ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

DESIGN AND APPLICATION OF NOVEL PHOTOINITATING SYSTEMS FOR RADICAL AND CATIONIC POLYMERIZATIONS UNDER UV AND VISIBLE LIGHT

Ph.D. THESIS

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Thesis Advisor: Prof. Dr. Yusuf YAĞCI

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

UV VE GÖRÜNÜR IŞIK ALTINDA RADİKAL VE KATYONİK POLİMERLEŞME YAPABİLEN YENİ FOTOBAŞLATICILARIN TASARIMI VE SENTEZİ

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Kerem Kaya, a Ph.D. student of **ITU Graduate School of Science Engineering and Technology** with student ID 509102066, successfully defended **the thesis** entitled **"DESIGN AND APPLICATION OF NOVEL PHOTOINITATING SYSTEMS FOR RADICAL AND CATIONIC POLYMERIZATIONS UNDER UV AND VISIBLE LIGHT"** which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family and my laboratory partners,

FOREWORD

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December 2018 Kerem KAYA
(MSc. Chemistry)

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ABBREVIATIONS

^{13}C-NMR	: Carbon-13 Nuclear Magnetic Resonance Spectroscopy
CHO	: Cyclohexene oxide
$CDCl_3$	: Deuterated chloroform
CTC	: Charge-Transfer complex
DCM	: Dichloromethane
DMA	: *N,N*-Dimethylaniline
DMSO-D6	: Deuterated dimethylsulfoxide
DPI	: Diphenyliodonium salt
$DPPS^+BF_4^-$	: Diphenylphenacylsulfonium tetrafluoroborate
DSC	: Differential Scanning Calorimeter
FT-IR(ATR)	: Fourier Transform Infrared-Attenuated Total Reflectance
GMA	: Glycidyl methacrylate
GPC	: Gel Permeation Chromatography
^{1}H-NMR	: Hydrogen Nuclear Magnetic Resonance Spectroscopy
HOMO	: Highest Occupied Molecular Orbital
IBVE	: Isobutylvinyl Ether
LUMO	: Lowest Unoccupied Molecular Orbital
***M*n**	: Number Average Molecular Weight
***M*w**	: Weigth Average Molecular Weight
MMA	: Methyl methacrylate
NVC	: *N*-Vinylcarbazole
PCHO	: Poly (cyclohexene oxide)
Photo-DSC	: Differential Scanning Calorimeter equipped with a light source
PIBVE	: Poly (isobutylvinyl ether)
PI	: Photoinitiator
PIS	: Photoinitiating systems
PMMA	: Poly(methyl methacrylate)
PS	: Photosensitizer
St	: Styrene
THF	: Tetrahydrofuran

$TPS^+BF_4^-$	: Triphenylsulfonium tetrafluoroborate
TEGDMA	: Triethyleneglycoldimethacrylate
TEGDVE	: Triethyleneglycoldivinyl ether
UV	: Ultraviolet

SYMBOLS

A	: Ampere
C	: Conversion
ΔHt	: Reaction heat evolved at time t
ΔH_0	: Reaction heat evolved at time 0
Đ	: Dispersity
ε	: Molar extinction coefficient
eV	: Electron volt
mW/cm^2	: Milliwatt by centimeter square
mV	: Milivolt
λ_{max}	: Maximum wavelength
V	: Volt

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DESIGN AND APPLICATION OF NOVEL PHOTOINITATING SYSTEMS FOR RADICAL AND CATIONIC POLYMERIZATIONS UNDER UV AND VISIBLE LIGHT

SUMMARY

Photopolymerization is a process utilizing electromagnetic radiation (light) as the energy source for polymerization of functional monomers and oligomers which is broadly applied in many industrial processes such as three-dimensional laser printing, ultraviolet (UV) curing of coatings and inks, pharmaceuticals, drug-delivery systems, dentistry and electronic materials. In these applications light is absorbed by the system to form reactive species to initiate the polimerization. The overall system consists of photoinitiators, mono and/or multi functional monomers and additives. Photoinitiators absorb light in the UV or visible spectral range (250–700 nm) and convert the light energy into chemical energy as reactive intermediates, such as free radicals and/or cations, which in turn initiate the polymerization of various monomers to form linear polymers and crosslinked networks. Light absorption by the photoinitiators or the photoinitiating systems requires that the emission from the light source overlaps with the absorption band of the photoinitiator.

Free radicals which are capable to initiate the polymerization of (meth)acrylic and styrenic monomers can be photochemically produced from a wide range of photoinitiators. Depending on the type of photoinitiating system employed, unimolecular or bimolecular actions of the excited state of the photoinitiator essentially lead to the generation of reactive radicals. In some cases photolytic excitation of the monomer itself can lead to free radicals if the absorption spectrum of the monomer lies in the spectral range of the excitation.

Although photoinitiated radical polymerizations have been known and investigated for a considerable period of time, photoinitiated cationic polymerizations have received little attention. The slow development of this field has largely been due to the lack of suitable photoinitiators capable of catalyzing ionic polymerizations. However, starting from late 1970’s significant progress has been made, particularly in the development of photoinitiators for cationic polymerization.

This thesis is formed of three different published studies related to the photoinititated radical and cationic polymerization of various monomers with different functionalities using novel photoinitiating systems under UV and/or visible light:

In the first part (Chapter 2) of this thesis, a phenacylium salt, namely diphenylphenacylsulfoniumtetrafluoroborate ($DPPS^+BF_4^-$) possessing both phenacyl and sulfonium chromophores was synthesized and characterized. Experimental and theoretical results revealed that $DPPS^+BF_4^-$ absorbed light at relatively higher wavelengths compared with its triphenyl analogue. The direct and sensitized initiation activity of the salt in both cationic and free radical photopolymerizations was also investigated and compared with that of its analogue triphenylsulfonium tetrafluoroborate ($TPS^+BF_4^-$). Differential scanning photocalorimetry and

conventional gravimetric analyses revealed that $DPPS^+BF_4^-$ showed higher efficiency for direct and sensitized photopolymerizations of most of the monomers investigated. Although, principally both homolytic and/or heterolytic cleavage is possible, theoretical (DFT) studies suggested that homolytic pathway is more favored for the generation of reactive initiating species.

In the second part, (Chapter 3) organotellurium-mediated polymerization of cyclohexene oxide (CHO), isobutyl vinyl ether (IBVE) and *N*-vinylcarbazole (NVC) in conjuction with diphenyliodonium hexafluorophosphate (DPI) was accomplished under visible light and sunlight. The chain transfer agent (CTA) ethyl 2-methyl-2-methyltellanylpropionate (EMPTeMe) and poly(methyl methacrylate) with an organotellurium group at the chain end (PMMATeMe) were used as photoinitiators for free-radical-promomted cationic polymerization reactions.

In the third of the thesis, (Chapter 4) a new double chromophoric sulfonium salt photoinitiator possessing both thioxanthone and phenacyl groups, namely 2-isopropylthioxanthonium phenacyl hexafluoroantimonate (ITXPhenS) was synthesized and characterized. ITXPhenS could form charge transfer complex (CTC) with the donor *N*, *N*-dimethyl aniline (DMA) with absorption characteristics in the visible range as confirmed by spectral analysis, cyclic voltammetry (CV) and density functional theory (DFT). CTC's were able to polymerize various monomer under visible light irradiation with high efficiency.

Finally, a general conclusion together with future work is presented in the last part of this thesis.(Chapter 5)

