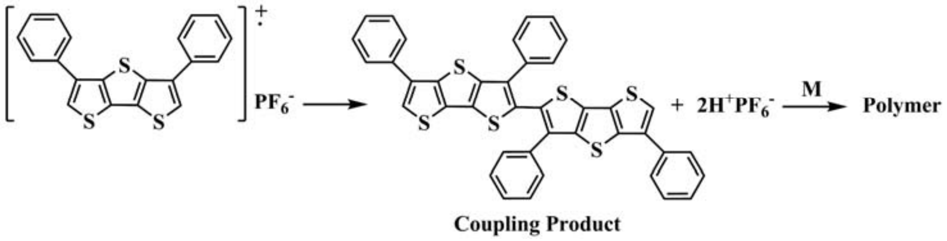


(4.3f)

Figure 4.6 shows the absorption spectra of highly conjugated thiophene derivatives and diphenyliodonium salt. The thiophene compounds, DTDT and DTDQ, absorb strongly above 400 nm presumably due to the extended conjugation of the thiophene groups through the central phenyl ring that makes them particularly useful for visible light applications.

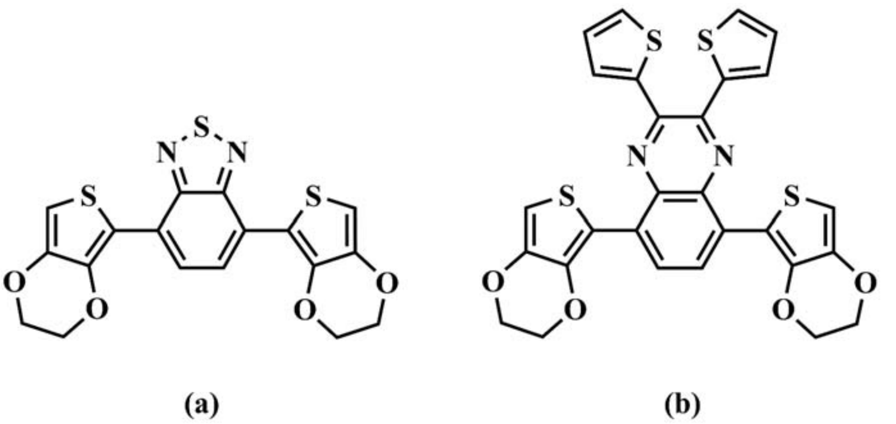


Figure 4.5 : Structures of (a) 4,7-di(2,3-dihydro-thieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (DTDT) and (b) 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl) quinoxaline (DTDQ).

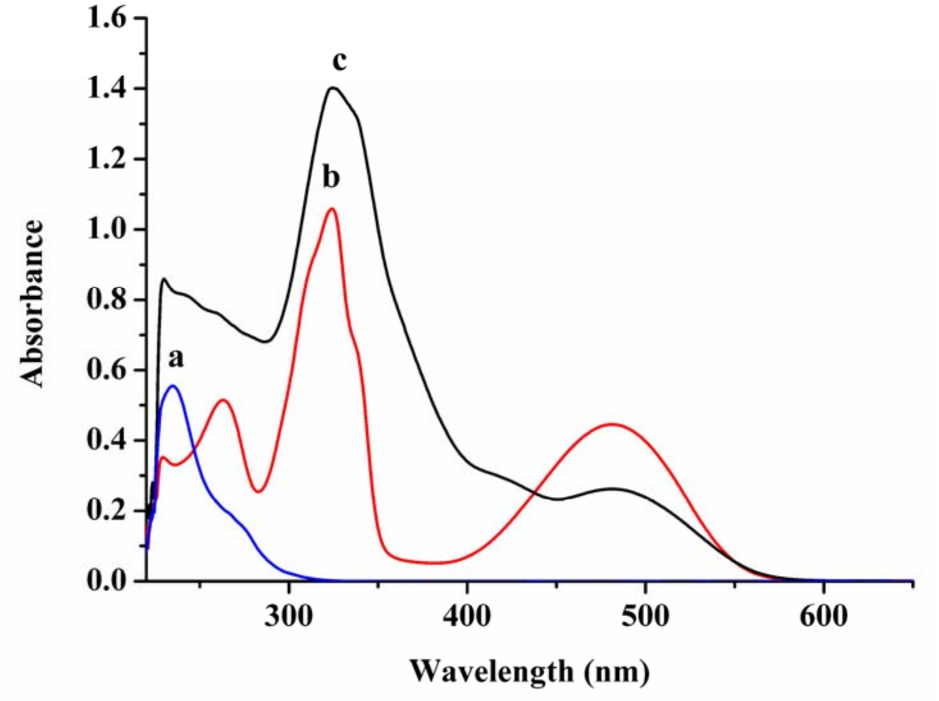


Figure 4.6 : UV spectra of 3.5 × 10^{-3} mol·L^{-1} $Ph_2I^+PF_6^-$ (a), 3.5 × 10^{-3} mol·L^{-1} 4,7-di(2,3-dihydro-thieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (DTDT) (b) and 3.5 × 10^{-3} mol·L^{-1} 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl) quinoxaline (DTDQ) (c) in CH_2Cl_2.

For the potential use of DTDT and DTDQ, as photosensitizers, the excited state emission characteristics were investigated by means of fluorescence and phosphorescence spectroscopic measurements. Figure 4.7 depicts the normalized fluorescence excitation and emission spectra of DTDT and DTDQ, in CH_2Cl_2 at room temperature. It is clear that structureless emissions were detected and a nearly mirror-image like relation exists between absorption and emission of both compounds. Both compounds did not exhibit phosphorescence emission at 77 K indicating rather low intersystem crossing efficiency between singlet and triplet excited states.

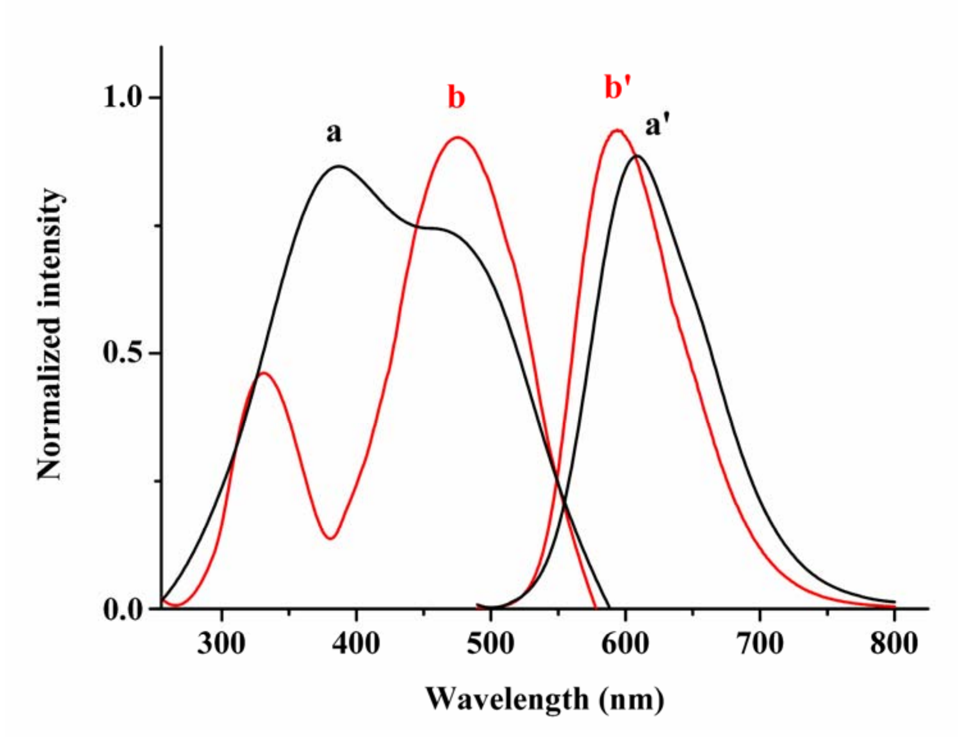


Figure 4.7 : Normalized excitation fluorescence spectra of DTDQ (a) and DTDT (b), and normalized emission spectra of DTDQ (a') and DTDT (b') in CH_2Cl_2 at room temperature.

In the presence of diphenyl iodonium salt, the fluorescence of the sensitizers is markedly quenched. Figure 4.8 shows a typical Stern-Volmer plot for the fluorescence quenching of DTDT and DTDQ, as a function of the concentration of the diphenyliodonium salt. The linear correlation shown in the plot strongly confirms the reaction of excited states of both DTDT and DTDQ, with the iodonium salt.

