ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

HIGHLY CONJUGATED VISIBLE AND NEAR-INFRARED LIGHT PHOTOINITIATING SYSTEMS FOR RADICAL AND CATIONIC POLYMERIZATION

M.Sc. THESIS

Ali SÜERKAN

Department of Chemistry

Chemistry Programme

JUNE 2021

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

HIGHLY CONJUGATED VISIBLE AND NEAR-INFRARED LIGHT PHOTOINITIATING SYSTEMS FOR RADICAL AND CATIONIC POLYMERIZATION

M.Sc. THESIS

Ali SÜERKAN
(509191244)

Department of Chemistry

Chemistry Programme

Thesis Advisor: Prof. Dr. Yusuf YAĞCI

JUNE 2021

ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

RADİKAL VE KATYONİK POLİMERİZASYON İÇİN YÜKSEK KONJUGASYONLU GÖRÜNÜR VE NIR BÖLGESİ FOTOBAŞLATICI SİSTEMLERİ

YÜKSEK LİSANS TEZİ

Ali SÜERKAN
(509191244)

Kimya Anabilim Dalı

Kimya Programı

Tez Danışmanı: Prof. Dr. Yusuf YAĞCI

HAZİRAN 2021

Ali Süerkan, a M.Sc. student of İTU Graduate School 509191244, successfully defended the thesis entitled “HIGHLY CONJUGATED VISIBLE AND NEAR-INFRARED LIGHT PHOTOINITIATING SYSTEMS FOR RADICAL AND CATIONIC POLYMERIZATION”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. Yusuf YAĞCI** ....
İstanbul Technical University

Jury Members : **Prof. Dr. Turan ÖZTÜRK** ....
İstanbul Technical University

Prof. Dr. Meral AYDIN ....
Yıldız Technical University

Date of Submission : 22 June 2021
Date of Defense : 1 July 2021

To my dear and beloved family,

FOREWORD

First and foremost, I want to express my gratitude to Professor Yusuf YAĞCI, my advisor, for his support, assistance, and unique perspective on the polymer area. He not only contributed to me scientifically with his own knowledge, but also his own experience in matters such as his view of life, working, persevering, not giving up, and being able to laugh at difficulties. It would not have been possible to complete my master's studies without his suggestions and scientific guidance.

I also would like to faithfully express my special thanks to Dr. Kerem KAYA. During my studies, he not only helped me in practice but also acquainted me with bedrock of scientific studies and taught me to find a way out.

My sincere thanks go to the group headed by Professor Levent TOPPARE from the Middle East Technical University for their contributions to the synthesis and electrochemical parts of the thesis.

I offer my sincere thanks to Dr. Semira BENER, Tuğba ÇELİKER, Azra KOCAARSLAN, Hüseyin Cem KILIÇLAR, Zeynep DELİBALLI, Assoc. Prof. Dr. Ali Görkem YILMAZ, Mehmet Bilgehan BİLGİÇ, Zehra Gül ÇOBAN, Mustafa Semih YILDIRIM for their help and companionship.

Finally, I would like to thank my family from the bottom of my heart, especially my mother Hacer SÜERKAN, my father Ramazan SÜERKAN, and my brother Yunus Emre SÜERKAN. I could not have achieved this without their support, inspiration, tolerance, patience, and common sense throughout my studies.

June 2021

Ali SÜERKAN
(Chemist)

TABLE OF CONTENTS

Page

ABBREVIATIONS

NMR : Nuclear magnetic resonance spectroscopy
UV-VIS : Ultraviolet-visible spectroscopy
THF : Tetrahydrofuran
FT-IR : Fourier-transform infrared spectroscopy
DCM : Dichloromethane
GPC : Gel permeation chromatography
NIR : Near-infrared Light
PET : Photoelectron transfer
DMA : Dynamic mechanical analysis
1a : 5H-[1,2,3]triazolo[40,50:4,5]benzo[1,2-c][1,2,5]thiadiazole
1b : 5H-[1,2,3]triazolo[40,50:4,5]benzo[1,2-c][1,2,5]selenadiazole
PS : Photosensitizer
PI : Photoinitiator
M : Monomer
CP : Cationic polymerization
FRP : Free radical polymerization
DPI : Diphenyliodonium hexafluorophosphate
PAH : Polycyclic aromatic hydrocarbons
MA : Methacrylate
GMA : Glycidyl methacrylate
MMA : Methyl methacrylate
CHO : Cyclohexene oxide
IBVE : Isobutyl vinyl ether
TEGDMA : Triethylene glycol dimethacrylate

SYMBOLS

$h\upsilon$: Radiation
R : Alkyl
R• : Radical
Ar : Aryl group
ε : Molar absorptivity
M_n : The number average molecular weight
M_w : The weight average molecular weight
Đ : Polydispersity index
M : Molar
ºC : The degree Celsius
L : Liter
s : Second
g : Gram
cm : Centimeter
nm : Nanometer
mmol : Milimole
mg : Milligram
mL : Milliliter

LIST OF TABLES

LIST OF FIGURES

HIGHLY CONJUGATED VISIBLE AND NEAR-INFRARED LIGHT PHOTOINITIATING SYSTEMS FOR RADICAL AND CATIONIC POLYMERIZATION

SUMMARY

Polymers are macromolecules that are formed by the covalent bonding of many monomer subunits which have small molecular weight. In general, small-molecule substances are found in the gas or liquid state of the substance, whereas polymers are generally solid and hard materials because they are larger molecules. The melting and boiling points of polymers are considerably higher than the monomers that form them. Due to these features, its usage areas are quite wide. Polymers can be classified as synthetic and natural, as well as organic and inorganic. In the structure of organic polymers, there is usually a hydrogen atom next to the carbon atom, while in inorganic polymers there may be atoms such as phosphorus, sulfur, and silicon next to the carbon atom. Synthetic and naturally occurring polymers are found in almost every part of daily life. Polynucleotides, polypeptides, and polysaccharides found in our body are natural biopolymers, while polymers such as polystyrene, polyvinylchloride, and polyethylene used in aviation, automotive, white goods, and electronics industries are synthetic. Semi-synthetic polymers have also been obtained by using additives over natural polymers over time. An example of this is the semi-synthetic celluloid used in the making of photographic films. Polymers are materials that are reasonably priced, whose mechanical properties can be adjusted as desired, can serve different purposes, and can be derivatized on purpose. The properties of polymers such as elasticity, crystalline, semi-crystalline, and amorphous can be adjusted by the selection of the monomers that make them up.

Polymer molecules were initially thought to be cyclic or colloidal. For the first time in 1920, Nobel laureate Hermann Staudinger suggested that these molecules are long molecules with a chain structure, but this proposition was not accepted until 1930. In the following years, the existence of polymers was supported by the studies of scientists such as Herman Francis Mark and Wallace Hume Carothers. Historically, the use of NMR, FTIR, Raman spectroscopy, and X-ray analysis techniques have also been important steps in the development of polymer chemistry. During this development period, widely used polymers such as polyacrylonitrile, polyvinyl acetate, polyurethane, and Teflon have emerged.

Polymerization methods can be kinetically divided into two classes: step-growth polymerization and addition (chain-growth) polymerization. These techniques can also be classified according to the propagation methods of polymer chains. While radical, cationic, and anionic reactions take part in the propagation steps of the chains in the addition polymerization technique, polyaddition and polycondensation reactions form the propagation steps of the chains in the step-growth polymerization method.

Photopolymerization is a polymerization process that uses electromagnetic radiation to convert functional monomers into polymers. Photopolymerization methods offer new approaches to synthesis techniques that have been studied with interest in industry and academic research. With the different polymerization techniques that these methods contain, they are used in many areas such as coatings, adhesives, 3-D printing, nanomaterials, artificial organs, dental filling materials.

In 1937, Paul Flory proposed that radical polymerization comprises of initiation, propagation, and termination steps. In the photopolymerization method initiated by electromagnetic radiation, chain reactions occur by following the initiation, propagation, and termination steps. First, molecules called photoinitiators absorb the rays of specific wavelengths and undergo photochemical decomposition and active species are formed. These active species start to add to their own structure from the monomer molecules in the environment and thus the first monomeric active center is formed and this is the initiation step. In addition, the active centers can be free radicals or they can be cationic or anionic. Then, other monomers in the environment begin to join this active center. Thus, after the initiation step, the propagation step is started and higher mass polymer chains are formed with each monomer molecule that joins the active centers. In the termination step, dead polymer chains are formed as a result of the interaction of the active chains with each other. In addition, chains in the propagation step are also terminated by hydrogen transfer between them, but since by-products may occur by virtue of chain transfer reactions, the molecular mass of the prepared polymer can often decrease.

Photoinduced cationic polymerization has received less attention than photoinitiated free-radical polymerization, which has been researched for more than 60 years. The main reason for the relatively slow development in this field is the lack of suitable photoinitiators that can effectively initiate cationic polymerization. Studies on diazonium salt initiators in the 1960s changed the situation significantly. In the same years, the discovery of onium salts or organometallic compounds, which have a high sensitivity to light and high activity, started a rapid and promising development in cationic polymerization, which also allowed radical and cationic reactions to occur simultaneously in hybrid systems.

Photopolymerization methods have superior features such as lower energy requirement, less solvent usage, and higher reaction rate compared to equivalent conventional methods. Light sources such as the Sun, fluorescent lamps, LEDs, incandescent bulbs and lasers can be used in such reactions. Although photopolymerization reactions can be carried out by initiating anionic, cationic, and radical centers, cationic and radical polymerization techniques are used more. In the industrial field, free radical photopolymerization methods play a more active role.

Photoinitiators present together with monomers in the reaction ambient play the main role in the initiation of photopolymerization reactions. Onium salt derivatives are widely used photoinitiators. Onium salt derivatives are widely used photoinitiators. While the cationic components of such onium salts determine the properties of the salt such as molar absorption coefficient, quantum yield, thermal stability, the anionic components affect properties such as acid strength, nucleophilic activity, initiation efficiency, and rate constant. Free radical species are formed as well as Bronsted acids formed by the decomposition of these salts, and for this reason, there are possibilities to be used in both radical and cationic polymerization techniques. In addition to these advantages, it is a disadvantage that they are activated with short-wavelength beams and therefore relatively higher energy beams. In this case, by adding molecules called photosensitizers to the reaction system, the wavelength of the light used is increased and photopolymerization reactions can be carried out with lower-energy beams. Photosensitizers absorb light and thus become excited, then transfer their energy to another molecule and do not participate in the reactions, with some exceptions. These molecules, which are generally polyaromatic hydrocarbons and have a conjugated structure, allow photopolymerization reactions to take place at relatively higher wavelengths.

Within the scope of this thesis, photoinitiator systems suitable for use in both cationic and radical photopolymerization techniques, which can operate at NIR region by increasing the wavelength at which photoinitiators, which generally have absorption in the UV region of the electromagnetic spectrum, are activated by using photosensitizer molecules, have been developed and presented to the literature.

RADİKAL VE KATYONİK POLİMERİZASYON İÇİN YÜKSEK KONJUGASYONLU GÖRÜNÜR VE NIR BÖLGESİ FOTOBAŞLATICI SİSTEMLERİ

ÖZET

Polimerler çok sayıda küçük mol kütleli monomer altbirimlerinin kovalent bağlar yapmasıyla meydana gelen makromoleküllerdir. Genelde küçük moleküllü maddeler maddenin gaz ya da sıvı halinde bulunurlar oysa polimerler daha büyük moleküller olmaları sebebi ile genelde katı ve sert malzemelerdir. Polimerlerin erime ve kaynama noktaları kendilerini oluşturan monomerlere göre oldukça yüksektir. Bu özellikleri sebebi ile kullanım alanları oldukça geniştir. Polimerler sentetik ve doğal olarak sınıflandırabilecekleri gibi organik ve inorganik olarak da sınıflandırılabilirler. Organik polimerlerde karbon atomu yanında genelde hidrojen atomu yer alırken, inorganik polimerlerde karbon atomu yanında fosfor, sülfür, silisyum gibi atomlar bulunabilmektedir. Sentetik ve doğal olarak bulunan polimerler günlük yaşamın hemen her yerinde bulunurlar. Havacılık, otomativ, beyaz eşya, elektronik sektörlerinde kullanılan polistiren, polivinilklorür, polietilen gibi polimerler sentetik iken vücudumuzda bulunan polinükleotitler, polipeptitler, polisakkaritler doğal biyopolimerlerdir. Doğal polimerler üzerinden zamanla katkı maddeleri kullanılarak yarı sentetik polimerler de elde edilmiştir. Fotoğraf filmlerinin yapımında kullanılan yarı sentetik selüloid buna bir örnek oluşturur. Polimerler makul fiyatlı, mekanik özellikleri arzulanan şekilde ayarlanabilen, farklı amaçlara hizmet edebilen ve amaca binaen türevlendiribilen maddelerdir. Polimerlerin elastikiyet, kristal, yarı kristal ve amorf gibi özellikleri, kendilerini oluşturan monomerlerin seçimleri ile ayarlanabilmektedir.

Polimer moleküllerinin ilk zamanlar halkalı veya kolloidal yapıda oldukları zannediliyordu. 1920 yılında ilk kez, Nobel ödülü sahibi Hermann Staudinger tarafından bu moleküllerin zincir yapısına benzeyen uzun zincirli makromoleküller olduğu öne sürülmüş ancak bu önerme 1930 yılına kadar kabul görmemiştir. Sonraki yıllarda Herman Francis Mark, Wallace Hume Carothers gibi bilim insanlarının yaptığı çalışmalarla polimerlerin varlığı önermesi destek görmüştür. Tarihsel süreçte NMR, FTIR, Raman spektroskopisi ve X-ışını analiz tekniklerinin kullanımı da polimer kimyasının gelişmesinde önemli basamaklar olmuştur. Bu gelişim yıllarında poliakrilonitril, polivinilasetat, poliüretan ve teflon gibi yaygın kullanılan polimerler ortaya çıkmıştır.

Polimerizasyon metodları kinetik olarak basamaklı polimerizasyon ve katılma polimerizasyonu olmak üzere iki sınıfta incelenebilirler: Basamaklı polimerizasyon ve katılma polimerizasyonu. Bu polimerizasyon yöntemleri de kendi içlerinde polimer zincirlerinin büyüme yöntemlerine göre sınıflandırılabilirler. Radikal, katyonik ve anyonik reaksiyonlar katılma polimerizasyon tekniğinde zincirlerin büyüme adımlarında rol alırlarken, polikatılma ve polikondenzasyon reaksiyonları

basamaklı polimerizasyon tekniğinde zincirlerin büyüme adımlarında yer alan reaksiyonlardır.

Fotopolimerizasyon yöntemi, fonksiyonel gruplara sahip monomerlerin elektromanyetik radyasyon kullanılarak polimerler haline getirildiği polimerizasyon tekniğidir. Fotopolimerizasyon yöntemleri, endüstri ve akademik araştırma alanlarında ilgiyle çalışılan sentez tekniklerine yeni yaklaşımlar sunar. Bu yöntemlerin içerisinde barındırdığı farklı polimerizasyon teknikleri ile kaplamalar, yapıştırıcılar, 3-D baskı, nanomateryaller, yapay organlar, diş dolgu malzemeleri, elektronik parçalar gibi birçok alanda amaca binaen kullanımları mevcuttur.

1937 yılında Paul Flory radikalik polimerizasyonun başlama, büyüme ve sonlanma adımlarından oluştuğunu öne sürmüştür. Elektromanyetik radyasyon ile başlatılan fotopolimerizasyon yönteminde de zincir reaksiyonlar başlama, büyüme ve sonlanma adımlarını izleyerek meydana gelirler. İlk olarak fotobaşlatıcı denen moleküller, üzerlerine gelen spesifik dalga boyundaki ışınları absorplayarak fotokimyasal bozunmaya uğrarlar ve aktif türler oluşur. Bu aktif türler kendi bünyelerine ortamda bulunan monomer moleküllerinden katmaya başlarlar ve böylelikle ilk monomerik aktif merkez oluşur ve bu ilk başlama adımıdır. Ayrıca aktif merkezler serbest radikaller olabileceği gibi katyonik veya anyonik türde de olabilirler. Ardından bu aktif merkeze ortamda bulunan diğer monomerler katılmaya başlar. Böylece başlama adımının ardından büyüme adımına geçilir ve aktif merkezlere katılan her bir monomer molekülü ile daha yüksek kütleli polimer zincirleri oluşur. Sonlanma aşamasında ise aktif zincirlerin birbirleriyle olan etkileşimleri sonucunda ölü polimer zincirleri meydana gelir. Ayrıca büyüme aşamasındaki zincirlerin aralarında hidrojen transferi yaparak da sonlanmaya uğramaları söz konusudur ancak zincir transfer tepkimeleri sonucunda yan ürünler meydana gelebileceğinden çoğu zaman hazırlanan polimerin molekül kütlesi azalabilir.