UV VE GÖRÜNÜR IŞIK ALTINDA RADİKAL VE KATYONİK POLİMERLEŞME YAPABİLEN YENİ FOTOBAŞLATICILARIN TASARIMI VE SENTEZİ

ÖZET

Fotopolimerizasyon, fonksiyonel monomerlerin polimerizasyonu için enerji kaynağı olarak elektromanyetik radyasyonun (ışık) kullanılmasıdır. Konvansiyonel polimerleşme teknolojisiyle kıyaslandığında fotopolimerizasyon çok daha temiz bir teknolojidir çünkü yüksek ısı ve fazla miktarda çözücüye ihtiyaç duymaz. Fotopolimerizasyon dişçilik, ilaç sanayisi, üç boyutlu lazer baskıları, boya kaplamaları gibi geniş bir endüstriyel alanda sıkça kullanılmaktadır. Bütün bu uygulamalar, sistem (foto-başlatıcılar, fotopolimerler ve/veya foto çapraz bağlanabilir polimerler) tarafından emilen ve yeni kimyasal bağlar oluşturmak için kullanılan ışığa ihtiyaç duyar: Foto-başlatıcılar, UV veya görünür spektral aralıktaki ışığı (250-700 nm) absorbe eder ve ışık enerjisini, serbest radikaller ve/veya katyonlar gibi reaktif ara maddeler olarak kimyasal enerjiye dönüştürür, bu da lineer polimerler veya çapraz bağlı polimerler oluşturmak üzere çeşitli monomerlerin polimerizasyonunu başlatır. Foto-başlatıcılar ve çok fonksiyonlu monomerlerin kombinasyonu üç boyutlu çapraz bağlanmış ağlar verir. Tarihte ilk kez 1940'larda Kodak firması polivinil sinamat eldesinde fotopolimerleşme teknolojisini kullanmış daha sonra Dupont firması 1950'lerde Dycril ürününü geliştirerek "tipo baskı" adıyla bildiğimiz fotopolimerleri üretmiştir. 1960'lardan itibaren fotopolimerleşme endüstrisi hızla büyüyen bir teknoloji olmuş ve 2017 yılında 7 milyar dolarlık bütçeye ulaşmıştır. Günümüzde fotopolimerizasyon yöntemi ile elde edilen endüstriyel ürünlerin kullanım alanları dişçilikten, yapay organ üretimine, arabaların hidrofobik yüzey ile kaplanmasından kişisel bilgisayarlarda kullanılan mikroçiplere kadar gitmektedir. Foto-başlatıcılar ya da foto-başlatma sistemleri tarafından ışık emilimi, fotokimyanın ilk yasası olan Grotthus-Draper yasasına göre ışık kaynağından gelen emisyonun foto-başlatıcının absorpsiyon bandı ile çakışmasını gerektirir. Akrilik monomerlerin polimerizasyonunu başlatabilen serbest radikaller, çok çeşitli foto-başlatıcılar kullanılarak fotokimyasal olarak üretilebilirler. Bununla birlikte, tüm serbest radikaller polimerizasyon reaksiyonlarını başlatamazlar. Bir serbest radikalin bir akrilik monomerin polimerizasyonunu başlatabilmesi bazı enerji kriterlerine bağlıdır: Birincisi, oluşan zincir radikali birincil radikale göre stabil olmalıdır, başka bir deyişle problem, bağ enerjilerini ve rezonansı içerir. Bazı durumlarda monomerin kendisinin fotolitik ayrışması da söz konusu olabilir. Her ne kadar foto-başlatılmış radikal polimerizasyonları bilinmekte ve hatırı sayılır bir süre boyunca araştırılmış olsa da, radikal polimerizasonun belli bazı dezavantajları bulunmaktadır. Bunların başında oksijene ve neme olan hassasiyet gelmektedir. Oksijen ve nemin radikal polimerizasyonun verimini ciddi bir biçimde azalttığı saptanmıştı. Ayrıca radikal polimerleşme yöntemi siklohegzen oksit, tetrahidrofuran, lakton ve benzeri epoksit türevi monmerlerin polimerizasyonunu gerçekleştirememektedir. Foto-başlatılmış katyonik polimerizasyonlar ise çok az ilgi görmüştür. Bu alandaki yavaş gelişme büyük ölçüde iyonik polimerizasyonları katalize edebilen uygun foto-başlatıcıların

eksikliğinden kaynaklanmıştır. Fakat 1970'lerin sonlarından başlayarak, özellikle katyonik polimerizasyon için foto-başlatıcıların geliştirilmesinde önemli ilerlemeler kaydedilmiştir. Bu konudaki en önemli çalışma James Crivello'nun 1977 yılında ariliyodonyum tuzlarını kullanarak siklik monomerlerin katyonik polimerizasyonunu yüksek verimlerle ışık altında gerçekleştirmesidir. Bu tez, yeni foto-başlatıcı sistemleri kullanılarak farklı fonksiyonlara sahip çeşitli monomerlerin polimerizasyonu ile ilgili üç farklı yayınlanmış çalışmadan oluşmaktadır:

İlk çalışmada (Bölüm 2) fenaçil ve sülfonyum kromofor gruplarına sahip (DPPS+BF4–) difenilfenaçil sülfonyum tetrafloroborat tuzu literatürdeki prosedüre göre sentezlendi ve yapısı farklı spektrospkopik yöntemler kullanılarak aydınlatıldı. Yapılan analizler sonucunda (DPPS+BF4–) tuzunun muadili olan trifenil sülfonyum (TPS+BF4–) tuzu ile kıyaslandığında ışığı daha yüksek dalga boyunda absorpladığı ve farklı monomerleri daha etkin biçimde polimerize ettiği ortaya çıktı. Fotosensitizasyon çalışmaları da (DPPS+BF4–) tuzunun (TPS+BF4–)'ye oranla daha yüksek polimer dönüşümlerine sahip olduğunu gösterdi. Yapılan teorik çalışmalar (YFT) hem homolitik hem de heterolitik bağ kırılmalarının mümkün olabileceğini ancak homolitik kırılmanın enerji açısından daha olası olduğunu ortaya çıkardı.

İkinci çalışmada (Bölüm 3) tellurium içeren organik yapılar difeniliyodonyum tuzu (DPI) varlığında siklohegzenoksit (CHO), izobütilvinileter (IBVE) ve N-vinilkarbazol (NVC) monomerlerinin polimerizasyonunda fotobaşlatıcı olarak kullanıldı. Zincir transfer ajanı etil 2-metil-2-metiltellanilpropiyonat (EMPTeMe) ve ucunda tellurium grubu ihtiva eden polimetil metakrilat (PMMATeMe) serbest-radikal-başlatmalı katyonik polimerizasyon reaksiyonlarında görünür bölge ışınması altında fotobaşlatıcısı olarak denendiler. Mikrobaşlatıcı kullanılarak farklı homopolimerler, makrofotobaşlatıcı kullanılarak metilmetakrilat izobütilvinileter blok kopolimeri elde edildi. Ayrıca bu fotobaşlatıcıların glisidilmetakrilat (GMA) gibi hibrid monomerlerin çapraz bağlanma tepkimelerini de gerçekleştirdiği saptandı. Böylece literatürde ilk defa tellurium içeren organik yapılar kullanılarak serbest-radikal başlatmalı katyonik fotopolimerizasyon tepkimeleri gerçekleştirildi.

Üçüncü çalışmada ise (Bölüm 4) tiyoksanton ve fenaçil kromoforları içeren yeni bir sülfonyum tuzu (2-izopropiltiyoksantonyum fenaçil hegzafloroantimonat) sentezlendi (ITXPhenS). Teorik çalışmalar yardımıyla (YFT) yapılan denemeler sonuncunda ITXPhenS yapısının N,N-dimetilanilin yapısıyla yük-transfer geçişleri oluşturduğu gözlemlendi. Oluşan yeni yük-transfer kompleksleri birçok farklı monomerin hem radikal hem de katyonik polimerizasyonunu görünür bölge ışıması altında başarılı bir şekilde gerçekleştirdi. Bu organotelluryum fotobaşlatıcılarının katyonik polimerizasyondaki verimlilikleri photo-dsc cihazı kullanılarak da kanıtlandı. Glisidil metakrilat (GMA) hibrit monomerini polimerleştirebilmeleri elde edilen sistemin hem radikal hem katyonik polimerleşme gerçekleştirdğini kanıtladı. Döngüsel voltametri çalışmaları elde edilen yük-transfer kompleksinin indirgenme potansiyelinin -0.36V gibi en iyi katyonik fotobaşlatıcıları olarak bilinen iyodonyum tuzlarının indirgenme potansiyeli (-0.25V) ile kıyaslanabilecek bir değer olduğu ortaya çıktı.

Son bölümde (Bölüm 5) tüm çalışmaların ortak sonucu ve gelecekte yapılması planlanan çalışmalara değinildi. Bu çalışmalar arasında yeni tek molekülden oluşan yük-transfer komplekslerinin sentezi ve yapılarının tek kristal x-ışınımı yöntemiyle aydınlatılması var. Bu yeni tip molekül-içi yük-transfer kompleksleri yapılarında bulundurdukları elektron alıcı ve elektron verici üniteler sayesinde yakın-infrared bölgesinde ışık absorplayabilen, bu sayede çok düşük enerji ihtiyacı duyan fotobaşlatıcılar olabilecektir.

1. INTRODUCTION –PHOTOPOLYMERIZATION

1.1 Principles of Photopolymerization

The process forming polymeric molecules by using light as the energy source, is generallly called as “photopolymerization”. In accordance with the mostly accepted terminology, photopolymerization means the synthesis of polymers by chain reactions that are initiated through the absorption of light (photon) by a photosensitive system. In conventional photopolymerization reactions, light is only an initiating tool. It does not have any role in the propagation and termination stages of the polymerization process. Both radical and cationic polymerizations can be initiated by light if appropriate photoinitiators and monomers are used. Photoinitiators are compounds that are most of the time thermally stable and capable of absorbing light with relatively high absorption coefficients in the UV or visible wavelength. Except special applications, only small amount of photoinitiators (0.001-0.00001 eq of monomer) are used in the photopolymerization reactions.