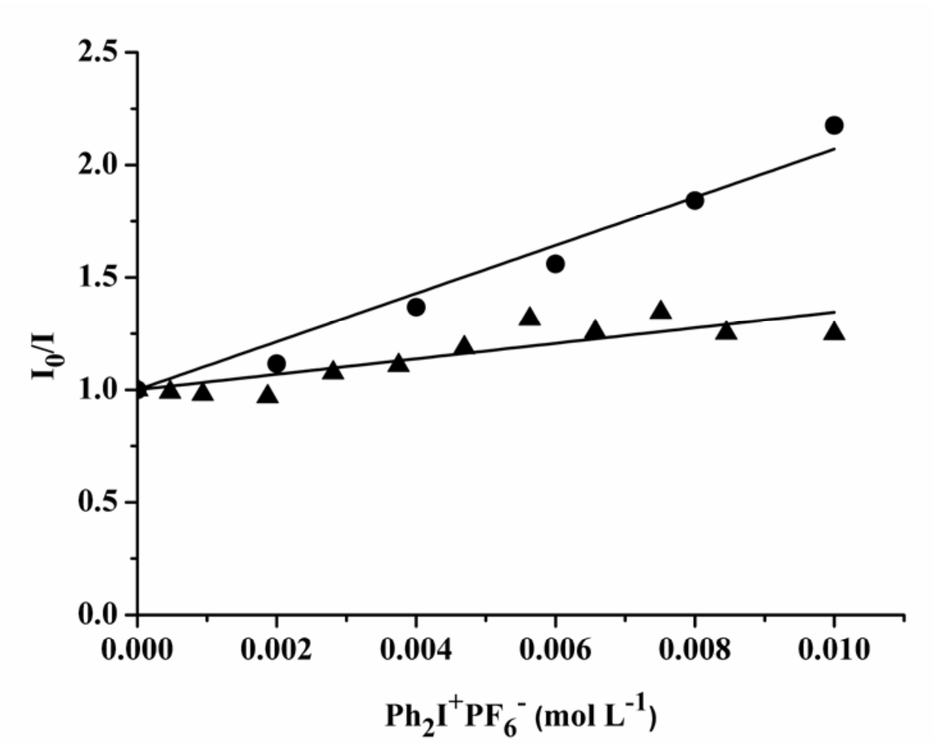


Figure 4.8 : Stern-Volmer plot for the fluorescence quenching of 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DTDQ) (1×10^{-5} mol·L^{-1}) (●) and 4,7-di(2,3-dihydro-thieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (DTDT) (1×10^{-5} mol·L^{-1}) (▲) by $Ph_2I^+PF_6^-$ in CH_2Cl_2 (I_0= fluorescence intensity of DTDT or DTDQ, I= fluorescence intensity in the presence of $Ph_2I^+PF_6^-$).

In our studies the photopolymerization were performed under irradiation at 480 nm e.g. at the wavelength where the light emission is well matched with absorption of sensitizers and iodonium salt is transparent. In Figure 4.9, the conversion of a typical epoxy monomer, cyclohexene oxide (CHO) into poly(cyclohexene oxide) is plotted versus time. As can be seen, the polymerization started without induction period and increased almost linearly with time.

The visible light photoinitiated polymerization of some representative monomers, namely n-butyl vinyl ether (BVE) and *N*-vinyl carbazole (NVC) with the thiophene derivatives in the presence of iodonium salt was also studied. As can be seen from Table 4.3, BVE and NVC were polymerized more effectively due to their strong electron donating nature. DTDT exhibited slightly better initiator efficiency for the polymerization of BVE than that of DTDQ which correlates well with their oxidation potentials (vide infra).

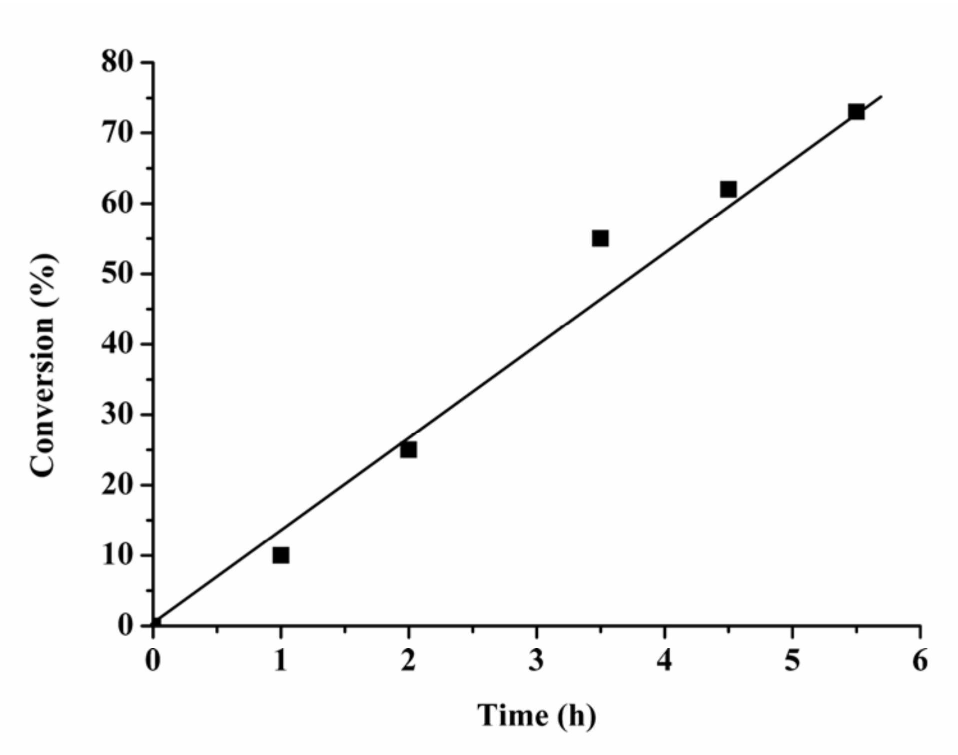


Figure 4.9 : Time-conversion plot for photoinduced polymerization of CHO in the presence of 0.03% 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DTDQ) and 0.06% $Ph_2I^+PF_6^-$ (room temperature, λ= 480 nm).

It is also interesting to note that the thiophene derivatives activate cationic polymerization more efficiently than the well-known visible light photosensitizer, camphorquinone even in the presence of a hydrogen donor such as benzyl alcohol. Although at reduced rate, polymerization also proceeds in the presence of air indicating oxygen inhibition observed with the aromatic carbonyl sensitizers is not an important process. Notably, irradiations with increased light intensity resulted in much faster polymerizations.

As for the all polynuclear aromatic compounds, electron transfer from the excited sensitizer to onium salt is feasible if the change in free energy (ΔG) is negative. Based on the oxidation potential (E_{ox}) and active excitation energy (E^*) of the photosensitizer (PS) and the reduction potential (E_{red}) of the initiator (PI), the free energy change (ΔG) for the photoinduced electron transfer process was estimated according to equation 4.1.

Table 4.3 : Photosensitized cationic polymerization[a] of various monomers in the presence of DTDT, DTDQ, CQ and $Ph_2I^+PF_6^-$ in CH_2Cl_2 at room temperature (λ= 480 nm).

M[b] **(mol·L^{-1})**	**PS[c]**	**$R_p \times 10^4$** **(mol·L^{-1}·s^{-1})**	**Conversion (%)**	**M_n** **(g·mol^{-1})**	**M_w/M_n**
CHO (5.6)	DTDT	2.02	26	10300	1.6
CHO (5.6)	DTDQ	1.96	25	11900	1.5
BVE (5.3)	DTDQ	4.75	78	51700	2.1
NVC (2.9)	DTDQ	3.17	80	23000	2.6
NVC (2.9)	DTDT	2.84	71	29500	3.2
CHO (5.6)[d]	DTDT	56.0	59	5570	1.6
CHO (5.6)[d, e]	DTDT	40.0	49	6060	1.7
CHO (5.6)[d]	CQ	23.0	28	3510	1.5
CHO (5.6)[d, f]	CQ	32.0	38	1620	1.3

[a] Light intensity = 0.045 mW·cm^{-2}, polymerization time= 2 h, [$Ph_2I^+PF_6^-$]= 3.4 × 10^{-3} mol·L^{-1}
[b] M: monomer, CHO: cyclohexene oxide, BVE: n-butyl vinyl ether, NVC: *N*-vinyl carbazole
[c] PS: photosensitizer, CQ: camphorquinone, [PS]= 1.7 × 10^{-3} mol·L^{-1}
[d] Light intensity = 25 mW·cm^{-2}, polymerization time= 10 min
[e] The polymerization was performed in aerated media.
[f] In the presence of benzyl alcohol as hydrogen donor.

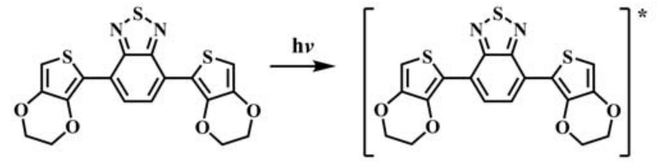
Table 4.4 summarizes the ΔG_S values of the free energy changes for the electron transfer from the singlet states of the photosensitizers to the ground-state iodonium salt. E_{ox} and E_S^* for DTDT and DTDQ were determined by cyclic voltammetry [207, 208] and fluorescence measurements, respectively. The free energy change (ΔG_T) for the electron transfer from the triplet states could not be estimated as phophoroscence studies of both sensitizer at 77 K failed to give any emission and the possibility of the initiation from triplet state was discarded. As can be seen from Table 4.4, electron transfer in singlet excited state of both thiophene compounds is thermodynamically favorable.