Fotobaşlatılmış katyonik polimerizasyon, 60 yıldan fazla bir süredir üzerinde çalışılan fotobaşlatılmış serbest radikal polimerizasyonundan daha az ilgi görmüş olan bir yöntemdir. Bu alandaki nisbi olarak yavaş gelişimin temel nedeni katyonik polimerizasyonu etkin şekilde başlatabilecek uygun fotobaşlatıcıların mevcut olmamasıdır. 1960'lı yıllarda diazonyum tuzu başlatıcılarının üzerinde çalışılması durumu önemli ölçüde değiştirmiştir. Aynı yıllarda ışığa karşı önemli derecede duyarlılık ve yüksek etkinliğe sahip olan onyum tuzlarının veya organometalik bileşiklerin keşfi katyonik polimerizasyonda hızlı ve umut vadedici bir gelişme başlatmıştır ve bu durum hibrit sistemlerde radikal ve katyonik reaksiyonların eşzamanlı olarak gerçekleşmesine de olanak sağlamıştır. Her iki polimerizasyon tekniği için de fotobaşlatıcı sistemler üzerinde araştırmalar devam etmektedir.

Fotopolimerizasyon methodlarının muadili konvansiyonel methodlara nazaran daha düşük enerji gereksinimi, daha az solvent kullanımı ve daha yüksek reaksiyon hızı gibi üstün özellikleri mevcuttur. Bu tür reaksiyonlarda en optimum ışık kaynağı olmakla Güneş, floresan lambalar, ledler, akkor ampuller ve lazerler gibi ışık kaynakları kullanılabilmektedir. Fotopolimerizasyon reaksiyonları anyonik, katyonik ve radikal merkezler üzerinden başlatılarak yürütülebilse de katyonik ve radikalik polimerizasyon tekniklerinden daha fazla yararlanılmaktadır. Endüstriyel alanda ise serbest radikal fotopolimerizasyon yöntemleri daha etkin rol oynar.

Fotopolimerizasyon reaksiyonlarının başlangıcında ortamda monomerlerle birlikte bulunan başlatıcılar rol oynar. Onyum tuzu türevlerinde bulunan moleküller yaygın olarak kullanılan fotobaşlatıcılardır. Bu tür onyum tuzlarının katyonik bileşenleri tuzun molar absorpsiyon katsayısı, kuantum verimi, termal kararlılık gibi özelliklerini belirlerken, anyonik kısımlarını asit kuvvetti, nükleofil özelliği, başlatma etkinliği, hız sabiti gibi özellikleri etkilerler. Bu tuzların bozunması ile oluşan Bronsted-Lowry asitlerinin yanı sıra serbest radikalik türler de meydana gelmektedir ve bu sebeple hem radikal hem de katyonik polimerizasyon tekniklerinde kullanılma olanakları mevcuttur. Bu avantajlarının yanı sıra düşük dalga boyunda ve dolayısı ile nisbi olarak daha yüksek enerjili ışınlarla aktive olmaları dezavantaj oluşturur. Bu durumda reaksiyon sistemine fotouyarıcı denen moleküller eklenerek, kullanılan ışığın dalga boyu yükseltilir ve daha düşük enerjili ışınlarla fotopolimerizasyon reaksiyonları gerçekleştirilebilir. Fotouyarıcılar ışığı absorplarlar ve böylelikle uyarılmış hale geçerler, ardından üzerlerindeki enerjiyi bir başka moleküle aktarırlar ve bazı istisnalar hariç reaksiyonlara katılmazlar. Poliaromatik hidrokarbonlardan oluşan ve konjuge bir yapıya sahip olan bu moleküller ile fotopolimerizasyon reaksiyonlarının nisbi olarak daha yüksek dalga boyunda gerçekleşmelerine olanak sağlanır.

Bu tez kapsamında, fotopolimerizasyon reaksiyonlarında kullanılan fotouyarıcılar ve fotobaşlatıcılar arasında gerçekleşen fotoeletkron transfer reaksiyonları incelenmiş ve bir mekanizmada gösterilmiştir. Bununla birlikte, genellikle elektromanyetik spektrumun UV bölgesinde absorpsiyona sahip olan fotobaşlatıcıların, fotouyarıcı moleküller kullanılarak aktive oldukları dalga boyu yükseltilip, NIR bölgede çalışabilen, hem katyonik hem de radikalik fotopolimerizasyon tekniklerinde kullanıma uygun fotobaşlatıcı sistemler geliştirilip literatüre sunulmuştur.

1. INTRODUCTION

Photopolymerization reactions are the types of reactions in which the monomers present in the reaction ambient undergo polymerization in the presence of photoinitiator molecules utilizing light energy [1]. When photoinitiator molecules absorb light at a certain wavelength, they create active species that can start polymerization processes, and thus the first monomeric active center is formed in the reaction medium with the interaction between monomers and these species. Monomeric active centers formed continue to add monomer molecules to themselves and thus polymer molecules start to form. The mechanisms of photoinduced radical and cationic polymerization reactions have been investigated within the scope of this thesis, and the polymer molecules obtained by using these polymerization methods have been examined by instrumental analysis methods. Light-induced polymerization reactions have some advantages compared to traditional polymerization methods with aspects such as less energy consumption [2,3], lessened solvent use [4,5], and higher efficiency [6,7]. These advantages have played a leading role in the production of a large number of products that can be obtained by photopolymerization methods. Coatings [8], 3-D printings [9], adhesives [10], electronics [11], artificial organs [12], nanomaterials [13], and dental filling [14,15] materials can be given as examples in the main areas where the products are obtained by applying photopolymerization methods. The majority of researches in the subject of photopolymerization has focused on free radical polymerization (FRP) methods. Recently, however, scientists have carried out studies to obtain polymer networks by utilizing radically and cationically polymerizable monomers with suitable photoinitiator systems [16-18]. When the formulations are exposed to UV light, onium salt type PIs are able to generate hybrid cross-linked systems. Iodonium salts with large, non-nucleophilic counter anions, such as diphenyl iodonium (DPI) salts, are the most common onium salts. When irradiated at the proper wavelength, these salts can easily undergo photochemical decomposition, resulting in active species capable of initiating both radical and cationic polymerizations. The main downside of DPI salts is their spectrum sensitivity in the UVB area (below 300 nm), which is a serious health problem since UVB is hazardous to living beings and can cause eye damage, as well as a substantial industrial disadvantage [19]. The spectral sensitivity of DPI salts can be widened to the visible region by the use of suitable free radical photoinitiators [20] and photosensitizers [21,22]. According to the mechanism given in Scheme, polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, anthracene, pyrene can successfully be employed for the photosensitization of aryliodonium salts in the visible light range, which has been shown by Crivello and coworkers (Figure 1.1) [23].

In our group, we also showed that highly conjugated thiophene derivatives can form radical and cationic active species by undergoing photoinduced electron transfer reactions when illuminated under the light corresponding to the visible region in the electromagnetic spectrum [24].

While most photoinitiators generate active species under visible light, photopolymerization reactions that can be carried out under NIR irradiation are very limited [25]. The ability of NIR light to penetrate deeper into the matter is also a desirable feature as well as lower energy consumption [26] and heat release [27] in photocuring applications [28].

Photopolymerization reactions conducted at NIR region are carried out using NIR light-absorbing dyes, which are electron donors that can undergo effective photoinduced electron transfer reactions with OS (OS couples/cyanine) [26,29,30] or upconverting nanoparticles (UCNP) that can upconvert the incident light to higher energy light corresponding to the near UV region. As a result, photopolymerization procedures are executed by transforming a high-wavelength entering beam into a lower-wavelength, higher-energy beam. The application of UCNPs in NIR irradiation polymerization reactions [31,32], on the other hand, is limited due to thermal loss of light energy [33,34] and the need for costly laser systems beaming intense light [35].

Given this context, we provide a novel class highly conjugated visible and NIR light photoiniating systems based on thiophene substituted [1,2,5]-thiadiazolo and [1,2,5]-selenadiazolo [3,4-f]-benzo [1,2,3] triazole, respectively in combination with diphenyliodonium hexafluorophosphate (DPI) for radical and cationic polymerizations of various monomers by utilizing a low-cost incandescent light source. The described method has also been shown to be appropriate to hybrid polymerizations in which both radical and cationic polymerizations occur concurrently.

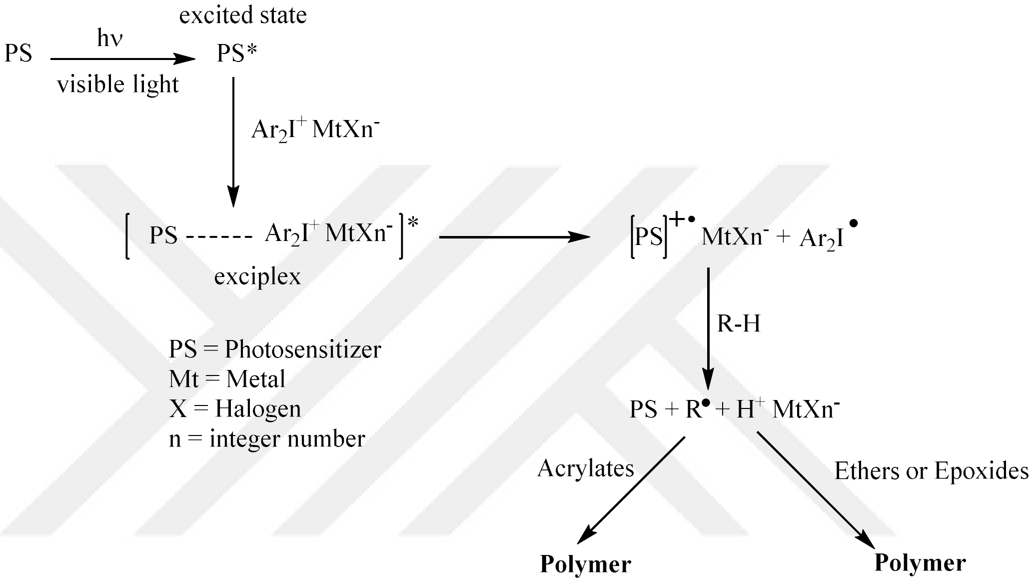


Figure 1.1 : PAH photosensitized radical and cationic polymerization pathway of aryliodonium salts.

2. THEORETICAL PART

2.1 Photopolymerization

Photopolymerization reactions have an important place in today's technology in academic research and industrial applications. It is a technique that is used in the production of polymer materials found in almost every part of our lives and continues to be developed day by day. In photopolymerization reactions, light energy replaces the thermal energy used in polymerization processes in conventional reactions [36,37]. By using light instead of heat energy, it provides advantages such as lower energy requirement, ability to carry out solvent-free reactions, high reaction rates at room temperature. There is also a wide range of monomer types suitable for use in photopolymerization reactions, providing an advantage in product diversity. Photopolymerization reactions are effectively utilized in areas such as 3-D printers, artificial organs, electronics, adhesives, coatings, and nanoparticles [38-44].

The components of the photopolymerization mechanism are photoinitiators, which can form reactive species when illuminated with light of appropriate wavelength, monomers containing functional groups on them, and photosensitizers, which sometimes form complexes with initiator molecules as a result of excitation with the light they absorb. The photoinitiator that absorbs the incoming light undergoes photochemical degradation, and active species are formed and the first active center is formed, which takes part in the formation of polymer chains by adding the existing monomers in reaction ambient to their structure (Figure 2.1) [1].

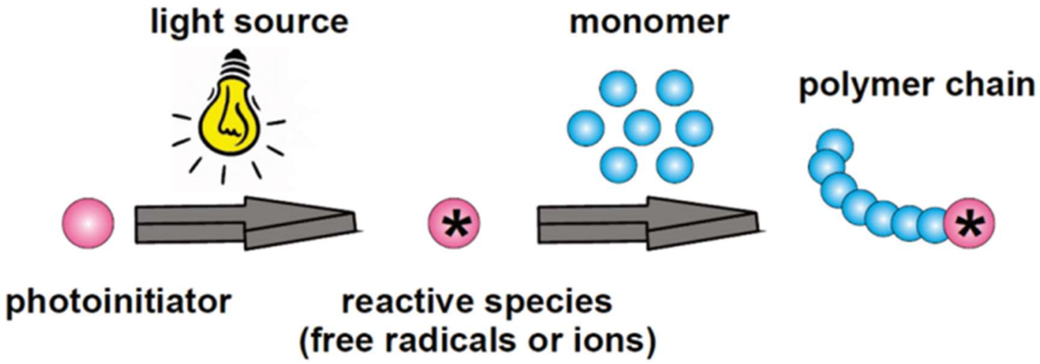


Figure 2.1 : A general aspect to photopolymerization reactions.

These active centers formed can be radical, cationic, or anionic and are preferred with suitable initiators selected according to the polymerization technique [45].

Addition polymerization methods can be classified as radical, cationic, and anionic mechanisms according to the active centers that play role in propagating chains. Photopolymerization techniques can also be examined under these headings.

2.1.1 Photoinitiated cationic polymerization

Although free radical polymerization has been a topic for a much longer time than cationic polymerization, it has shortcomings such as being affected by the inhibition of diradical oxygen in the air and limitations in post-cure modifications that can affect the main product. Due to the lack of suitable photoinitiators in cationic polymerization, its progress was slower than in radical polymerization. In the late 1970s, the synthesis of onium salts suitable for the initiator role in cationic polymerization increased the interest in studies on cationic polymerization. Iodonium and sulfonium salts are the most commonly used photoinitiators in cationic polymerization [46-48].

Cationic polymerization has advantages over radical polymerization such as lower volume shrinkage and not being affected by oxygen inhibition. Cationic photopolymerization eliminates volatile emissions, high viscosity, molecular oxygen inhibition limits, and toxicity issues. Furthermore, cationically polymerizable monomers like vinyl ethers [49,50] and epoxides go through a process known as dark polymerization, in which they slowly polymerize without being exposed to light [51]. The most common cationically polymerized monomers are epoxides [52] and vinyl ethers [53].

Epoxy monomers have rings in their structure, and when they react, these rings open, and other chemical bonds are formed. The volume change in ring-opening reactions is very small because the number and type of chemical bonds are the same before and after the reaction. Surface coatings, printing plates, and photoresists are some of the most popular areas for cationic polymerization. [54].

The photoinitiated cationic polymerization method can be examined under two subheadings, direct and indirect, in terms of the initiation of the reactions [55].

2.1.1.1 Direct initiation

In the cationic photopolymerization method, in which the polymerization process starts directly, the photoinitiator decomposes by absorbing the light at the appropriate wavelength, and the reactive species radical cation and protonic acid are formed, and these active species react with the cationically polymerizable monomer and the polymer chain starts to propagate (Figure 2.2) [56].

Generally, the photoinitiator molecules used here are those that absorb the light at the wavelength in the UVA/UVB/UVC regions of the electromagnetic spectrum [57], and it has been desired to operate the initiator systems at higher wavelengths than the wavelengths at which they are activated, in order to protect healthy problems caused by UV light and to develop an alternative in the industry [58].

One of the most beneficial properties of onium salts used in cationic polymerization is that the anions they contain are non-nucleophilic and do not have a negative effect on the course of the polymerization, which could suppress the propagation of polymer chains if these anions were not non-nucleophilic [59].

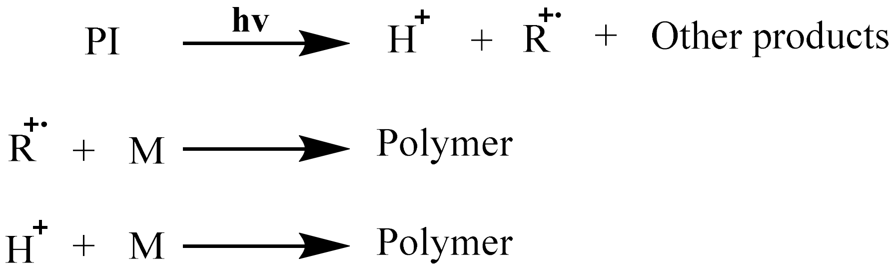
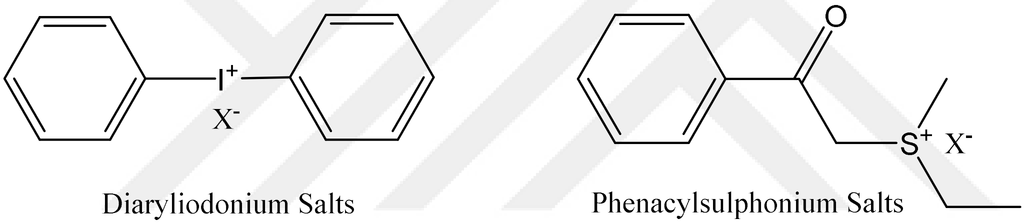


Figure 2.2 : Direct initiation in photoinduced cationic polymerization.