Industrial photopolymerization reactions mostly depend on the use of UV light sources emitting in the 250–400 nm wavelength range (UV range). The handling of these UV-sensitive photoinitiators are easy and does not require any special precautions, which are not necessary sensitive or have limited sensitivity to visible light. Due to the many advantages offered, photoinitiation continued to replace the other coventional initiation techniques involving thermochemical or electrochemical processes [1]. Photoinitiation is also considered to be an alternative to initiation by high-energy radiation, such as electron beam radiation. Initiation by high-energy radiation is less specific than photoinitiation because high-energy radiation can simultaneously generate different free radical species of differing reactivity as well as different ions with different reactivities.

Free radical and cationic polymerizations are both limited to certain kinds of monomers. Olefinic and acrylic monomers can only be polymerized by free radical mechanism. On the other hand, other compounds such as oxiranes and vinyl ethers can only be polymerized by cationic mechanisms. Photopolymerizations can most of time be performed at room temperature and sometimes even at much lower temperature (below 0 ^oC).

1.2 Types of Photoinitiators

Two types of compounds are used as photoinitiators of free radical polymerization reactions which differ in their mode of generating reactive free radicals.

- Type I initiators undergo a very rapid bond cleavage after they absorp a photon.
- Type II initiators form relatively long-lived excited triplet states which are capable of undergoing hydrogen-abstraction or electron-transfer reactions with a co-initiator molecule that is intentionally added to the system having monomer.

Some of the Type I photoinitiators are listed in Figure 1.1.

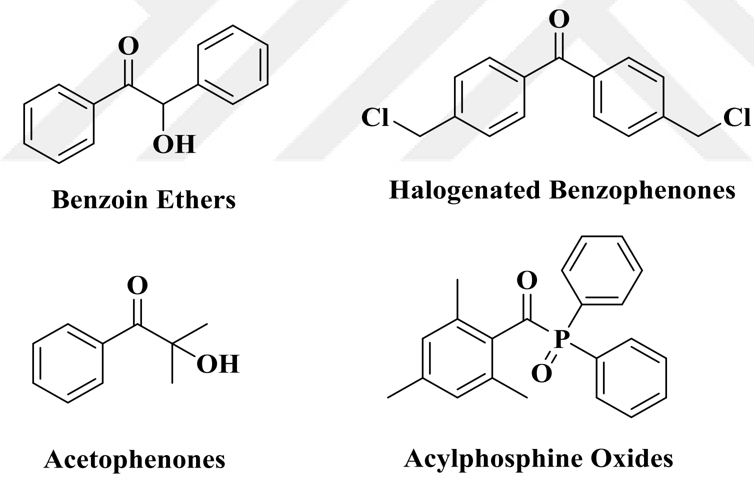


Figure 1.1 : Mostly used Type I photoinitiators.

Nearly all of these compounds contain aromatic carbonyl groups which act as chromophores. Since the dissociation energy of the C–C bond adjacent to the benzoyl group is lower than the excitation energy of the excited state, these compounds can undergo rapid bond cleavage resulting in the formation of radicals, one of them being a benzoyl-type radical (Figure 1.2) [2]. Phosphinoyl radicals are more reactive towards olefinic compounds than carbon-centered radicals.

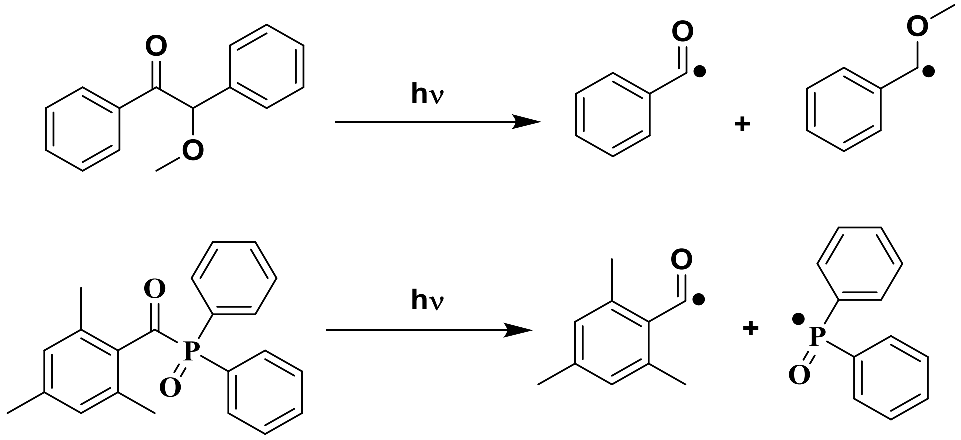


Figure 1.2 : Photocleavage of benzoyl containing photoinitiators.

Typical type II initiators contain carbonyl chromophores and are listed in Figure 1.3.

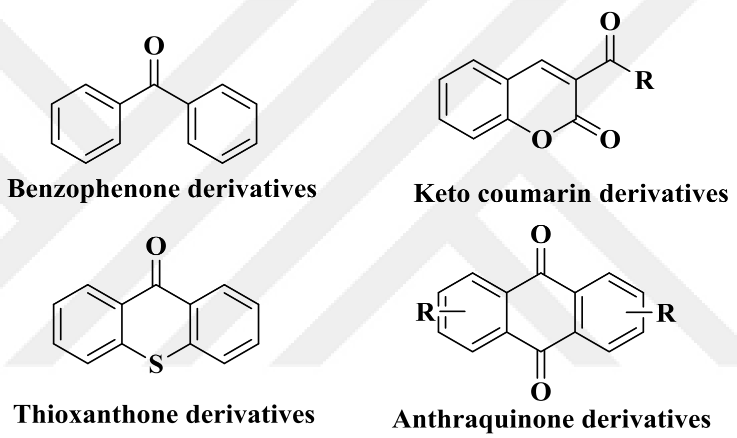


Figure 1.3 : Most common Type II Photoinitiators.

After irradiation, they form long-lived triplet states, which do not undergo cleavage reactions since the triplet energy is lower than the bond dissociation energy. The triplet species react with co-initiators (Figure 1.4.) [3].

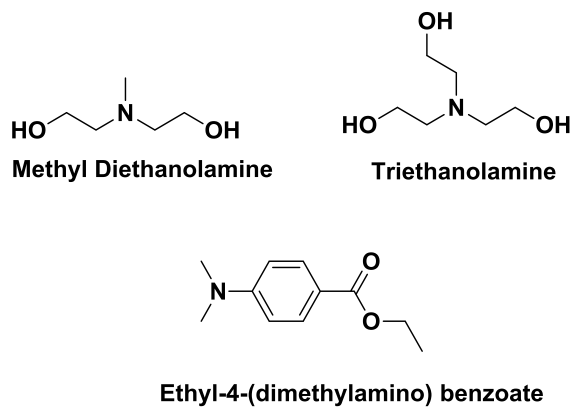


Figure 1.4 : Some co-initiators for Type II Free Radical Photoinitators.

For example, diaryl ketones can abstract hydrogen atoms from alcohols that the triplet energy exceeds the bond dissociation energy of the C–H bond to be broken. Type II initiators containing carbonyl groups can also undergo electron-transfer reactions, which lead to hydrogen abstraction after an intermediate “exciplex” [4] (excited complex) is formed between the diaryl ketone radical anion and the amine radical cation, as illustrated in Figure 1.5.

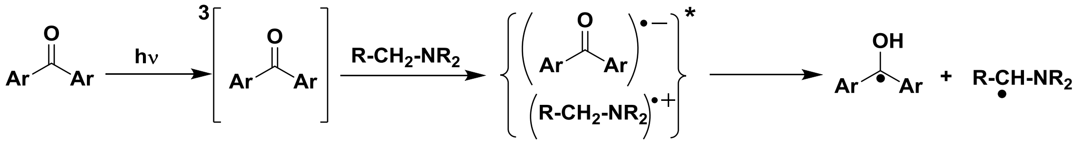


Figure 1.5 : Generation of reactive species using Type II initiators.

Nowadays, visible-light photoinitiators are very often used in many special applications using visible-light emitting lasers of low cost and high performance. These applications are photoimaging processes, such as laser direct imaging, LDI, and computer-assisted design, CAD, which are used for the imaging of printed circuit boards [5]. Other visible light applications are the production of holograms and color printing. In the literature, thousands of photoinitiator system for visible light exposure have been synthesized.

1.3 Cationic Photoinitiators

Although photoinitiated radical polymerizations have been known and investigated for long time, photoinitiated cationic polymerization has received little attention. The slow development of the photocationic polymerization was due to the difficulty of finding suitable photoinitiators which could catalyze cationic polymerization.

Photoinitiated cationic polymerizations are rapid polymerizations that proceed without oxygen inhibition, have minimal sensitivity to water and they are able to polymerize vinyl ethers, oxiranes (epoxides), and other heterocyclic monomers (Figure 1.6) which can not be polymerized by free radical mechanisms. Cationic photopolymerizations proceed as chain reactions involving initiation and propagation steps [3].