Table 4.4 : Free energy changes (ΔG_S) for the electron transfer from singlet excited states of DTDT and DTDQ to $Ph_2I^+PF_6^-$.

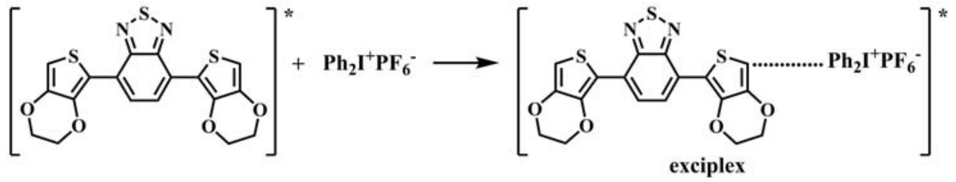
Photosensitizer	**E_{ox}** **(kcal·mol^{-1})**	**E^*** **(kcal·mol^{-1})**	**ΔG_S** **(kcal·mol^{-1})**
DTDT	0.95	48.00	-21.48
DTDQ	0.70	47.13	-26.38

E_{red} = - 0.20 (V) vs. SCE
DTDT: 4,7-di(2,3-dihydro-thieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole
DTDQ: 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline

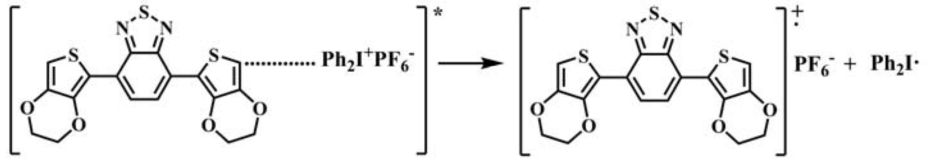
A mechanism based on electron transfer concerning the reaction of excited DTDT with iodonium ion is described in reactions. The same mechanism may also be postulated for the other thiophene derivative DTDQ.



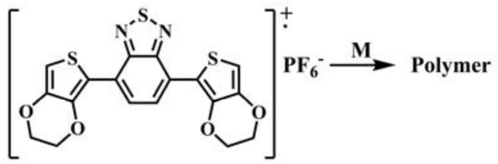
(4.4a)



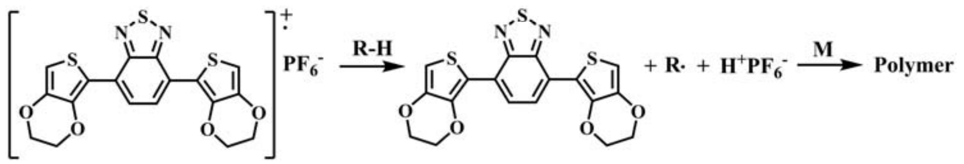
(4.4b)



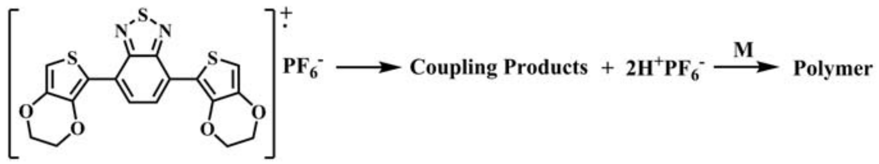
(4.4c)



(4.4d)



(4.4e)



(4.4f)

The radical cations formed by reaction 4.4c would be capable of initiating cationic polymerization since direct initiation by the species formed from polynuclear aromatic compounds is a well known process [112, 209-211] and, because of the non-nucleophilicity of PF_6^- ions, cationic chain propagation would not be prevented. Principally, polymerization could also be initiated by the Brønsted acids formed via hydrogen abstraction (4.4e) or coupling reactions (4.4f). Of particular importance is to evaluate if the Brønsted acids formed from the above reactions are the actual initiating species. Thus, photopolymerization experiments with CHO in the presence of a strong proton scavenger, 2,6-di-*tert*-butyl-4-methylpyridine (DBMP) were performed. It was observed that polymerization of CHO was totally inhibited when

DBMP was present in the system (Table 4.5). Such inhibition indicates that protons generated according to reactions 4.4e and 4.4f play important role regarding the initiation of cationic polymerization and direct initiation by the reaction of the radical cations with the monomer (4.4d) can be neglected. In order to gain more insight to the polymerization process, experiments were performed where either the thiophene compound or iodonium ion was omitted. This omission of either of the two components failed to produce polymer, which is consistent with the proposed mechanism shown in reactions 4.4a-f.

Table 4.5 : Photosensitized cationic polymerization of cyclohexene oxide (CHO) for 2 h at λ= 480 nm.

CHO[a]	**DTDQ**[b]	**$Ph_2I^+PF_6^-$**[c]	**Conversion (%)**
+	+	+	25
+	-	+	-
+	+	-	-
+[d]	+	+	-

[a] $[96] = 5.6$ mol·L^{-1}

[b] $[DTDQ]= 1.7 \times 10^{-3}$ mol·L^{-1}

[c] $[Ph_2I^+PF_6^-]= 3.4 \times 10^{-3}$ mol·L^{-1}

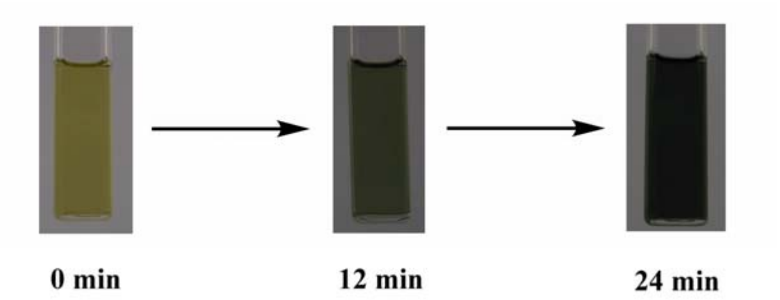
[d] In the presence of 2,6-di-*tert*-butyl-4-methyl pyridine.

Evidence for the practical value of the promoting effect of conjugated thiophene derivatives on cationic polymerization induced by onium salts was obtained from cross-linking monomer 1,3-bis(3,4epoxycyclohexylethyl)tetramethyl disiloxane (EPOX). Bulk polymerizations of the bis-epoxide containing 3.4×10^{-3} mol·L^{-1} $Ph_2I^+PF_6^-$ were carried out. In the absence of the thiophene derivatives photoirradiations from a Bluephase light source emmiting at 430-490 nm failed to produce a gel after 2 h irradiation. In contrast addition 1.7×10^{-3} mol·L^{-1} DTDQ produced complete gelation after 10 min irradiation at room temperature.

4.2 Polythiophene Derivatives by Step-growth Polymerization via Photoinduced Electron Transfer Reactions

As it was described above, DDT is an efficient electron-transfer photosensitizer for diaryliodonium salt initiated cationic polymerization. The proposed mechanism based on electron transfer concerning the reaction of excited DDT with iodonium ion was explained in detail (reactions 4.3a-f). Polymerizations were initiated either by

DDT radical cations or the protons formed via hydrogen abstraction or coupling reactions. By virtue of the thiophene type radical cation formation and the crusial role of these species in the electropolymerization, the described photoinduced process has the potential of forming polymeric molecules. Thus, step-growth polymerization of DDT was triggered by generating radical cations not by electrochemical means but by the decsribed photochemical process.



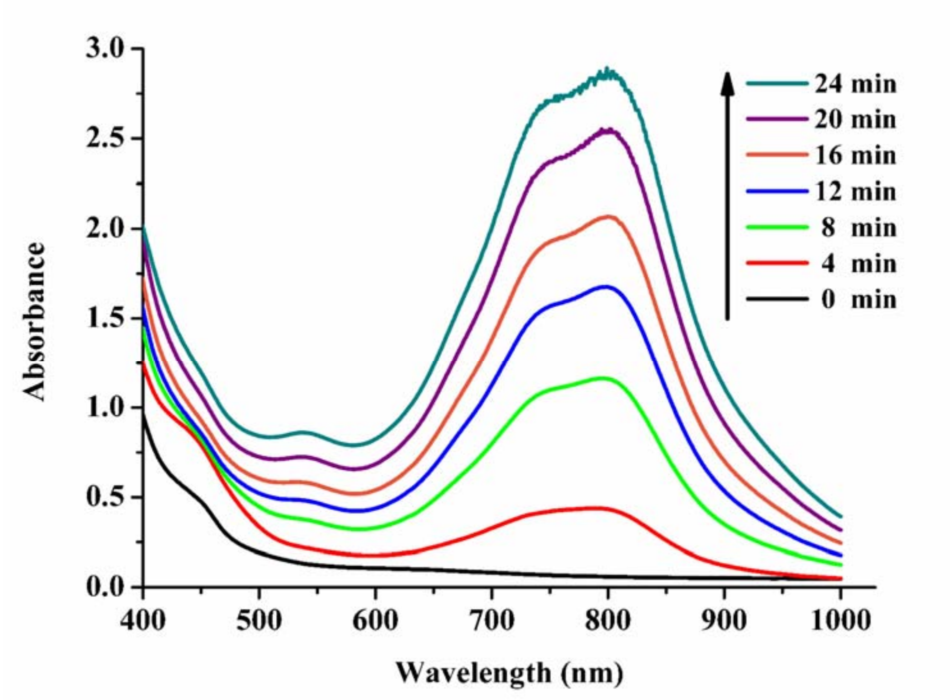


Figure 4.10 : UV-Vis spectral change during irradiation of 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) (1.9 x 10-3 mol L-1) in the presence of $Ph_2I^+PF_6^-$ (3.8 x 10^{-3} mol L^{-1}) in CH_2Cl_2 solution.