Onium salts

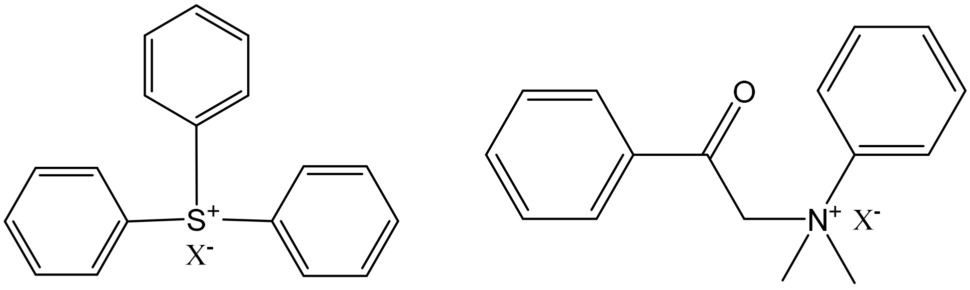
Among the cationic photoinitiators, onium salts are the most often utilized photoinitiators with short-wavelength absorption in the UV region of the electromagnetic spectrum [60]. The spectral sensitivity of onium salts can be tuned to the visible region by techniques such as charge transfer complex formation and free radical promotion. Photosensitizers such as anthracene, perylene, phenothiazine can form excited complexes with onium salts when they absorb light of a particular wavelength [61].

Ground state charge transfer complex generation between electron donor compounds and alkoxy pyridinium salts is another way to initiate cationic polymerization in the visible region [62]. Some often use onium salts were as given below (Figure 2.3).



Diaryliodonium Salts

Phenacylsulphonium Salts



Triarylsulphonium Salts

Phenacylammonium Salts

Alkoxypyridinium Salts

Diazonium Salts

Figure 2.3 : Some often use onium salt photoinitiators.

Cationic components of onium salts determine their photochemical properties (quantum yield, molar absorption coefficient, thermal stability, photosensitization), while anionic components determine dominant properties (nucleophilicity(ion pairing), anion stability, acid strength, propagation rate constants, initiation efficiency) in polymerization reactions. The most commonly used onium salts are diaryliodonium salts, which are easy to obtain, and the photolysis mechanism is as follows (Figure 2.4) [63-64].

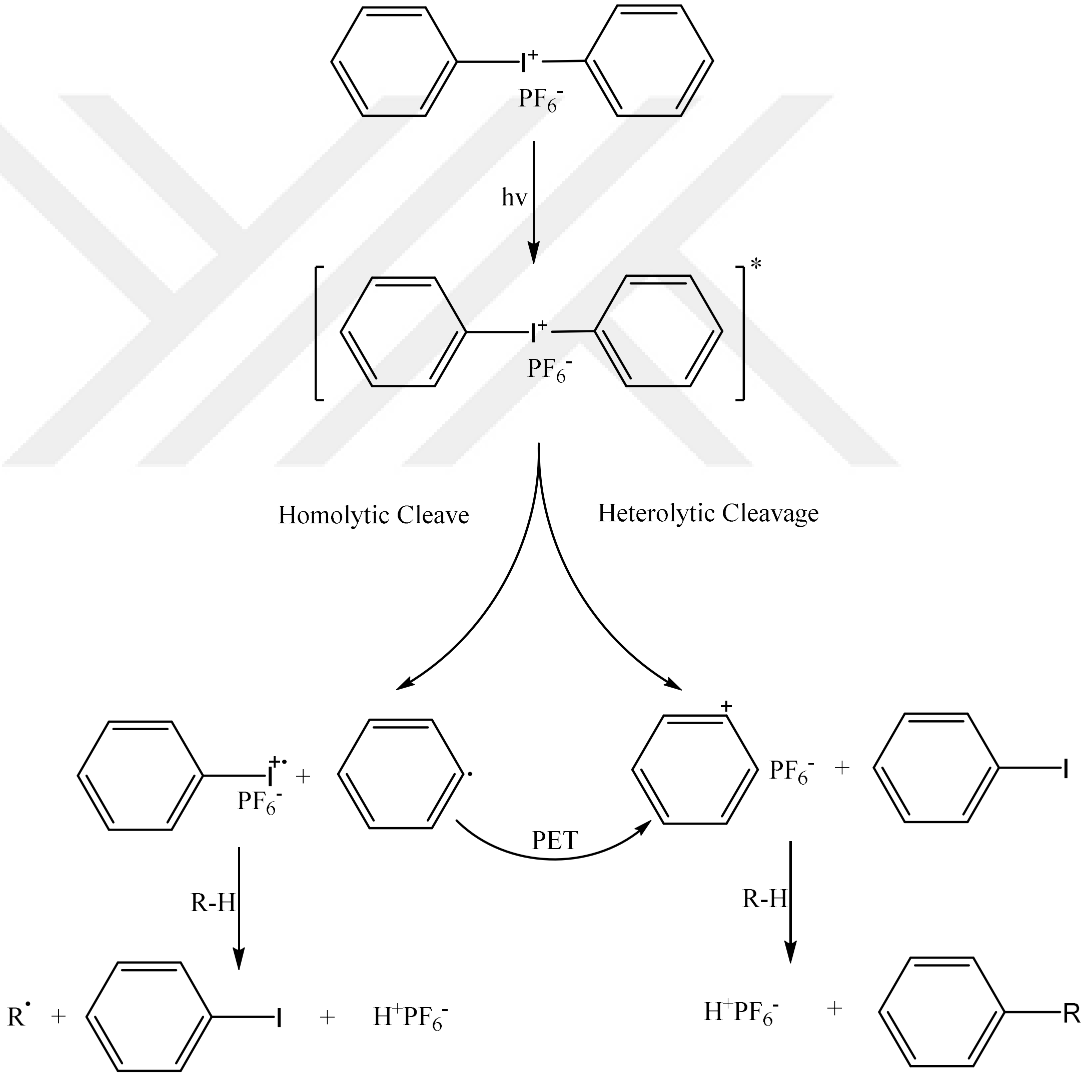


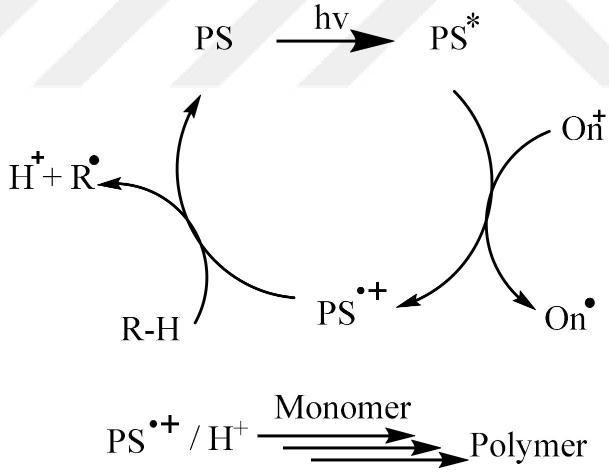
Figure 2.4 : Photodegradation of diphenyliodonium hexafluorophosphate photonitiator.

2.1.1.2 Indirect initiation

In photopolymerization processes, chemical reactions are initiated by incident light at the wavelength initiating molecules absorb, and therefore the wavelength of the light to be used is selected according to the initiator molecule. However, most initiator molecules have the ability to absorb in the UV region, which requires relatively higher energy. In order to overcome this problem, complexes are formed by using some electron-rich compounds in addition to the initiator molecules. In such alternative ways, the wavelength of the light to be used can be made longer than the wavelength at which the photoinitiator absorbs [65,66].

Photosensitization via exciplex formation

The photosensitization process is the electron transfer process that takes place in the near-UV or visible region between the photosensitizer molecules and onium salts, and it is also known as photoinduced electron transfer (Figure 2.5) [67,68].



RH: solvent or monomer

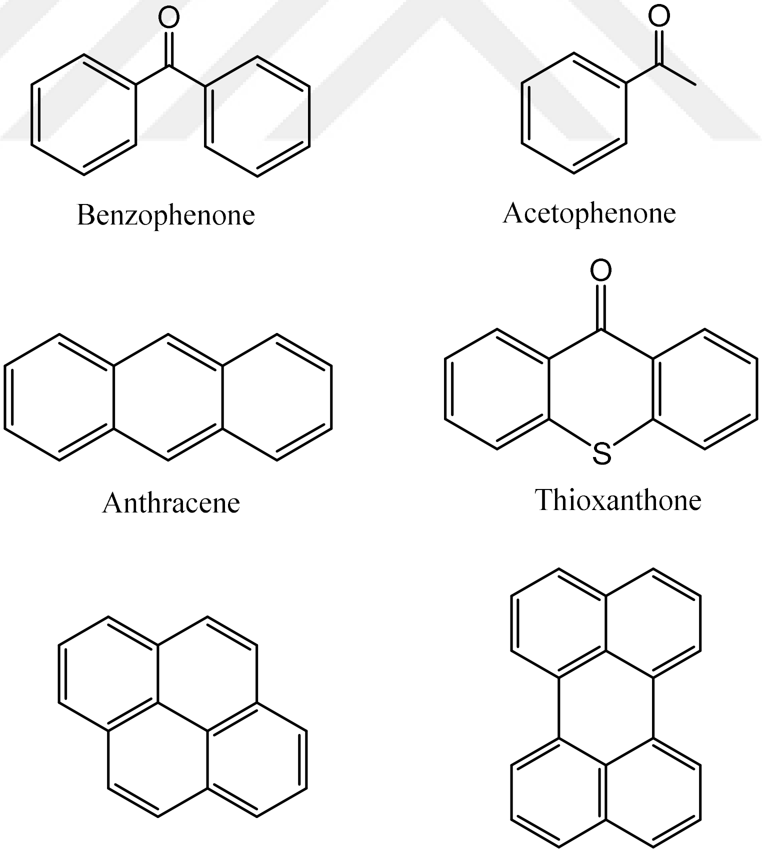
Figure 2.5 : Photosensitization between photosensitizer and onium salt in initiation of cationic polymerization.

It is assumed that the photosensitization process between the photosensitizer and the ground state onium salt will only take place when the Gibbs free energy change value for the PET process is negative. The free energy change is estimated utilizing the Rehm-Weller equation (Eq: 2.1).

$$\Delta G_{et} = f_c\left[E^{ox}_{1/2}(D/D^{\cdot+}) - E^{red}_{1/2}(A/A^{\cdot-})\right] - E^* + \Delta E_c \qquad \mathbf{(2.1)}$$

where f_c is the Faraday constant, $E^{ox}_{1/2}(D/D^{\cdot+})$ is the oxidation potential of the donor (D), $E^{red}_{1/2}(A/A^{\cdot-})$ is the reduction potential of the acceptor(A), E^* is the singlet or excited-state energy of the photosensitizer, and ΔE_c is the Coulombic stabilization energy [69,70].

Photosensitizers, which have the ability to absorb higher wavelength light than onium salts, are widely used in industry and medical applications. There are also photosensitizers such as IR-780 iodide, IR-740 perchlorate, indocyanine green, which have absorption in the NIR region of the electromagnetic spectrum. Examples of commonly used photosensitizers are benzophenone, acetophenone, anthracene, thioxanthone, perylene, pyrene (Figure 2.6). In addition, porphyrin, chlorin, and bacteriochlorin are photosensitizers that are widely used in photodynamic therapy applications in the medical field [71].



Benzophenone Acetophenone

Anthracene Thioxanthone

Pyrene Perylene

Figure 2.6 : Some often used photosensitizers.

Ground state charge transfer complexes (CTCs)

It has been shown that pyridinium salts form ground state charge transfer complexes with electron-rich donors such as methoxy-substituted benzene [72]. In such complexes, the absorption values of the species forming the complex are lower than their values in the complex state, which means that when they come together, the absorption value increases with the interaction that occurs. In the following mechanism, charge transfer complex formation between N-ethoxy-4-cyano pyridinium hexafluorophosphate and 1,2,4 trimethoxybenzene and subsequent electron transfer mechanism was depicted in Figure 2.7 [73]. While the individual absorption values of the components were 270 and 265 nm, respectively, they showed maximum absorption at 420 nm in the complex.

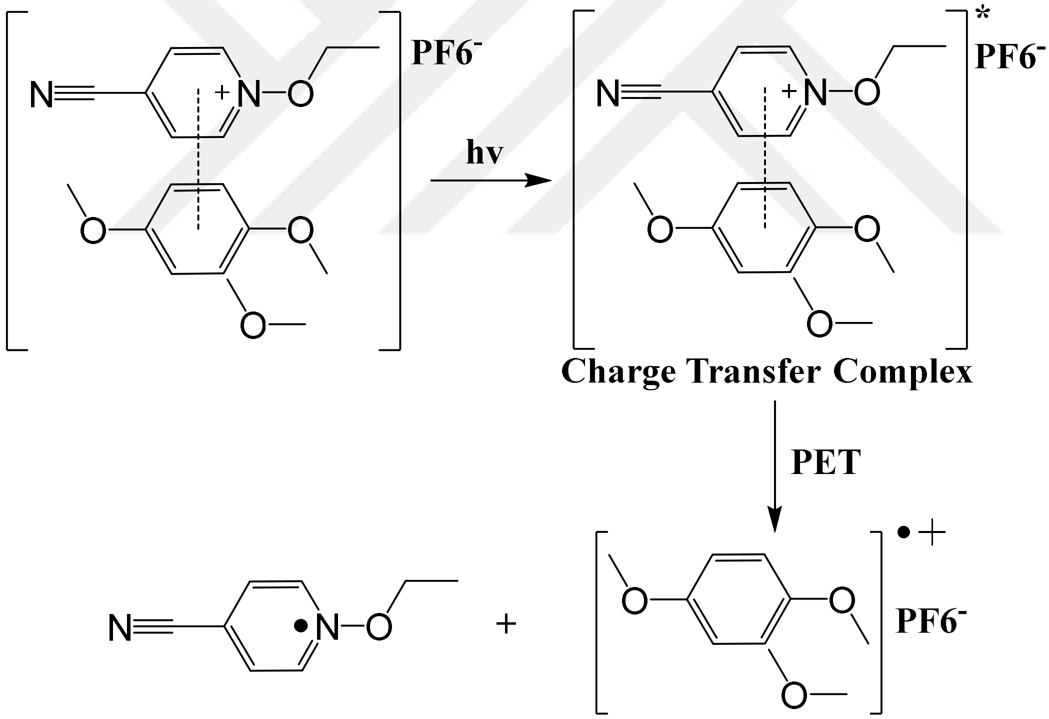


Figure 2.7 : The mechanism of PET reactions in charge-transfer complexes.

2.1.1.3 Photoinduced free-radical promoted cationic polymerization

One of the disadvantages of the commonly used onium salts is that they absorb light at the short-wavelength and therefore it is necessary to use higher energy light sources for their photoactivity. In order to overcome this problem, indirect photolysis processes have been applied [74].

Onium salts are compounds that can be easily reduced by electron donor compounds, and they oxidize electron donor free radicals to form carbocations necessary for the initiation of cationic polymerization. This method, known as free-radical promoted cationic polymerization, enables the cationic polymerization process with onium salts to take place with longer wavelength light [75-77]. In this method, the spectral sensitivity of the system can be adjusted with the meticulously selected initiators. *Type I* photoinitiators are excellent promoters for cationic polymerization as they can easily oxidize free radicals by unimolecular bond cleavage (Figure 2.8) [78]. In addition, derivatives of *Type I* photoinitiators have also been synthesized for use in such reactions [79].

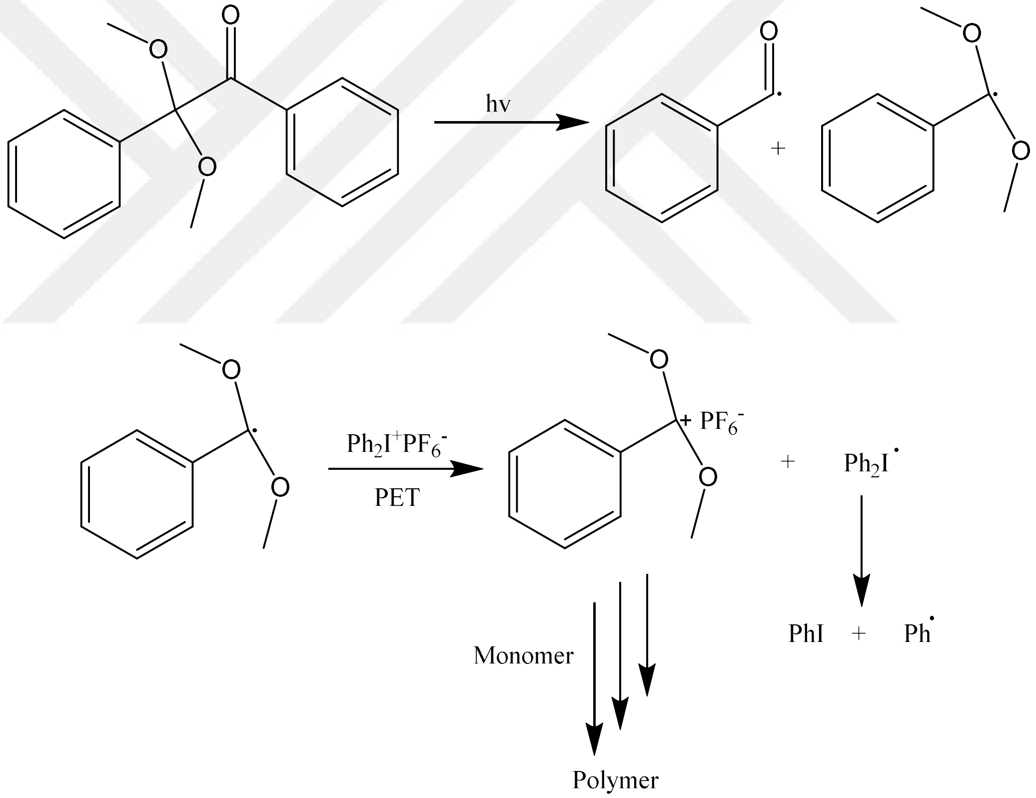


Figure 2.8 : Photoinduced free-radical promoted cationic polymerization mechanism.