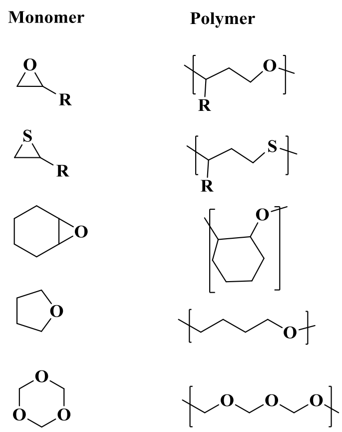


Figure 1.6 : Monomers polymerizable by cationic mechanism.

However, in most of the cases there is no termination step and the growing chains are terminated by nucleophilic impurities which are present in the system. Cationic reactions are photoinitiated with the aid of special initiators [6]. Typical cationic photoinitiators are listed below (Figure 1.7).

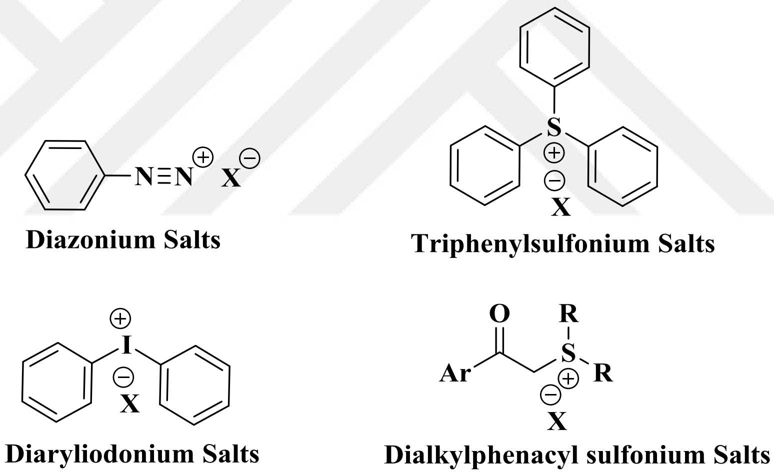


Figure 1.7 : Monomers polymerizable by cationic mechanism.

Reactive cations can be generated via three different routes: (a) by direct photolysis of the initiator, (b) by sensitized photolysis of the initiator, and (c) by free radical mediation.

Crivello's pioneering work on onium based salts (mostly sulfonium and iodonium salts) had great impact on the investigations of cationic photoinitiators [7]. The polymerization mechanism proposed for the onium salt type photoinitiators of the general structure $\{(A–B)^+ X^-\}$s is the generation of Brønsted acids (superacids) (Figure 1.8) of the structure H^+X^- based on non-nucleophilic anions X^-. These superacids play a prominent role in the initiation process.

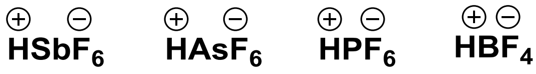


Figure 1.8 : Typical superacids used in cationic polymerization reactions.

On the other hand, radical cations A^{+}, formed by irradiation can also react with the polymerizable monomers. According to the general mechanism of the photolysis, shown in Figure 1.9, the radical cation $A^{+\cdot}$ may abstract a hydrogen from surrounding molecules RH. The resulting cation AH^{+} then releases a proton.

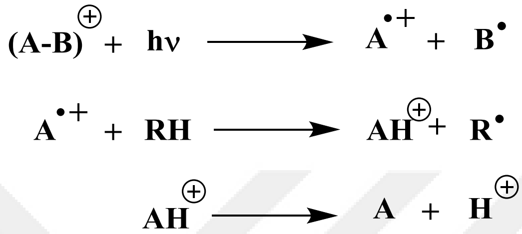


Figure 1.9 : Photolysis mechanism of an onium salt.

The detailed mechanism of the photolysis of a diaryl iodonium ion is presented in Figure 1.10. Both the initially formed radical cation and the proton are possible initiating species for polymerization reactions.

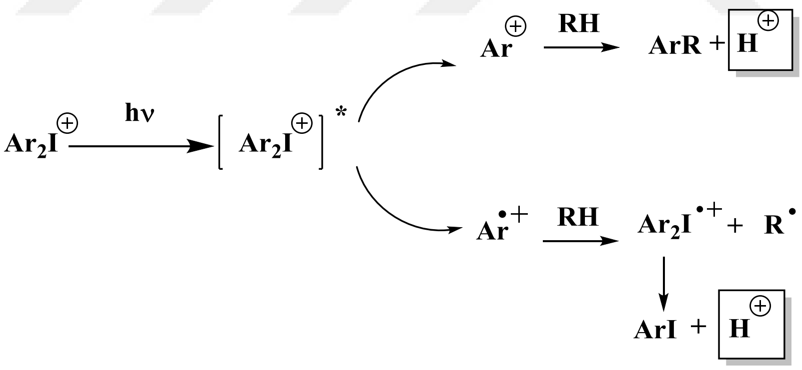


Figure 1.10 : Photolysis mechanism of a diaryliodonium salt.

1.4 Sensitized Photoinitiation

The First Law of Photochemistry states that light or photons must be absorbed to have an effect. In some experiments, the molecule that absorbs the light is chemically changed, but this absorption does not change any other molecule in the system. In other experiments, the molecule that absorbs the light changes the chemistry of another molecule in the system. The latter case is called “Photosensitization” and the molecule that absorbs the photon is called the photosensitizer and the altered molecule is the acceptor or substrate. Both the photosensitizer and light are required for photosensitization. Since diaryliodonium and triarylsulfonium salts absorb light mainly at wavelengths below 300 nm, these compounds are not useful photoinitiators when irradiated at wavelengths above 300 nm. Crivello has demonstrated that the photolysis of diaryliodonium salts may be photosensitized in the visible light region using several dyes, while perylene and other polynuclear hydrocarbons worked as photosensitizers for the photolysis of triarylsulfonium salts [8]. Pappas and Jilek have also suggested that an exciplex can be formed between the excited dye and the aryl onium salt [9]. In most cases, energy transfer from PS* to $(A–B)^+$ can be excluded. However, PS* can be oxidized by the onium ion, i.e. radical cations $PS^{\cdot+}$ can be formed by electron transfer from the electronically excited photosensitizer PS* to the onium ion (see Figure 1.11), provided that the free energy ΔG of this reaction is low. Anthracene and carbazole derivatives are typical electron-transfer photosensitizers.

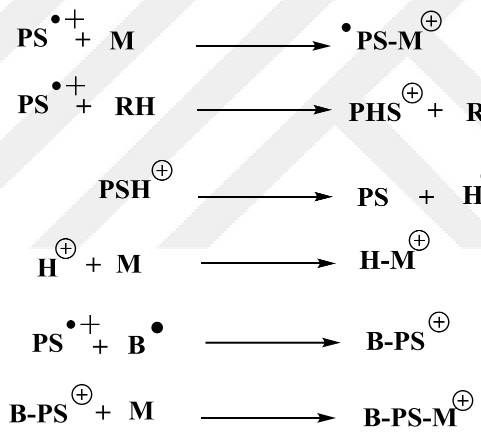


Figure 1.11 : Possible initiation route of photosensitized cationic polymerization.

1.5 Free-Radical Promoted Cationic Photoinitiation

Some of the carbon-centered free radicals, which are formed by irradiation or by heating of commercially available free radical initiators, can be oxidized using onium salts $(A\text{-}B)^+$ the reaction according to Figure 1.12 [10].

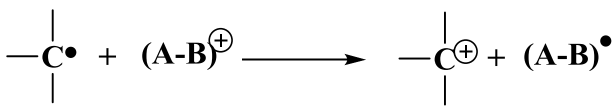


Figure 1.12 : Initiation route for free-radical promoted cationic polymerization.

Carbocations generated this way can directly add to monomers like tetrahydrofuran, cyclohexene oxide or vinyl ether, they can form Brønsted acids by abstracting hydrogen from surrounding molecules. This method, which is called “Free-Radical-Promoted Cationic Polymerization” is quite effective providing possibility to use a large variety of radical photoinitiators.

1.6 Purpose of Thesis

The objective of this thesis is to design and synthesize novel photoinitiators which can absorp light in UV and/or visible region, capable of polymerizing different monomers with different functionalities. To investigate their ability of photopolymerization different spectroscopic techniques like NMR, FT-IR, UV-Vis and fluorescence spectroscopy together with other measurement methods such as cyclic voltammetry, GPC, DSC, Photo-DSC and single crystal X-ray diffraction were used. The thesis is written in a way that each chapter has its own introduction, results and conclusion parts.

Chapter 2 (First part) is about the synthesis of a novel sulfonium salt, diphenylphenacyl sulfonium tetrafluoroborate ($DPPS^+BF_4^-$), its investigation of photopolymerization activity and the comparison of its activity with a commercially available analogue triphenyl sulfonium tetrafluoroborate ($TPS^+BF_4^-$) to reveal that the phenacyl salt has better photocatalytic activities.

Chapter 3 demonstrates the use of previously synthesized organotellurium compounds in the presence of diphenyliodonium salt as a new strategy for the free-radical promoted cationic polymerization of different monomers such as CHO, IBVE, NVC under visible and sun light irradiation.