Since the diphenyliodonium ion does not absorb at the irradiation wavelength, λ > 350 nm, all the light is absorbed by DDT (Figure 4.2). Experimentally, DDT was polymerized quite effectively when the solution containing DDT and diphenyliodonium hexafluorophosphate in CH_2Cl_2 was irradiated for about 30 min. As can be seen from Figure 4.10, the polymerization was accompanied with darkening of the solution and a new absorption band at 740-800 nm appeared indicating extended conjugation due to polymer formation. Similar absorption characteristics were observed with the polymers obtained by electrochemical means [206].

The GPC profile of the resulting PDDT suggests that only oligomers with different chain lengths were formed (Figure 4.11). However, the molecular weight measurements with light scattering gave much higher value ($M_w = 6 \times 10^5$ g·mol^{-1}) (Figure 4.12). The low value obtained by GPC method may be due to the different hydrodynamic volume of the polymer compared to the polystyrene standards. The higher absorbtion at longer wavelengths compared to that found with other polythiophenes also confirms the formation of high molecular weight polymers.

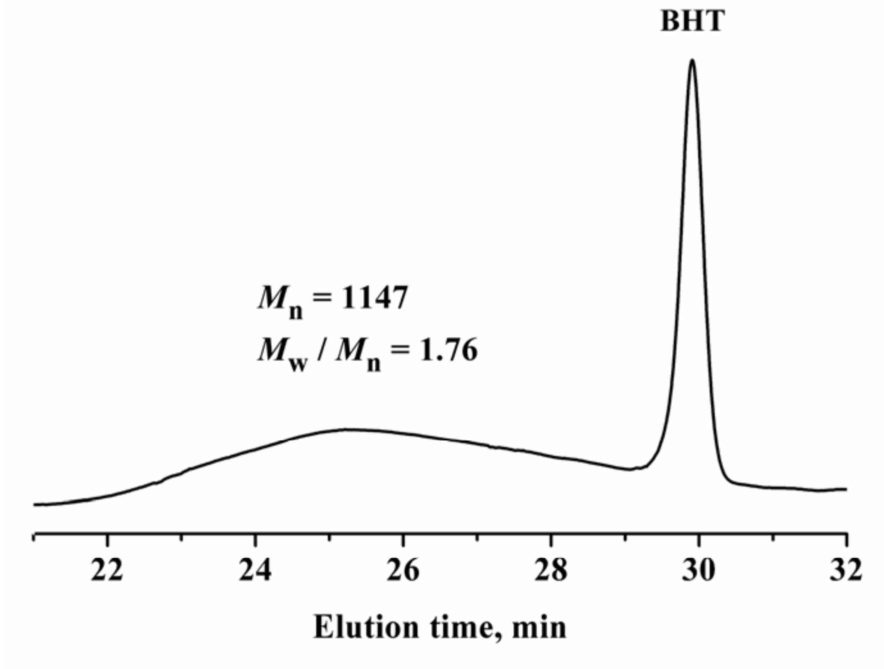


Figure 4.11 : The GPC profile of PDDT formed after irradiation of 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) in the presence of $Ph_2I^+PF_6^-$.

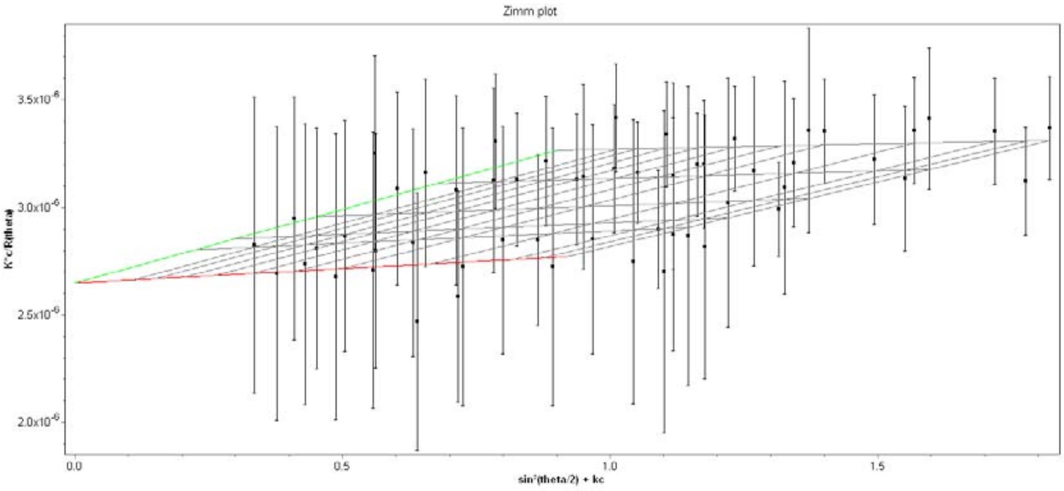


Figure 4.12 : Zimm plot for PDDT in THF.

The structure of the polymer was confirmed by ^{1}H NMR and IR analysis. ^{1}H NMR spectra of DDT and the photolysis product are shown in Figure 4.13a and b, respectively. The broadening of the peaks together with the decrease of the peak at about 8.0 ppm in the spectrum (b), corresponding to thiophene protons at 2 position clearly indicates the PDDT formation.

IR spectral analysis of the PDDT also revealed the proposed structure (Figure 4.14). As can be seen, the FT-IR spectrum of monomer exhibits most of the characteristic peaks at 1592, 1441, 1350 and 1257 cm^{-1} originating from C=C and C-C. Broadening of these peaks in the spectrum of PDDT indicates the formation of polymeric material. The band at 730 cm^{-1} corresponds to the monosubstituted benzene. The bands at 847 and 3100 cm^{-1} corresponding to C-H bending and streching of the thiophene ring, respectively, were much reduced in the spectrum of PDDT (Figure 4.14) indicating loss of those bonds due to polymerization. The shoulder at 1677 cm^{-1} and the intense band at 1070 cm^{-1} revealed the formation of polyconjugation.

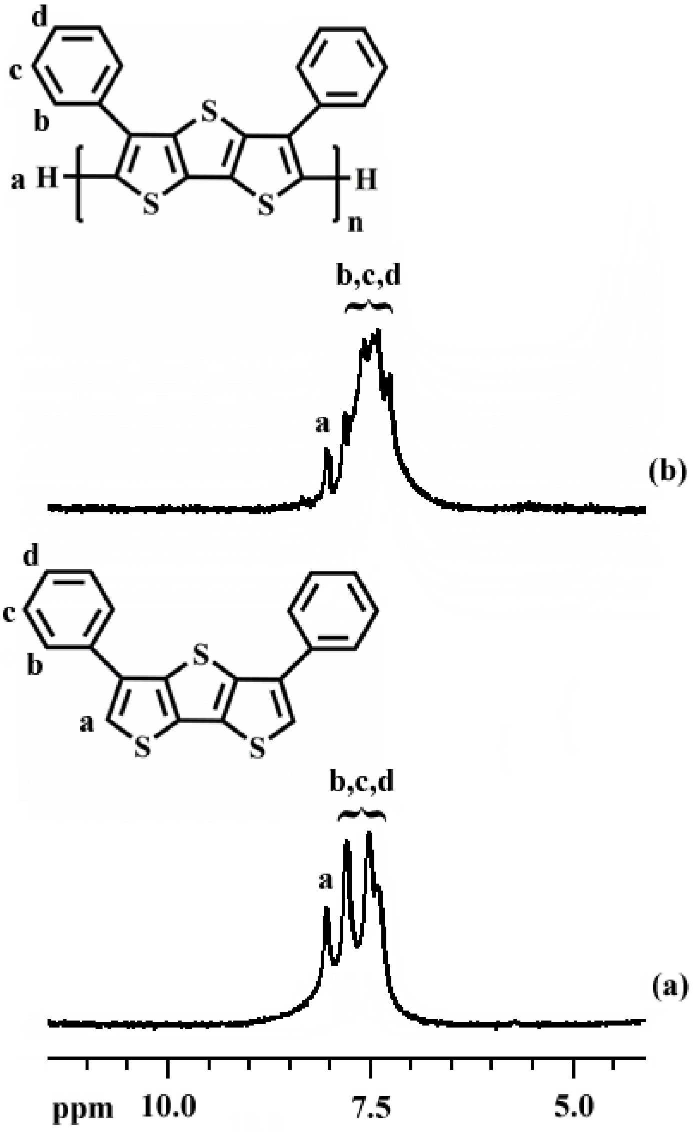


Figure 4.13 : ^{1}H NMR spectra of a) DDT and b) PDDT in d_6-DMSO.