2.1.1.4 Photoinduced living cationic polymerization

In this method, controlled/living cationic polymerization can be performed using Lewis acids. For example, there is a growing cationic chain in the cationic polymerization of vinyl ether monomers, and the carbocation centers in this growing chain are stabilized by Lewis acids (Figure 2.9). Thus, cationic polymerization proceeds in a controlled/living manner accompanied by the coordination of Lewis acids, and the molecular weight distributions of the polymers can be controlled [80-83].

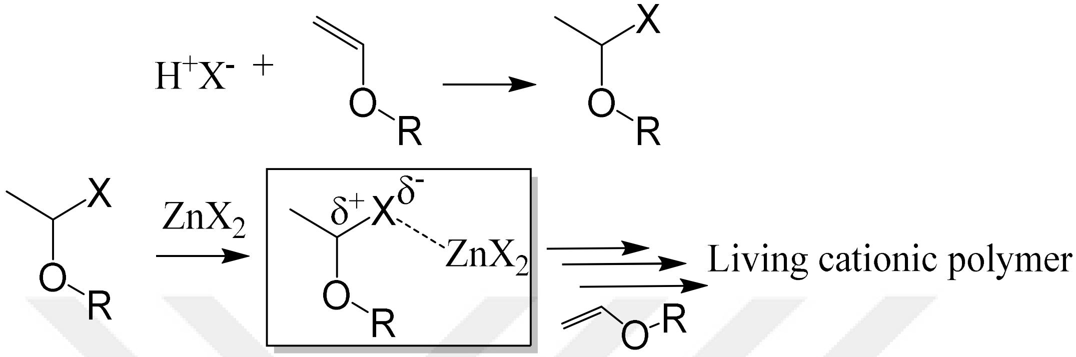


Figure 2.9 : Controlled living cationic polymerization towards Lewis acids.

2.1.2 Photoinitiated free radical polymerization

Free radical polymerization is a polymerization technique that has been studied for more than 60 years and the mechanisms of the reactions have been clarified as much as possible. Acrylate and methacrylate monomers have been widely used in radical polymerization for years. The reason for this is that these substances have high reactivity and allow the production of substances with different properties. Despite its widespread use, an important disadvantage of radical polymerization is the inhibition effect of atmospheric oxygen during the polymerization process.

The reaction mechanism of photoinitiated radical polymerization can be distinguished as initiation, propagation, chain transfer, and termination steps [84]. Photoinitiators used in photoinitiated radical polymerization are examined under two headings: *Type I* photoinitiators, which form radical species with α-cleavage as a result of light absorption, and *Type II* photoinitiators, which react with an H-donor molecule to form initiating radicals [85].

In this polymerization technique, the photoinitiator molecule, which undergoes decomposition by absorbing light, takes part in the initial step. The interaction of the radicals generated by photolysis with the monomers in the reaction medium results in the formation of monomeric active centers. The initial step can be summarized in two steps as the formation of free radicals formed by the degradation of the photoinitiator and the addition of monomers to form chains (Figure 2.10).

$$\begin{aligned} \mathrm{PI} &\xrightarrow{h\nu} \mathrm{PI}^{*} \\ \mathrm{PI}^{*} &\longrightarrow \dot{R}_1 + \dot{R}_2 \\ \dot{R}_1 + \mathrm{M} &\longrightarrow R_1\text{-}\mathrm{M} \end{aligned}$$

Figure 2.10 : Initiation mechanism of photoinduced free radical polymerization.

Propagation is the step where monomers join active centers one after the other to form polymer chains. The general assumption is that the reactivity of radicals is independent of chain length, meaning that all propagation reactions have the same rate constant. During propagation, a chain is terminated by abstraction of a H atom from the species in the reaction ambient while the formed radical may continue to polymerize. In theory, the propagation step continues until all the monomers in the medium are exhausted, but regardless of the monomers, the radical pairs can react with each other and terminate their activities (Figure 2.11). In addition, the termination step takes place through combination or disproportionation reactions. The combination is a reaction where two growing polymer chains react with each other to form a nonreactive polymer chain. In the disproportionation reaction, a hydrogen atom is transferred from one radical to the other, thus forming two polymer chains with one saturated and the other unsaturated.

$$\left.\begin{aligned} R_1\text{—}M^{\bullet} + M &\longrightarrow R_1\text{—}MM^{\bullet} \\ R_1\text{—}MM^{\bullet} + (n\text{-}2)M &\longrightarrow R_1\text{—}Mn^{\bullet} \end{aligned}\right\}\ \text{Propagation}$$

$$\left.\begin{aligned} R_1\text{—}Mn^{\bullet} + R\text{-}H &\longrightarrow R_1\text{—}MnH + R^{\bullet} \\ R^{\bullet} + M &\longrightarrow R\text{-}M^{\bullet} \end{aligned}\right\}\ \text{Chain Transfer}$$

$$\left.\begin{aligned} R_1\text{—}M_n^{\bullet} + R_1\text{—}M_m^{\bullet} &\longrightarrow R_1\text{—}M_{n+m}\text{—}R_1 \\ R_1\text{—}M_n^{\bullet} + R_2^{\bullet} &\longrightarrow R_1\text{—}M_n\text{—}R_2 \\ R_1\text{—}M_n^{\bullet} + R_1\text{—}M_m^{\bullet} &\longrightarrow R_1\text{—}M_n + R_1\text{—}M_m \\ R_1\text{—}M_n^{\bullet} + R_2^{\bullet} &\longrightarrow R_1\text{—}M_n + R_2 \end{aligned}\right\}\ \text{Termination}$$

Figure 2.11 : The main principal reactions proceeding during photoinduced free radical polymerization.

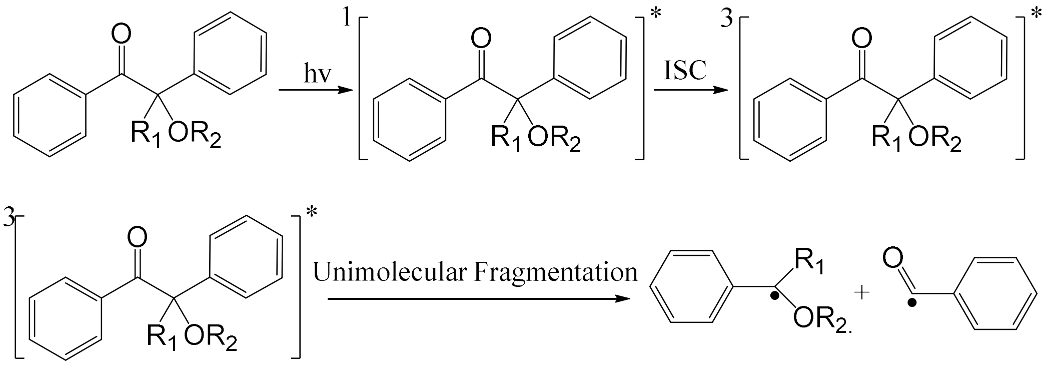
Photoinitiators are molecules that are degraded under light and used to form radicals, and they can be examined under two separate headings as *Type I* and *Type II* according to their photolysis mechanism.

2.1.2.1 *Type I* photoinitiators

Type I photoinitiators are compounds that can form initiator radicals by unimolecular bond cleavage. *Type I* photoinitiators undergo direct fragmentation and active species are formed as a result of homolytic cleavage. Photolysis of the benzoin ether derivative, a Type I photoinitiator, occurs via unimolecular bond cleavage as shown below (Figure 2.12). Almost all *Type I* photoinitiators contain aromatic carbonyl groups, and the commonly used derivatives are compounds such as benzoin ethers, benzyl ketals, acetophenone, benzyl oximes, as shown in Table 2.1 [84, 86-88].

Another term used for photoinitiators is quantum yield. The quantum yield is the ratio of the number of initiating radicals to the number of photons absorbed by the photoinitiator. [89]. Assuming the formation of two radical initiator species with a photon absorbed by a photoinitiator, the quantum yield should theoretically be 2, but the situation is slightly different from this because each initiating radical can give coupling or disproportionation reactions by not adding a monomer to its structure.

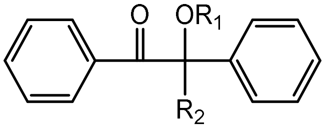
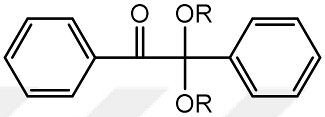
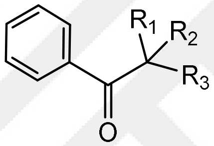
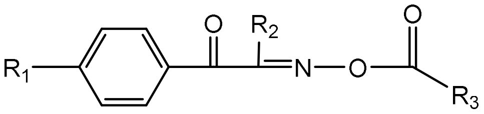
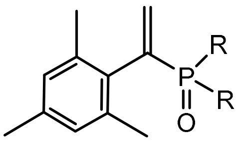
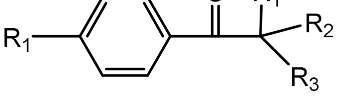
Thus, it can be understood that the quantum efficiency is lower than two, since not every radical species formed does not play an initiator role in initiating the polymerization.



R_1: H, Alkyl, Substituted Alkyl R_2: H, Alkyl, Substituted Alkyl

Figure 2.12 : Direct photolysis mechanism of a *Type I* photoinitiator.

Table 2.1 : Structures and maximum absorption wavelengths of *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_2, CH_3, C_3H_7	365
Acetophenones	 R_1: OCH_3, OC_2H_5 R_2: OCH_3, H R_3: C_6H_5	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 or C_2H_5 R_3: $N(CH_3)_3$, morpholine	320

2.1.2.2 Type II photoinitiators

A Type II photoinitiator, which reacts with a second molecule called co-initiator, undergoes a bimolecular reaction. Thioxanthone can be given as a typical example of photoinduced free radical polymerization using *Type II* photoinitiators (Figure 2.13) [90].

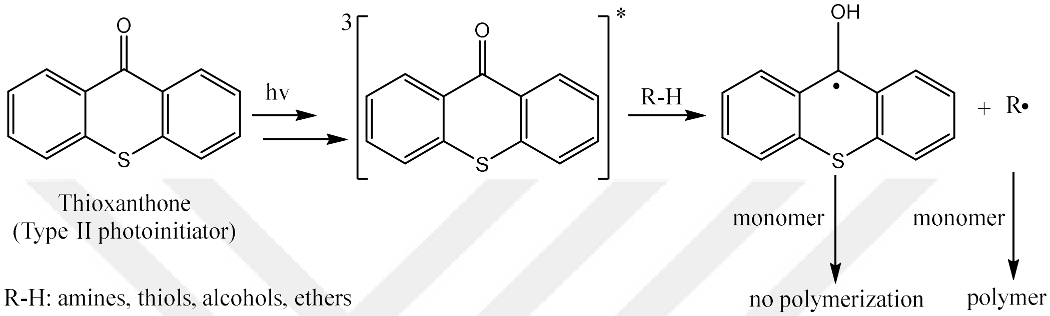
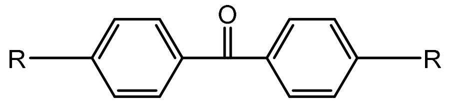
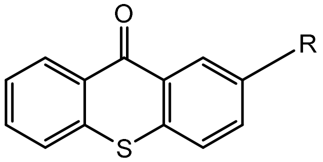
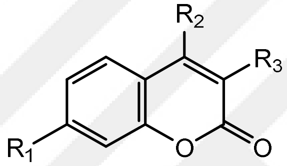
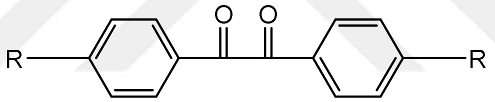
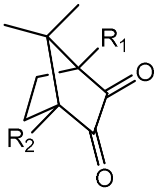


Figure 2.13 : Photoinitiated free radical polymerization by a *Type II* photoinitiator.

Such photoinitiators, after absorbing light of the appropriate wavelength, cause free radical formation by abstraction of an H atom from a co-initiator molecule in the reaction medium. The co-initiator molecule, which forms a free radical with an H abstraction, plays an initiator role in the polymerization reaction by adding monomer to its structure, on the other hand, the radical derivatives of *Type II* photoinitiator molecule can undergo coupling or disproportionation reactions without adding any monomer molecule to its structure [91]. The co-initiator molecules designated herein by R-H may be amine, thiol, alcohol, or ether derivatives. Commonly used *Type II* photoinitiators are thioxanthone [92], benzophenone [93], coumarin [94], benzyl[95], and comphorquinone [96] derivative compounds (Table 2.2) [84].

Table 2.2 : Structures and maximum absorption wavelengths of *Type II* radical photoinitiators.

Photoinitiators	Structure	λ_{max}(nm)
Benzophenones	 R: H, OH, $N(C_2H_5)_2$, C_6H_5	335
Thioxanthones	 R: H, Cl, isopropyl	390
Coumarins	 R_1: $N(C_2H_5)_2$, $N(CH_3)_2$ R_2: CH_3, cyclopentane R_3: H, benzothiazole	370
Benzils	 R: H, CH_3	340
Comphorquinones	 R_1: H, CH_3 R_2: H, CH_3	470

2.1.3 Photoinitiated anionic polymerization

In anionic polymerization method, the active centers in the polymer chains are anionic, and the growth of the chains generally develops over carbanions. The monomers used in this method carry electron-withdrawing groups and these groups make the monomer prone to anionic polymerization. For example, the presence of two electron-withdrawing groups on the methyl cyanoacrylate monomer makes the monomer suitable for anionic polymerization. In addition to vinyl monomers [97] containing electron-withdrawing groups, ethylene oxide [98] and styrene [99] are monomer types that can be polymerized by the anionic polymerization method.

There is not much research on anionic photoinitiators compared to their photoinitiator counterparts in other types of polymerization. Organometallic complexes such as metallocenes, alkyl aluminum porphyrins, and inorganic complexes such as chromium amine thiocyanate are examples of anionic photoinitiators [100]. In anionic polymerization, as in other chain reactions, initiation, propagation, chain transfer, and termination steps are available. The negatively charged part of the initiator molecule joins the monomer to form the first anionic active center and polymerization proceeds over this center as in the ring-opening polymerization of epoxides shown below (Figure 2.14) [101].

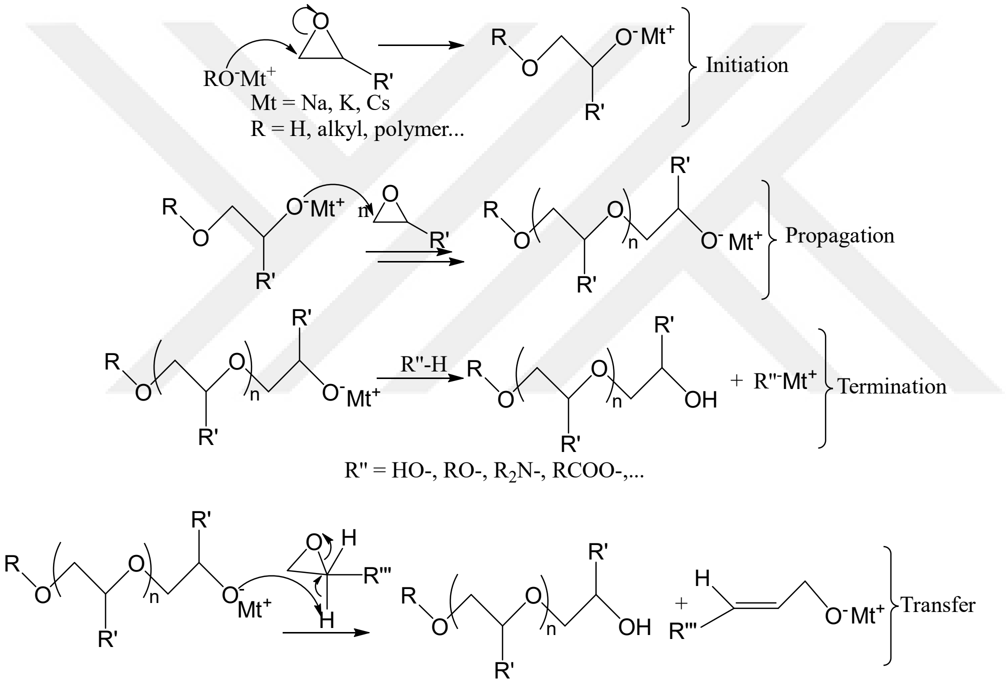


Figure 2.14 : Alkali metal alkoxides initiated anionic ring-opening polymerization.