Chapter 4 concerns the synthesis of a new thioxanthonium (type of sulfonium) salt which can form different charge-transfer complexes (CTC’s) with *N*,*N*-Dimethylaniline (DMA) in different ratios (2:1-1:1). These charge-transfer complexations and their photocatalytic activites for the photopolymerization of a variety of monomers are investigated with different spectroscopic techniques.

Finally, conclusions are summarized in Chapter 5 including remarks for future work.

2. DIPHENYLPHENACYL SULFONIUM SALT AS DUAL INITIATOR FOR BOTH RADICAL AND CATIONIC POLYMERIZATIONS[1]

2.1 Introduction

Photopolymerization is currently one of the most important polymerization techniques in a wide range of applications such as coatings, adhesives inks, printing, and microelectronics [11-15]. While most of the industrial applications of photocuring focus on free radical polymerization techniques, the cationic mode also receives considerable attention in industry and academia mainly due to its insensitivity to oxygen [16]. The further growth of such interest is strongly coupled to the development of initiators which fulfill requirements for specific applications. High curing speed, wavelength selectivity, low migration, and solubility are the most important criteria for successful application of initiators in industrial curing processes. Onium salts are known to initiate both free radical and cationic polymerizations [17, 18]. Among them, iodonium [7, 19-22], pyridinium [23], phosphonium [24, 25] and sulfonium salts [26, 27] are most extensively used as initiators for cationic polymerization. The major drawback of onium type initiators is their low spectral response at high wavelengths. In attempt to extend the sensitivity to higher wavelengths, onium salts were combined in a two component system in conjunction with photosensitizers [28, 29].Onium salts can, thus, be activated by photosensitizers with favorable absorption characteristics in mechanistically different pathways involving electron transfer reactions in exciplexes [30, 31], charge transfer complex [32] and with free radicals [33, 34]. However, solubility, compatibility, migration, and cost make bi-component systems less attractive for industrial applications. Phenacyl salts are a class of onium salts that can overcome this problem to some extent by incorporating a chromophore group in the structure and slightly shifting the absorption to longer wavelengths [35, 36]. They are easily synthesized by the reaction of phenacyl halides and the corresponding heteroatom nucleophiles and subsequent ion exchange with the sodium, potassium, or silver salt of a non-nucleophilic counter anion [37]. As

[1] This chapter is based on the paper "Diphenylphenacyl Salt as Dual Initiator For Both Radical and Cationic Polymerizations" by Kaya K., Kreutzer J., Yagci Y., Journal of Polymer Science, Part A; vol. 56, issue 4, 451-457.

presented on the example of phenacyl pyridinium salt (Figure 2.1), cleavage occurs upon photolysis either homolytically to give a phenacyl radical and the corresponding heteroatom radical cation or heterolytically resulting in the formation of the phenacyl cation directly. In the former case, internal electron transfer also yields phenacylium cation. Thus, formed species were shown to initiate both free radical and cationic polymerizations [38]. Several phenacyl sulfonium salts were previously designed and successfully used in free radical and/or cationic polymerization reactions [39-42]. However, due to the aliphatic and cyclic nature, limited spectral shift and efficiency was obtained. To combine advantages from phenacyl and aryl sulfonium structures, characterization of a novel diphenylphenacyl sulfonium salt and its application as a dual initiator for radical and cationic photopolymerizations. Both direct and sensitized polymerizations were investigated and initiation efficiencies were compared with that of the analogous triphenyl sulfonium salt.

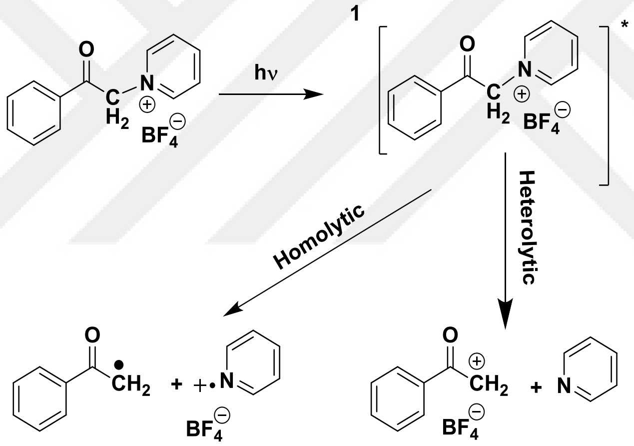


Figure 2.1 : Photoinduced decomposition of phenacylpyridinium salts.

2.2 Experimental

Diphenyl sulfide (98%, Alfa Aesar), 2-bromoacetophenone (phenacylbromide, 99%, Merck), silver tetrafluoroborate (98%, Sigma-Aldrich), diphenyliodonium bromide, 97%, bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (BAPO, Ciba specialty chemicals), 2,2-dimethoxy-2 phenylacetophenone (DMPA, Ciba), tetrabutylammonium hexafluorophosphate (98%, Sigma-Aldrich), and perylene (99%, Sigma-Aldrich) were used as received without further purification. Methyl methacrylate (MMA; 99%, Sigma-Aldrich) and styrene (St; 99%, Sigma-Aldrich) were purified by passing through a basic alumina column to remove the inhibitor before use. NVinylcarbazole (NVC; 98%, Sigma-Aldrich) was crystallized from absolute ethanol. Cyclohexene oxide (CHO) was purified by vacuum distillation over calcium hydride and stored under nitrogen. All solvents were purchased from Merck and purified by conventional procedures.

^{1}H-NMR and ^{13}C-NMR spectra were recorded in deuterated chloroform ($CDCl_3$ with tetramethylsilane as an internal standard at 500 and 125MHz, respectively, on an Agilent VNMRS 500 spectrometer at 25^{o}C). Fourier-transform infrared (FTIR) spectra were recorded on Perkin–Elmer Spectrum One spectrometer with an ATR Accessory (ZnSe, PikeMiracle Accessory) and mercury cadmium telluride detector. Sixtyfour scans were averaged. UV-visible spectra were recorded with a Shimadzu UV-1601 double-beam spectrometer equipped with a 50-W halogen lamp and a deuterium lamp which can operate between 190 and 1100 nm. Gel permeation chromatography (GPC) measurements were performed on a TOSOH EcoSEC GPC system equipped with an auto sampler system, a temperature controlled pump, a column oven, a refractive index (RI) detector, a purge, and degasser unit and TSKgel superhZ2000. Tetrahydrofuran was used as an eluent at flow rate of 1.0 mL/min at 40^{o}C. Refractive index detector was calibrated with polystyrene standards having narrow molecular weight distributions. GPC data were analyzed using Eco-SEC Analysis software. The photo-differential scanning calorimetry (photo-DSC) measurements were carried out by means of a modified PerkinElmer Diamond DSC equipped with a high-pressure mercury arc lamp emitting light at 320–500 nm. Cyclic voltammetry (CV) was performed on Princeton Applied Research VersaStat3 potentiostat under the control of VersaStudio Software with a three-electrode cell in a solution of 0.1 M tetrabutylammonium hexafluorophosphate ($Bu4N^+PF_6^-$) dissolved in dry acetonitrile at a scan rate of 50 mV/s. The solution in the three-electrode cell was purged with pure nitrogen for at least 10 min before each measurement. A Pt (platinum) wire was used as the counter electrode and Ag/AgCl electrode was used as the reference electrode. LUMO energies were estimated by the empirical equation LUMO5 (E_{onset} red 14.4) eV. The single crystal X-ray measurement was carried out on a Bruker D8 VENTURE diffractometer equipped with a shuterless detector using graphite monochromatic Mo-Kα radiation (0.71073 Å) and scanned with ω-rotation frames at room temperature. Triphenylsulfonium tetrafluoroborate ($TPS^+BF_4^-$) was prepared according to a known procedure [43] by reacting diphenyliodonium bromide with sodium tetrafluoroborate and diphenyl sulfide. Pure $TPS^+BF_4^-$ was obtained by recrystallization from ethanol in 85% yield. Diphenylphenacylsulfonium tetrafluoroborate ($DPPS^+ BF_4^-$) was prepared according to a known procedure [44]. Typically, a mixture of diphenylsulphide (5.0 g, 27 mmol), 2-bromoacetophenone (5.4 g, 27 mmol), and $AgBF_4$ (5.3 g, 27 mmol) was stirred in 100 mL of dry dichloromethane for 48 h at room temperature. (Figure 2.2) After filtration, the solvent was removed to afford a tan-colored solid that could be recrystallized from dichloromethane. Single crystals suitable for single crystal XRD measurement were obtained by slow evaporation of a concentrated dichloromethane solution in 7 days.