The proposed mechanism involves the intermediate DDT radical cation formed by the electron transfer from the excited state DDT to the iodonium as described for the sensitization of cationic polymerization (reaction 4.3a-f). Such redox process between photoexcited DDT and ground state iodonium salt is thermodynamically favorable for both singlet and triplet excited states since the corresponding free energy changes (ΔG) were found to be -57.8 and -38.8 kcal mol^{-1}, respectively.

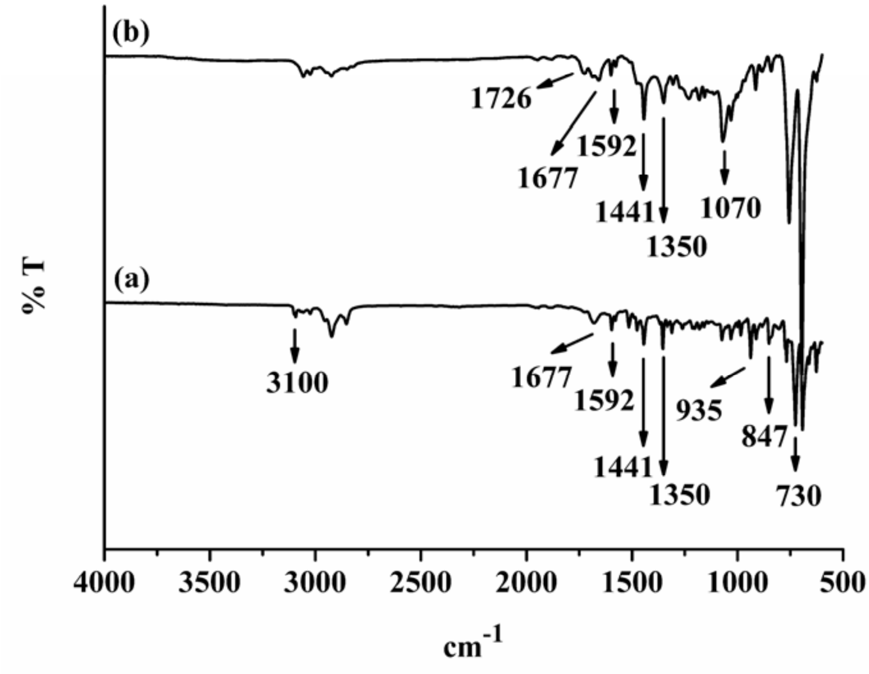


Figure 4.14 : FT-IR spectra of a) DDT and b) PDDT.

Although the participation of the triplet state in the redox process can not be discarded, the more favorable Δ*G* value and fluorescence quenching of DDT with iodonium ion indicates that electron transfer from singlet state to the salt contributes strongly to the generation of radical cation. In the following step, a spin-pairing of two radical cations results in the formation of a dihydrodimer dication, which subsequently undergoes a loss of protons and rearomatization. The polymerization proceeds with the oxidation of the dimer, which undergoes further coupling reactions with the other radical cations formed in a similar manner as in electrochemical polymerization mechanism (Figure 4.15).

Thermal stability of PDDT was investigated by thermal gravimetric analysis (TGA) under nitrogen exposure. TGA profiles of DDT and PDDT are shown in Figure 4.16. It is clear from the figure that the monomer decomposes at the temperatures above 400°C. In contrast, the polymer decomposes only slightly (10%) even it is heated up to 600°C. The char yield at 800°C (70%) is higher than thiophene polymers [212]. This behaviour may be attributed to the constructive effect of extra phenyl and fused thiophene rings. The excellent thermal stability indicates that this polydithienothiophene derivative can be applied in a wide temperature scale.

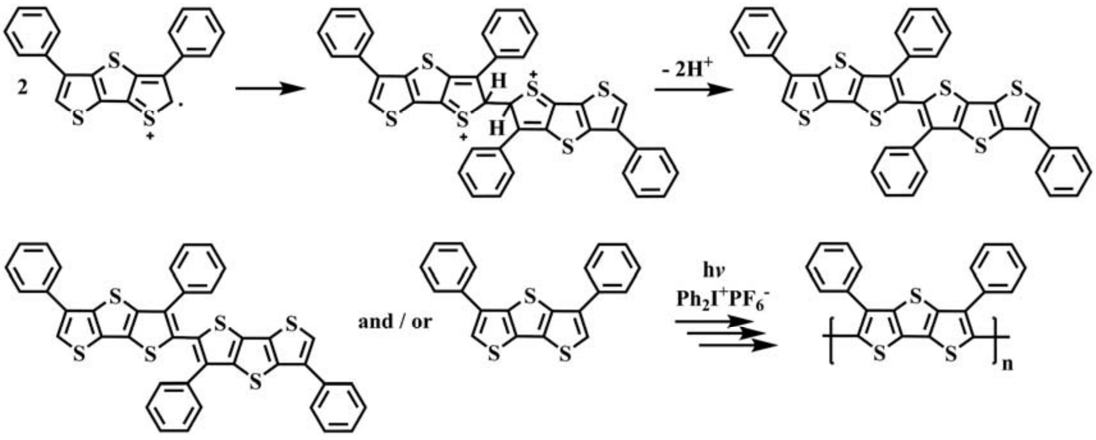


Figure 4.15 : Polymerization of 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT).

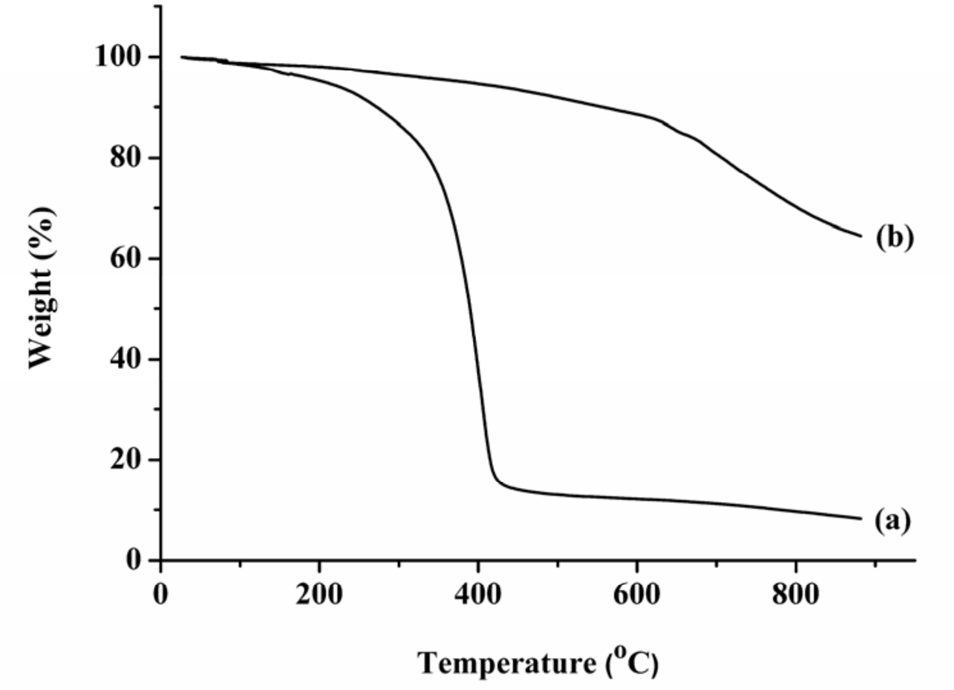


Figure 4.16 : TGA thermograms of a) DDT and b) PDDT.

4.3 Novel Free Radical Photoinitiating System by Combination of Cleavage and Electron Transfer Reactions

Conventional free radical polymerization is often based on the thermal homolytic cleavage of covalent bonds. Recently, Yoshida and co-workers [213] introduced a new initiating system for free radical polymerization using electron transfer driven C-Si bond cleavage. As it is shown in Figure 4.17, in this binary system the initiation begins with single electron transfer from benzylsilane(stannane) to triarylaminium salt to generate the corresponding radical cation. Benzyl radical is fromed by the selective C-Si (C-Sn) bond cleavage that is supported by nucleophilic attack on Si (or Sn) by the solvent. Benzyl radical, which may also be trapped by residual aminium salt [214, 215], initiates polymerization.