3. EXPERIMENTAL PART

3.1 Materials and Solvents

3.1.1 Materials

Diphenyliodonium Hexafluorophosphate (Ph2I^{+}PF6^{-} ; 98%, Sigma-Aldrich), Methylcrylate (99%, Sigma-Aldrich), Glycidyl Methacrylate (GMA; ≥97.0%, Sigma-Aldrich), Methyl Methacrylate (MMA; 99%, Sigma-Aldrich), Cyclohexene Oxide (98%, Sigma-Aldrich), Isobutyl Vinyl Ether (99%, Sigma-Aldrich), Triethylene glycol dimethacrylate (95%, Sigma-Aldrich), 5H-[1,2,3]triazolo [40,50:4,5]benzo[1,2-c][1,2,5]thiadiazole (1a), 5H[1,2,3]triazolo[40,50:4,5]benzo [1,2-c][1,2,5]selenadiazole (1b), Poly(propylene glycol) diglycidyl ether (Mn ~380, Sigma-Aldrich) (Figure 3.1).

3.1.2 Solvents

Dichloromethane (DCM; Aldrich, ≥99%) was distilled over phosphorus pentoxide previous to use and Tetrahydrofuran (THF; VWR Chemicals, 99.7%) was used as received.

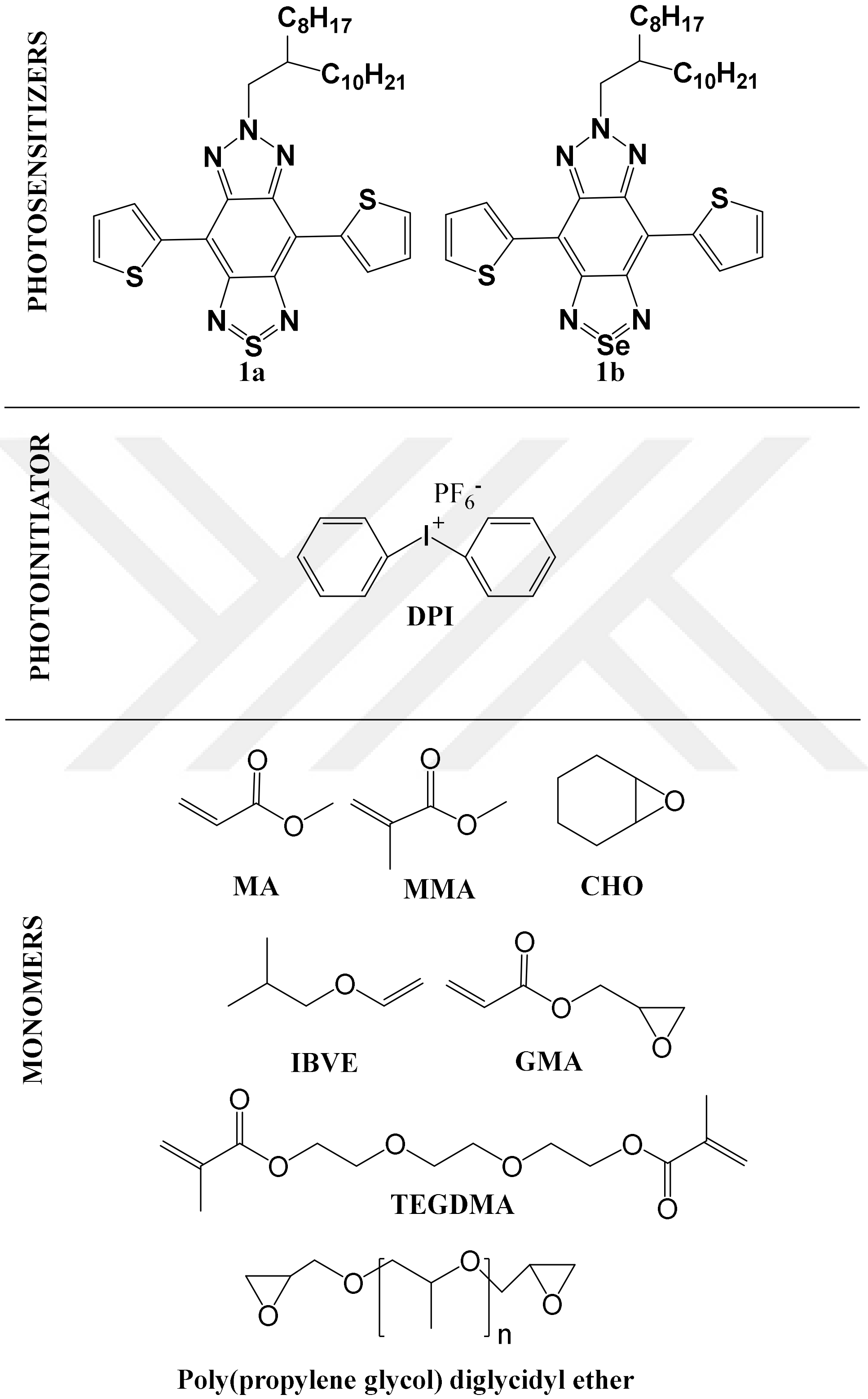


Figure 3.1: Structures of photosensitizers, photoinitiator and monomers used in the experiments.

3.2 Instruments and Characterization

3.2.1 Gel permeation chromatography (GPC)

A TOSOH EcoGPC system with a temperature-controlled pump, an autosampler system, a refractive index (RI) detector, a column oven, a degasser unit, and a purge, and a TSK gel superhZ2000 column with 4.6 mm ID 2 cm column dimensions was used to determine the molecular weights of the polymers. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL.min- 1 at 40 ˚C. RI detector was calibrated with polystyrene standards having very narrow molecular weight distributions. Eco-GPC Analysis software was used to examine GPC data.

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

^{1}H-NMR (500 MHz) spectra were measured in deuterated chloroform with tetramethylsilane as an internal standard on Agilent VNMRS500 spectrometer at 25 ˚C.

3.2.3 Photoreactor and bulb

The light bulb was attached to the top of a photoreactor setup equipped with a large air-cooling fan and the reaction temperature was maintained at room temperature. (24−25˚C). A Philips 150 W PAR38E E27 halogen pressed glass type bulb with strong IR-A (NIR) emission was utilized for the photopolymerization reactions. The light intensity inside the reaction tube was determined to be ~200 mW.cm^{-2}.

3.2.4 UV-Vis spectrometer

A Shimadzu UV1601 double-beam spectrometer with a 50 W halogen lamp and a deuterium lamp that can function between 200 and 1100 nm was used to collect UV–vis spectra.

3.2.5 Fluorescence spectrometer

A Perkin-Elmer LS55 device with a pulsed Xenon source was used to take fluorescence measurements. The slit widths were set to 10 nm. The measurement speeds were kept constant at 250 nm/min.

3.2.6 Dynamic mechanical analysis

Dynamic mechanical analyses were carried out using 15 mm of polymer films on a Perkin–Elmer Pyris Diamond DMA device working with a maximum force of 5 N between 10 ˚C–200 ˚C with 4 ˚C min^{-1} temperature rise.

3.2.7 Electrochemical measurements by cyclic voltammetry

The electrochemical properties of the photosensitizers 1a and 1b were analyzed by cyclic voltammetry (CV) in a solution of 0.1 M $Bu_4N^+PF6^-$/DCM/ACN electrolyte/solvent pair at a scan rate of 100 mV/s. In a three-electrode cell system, CV analyses were carried out with ITO-coated glass as working electrodes and platinum and silver wires as the counter and reference electrodes, respectively.

3.3 Synthesis of Polymers

25 mg of DPI (~0.06 mmol), 6.5 mg of PS (~0.01 mmol) and 1 mL of monofunctional and 2 mL of bifunctional monomers (0.1-0.2 mmol) were dissolved in 1 mL of dichloromethane (DCM) and were transferred inside a 20 mL Schlenk tube that had been heated, degassed, and flushed three times with nitrogen. After 2 h of irradiation (except for GMA which was irradiated for 24 h) inside the photoreactor, the polymers formed were precipitated into methanol. The obtained polymers were all colored, and the unreacted PSs were washed out with hot methanol. Following the washing step, the polymers were dried in a vacuum oven at 50°C for at least 24 hours to get rid of any solvent impurities. ^{1}H-NMR analysis was used to determine the conversions.

3.4 Curing of Hybrid Monomer

For dynamic mechanical analysis (DMA), 2 mL of TEGDMA / poly (propylene glycol) diglycidyl ether hybrid monomer, 25 mg of DPI (~ 0.06 mmol), 6.5 mg of PS 1a (~ 0.01 mmol) were charged into a Teflon mold (5 cm length, 2 cm width, 0.5 cm depth) and another one of the same mold was prepared for the other curing process, which was carried out by exposing one of the systems under UV light and the other under NIR light for 8 hours.

4. RESULTS AND DISCUSSION

As visible or NIR light sensitizer, photosensitizers have a strong absorbance with broad maximum absorbance peaks at 620 and 710 nm. The emission spectra of the light source emitting in this region are also shown in Figure 4.1. When the photosensitizers 1a and 1b dissolved in dichloromethane (DCM) were excited at 600 and 655 nm, respectively, they demonstrate a mirror image of the absorbance peaks at 725 and 800 as the emission spectrum. Between the maxima of the absorption and emission peaks of the photosensitizers, a shift in the electromagnetic spectrum corresponding to the so-called Stokes shift of 90 nm to the IR-A region was observed (Figure 4.2).

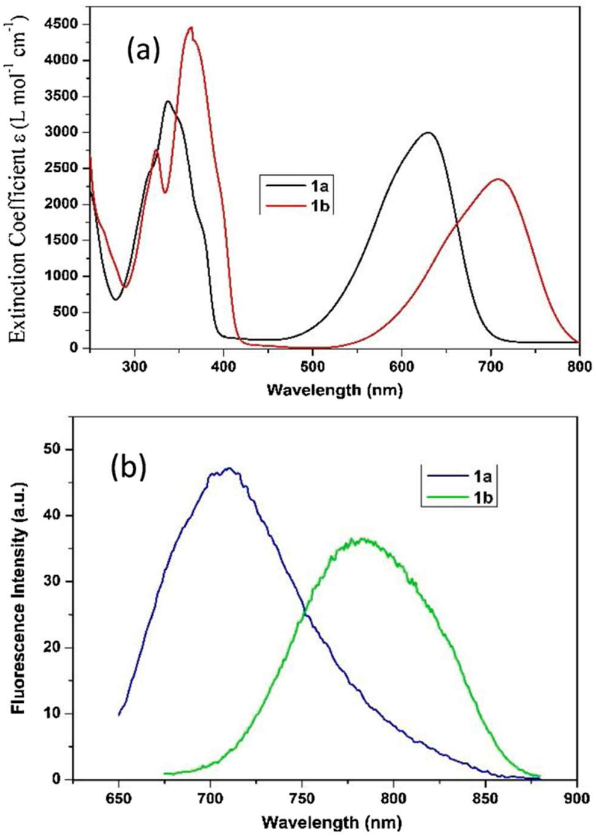


Figure 4.1 : (a) Optical absorption spectra of 3x10^{-5} M dichloromethane solution of 1a (black) and 1b (red) (b) fluorescence spectra of 3x10^{-8} M dichloromethane solution of 1a (blue) and 1b (green) excited at 600 nm and 655 nm, respectively.

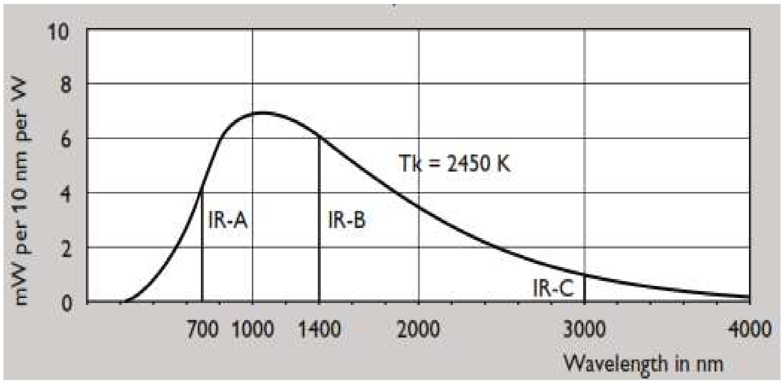


Figure 4.2 : Emission Spectrum of the incandescent bulb used in the photopolymerization reactions.

Considering the oxidation potentials of thiophene units, which are electron donors, in the structure of PSs, reactive species are expected to be formed by photoelectron transfer (PET) reactions (Figure 4.3).

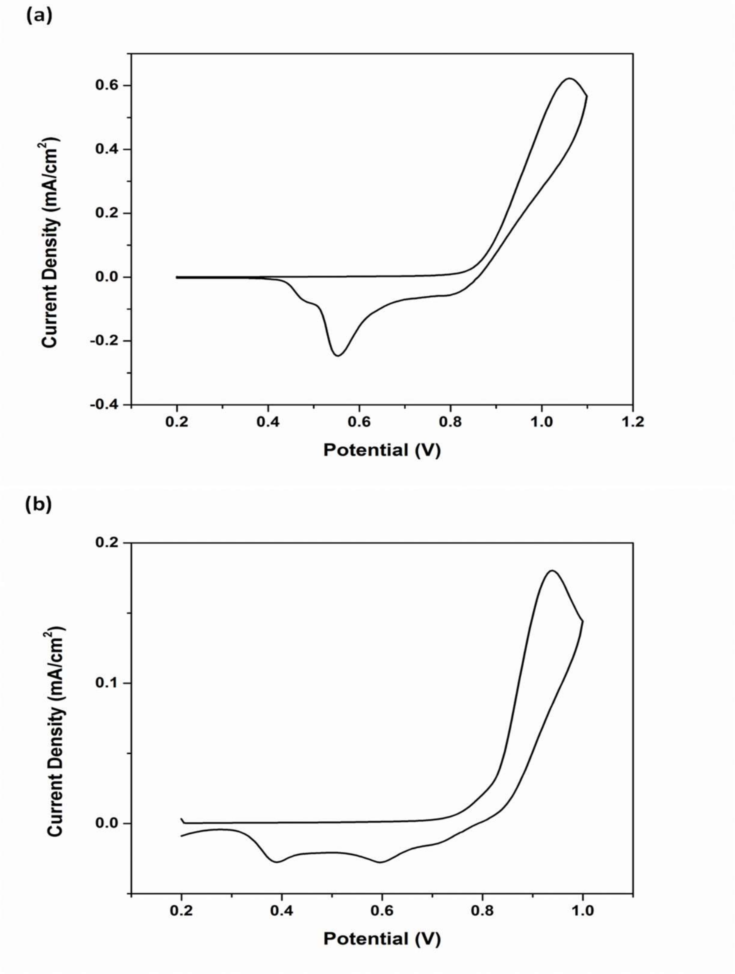


Figure 4.3 : Cyclic voltammograms of (a) 1a and (b) 1b in a solution of 0.1 M Bu_4NPF_6/DCM/ACN electrolyte/solvent couple at a scan rate of 100 mV/s.

It is well known that these PET reactions cause changes in fluorescence emissions of related species due to quenching. Therefore, in order to see this phenomenon in fluorescence emission, we took emission measurements of different concentrations of the DPI mixture prepared with both PSs. A fluorescence quenching experiment was performed by excitation of PS using increasing amounts of DPI salt (Fig 4.4). According to the results, a sharp decrease in the emission spectrum was observed with the addition of DPI to PS 1a. However, as compared to PS 1a, the emission spectrum of PS 1b changed very little and thus it was concluded that there was a less efficient PET reaction between PS 1b and DPI. We suggested that this may be due to steric obstacles or restrictions due to the fact that the selenium atom in PS 1b is larger than the sulfur atom in PS 1a. Considering the Stern-Volmer graphs calculated from the fluorescence emission spectrum, it shows that both PSs perform dynamic quenching with DPI. The interaction between PSs and DPI after excitation resulting from the dynamic quenching process appears with a linear curve in Stern-Volmer graphs (Figure 4.5) [102].