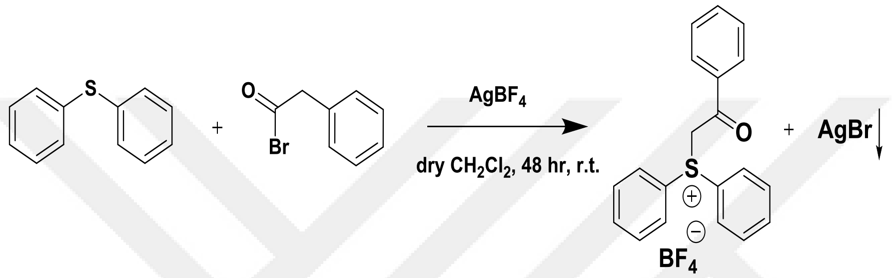


Figure 2.2 : Synthesis of $DPPS^+BF_4^-$.

2.3 Results and Discussion

Theoretical calculations were performed with the Gaussian09 program package [45]. Geometries were optimized with the M06 functional in combination with the 6–311G** basis set in gas phase. All geometries were confirmed as minimum structures displaying all frequencies real. Transition states were calculated with the Synchronous Transit-Guided Quasi Newton method as implemented in Gaussian09 using the optimized structures of the educt and product and a guess structure for the transition state. The nature of the transition state was confirmed by displaying one imaginary frequency and connecting the educt, transition state, and product via an internal reaction coordinate calculation. Gibbs free energies and enthalpies include thermal corrections at 298 K. Excitation energies were calculated by density functional theory in its time dependent framework (TD-DFT) with the functional and basis set combination as described before the spectra were modeled with a lorentzian broadening of each transition line with a half width of 0.18 eV. Yield: 6.0 g (57%), (m.p. 160–161). FT-IR (ATR): 51685cm^{-1} (s), 2987 cm^{-1} (m), 3070 cm^{-1} (m). ^{1}H-NMR (500 MHz, $CDCl_3$, d): 8.00 (dd, J58.0 Hz, 2H, Ar), 7.68 (t, J=7.60 Hz, 1H, Ar), 7.50(t, J=7.50Hz, 1H, Ar), 7.38–7.35 (m, 4H, Ar), 7.33-7.30 (m, 4H, Arl), 7.26 (d, J=7.25Hz, 2H, Ar), 7.24 (t, J=7.25 Hz, 1H, Ar), 4.47(s, 2H, CH2) ppm (Fig. 1). ^{13}C-NMR (125 MHz, $CDCl_3$, d): 191.22 (C=O), 134.70 (C, Ar.), 135.94 (C, Ar) 134.00 (C, Ar), 129.39 (C, Ar), 126.93 (C, Ar.), 31.16 (C, CH2).

For polymerization, a quartz tube with a magnetic bar was heated and degassed for 20 min before it was filled with monomer (0.50 mL, 4.70 mmol) and photoinitiator (0.07 mmol) in 0.5 mL dichloromethane under nitrogen atmosphere. The solution was irradiated in a Rayonet photoreactor equipped with 12 lamps emitting at 300 nm. Before the polymerization trials, thermal and photochemical stabilities of the salts were investigated. Both salts are thermally stable up to 200^{o}C. UV-vis absorption changes in both photoinitiators under 300 nm light are presented in the supporting infromation. After irradiation, the solution was precipitated in 10-fold excess methanol and the precipitated polymer was filtered and dried under vacuum. All the photosensitized polymerization reactions of CHO were carried out in a capped borosilicate tube, the irradiation was achieved by a photoreactor equipped with six lamps emitting polychromatic light at 400–500 nm except DMPA sensitization in which lamps emitting light at 350 nm were used. For the photopolymerizations followed by photo-DSC, a uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 62 mW/cm^2 by a UV radiometer capable of broad UV range coverage. The mass of the sample was 3 mg, and the measurements were carried out in an isothermal mode at 30^{o}C under a nitrogen flow of 20 mL/min. The reaction heat liberated in the polymerization is directly proportional to the number of acrylate groups reacted in the system. The structure of the salt was confirmed by NMR, ATR-FTIR, single crystal X-ray, and UV-Vis spectral analysis. As can be seen from Figure 2.3, the ^{1}H-NMR spectrum exhibits signals for the aromatic and methylene protons at 8.0–7.2 ppm and 4.4 ppm, respectively. In Figure 2.4, the calculated and experimentally measured UV-vis spectra of the salts are compared. Notably, the absorption of the phenacyl salt appears at higher wavelengths.

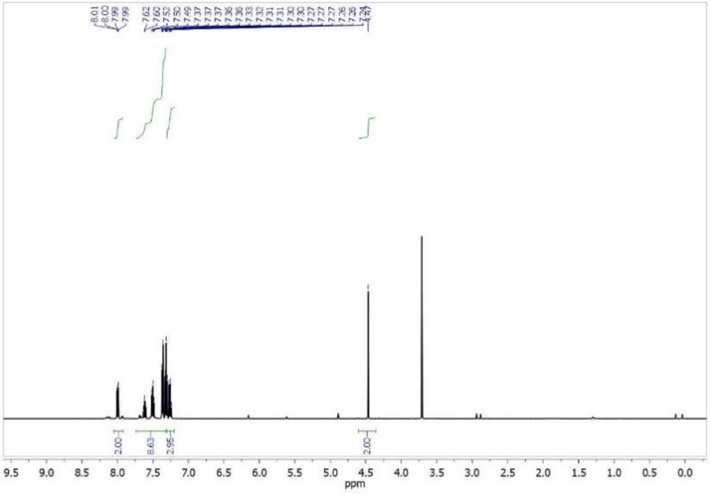


Figure 2.3 : ^{1}H-NMR spectrum of $DPPS^{+}$ BF_4^{-}.

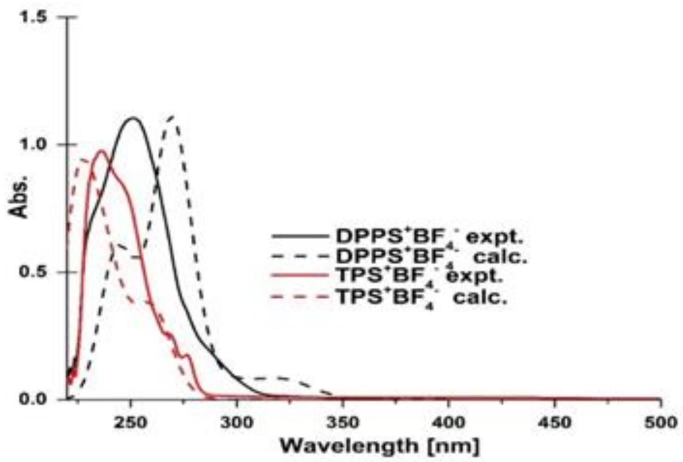


Figure 2.4 : Calculated and measured UV-Vis spectra of $DPPS^{+}BF_4^{-}$ and $TPS^{+}BF_4^{-}$.

For single crystal XRD study, a single crystal of $DPPS^{+}$ BF_4^{-} with dimensions 0.01x 0.04x0.20 mm was grown by slow evaporation of dichloromethane solution. Molecular drawings are generated using OLEX2. Ver. 1.2-dev [46]. Thermal ellipsoids are plotted at the 50% probability level. The crystal and instrumental parameters were used in data collection. CCDC 1545578 contains the supplementary crystallographic data. Crystal parameters and refinement details for $DPPS^{+}BF_4^{-}$ are summarized in the supporting information. Further details on crystal data, data collection, refinements, and oak ridge thermal ellipsoid plot (ORTEP) drawings with the atom numbering schemes are given in the Supporting Information. The structure of the salt was further confirmed by single crystal XRD. The compound crystallized in the orthorhombic lattice system. The SAC bond lengths are in the normal range of

1.76–1.81 Å for a pyramidal sulfonium cation and lone pair repulsions of sulfur decrease the C-S-C bond angles below the tetrahedral values which are in the range of 102°–103° and in good agreement with the reported value for sulfonium cations [47, 48]. The B-F bond lengths are in the range of 1.33–1.34 Å close to that given for BF_4^- anion [49]. No inter- or intra-molecular interaction in the crystal lattice could be observed.

To investigate the applicability of this photoinitiator in the initiation of radical polymerization, a series of vinyl monomers namely MMA, styrene (St), and NVC were used. Polymerization of all monomers was successfully achieved and compared with the conventional sulfonium salt, $TPS^+BF_4^-$, relatively higher monomer conversions were attained (Table 2.1). It should be noted that NVC is a strong electron rich monomer and can undergo both free radical and cationic polymerizations.

Table 2.1 : Photoinduced polymerization using $DPPS^+BF_4^-$ for different monomers.

Monomer	**Time (min)**	**Conversion[b] (%)**	**M_n[c] x 10^{-3} (g mol^{-1})**	**$Đ$[d]**
MMA	15	25	22.26	1.27
MMA	30	56	37.62	1.78
MMA	60	64	25.13	2.42
MMA	120	68	26.75	1.71
St	120	59	11.43	2.42
NVC	120	52	1.39	5.19
CHO	120	31	26.40	1.85

Interestingly, similar conversions were obtained for the cationic polymerization of the oxirane monomer, CHO that polymerizes only by a cationic mechanism indicating that the same cationic species were involved in the initiation process. The observed higher efficiency in the free radical process may be related to faster decomposition rate of the phenacyl salt. In the corresponding cationic mode, however, the initiating species are formed after the subsequent electron transfer process (vide infra). Principally, the initiation action of phenacylium salts is based on either homolytic or heterolytic cleavage of the excited salt. Homolytic cleavage (pathway a in Figure 2.5) results in the formation of either a phenyl or a phenacyl radical, together with a diphenylsulfonium radical cation. The formed radical species are able to initiate the free radical polymerization in a further step (Figure 2.5).