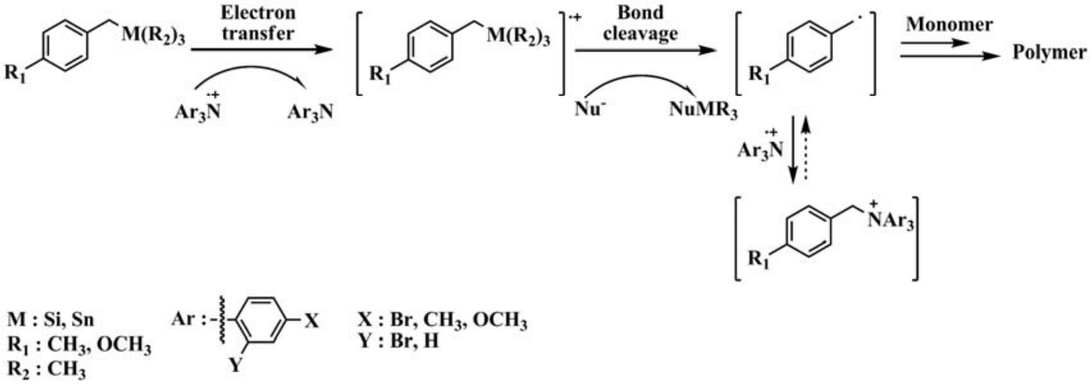


Figure 4.17 : Free radical polymerization mechanism using electron transfer driven C-Si bond cleavage.

It seemed appropriate to use the same strategy for photoinitiated radical polymerization by using phenacyl salts as radical cation sources. It is known that phenacyl anilinium and pyridinium salts undergo irreversible photolysis leading to complete fragmentation of the photoinitiator (Figure 2.9). Although electronically excited salt undergoes heterolytic and/or homolytic cleavage resulting eventually in the formation of phenacylium cations, aminium salt is the intermediate product in the homolytic cleavage. Based on the formation of such radical cations a new free radical photoinitiating system was designed. For this purpose, first two phenacyl salts, namely *N*-phenacyl-*N,N*-dimethylanilinium hexafluoroantimonate ($PDA^+SbF_6^-$) and *N*-phenacylpyridinium hexafluoroantimonate ($PPy^+SbF_6^-$) were synthesized according to the previously reported procedures [111-113]. A benzylsilane, namely (4-methoxybenzyl)trimethylsilane (MBTMS), was also synthesized as a second component of the initiating system. The structures of the components of the initiating system were confirmed by means of ^{1}H NMR spectroscopy and the results were in accordance with previously reported data.

Figure 4.18 shows the absorption spectra of phenacyl salts and MBTMS. The absorption spectra of both $PDA^+SbF_6^-$ and $PPy^+SbF_6^-$ exhibit n–π* absorption with a maximum at about 300 nm, characteristic of acetophenone derivatives. Differently, $PPy^+SbF_6^-$ possesses an absorption in the visible region that is a characteristic of pyridinium salts. The benzylsilane compound (MBTMS) exhibits an absorption with a maximum at about 300 nm.

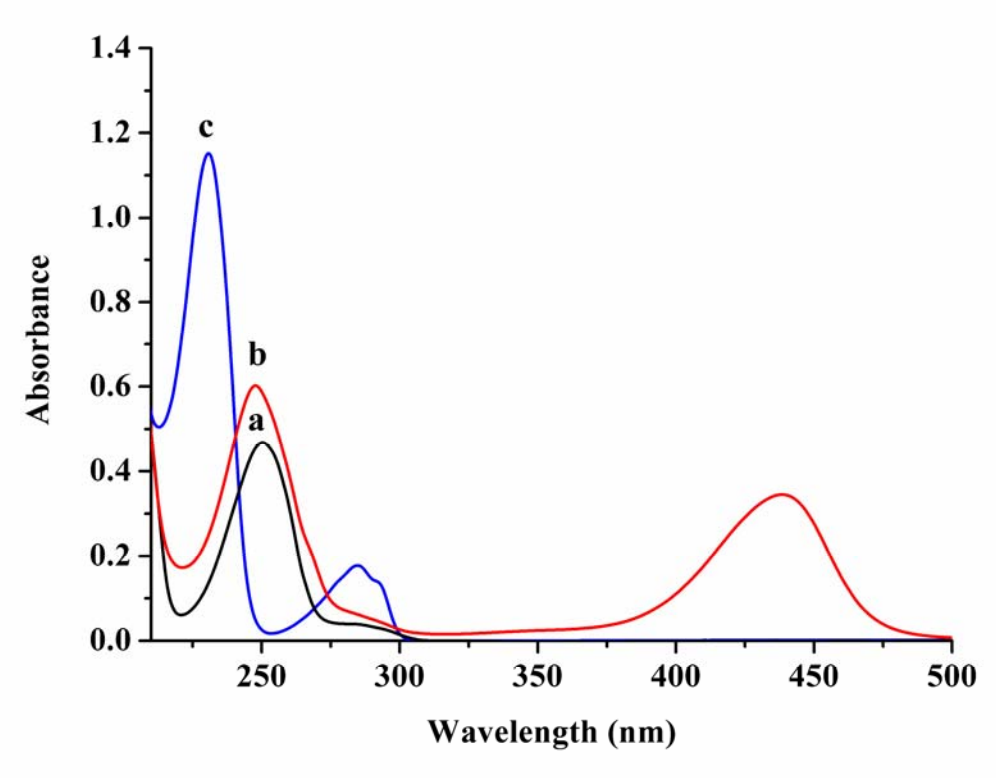


Figure 4.18 : Absorption spectra of a) $PDA^+SbF_6^-$ (4.75×10^{-5} mol·L^{-1}), b) PPy $^+SbF_6^-$ (4.75×10^{-5} mol·L^{-1}) and c) MBTMS (9.5×10^{-5} mol·L^{-1}) in MeCN.

The polymerization of methyl methacrylate (MMA) was examined. Typical results are presented in Table 4.6. As can be seen, MMA was polymerized efficiently in the presence of MBTMS and phenacyl salt ($PDA^+SbF_6^-$ or PPy $^+SbF_6^-$) (Table 4.6, Run 1 and 4). In order to gain more insight to the polymerization process, experiments were performed where either the benzylsilane compound or phenacyl salt was omitted. Either no polymer or negligible amount of polymer was formed in the absence of MBTMS or phenacyl salts, indicating that both of the two components of the initiating system are indispensable for the polymerization to occur.

Table 4.6 : Photoinitiated free radical polymerization of MMA in the presence of $PDA^+SbF_6^-$ or $PPy^+SbF_6^-$, and MBTMS at room temperature.[a]

Run	Phenacyl salt[b]	MBTMS[c]	Yield (%)	M_n (g·mol^{-1})	M_w/M_n
1	**$PDA^+SbF_6^-$**	+	18	37770	2.04
2	**$PDA^+SbF_6^-$**	-	0	-	-
3	-	+	2	32550	2.05
4	**$PPy^+SbF_6^-$**	+	19	50260	2.20
5	**$PPy^+SbF_6^-$**	-	0	-	-
6	-	+	0.6	47660	2.12

[a] Light intensity = 0.045 mW·cm^{-2}, polymerization time= 2 h
[b] [Phenacyl salt] = 6.67×10^{-2} mol·L^{-1}
[c] [MBTMS] = 13×10^{-2} mol·L^{-1}

In Figures 4.19 and 4.20, the conversion of MMA is plotted versus time. As can be seen, the polymerization started without induction period and increased almost linearly with time.

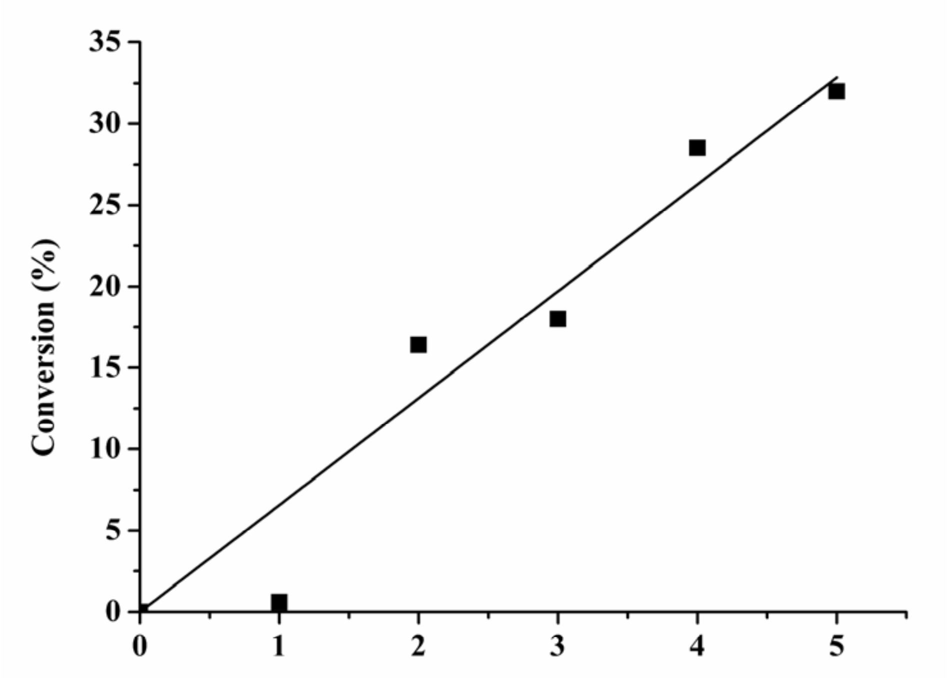


Figure 4.19 : Time-conversion plot for photoinduced polymerization of MMA by using $PDA^+SbF_6^-$ (6.67×10^{-2} mol·L^{-1}) and MBTMS (13.0×10^{-2} mol·L^{-1}) (room temperature, λ> 300 nm).