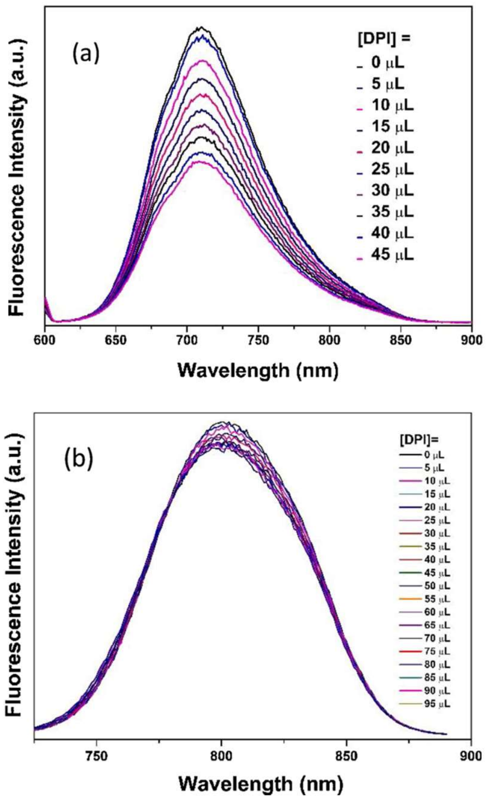


Figure 4.4 : Fluorescence spectra of 3 mL of (a) 1a excited at 600 nm and (b) 1b excited at 655 nm upon addition of 50 mM x 5µL DPI ($Ph_2I^+ PF_6^-$) in dichloromethane.

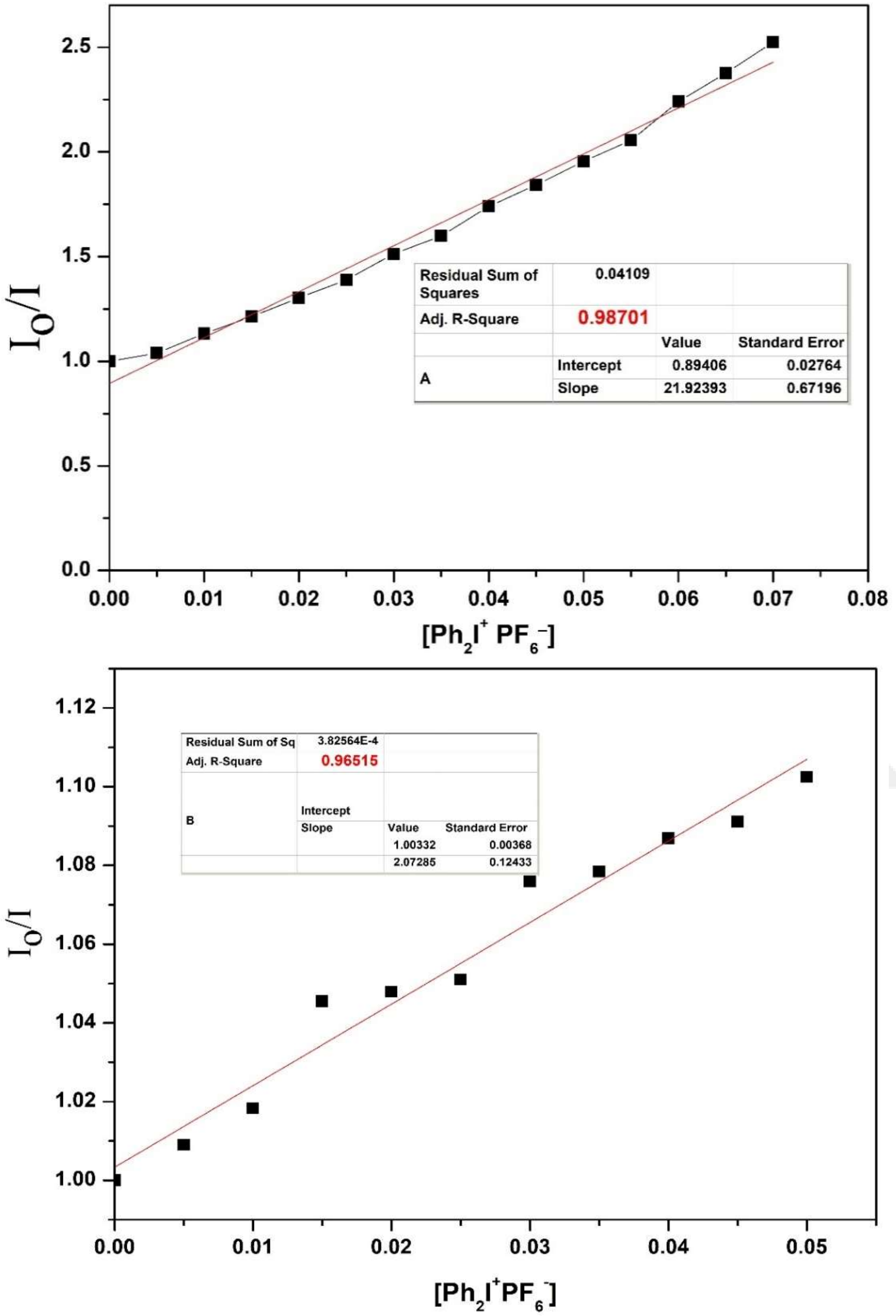


Figure 4.5 : Stern-Volmer plots of the quenching of 1x10^{-8} M (a) 1a and (b) 1b.

Photopolymerization reactions were performed with monomers that can be polymerized radically and cationically in order to determine the activities of photosensitizers with iodonium salt under NIR radiation. Photographs of the polymers obtained with a colored appearance can be seen in Figure 4.6.

Figure 4.6 : Images of the resultant polymers after NIR irradiation: (a) PCHO using 1a. (b) PMMA using 1b. (c) PMMA using 1a. (d) PGMA using 1a. (e) PIBVE using 1b. (f) PIBVE using 1a. (g) PMA using 1b. (h) PMA using 1b.

In the Table where yield values, molecular weights of polymers and polydispersity indices are shown, data from a series of polymerization reactions using various monomers in which PS are used as NIR region sensitizers and DPI salt as photoxidants are shown. (Table 4.1)

Table 4.1: NIR induced photopolymerization of a variety of monomers by using photosensitizers, 1a and 1b, in the presence of $Ph_2I^+PF_6^-$.

Photosensitizer	Monomer	Conversion (%)	M_n(kg mol^{-1})	Đ
1a	CHO	82.6	6.4	1.6
1a	IBVE	92.0	84.0	1.7
1a	MMA	8.2	56.5	1.6
1a	TEGDMA	75.3	nd	-
1a	MA	26.2	4.5	3.1
1a	GMA	92.2	nd	-
1b	CHO	79.5	4.9	1.7
1b	IBVE	69.6	96.8	1.5
1b	MMA	1.6	48.5	1.8
1b	TEGDMA	1.0	nd	-
1b	MA	5.0	73.7	1.5
1b	GMA	90.8	nd	-

In addition, the yields obtained in the table were revised as a result of the measurements made with the ^{1}H-NMR analysis. The peaks that PS 1a and 1b sensitizers appeared in the aromatic region in ^{1}H-NMR were an indication of their presence in the structures of the polymers. When the integral areas of the polymer peaks formed in the aliphatic region were proportioned to those formed in the aromatic region, how many PS molecules remained in the structure was determined (0.03-0.08%), and this situation was taken into account in the yield calculations (Figure 4.8). In addition, the fact that PS molecules encoloured their own colors to the solutions in NMR tubes where PSs were found was an indicator of their presence in polymer structures (Figure 4.7).

Figure 4.7: Photos of the chloroform D-1 solutions of the polymers

The photoelectron transfer process was expected to be similar to the typical photosensitization behavior of conjugated thiophene derivatives. In this direction, if we examine this scheme, the radiation made in the NIR region results in the formation of the photosensitizer radical cation and the iodo radical by transferring an electron from PS to DPI. In addition to the formation of radical species in this way, the Bronsted acids originating from the PS radical cation are in charge of initiating the cationic polymerization process. Since transitions of structurally identical thiophene derivatives cannot be effectively quenched by epoxy monomers, direct initiation by the PS radical cation can be neglected. The concurrently formed diphenyl iodo radical decomposes swiftly to phenyl radicals and iodobenzene, and these radicals play a role in initiating radical polymerization (Figure 4.9).

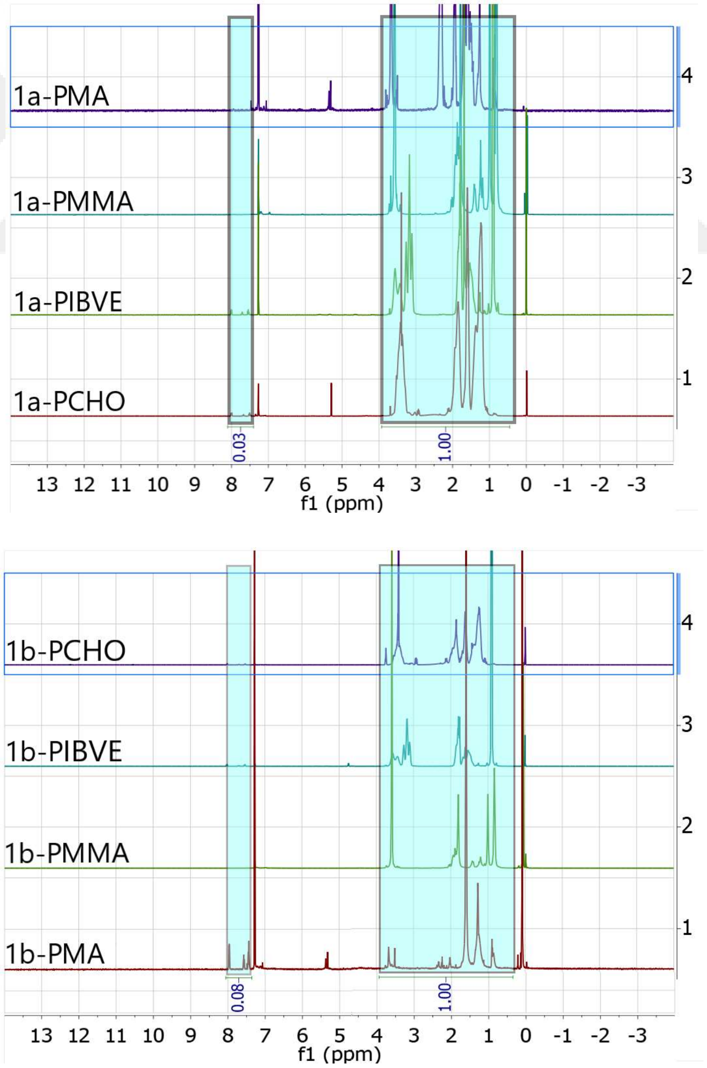


Figure 4.8: ^{1}H-NMR Spectra of the polymers in $CDCl_3$ (500 MHz).

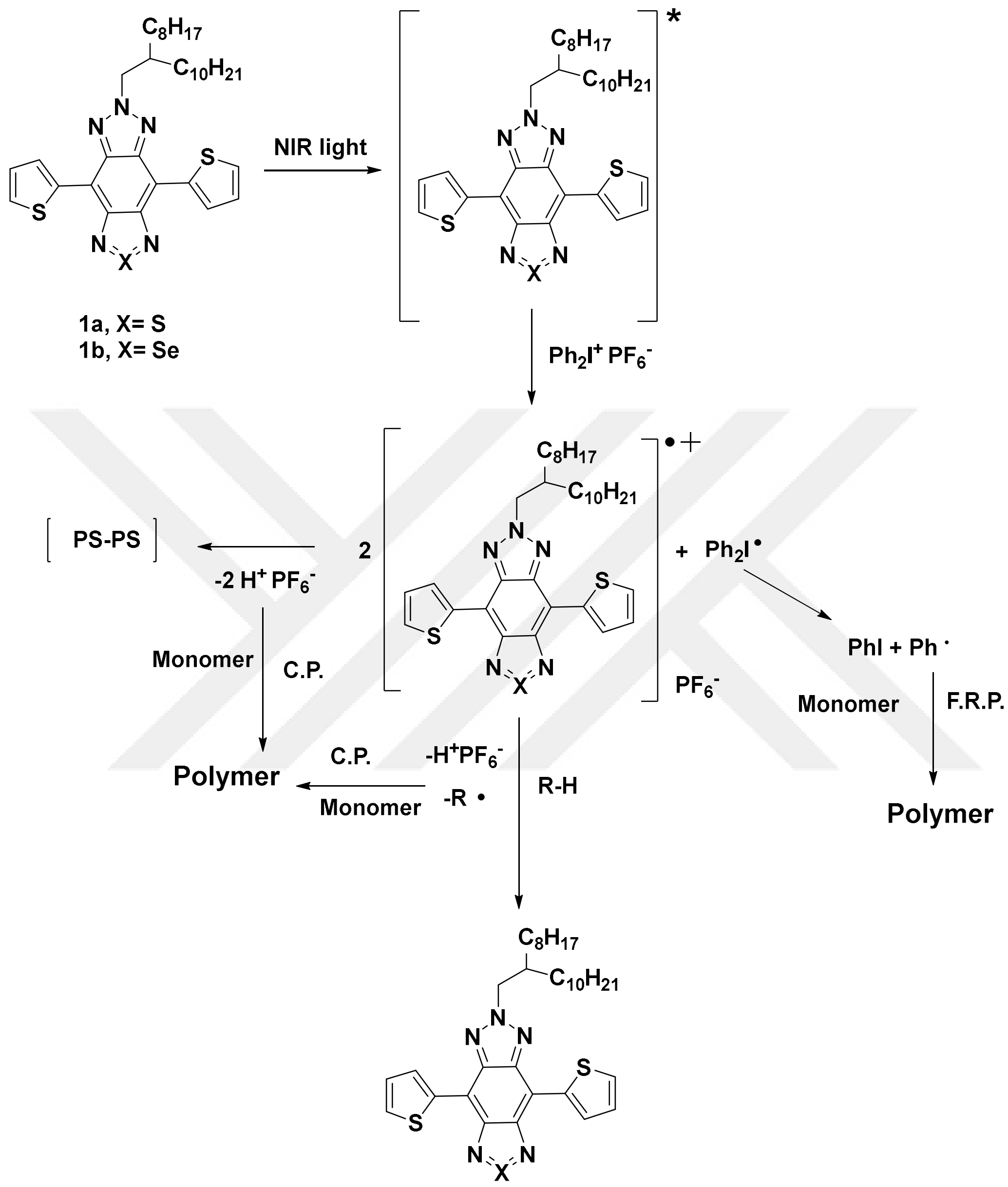


Figure 4.9 : Proposed reaction mechanisms with different routes for NIR-sensitized polymerization.

Both PS molecules have low initiation effectivity for radical polymerization compared to the cationic polymerization as shown above. This fact may be due to coupling reactions accompanied by proton release that can occur between the growing radicals species and the PS radical cation (Figure 4.10). This behavior was indicated in Figure 4.11 by the spectral identification of the polymers formed. As can be seen from these absorption spectra, it has been observed that PS molecules were trapped in polymers and therefore, the polymers showed peaks in the absorption area of PS molecules. In addition, if we examine the PMMA absorption in the spectrum, it is seen that the polymer has relatively stronger absorbance in the region where the PSs absorb. This situation points to the possible coupling reactions with the growing polymer chains with PS-derived radicals.

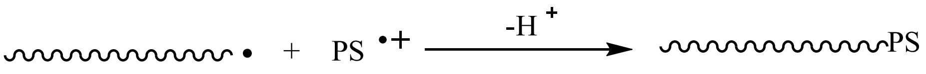


Figure 4.10 : The proposed coupling reaction of propagating radicals with photosensitizer radical cation.

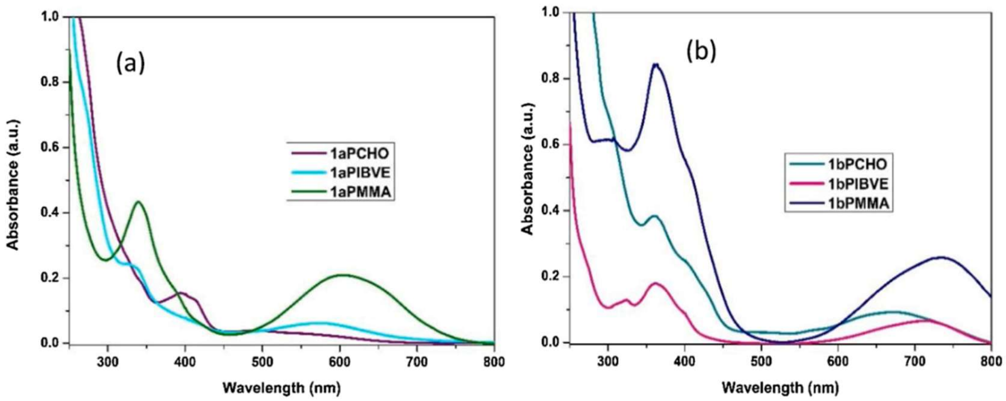


Figure 4.11 : UV absorbance spectra of the polymers obtained using (a) 1a and (b) 1b.