In the heterolytic cleavage pathway (pathway c in Figure 2.5), diphenylsulfide and a phenyl cation are formed. The same products can, however, be obtained after homolytic cleavage (pathway a) followed by electron transfer from the radical species to the sulfonium radical (pathway b in Figure 2.5). The cationic species obtained by heterolytic cleavage or homolytic cleavage with subsequent electron transfer are able to initiate cationic polymerization reactions. Furthermore, it is known that hydrogen abstraction from the solvent can generate superacid which is able to initiate cationic polymerization. We will start our discussion with the free radical polymerization reaction. Homolytic cleavage results in the formation of phenyl or phenacyl radical and the diphenylsulfinyl radical.

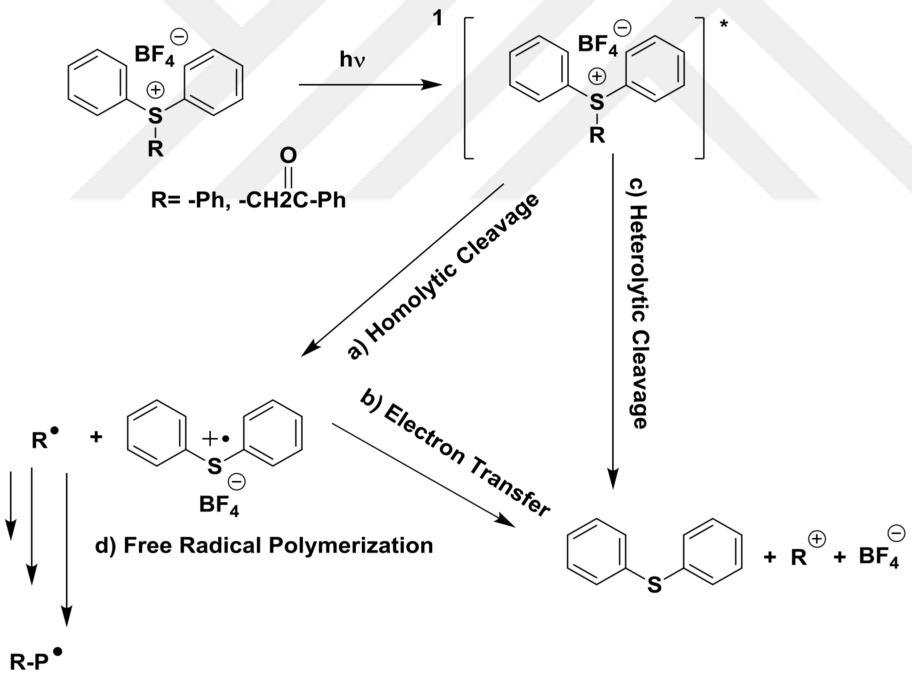


Figure 2.5 : Initiation pathways for both radical and cationic polymerizations.

This reaction is exothermic for both, $TPS^+ BF_4^-$ and $DPPS^+ BF_4^-$ initiators; however, the formation of the phenyl radical is energetically slightly favored. Addition of the first MMA monomer unit either to the phenyl or phenacyl radical proceeds via a transition state which lies at 700 kJ/mol for the phenyl-MMA reaction and 830 kJ/mol for the phenacyl-MMA reaction. (Figure 2.6)

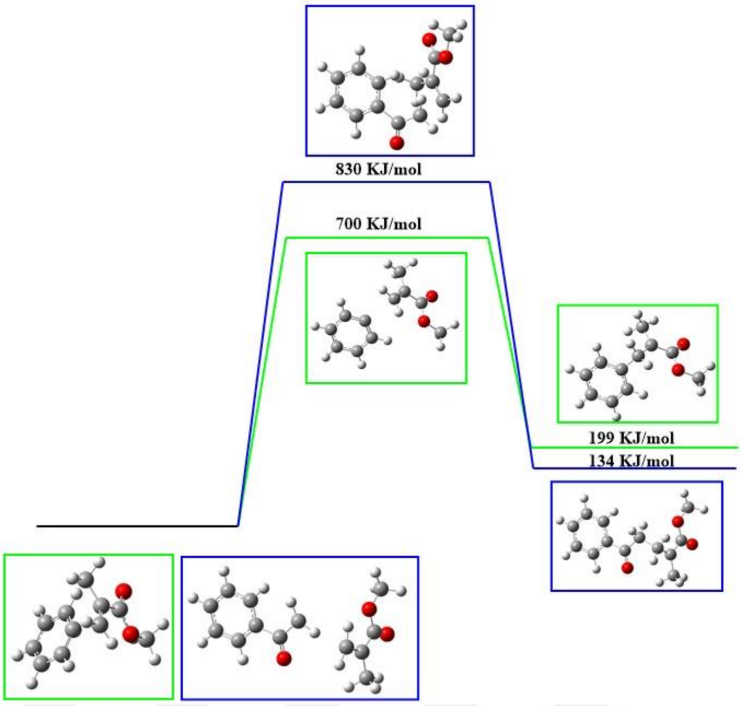


Figure 2.6 : Energy diagram for the initiation of radical polymerization of MMA.

The products of the first monomer addition lie energetically close to each other (199 kJ/mol for phenyl-MMA compared with 134 kJ/mol for phenacyl-MMA) with phenacyl-MMA being the energetically favored product. However, this might be one reason among others for the increased polymer conversion when $DPPS^+ BF_4^-$ is used as initiator in the polymerization of MMA and St. The cationic polymerization mechanism can proceed via two pathways: homolytic cleavage and subsequent electron transfer results in the formation of phenacyl cations and diphenyl sulfide. As outlined before, homolytic cleavage is energetically favored for the $TPS^+BF_4^-$ initiator. The electron transfer to diphenyl sulfide and formation of the respective cations is energetically disfavored for both the initiator species, however, energetically almost neutral for the $TPS^+BF_4^-$ initiator. The second possibility, heterolytic cleavage seems energetically disfavored for both initiating systems. We, therefore, speculate that the initiation pathway in cationic polymerization proceeds via homolytic cleavage and subsequent electron transfer from the phenyl or phenacyl radical to the diphenyl sulfinium species. Energetically, the first step, which is the homolytic cleavage is favored for $TPS^+ BF_4^-$; however, the second step, the electron transfer, proceeds more likely for the $DPPS^+ BF_4^-$ initiator. The difference in the reaction enthalpies and reaction free energies between $DPPS^+BF_4^-$ and $TPS^+BF_4^-$ is rather small. Experimentally, this is reflected in similar conversions for the polymerization of CHO or NVC. To further extend spectral sensitivity to longer wavelengths, indirect systems involving free radical promotion and sensitization by electron transfer reaction in the exciplex in cationic polymerizations by using CHO as a model monomer were conducted. DMPA, BAPO, and perylene were selected as free radical source and sensitizer, respectively. In all cases, $DPPS^{+}BF_4^{-}$ was found to be more reactive due to the more favorable thermodynamic conditions, as would be expected on the basis of their reduction potentials. Upon irradiations at selected wavelengths, both DMPA and BAPO generate electron donor radicals that can readily be oxidized to the corresponding cationic species capable of initiating cationic polymerization of CHO (Figure 2.7).