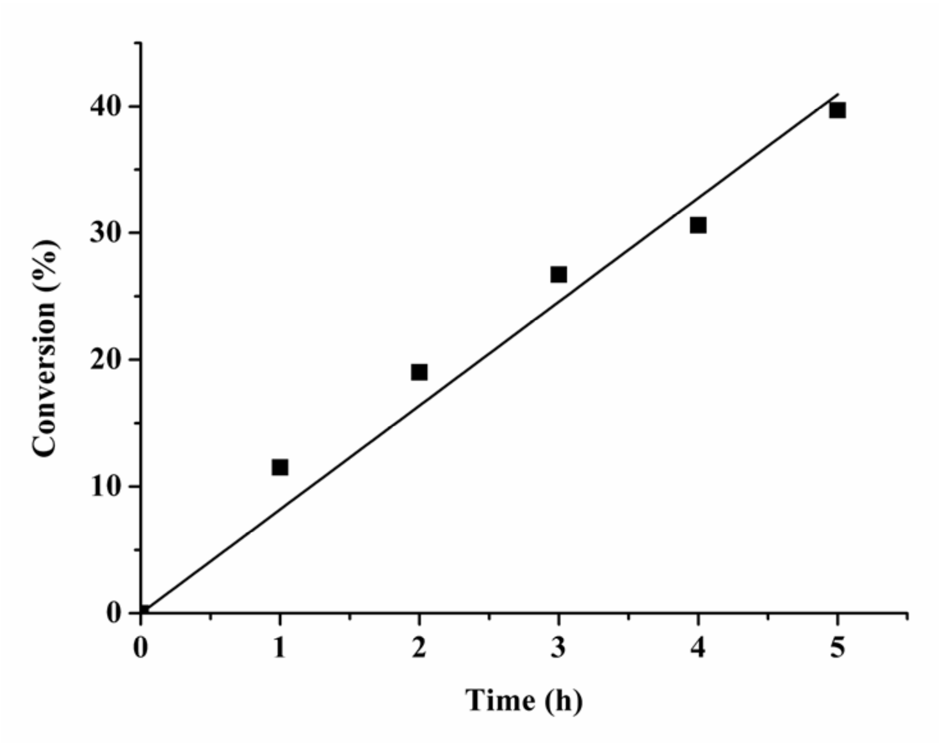


Figure 4.20 : Time-conversion plot for photoinduced polymerization of MMA by using $PPy^{+}SbF_{6}^{-}$ (6.67×10^{-2} mol·L^{-1}) and MBTMS (13.0×10^{-2} mol·L^{-1}) (room temperature, $\lambda > 300$ nm).

The photoinitiated free radical polymerization of some representative monomers, namely butyl acrylate (BA) and styrene (S) with the phenacyl salts in the presence of MBTMS was also studied. As can be seen from Table 4.7, polymerization of BA also proceeded under the similar conditions and gave the poly(BA) in moderate yields (Table 4.7, Run 3 and 4). Interestingly, S was polymerized in low yields and the molecular weights of the polymers were smaller. Higher activity with more electrofilic (meth)acrylate monomers may be due to the possibility of zwitterionic polymerization through the weak bases pyridine and *N,N*-dimethylaniline formed concomitantly.

Table 4.7 : Photoinitiated free radical polymerization of various monomers in the presence of $PDA^{+}SbF_6^{-}$ or $PPy^{+}SbF_6^{-}$, and MBTMS at room temperature.[a]

Run	Monomer[b]	Phenacyl salt[c]	Yield (%)	M_n ($g \cdot mol^{-1}$)	M_w/M_n
1	MMA	$PDA^{+}SbF_6^{-}$	18	3777	2.04
2	MMA	$PPy^{+}SbF_6^{-}$	19	50260	2.20
3	BA	$PDA^{+}SbF_6^{-}$	53	129340	2.02
4	BA	$PPy^{+}SbF_6^{-}$	20	138250	2.09
5	S	$PDA^{+}SbF_6^{-}$	3	2900	1.37
6	S	$PPy^{+}SbF_6^{-}$	4	4650	2.29

[a] Light intensity = 0.045 $mW \cdot cm^{-2}$, polymerization time= 2 h, [MBTMS] = 13×10^{-2} $mol \cdot L^{-1}$
[b] [MMA] = 6.2 $mol \cdot L^{-1}$, [BA] = 5.2 $mol \cdot L^{-1}$, [S] = 5.8 $mol \cdot L^{-1}$
[c] [Phenacyl salt] = 6.67×10^{-2} $mol \cdot L^{-1}$

The proposed mechanism based on electron transfer concerning the reaction of $PDA^{+}SbF_6^{-}$ with MBTMS is described in Figure 4.21. The same mechanism may also be postulated for $PPy^{+}SbF_6^{-}$ (Figure 4.22). The initiation reaction begins with homolytic cleavage of $PDA^{+}SbF_6^{-}$ to generate aminium salt. The next step consists of single electron transfer from MBTMS to aminium salt to generate benzylsilane radical cation (a). The benzyl radical, which initiates the polymerization, is formed by the nucleophile-assisted C-Si bond cleavage of benzylsilane radical cation. The solvent (MeCN) is acting as the nucleophile. An electron transfer between aminium salt and phenacyl radical (b) should also be considered. However, higher reactivity of the radical cations with silane compounds reveals that the probability of such electron transfer is limited.

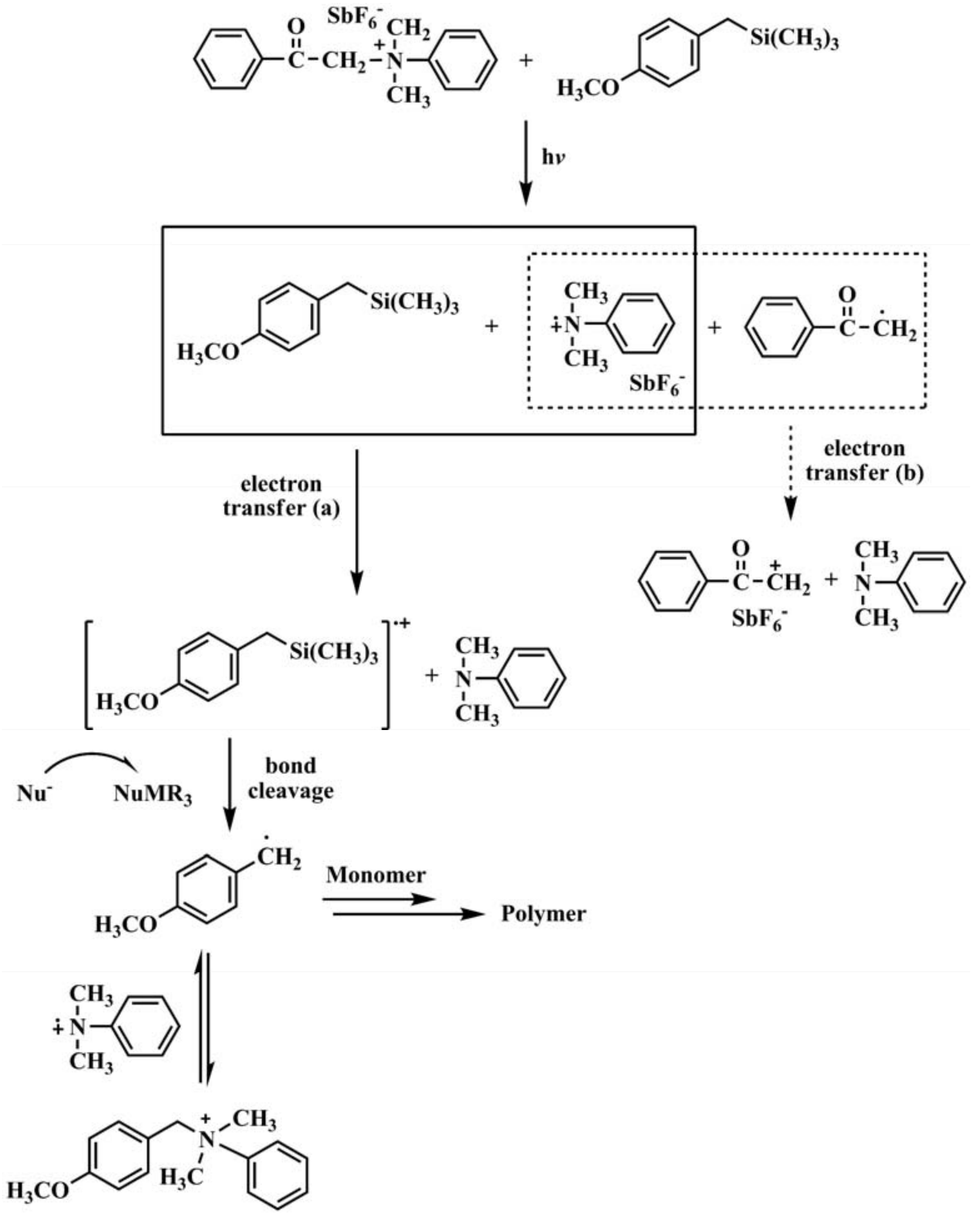


Figure 4.21 : Proposed mechanism for the photoinitiated radical polymerization by using $PDA^+SbF_6^-$ in the presence of MBTMS.