In particular, 1a PS appears to be more effective in both types of polymerization. Although 1b PS has redox potential for electron transfer processes that is thermodynamically more favorable, this low efficiency observed compared to PS 1a can be attributed to the lower absorbance value of PS 1b and the radius size of the selenium atom it contains. Subsequently, it may be taken into account that the outermost shell orbitals of the selenium atoms overlap with neighboring carbon atoms relatively weaker than that of sulfur atoms. Higher yields were obtained with the electron donor monomer, IBVE, which has higher reactivity than other monomers. Besides initiation with Bronsted acids, electron donor radicals can oxidize to corresponding carbocations. Therefore, polymerization reactions can go through both initiation routes.

In addition, an experiment was conducted with glycidyl methacrylate (GMA), which has both radical and cationically polymerized functional groups capable of hybrid polymerization. Here, in real-time H-NMR measurements, the effectiveness of sensitizers was examined while DPI, PS, and monomer were present in an NMR tube. Here, too, the higher efficiency of PS 1a compared to that of PS 1b was shown in accordance with Stern-Volmer quenching experiments and gravimetric efficiency calculations. In the reaction of GMA with sulfur atom-containing PS 1a under NIR light for 1 hour, new peaks were observed in CH_2 protons attached to oxirane units and corresponding to new methyl groups (acrylate methyl) around 1 ppm. After 2h lighting, complete gelation occurred and wider peaks were observed due to cross-linking. This change in the NMR spectrum was observed to be much slower in the reaction with the selenium-containing PS 1b relative to that of PS 1a (Figure 4.12).

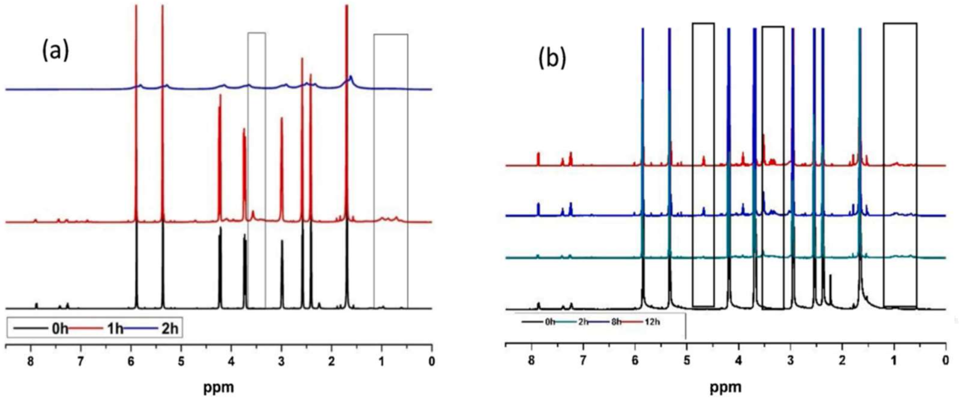


Figure 4.12 : 1H-NMR spectra changes over time of GMA after NIR irradiation (a) using 1a and (b) using 1b in CDCl3 (500 MHz).

Since the network formed by the GMA hybrid monomer has a very fragile structure, DMA analysis was performed with a hybrid system consisting of an oligomer, TEGDMA/POLY(PROPYLENE GLYCOL) Diglycidyl ether, in the presence of PS 1a and DPI. The different transition temperatures of the films formed as a result of the preparation of these mixtures in the presence of PS 1a under 350 nm UV light and also under NIR were observed, as can be seen in the figure (Figure 4.13). The peaks of the tanD curves signal the glass transition temperatures of the films formed. It was observed from the graphic obtained with DMA that the glass transition temperature of the monomer mixture, which was cured with the UV system and turned into a film, was at around 60 °C, and that of the monomer mixture, which was turned into a film with the NIR system, was at around 120 °C. The reason for this is the ability of NIR light to release heat to irradiated area compared to UV light (Figure 4.14).

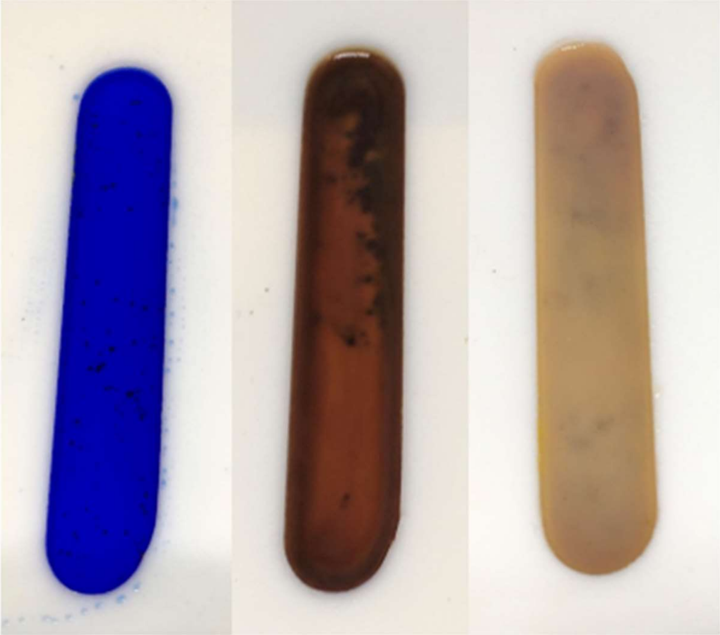


Figure 4.13 : Images of the monomer mixtures /1a before (left), after UV (middle) and NIR irradiation (right).

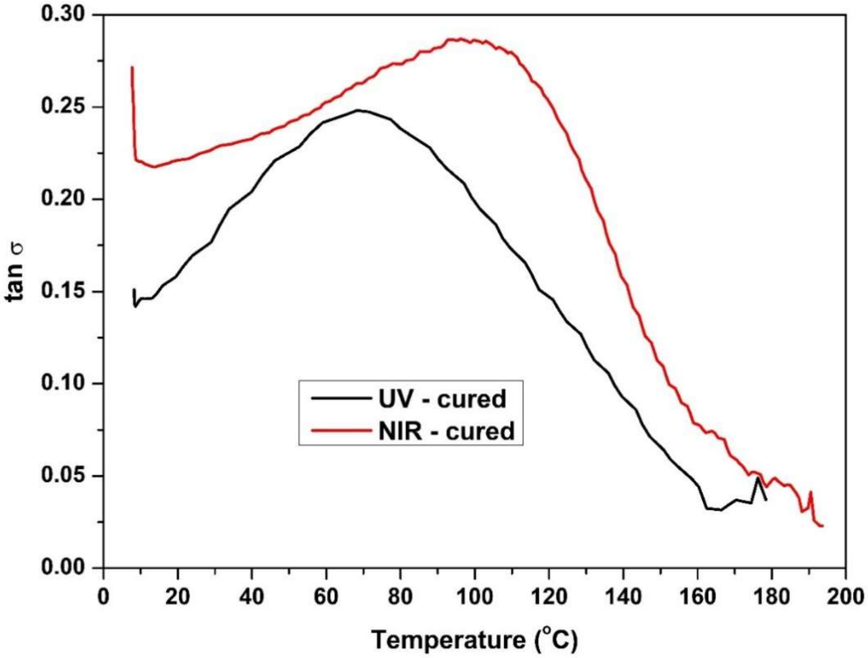


Figure 4.14 : Dynamic mechanical analysis of UV-cured (black) and NIR-cured (red) polymers.

5. CONCLUSION

In this paper, we have developed a new photoinitiator system. Highly conjugated visible and near-infrared (NIR) photosensitizer molecules containing sulfur and selenium heteroatoms have been reported for the first time for both radical and cationic types of polymerization. By using this photoinitiator system, we have shifted the wavelength of the light used in cationic and radical polymerization to a higher wavelength, and thus a system with lower energy than its counterparts has been developed. In addition to its lower energy use, the ability of the near-infrared (NIR) light to penetrate deeper, which is a superior property compared to ultraviolet (UV) light, was demonstrated by dynamic mechanical analysis (DMA) of a monomer mixture. The initiator system was used on monomers polymerizable as radical, cationic, and hybrid. The initiation step, which is the first step of the photoinitiator system we have developed, is based on photoelectron transfer (PET) reactions that take place between the photosensitizer and the onium salt. The radical and cationic active species formed in this way played a role as the starting product in their polymerization types. It has been observed that the cationic polymerization type is more effective than the radical polymerization type due to the coupling reactions that may occur in radical polymerization. The initiator system has been demonstrated to have a possible utility in dual polymerization using a bifunctional monomer having both radical and cationic polymerizable groups. Therefore, a new photoinitiator system for radical and cationic polymerization has been introduced to the literature.

REFERENCES

[1] **Yagci, Y., Jockusch, S., Turro, N. J.** (2010). Photoinitiated Polymerization: Advances, Challenges, and Opportunities, *Macromolecules*, ***43***(15), 6245–6260.

[2] **Dadashi-Silab, S., Doran, S., Yagci, Y.** (2016)**.** Photoinduced Electron Transfer Reactions for Macromolecular Syntheses., *Chemical Reviews*, ***116***(17)**,** 10212–10275.

[3] **Fouassier, J. P., Allonas, X., Burget, D.** (2003). Photopolymerization reactions under visible lights: principle, mechanisms, and examples of applications, *Progress in Organic Coatings*, ***47***(1), 16–36.

[4] **Dubé, M. A., Salehpour, S.** (2014). Applying the Principles of Green Chemistry to Polymer Production Technology, *Macromolecular Reaction Engineering*, ***8***(1), 7–28.

[5] **Fouassier, J. P., Allonas, X., Lalevêe, J., Dietlin, C.** (2010). Photoinitiators for free radical polymerization reactions, *Photochemistry and Photophysics of Polymer Materials*, 1351–419.

[6] **Andrzejewska, E.** (2001). Photopolymerization kinetics of multifunctional monomers, *Progress in Polymer Science*, ***26***(4), 605-665.

[7] **Sangermano M., Roppolo, I., Chiappone, A.** (2018). New horizons in cationic photopolymerization, *Polymers*, ***10***(2), 136.

[8] **Mendes-Felipe, C., Oliveira, J., Etxebarria, I., Vilas-Vilela, J. L., Lanceros-Mendez, S.** (2019). State-of-the-Art and Future Challenges of UV Curable Polymer-Based Smart Materials for Printing Technologies, *Advanced Materials Technologies*, ***4***(3), 1800618.

[9] **Bagheri, A., Jin, J.** (2019). Photopolymerization in 3D Printing, *ACS Applied Polymer Materials*, **1**(4), 593–611.

[10] **Gong, H., Guo, X., Cao, D., Gao, P., Feng, D., Zhang, X., Shi, Z., Zhang, Y., Zhu, S., Cui, Z.** (2019). Photopolymerizable and moisture-curable polyurethanes for dental adhesive applications to increase restoration durability, *Journal of materials chemistry. B*, ***7***(5), 744–754.

[11] **Layani, M., Wang, X., Magdassi, S.** (2018). Novel Materials for 3D Printing by Photopolymerization, *Advanced materials* (Deerfield Beach, Fla.), ***30***(41), 1706344.

[12] **Baroli, B.** (2006). Photopolymerization of biomaterials: issues and potentialities in drug delivery, tissue engineering, and cell encapsulation applications, *Journal of Chemical Technology & Biotechnology*, ***81***(4), 491–499.

[13] **Medellin, A., Du, W., Miao, G., Zou, J., Pei, Z., Ma, C.** (2019). Vat Photopolymerization 3D Printing of Nanocomposites: A Literature Review, *Journal of Micro and Nano-Manufacturing*, *7*(3), 031006-2.

[14] **Stansbury, J.W.** (2000). Curing dental resins and composites by photopolymerization, *Journal of Esthetic and Restorative Dentistry*, ***12***(6), 300–308.

[15] **Topa, M., Ortyl, J.** (2020). Moving Towards a Finer Way of Light-Cured Resin-Based Restorative Dental Materials: Recent Advances in Photoinitiating Systems Based on Iodonium Salts, *Materials* (Basel, Switzerland), ***13***(18), 4093.

[16] **Shao, J., Huang, Y., Fan, Q.** (2014). Visible light initiating systems for photopolymerization: status, development and challenges, *Polymer Chemistry*, ***5***(14), 4195–4210.

[17] **Shi, S., Karasu, F., Rocco, C., Allonas, X., Croutxê-Barghorn, C.** (2015). Photoinitiating systems for LED-Cured interpenetrating polymer networks, *Journal of Polymer Science*, ***28***, 31-35.

[18] **Ortyl, J., Fiedor, P., Chachaj-Brekiesz, A, Pilch, M., Hola, E, Galek, M.** (2019). The applicability of 2-amino-4,6-diphenyl-pyridine-3-carbonitrile sensors for monitoring different types of photopolymerization processes and acceleration of cationic and free-radical photopolymerization under near UV light, *Sensors* (Basel), ***19***(7), 1668.

[19] **Fouassier, J. P.** (1995). Photoinitiation, photopolymerization, and photocuring: fundamentals and applications. Hanser.

[20] **Kaya, K., Seba, M., Fujita, T., Yamago, S., Yagci, Y.** (2018). Visible light-induced free radical promoted cationic polymerization using organotellurium compounds, *Polymer Chemistry*, ***9***(48), 5639–5643.

[21] **Kostrzewska, K., Ortyl, J., Dobosz, R., Kabatc, J.** (2017). Squarylium dye and onium salts as highly sensitive photoradical generators for blue light, *Polymer Chemistry*, ***8***(22), 3464–3474.

[22] **Kabatc, J., Ortyl, J., Kostrzewska, K.** (2017). New kinetic and mechanistic aspects of photosensitization of iodonium salts in photopolymerization of acrylates, *RSC Advances*, *7*(66), 41619–41629.

[23] **Crivello, J. V., Jiang, F.** (2002). Development of Pyrene Photosensitizers for Cationic Photopolymerizations, *Chemistry of Materials*, ***14***(11), 4858–4866.

[24] **Beyazit, S., Aydogan, B., Osken, I., Ozturk, T., Yagci, Y.** (2011). Long wavelength photoinitiated free radical polymerization using conjugated thiophene derivatives in the presence of onium salts, *Polymer Chemistry*, ***2***(5), 1185.

[25] **Strehmel, B., Schmitz, C., Bromme, T., Halbhuber, A., Oprych, D., Gutmann, J.S.** (2016). Advances of near infrared sensitized radical and cationic photopolymerization: from graphic industry to traditional coatings, *Journal of Polymer Science and Technology*, ***29***(1), 111–121.

[26] **Bonardi, A. H., Dumur, F., Grant, T. M., Noirbent, G., Gigmes, D., Lessard, B. H., Fouassier, J.-P., Lalevée, J.** (2018). High Performance Near-Infrared (NIR) Photoinitiating Systems Operating under Low Light Intensity and in the Presence of Oxygen, *Macromolecules*, ***51***(4), 1314–1324.

[27] **Schmitz, C., Oprych, D., Kutahya, C., Strehmel, B.,** (2018). NIR light for initiation of photopolymerization, *The Royal Society of Chemistry*, (Chapter 14, pp. 431–478).

[28] **Liu, R., Zou, X., Xu, Y., Liu, X., Li, Z.** (2016). Deep Thiol-ene Photopolymerization Using Upconversion Nanoparticle-assisted Photochemistry, *Chemistry Letters*, ***45***(9), 1054–1056.

[29] **Brömme, T., Oprych, D., Horst, J., Pinto, P. S., Strehmel, B.** (2015). New iodonium salts in NIR sensitized radical photopolymerization of multifunctional monomers, *RSC Advances*, ***5***(86), 69915–69924.

[30] **Kabatc, J., Iwińska, K., Balcerak, A., Kwiatkowska, D., Skotnicka, A., Czech, Z., Bartkowiak, M.** (2020). Onium salts improve the kinetics of photopolymerization of acrylate activated with visible light, *RSC Advances*, ***10***(42), 24817–24829.

[31] **Meng, X., Lu, H., Li, Z., Wang, C., Liu, R., Guan, X., Yagci, Y.** (2019). Near-infrared light induced cationic polymerization based on upconversion and ferrocenium photochemistry, *Polymer Chemistry*, ***10***(41), 5574–5577.

[32] **Kocaarslan, A., Tabanli, S., Eryurek, G., Yagci, Y.** (2017). Near-Infrared Free-Radical and Free-Radical-Promoted Cationic Photopolymerizations by In-Source Lighting Using Upconverting Glass, *Angewandte Chemie* (International ed. in English), ***56***(46), 14507–14510.

[33] **Ravetz, B. D., Tay, N. E. S., Joe, C. L., Sezen-Edmonds, M., Schmidt, M. A., Tan, Y., Janey, J. M., Eastgate, M. D., Rovis, T.** (2020). Development of a Platform for Near-Infrared Photoredox Catalysis, *ACS central science*, ***6***(11), 2053–2059.

[34] **Yagci, Y., Jockusch, S., Turro, N. J.** (2007). Mechanism of Photoinduced Step Polymerization of Thiophene by Onium Salts: Reactions of Phenyliodinium and Diphenylsulfinium Radical Cations with Thiophene, *Macromolecules*, ***40***(13), 4481–4485.