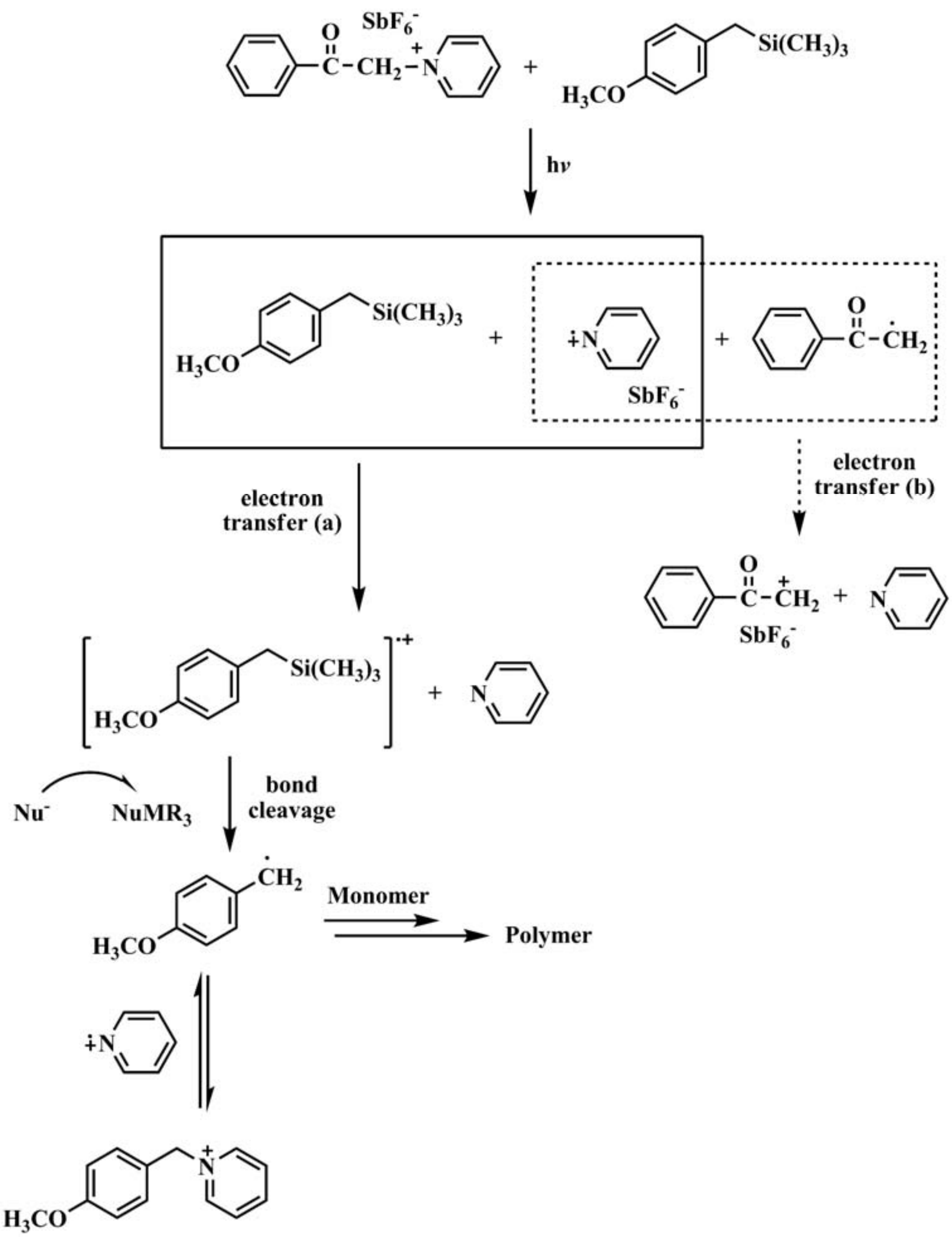


Figure 4.22 : Proposed mechanism for the photoinitiated radical polymerization by using $PPy^+SbF_6^-$ in the presence of MBTMS.

5. CONCLUSION

In this thesis, possibility of electron transfer reactions to initiate polymerizations by photochemical means was described. Three different strategies were employed for extending absorptivity of the initiating systmes to longer wavelengths.

The first strategy is composed of electron transfer photosensitization by using highly conjugated thiophene derivatives, namely 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT), 4,7-di(2,3-dihydro-thieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (DTDT) and 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl) quinoxaline (DTDQ). For the potential use of these conjugated thiophene compounds as photosensitizers, the excited state emission characteristics were investigated by means of fluorescence and phosphorescence spectroscopic measurements.

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 and 1,3-bis(3,4epoxycyclohexylethyl)tetramethyl disiloxane (EPOX) were readily polymerized in bulk or dichloromethane solutions at appropriate wavelengths where the light emission is well matched with absorption of sensitizers and iodonium salt is transparent. Interestingly, thiophene derivatives activated cationic polymerization more efficiently than the well-known visible light photosensitizers, anthracene and camphorquinone.

A mechanism based on electron transfer concerning the reaction of excited sensitizers with iodonium ion was proposed. Polymerizations achieved in the presence of a strong proton scavenger (2,6-di-*tert*-butyl-4-methylpyridine (DBMP)) revealed that the Brønsted acids formed via hydrogen abstraction or coupling reactions are the actual initiating species and direct initiation by the reaction of the radical cations with the monomer can be neglected.

The second strategy relies on the synthesis of conjugated thiophene polymers by photoinduced step-growth polymerization using onium salts. The process is based on the thiophene type radical cation formation explained in the first strategy and the crusial role of these species in the electropolymerization. Formation of the polymer was followed by UV-Vis spectroscopy and a new absorption band at 740-800 nm appeared indicating extended conjugation. The synthesized polymer was characterized by spectral methods (^{1}H NMR and IR analysis), GPC and light scattering measurements. The excellent thermal stability obtained by thermal gravimetric analysis (TGA) indicated that PDDT can be applied in a wide temperature scale.

The described method may be useful particularly when the polymers are desired to be coated on various surfaces such as glasses, since unless they function as electrodes where electropolymerizations typically occur. In contrast to electrochemical and chemical oxidation processes, the descibed photoinduced polymerization is simple and straightforward. Because the protonic acid, formed during the polymerization, can induce the polymerization of cationically polymerizable monomers under appropriate conditions, the process is potentially useful for the *in situ* preparation of hybrid sytems consisting of epoxy networks and conjugated polymers.

In the final strategy, a novel free radical photoinitiating system by combination of cleavage and electron transfer reactions was suggested. The initiating system is composed of two components, a phenacyl salt and a benzylsilane compound.

N-Phenacyl-*N,N*-dimethylanilinium hexafluoroantimonate ($PDA^+SbF_6^-$), *N*-phenacylpyridinium hexafluoroantimonate ($PPy^+SbF_6^-$) and (4-methoxybenzyl)trimethylsilane (MBTMS) were synthesized, and characterized by ^{1}H NMR and UV spectroscopy. Several types of monomers such as methyl methacylate (MMA), butyl acrylate (BA) and styrene (S) were efficiently polymerized by using $PDA^+SbF_6^-$ or $PPy\ ^+SbF_6^-$ in the presence of MBTMS. The control experiments showed that both of the two components of the initiating system are indispensable for the polymerization to occur.

The postulated mechanism is based on the electron transfer reaction between phenacyl salt and MBTMS. The initiation is achieved by the bezyl radical, which is formed by the nucleophile-assisted C-Si bond cleavage of benzylsilane radical cation. Although mechanistic details still remain to be evaluated it is clear that photoinitiated free radical polymerization of vinyl monomers can efficiently be realized with the aid of phenacyl salts and MBTMS.

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Projects:

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2006-2008	TUBITAK Project (Project No: 106T075) A Novel Route for the Synthesis of Linear and Functional Polymers: Atom Transfer Radical Coupling

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