[35] **Yeh, J., Tsou, C., Li, Y., Xiao, H., Wu, C., Chai, W., Lai, Y.-C., Wang, C.-K.** (2012). The compatible and mechanical properties of biodegradable poly(Lactic Acid)/ethylene glycidyl methacrylate copolymer blends, *Journal of Polymer Research*, ***19***(2), 9766.

[36] **Abdulrasoul, F. A. M., Ledwith, A. and Yagci, Y.** (1978). Photo-Chemical and Thermal Cationic Polymerizations, *Polymer*, ***19***(10)**,** 1219-1222.

[37] **Denizligil, S., Yagci, Y. and McArdle, C.** (1995). Photochemically and Thermally-Induced Radical Promoted Cationic Polymerization Using an Allylic Sulfonium Salt, *Polymer*, ***36***(16)**,** 3093-3098.

[38] **Gibson, I., Rosen, D., Stucker, B., Khorasani, M.** (2021). Additive Manufacturing Technologies, *Springer-Verlag New York*, (3).

[39] **Bagheri, A., Jin, J.** (2019). Photopolymerization in 3D Printing, *ACS Applied Polymer Materials*, ***1***(4), 593–611.

[40] **Ye, Q., Wang, Y., Williams, K., & Spencer, P.** (2007). Characterization of photopolymerization of dentin adhesives as a function of light source and irradiance, *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, ***80***(2), 440–446.

[41] **Khudyakov, I. V.** (2018). Fast photopolymerization of acrylate coatings: Achievements and problems, *Progress in Organic Coatings*, ***121***, 151–159.

[42] **Wang.** (2019). Advanced Polymers for Three-Dimensional (3D) Organ Bioprinting, *Micromachines*, ***10***(12), 814.

[43] **Check, C., Chartoff, R., & Chang, S.** (2015). Effects of nanoparticles on photopolymerization of acrylate monomers in forming nano-composites, *European Polymer Journal*, ***70***, 166–172.

[44] **Rocheva, V. V., Koroleva, A. V., Savelyev, A. G., Khaydukov, K. V., Generalova, A. N., Nechaev, A. V., Khaydukov, E. V.** (2018). High-resolution 3D photopolymerization assisted by upconversion nanoparticles for rapid prototyping applications, *Scientific Reports*, ***8***(1), 3663.

[45] **Fouassier, J. ., Allonas, X., & Burget, D.** (2003). Photopolymerization reactions under visible lights: principle, mechanisms and examples of applications. *Progress in Organic Coatings*, ***47***(1), 16–36.

[46] **Sangermano, M.** (2012). Advances in cationic photopolymerization, *Pure and Applied Chemistry*, ***84***(10), 2089–2101.

[47] **Crivello, J. V.** (1983). Cationic polymerization: Iodonium and sulfonium salt photoinitiators. Initiators, 1–48.

[48] **Crivello, J. V.** (1999). The discovery and development of onium salt cationic photoinitiators. *Journal of Polymer Science Part A: Polymer Chemistry*, ***37***(23), 4241–4254.

[49] **Kahveci, M., U., Uygun, M., Tasdelen, M., A. Schnabel, W. Cook, W., D., Yagci, Y.** (2009). Photoinitiated Cationic Polymerization of Vinyl Ethers Using Substituted Vinyl Halides. *Macromolecules*, ***42***(13), 4443−4448.

[50] **Yonezumi, M., Kanaoka, S., Okumoto, S., Aoshima, S.** (2009). Living Cationic Polymerization of Vinyl Ethers Using a Strong Lewis Acid without Stabilizing Additives: Effective Interaction of Monomers with Growing Ends and/or SnCl4, *Polymer Journal*, ***41***(1), 16–17.

[51] **Sangermano, M., Rodriguez, D., Gonzalez, M. C., Laurenti, E., & Yagci, Y.** (2018). Visible Light Induced Cationic Polymerization of Epoxides by Using Multiwalled Carbon Nanotubes, *Macromolecular Rapid Communications*, ***39***(13), 1800250.

[52] **Bulut, U., & Crivello, J. V.** (2005). Investigation of the Reactivity of Epoxide Monomers in Photoinitiated Cationic Polymerization, *Macromolecules*, ***38***(9), 3584–3595.

[53] **Kahveci, M. U., Tasdelen, M. A., & Yagci, Y.** (2007). Photochemically initiated free radical promoted living cationic polymerization of isobutyl vinyl ether, *Polymer*, ***48***(8), 2199–2202.

[54] **Puskas, J. E., Michel, A., & Barghi, S.** (1999). Ionic Polymerizations and Related Processes, NATO Science Series, 369.

[55] **Yagci, Y., & Schnabel, W.** (1994). Direct and sensitized photoinitiated cationic polymerization using pyridinium salts, Macromolecular Symposia, ***85***(1), 115–127.

[56] **Toba, Y., Saito, M., & Usui, Y.** (1999). Cationic Photopolymerization of Epoxides by Direct and Sensitized Photolysis of Onium Tetrakis(pentafluorophenyl)borate Initiators, *Macromolecules*, ***32***(10), 3209–3215.

[57] **Yagci, Y., Durmaz, Y. Y., & Aydogan, B.** (2007). Phenacyl onium salt photoinitiators: synthesis, photolysis, and applications, *The Chemical Record*, ***7***(2), 78–90.

[58] **Aydogan Temel, B., Gacal, B., Yildirim, A., Yonet, N., Yuksel, Y., Yagci, Y.** (2006). Wavelength tunability in photoinitiated cationic polymerization. Photochemistry and UV Curing: New Trends.

[59] **Villotte, S., Gigmes, D., Dumur, F., & Lalevée, J.** (2019). Design of Iodonium Salts for UV or Near-UV LEDs for Photoacid Generator and Polymerization Purposes, *Molecules*, ***25***(1), 149.

[60] **Crivello, J. V., Lam, J. H. W.** (1977). Diaryliodonium Salts. A New Class of Photoinitiators for Cationic Polymerization, *Macromolecules*, ***10***(6), 1307–1315.

[61] **Crivello, J. V.** (2002). Advances in the design of photoinitiators, photosensitizers and monomers for photoinitiated cationic polymerization, *Designed Monomers and Polymers*, ***5***(2-3), 141–154.

[62] **Garra, P., Fouassier, J. P., Lakhdar, S., Yagci, Y., & Lalevée, J.** (2020). Visible Light Photoinitiating Systems by Charge Transfer Complexes: Photochemistry without dyes, *Progress in Polymer Science*, 101277.

[63] **Crivello, J. V., & Lee, J. L.** (1990). The synthesis, characterization, and photoinitiated cationic polymerization of silicon-containing epoxy resins, *Journal of Polymer Science Part A: Polymer Chemistry*, ***28***(3), 479–503.

[64] **Merritt, E., & Olofsson, B.** (2009). Diaryliodonium Salts: A Journey from Obscurity to Fame, *Angewandte Chemie International Edition*, ***48***(48), 9052–9070.

[65] **Crivello, J.** (2015). Sensitization of Cationic Photopolymerizations, *Dyes and Chromophores in Polymer Science*, 45–79.

[66] **Erdur, S., Yilmaz, G., Goen Colak, D., Cianga, I., & Yagci, Y.** (2014). Poly(phenylenevinylene)s as Sensitizers for Visible Light Induced Cationic Polymerization, *Macromolecules*, ***47***(21), 7296–7302.

[67] **Aydogan, B., Yagci, Y., Toppare, L., Jockusch, S., Turro, N. J.** (2012). Photoinduced Electron Transfer Reactions of Highly Conjugated Thiophenes for Initiation of Cationic Polymerization and Conjugated Polymer Formation, *Macromolecules*, ***45***(19), 7829–7834.

[68] **Yagci, Y., Sangermano, M., & Rizza, G.** (2008). Synthesis and Characterization of Gold−Epoxy Nanocomposites by Visible Light Photoinduced Electron Transfer and Cationic Polymerization Processes, *Macromolecules*, **41**(20), 7268–7270.

[69] **Hola, E., Pilch, M., Galek, M., Ortyl, J.** (2020). New versatile bimolecular photoinitiating systems based on amino- m -terphenyl derivatives for cationic, free-radical and thiol–ene photopolymerization under low intensity UV-A and visible light sources, *Polymer Chemistry*, ***11***(2), 480–495.

[70] **Schmitz, C., Halbhuber, A., Keil, D., Strehmel, B.** (2016). NIR-Sensitized Photoinitiated Radical Polymerization and Proton Generation with Cyanines and LED Arrays, *Progress in Organic Coatings*, ***100***, 32–46.

[71] **Abrahamse, H., & Hamblin, M. R.** (2016). New photosensitizers for photodynamic therapy, *Biochemical Journal*, ***473***(4), 347–364.

[72] **Hizal, G., Yagci, Y., Schnabel, W.** (1994). Charge-Transfer Complexes of Pyridinium Ions and Methyl- and Methoxy-Substituted Benzenes as Photoinitiators for the Cationic Polymerization of Cyclohexene Oxide and Related Compounds, *Polymer*, ***35***(11), 2428−2431.

[73] **Hizal, G., Emiroglu, S. E., Yagci, Y.** (1998). Photoinitiated radical polymerization using charge transfer complex of N-ethoxy-pcyanopyridinium salt and 1,2,4-trimethoxybenzene, *Polymer International*, ***47***(4), 391−392.

[74] **Yagci, Y.** (1998). Initiation of cationic polymerization by photoinduced electron transfer, *Macromolecular Symposia*, ***134***(1), 177–188.

[75] **Yagci, Y., Schnabel, W., & Ledwith, A.** (1987). Synthesis and reactions of polymers with photoactive terminal groups-3. The use of radical promoted cationic polymerization for the synthesis of poly(n-butyl vinylether) with n-acyl dibenz(b, f)azepine terminal units, *European Polymer Journal*, ***23***(10), 737–740.

[76] **Yagci, Y., & Schnabel, W.** (1992). New aspects on the photoinitiated free radical promoted cationic polymerization. Makromolekulare Chemie, *Macromolecular Symposia*, ***60***(1), 133–143.

[77] **Tasdelen, M. A., Lalevée, J., & Yagci, Y.** (2020). Photoinduced Free Radical Promoted Cationic Polymerization after 40 Years of the Discovery, *Polymer, **11**, 1111-1121.*

[78] **Hepuzer, Y., Yagci, Y., Biedron, T., & Kubisa, P.** (1996). Photoinitiated free-radical and promoted cationic polymerization by using

polyepichlorohydrin with benzoin terminal groups, *Angewandte Makromolekulare Chemie*, ***237***(1), 163–171.

[79] **Tehfe, M.-A., Dumur, F., Graff, B., Morlet-Savary, F., Gigmes, D., Fouassier, J.-P., & Lalevée, J.** (2013). Design of new Type I and Type II photoinitiators possessing highly coupled pyrene–ketone moieties, *Polymer Chemistry*, ***4***(7), 2313.

[80] **Yonezumi, M., Kanaoka, S., Okumoto, S., Aoshima, S.** (2009). Living Cationic Polymerization of Vinyl Ethers Using a Strong Lewis Acid without Stabilizing Additives: Effective Interaction of Monomers with Growing Ends and/or SnCl4, *Polymer Journal*, ***41***(1), 16–17.

[81] **Kahveci, M. U., Oytun, F., Yagci, Y.** (2013). Influence of Type of Zinc Salts on Photoinitiated Living Cationic Polymerization of Vinyl Ethers, *Polymer*, ***54***(18), 4798−4801.

[82] **Kahveci, M. U., Tasdelen, M. A., Yagci, Y.** (2008). Photo-Induced Cross-Linking of Divinyl Ethers by Using Diphenyliodonium Salts With Highly Nucleophilic Counter Anions in the Presence of Zinc Halides, *Macromolecular Rapid Communication*, ***29***(3), 202−206.

[83] **Kahveci, M. U., Yagci, Y.** (2011). Photoinitiated Cationic Polymerization of Vinyl Ethers Using Substituted Vinyl Halides in the Presence of Metallic Zinc, *Macromolecules*, ***44***(14), 5569−5572.

[84] **Tasdelen, M., A.** (2007). New initiating systems for free radical photopolymerization, (Doctoral dissertation). Retrieved from https://tez.yok.gov.tr/.

[85] **Eibel, A., Fast, D. E., & Gescheidt, G.** (2018). Choosing the ideal photoinitiator for free radical photopolymerizations: Predictions based on simulations using established data, *Polymer Chemistry*, ***17***(6), 953-1044.

[86] **Lissi, E. A., Garrido, J., & Zanocco, A.** (1984). Photopolymerization of methyl methacrylate by benzoin methyl ether irradiated at 366 nm: Effect of the initiator absorbance upon the polymerization rate, *Journal of Polymer Science: Polymer Letters Edition*, ***22***(7), 391–393.

[87] **Temel, G., Enginol, B., Aydin, M., Balta, D. K., & Arsu, N.** (2011). Photopolymerization and photophysical properties of amine linked benzophenone photoinitiator for free radical polymerization, *Journal of Photochemistry and Photobiology A: Chemistry*, ***219***(1), 26–31.

[88] **Chen, S., Jin, M., Malval, J.-P., Fu, J., Morlet-Savary, F., Pan, H., & Wan, D.** (2019). Substituted Stilbene-based Oxime Esters used as Highly Reactive Wavelength-dependent Photoinitiators for LED Photopolymerization, *Polymer Chemistry*, ***48***(10), 6609-6621.

[89] **Neumann, M. G., Schmitt, C. C., Ferreira, G. C., & Corrêa, I. C.** (2006). The initiating radical yields and the efficiency of polymerization for various dental photoinitiators excited by different light curing units, *Dental Materials*, ***22***(6), 576–584.

[90] **Amirzadeh, G., & Schnabel, W.** (1981), *Die Makromolekulare Chemie*, ***182***(10), 2821–2835.

[91] **Berner, G., Kirchmayr, R., and Rist, G.,** (1978). Recent Developments in Photoinitiators, *Journal of the Oil & Colour Chemists Association*, ***61***, 105-113.

[92] **Aydin, M., Arsu, N., & Yagci, Y.** (2003). One-Component Bimolecular Photoinitiating Systems, 2, *Macromolecular Rapid Communications*, ***24***(12), 718–723.

[93] **Block, H., Ledwith, A., & Taylor, A. R.** (1971). Polymerization of methyl methacrylate photosensitized by benzophenones, *Polymer*, ***12***(4), 271–288.

[94] **Rahal, M., Mokbel, H., Graff, B., Toufaily, J., Hamieh, T., Dumur, F., & Lalevée, J.** (2020). Mono vs. Difunctional Coumarin as Photoinitiators in Photocomposite Synthesis and 3D Printing, *Catalysts*, ***10***(10), 1202.

[95] **Moszner, N., Fischer, U. K., Ganster, B., Liska, R., & Rheinberger, V.** (2008). Benzoyl germanium derivatives as novel visible light photoinitiators for dental materials, *Dental Materials*, ***24***(7), 901–907.

[96] **Kamoun, E. A., Winkel, A., Eisenburger, M., & Menzel, H.** (2016). Carboxylated camphorquinone as visible-light photoinitiator for biomedical application: Synthesis, characterization, and application, *Arabian Journal of Chemistry*, ***9***(5), 745–754.

[97] **Morton, M., & Fetters, L. J.** (1975). Anionic Polymerization of Vinyl Monomers, *Rubber Chemistry and Technology*, ***48***(3), 359–409.

[98] **Yagci, Y., & Ito, K.** (2005). Macromolecular Architecture Based on Anionically Prepared Poly(ethylene oxide) Macromonomers, *Macromolecular Symposia*, ***226***(1), 87–96.

[99] **Worsfold, D. J., & Bywater, S.** (1960). Anionic Polymerization of Styrene, *Canadian Journal of Chemistry*, ***38***(10), 1891–1900.

[100] **Fouassier, J. P., Lalevêe, J.** (2012). Anionic Photoinitiators, *Photoinitiators for Polymer Synthesis*, 343–345.

[101] **Hadjichristidis N., Hirao, A.** (2015). Anionic Polymerization: Principles, Practice, Strength, Consequences and Applications, Springer Tokyo Heidelberg New York Dordrecht London.

[102] **Gehlen, M. H.** (2020). The centenary of the Stern-Volmer equation of fluorescence quenching: From the single line plot to the SV quenching map, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, ***42***, 100338.

CURRICULUM VITAE

Name Surname : Ali SÜERKAN

[redacted]

EDUCATION

- **B.Sc.** : 2020, Kocaeli University, Faculty of Arts and Science, Chemistry Department
- **M.Sc.** : 2021, Istanbul Technical University, Faculty of Science and Letter, Chemistry Department

PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

- **Suerkan, A., Alkan, E. A., Kaya, K., Udum, Y. A., Toppare, L., Yagci, Y.** (2021). Highly Conjugated Visible and Near-Infrared Light Photoinitiating Systems for Radical and Cationic Polymerization. *Progress in Organic Coatings*, 154, 106189.