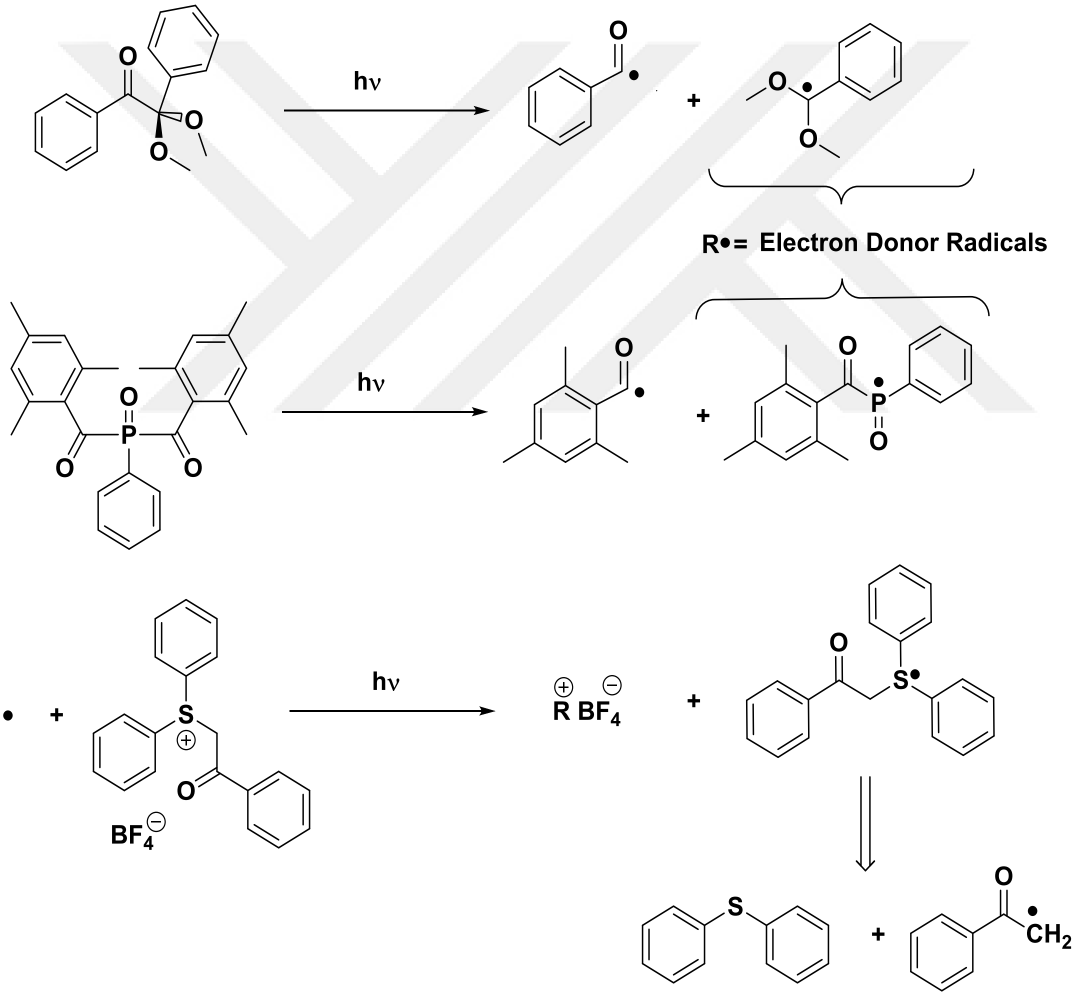


Figure 2.7 : Free radical promoted cationic polymerization using $DPPS^{+}$ BF_4^{-}.

Similarly, with perylene as photosensitizer relatively higher conversions were attained (Table 2.2.).

Table 2.2 : Sensitized cationic polymerization of CHO using $DPPS^+BF_4^-$, $TPS^+BF_4^-$.

Initiator	Monomer	Sensitizer	Time (min)	Conversion[b](%)	M_n[c]x10^{-3} (g mol^{-1})	$Đ$[d]
$DPPS^+BF_4^-$	CHO	BAPO	60	62	14.50	2.34
$TPS^+BF_4^-$	CHO	BAPO	60	45	21.00	2.12
$DPPS^+BF_4^-$	CHO	DMPA	60	42	16.02	1.82
$TPS^+BF_4^-$	CHO	DMPA	60	30	16.14	2.26
$DPPS^+BF_4^-$	CHO	Perylene	60	45	14.18	1.89
$TPS^+BF_4^-$	CHO	Perylene	60	38	37.83	1.39

According to Pappas et al., sensitization by polynuclear aromatic compounds proceeds via electron transfer processes within exciplexes [50]. (Figure 2.8).

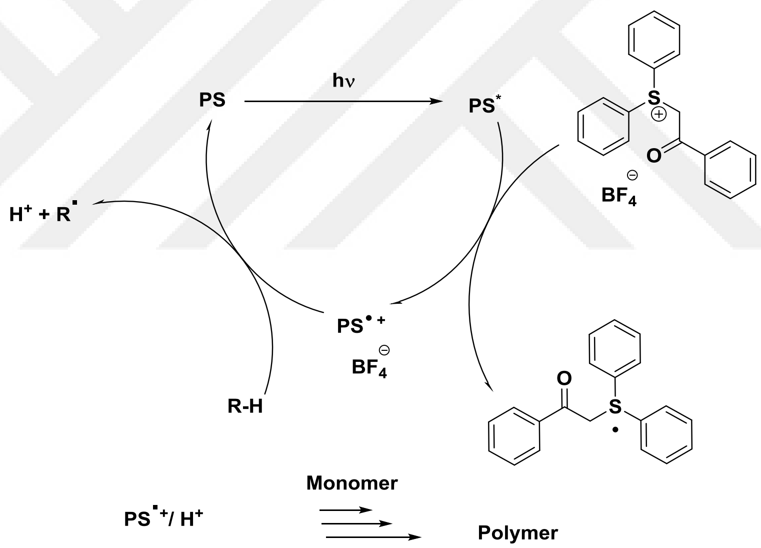


Figure 2.8 : Photosensitization of $DPPS^+BF_4^-$ for the cationic polymerization.

In our case, it is quite likely that the phenacyl radicals thus formed may further undergo electron transfer to generate additional cationic species. Photo-DSC appeared to be very useful in investigating the initiation efficiency of initiators. We applied this method to shed light on the initiation efficiency of our initiators for the polymerization of a multifunctional monomer, namely, triethyleneglycol dimethacrylate (TEGDMA). Figure 2.9 shows the photo-DSC curves for the polymerization TEGDMA initiated by both TPS^+ BF_4^- and $DPPS^+$ BF_4^- under polychromatic light.

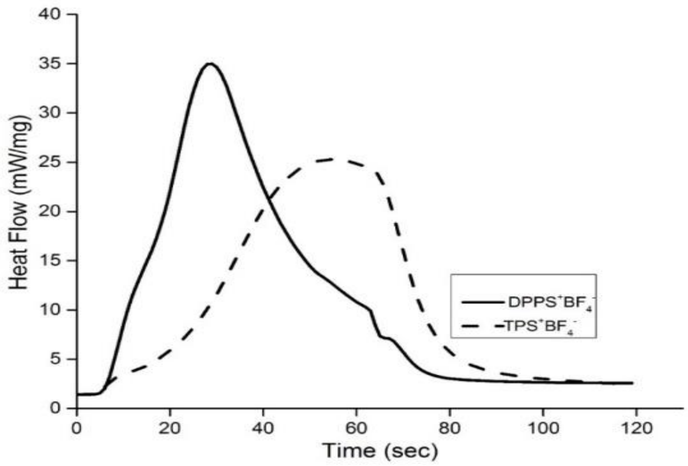


Figure 2.9 : Photo-DSC profiles of photopolymerization of TEGDMA using $DPPS^+$ BF_4^- and TPS^+ BF_4^-.

The inset shows the plot of the conversion versus irradiation time derived from the polymerization system. (Figure 2.9) It is clear that $DPPS^+$ BF_4^- polymerizes TEGDMA monomer in a shorter time with higher conversion in accordance with polymerization behavior observed for the monofunctional monomers.

2.4 Conclusion

A novel phenacyl-type sulfonium photoinitiator ($DPPS^+$ BF_4^-) which is capable of sinitiating both radical and cationic polymerization was synthesized. $DPPS^+$ BF_4^- is thermally stable until 198°C and showed higher absorption characteristics with relatively higher polymerization conversions for most of the monomers compared with its triphenyl sulfonium analogue, TPS^+ BF_4^-. Photosensitization studies also revealed that $DPPS^+$ BF_4^- gave higher conversions compared with that of TPS^+ BF_4^- probably due to the additional cationic species formed. CV studies revealed that $DPPS^+$ BF_4^- undergoes redox processes more efficiently due to the favorable thermodynamic conditions. Potential coating application of the initiating system was demonstrated by photo-DSC studies using a multifunctional monomer TEGDMA.

3. VISIBLE LIGHT-INDUCED FREE RADICAL PROMOTED CATIONIC POLYMERIZATION USING ORGANOTELLURIUM COMPOUNDS[2]

3.1 Introduction

Photoinitiated polymerization processes are widely used in various conventional applications [51], and they continue to advance at a rapid pace as new applications are introduced. This is due to their attractive productivity, energy saving potential, and favorable environmental impact [52] and the possibility of spatial and temporal control presented [53-59]. Although free radical polymerizations are in a more advanced state as most industrial applications of photopolymerization concern free radical systems [60], the corresponding cationic mode has recently received revitalized interest [57, 61] due to its inertness to oxygen and the lifetime of the propagating ionic species. Favored by the non-nucleophilic nature of their counter ions, photoinitiated cationic polymerizations proceed even in the dark once they have been initiated by light [18].

Commercially important and well-studied cationic photoinitiators include iodonium [62, 63], sulfonium [64], alkoxy pyridinium [65], ammonium [66] and phosphonium salts [67]. However, unless specially designed, all of the salts exhibit a poor spectral response at high wavelengths. Spectral sensitivity of these salts can be extended to longer wavelengths from the UV to the near-IR region [68-70] by three modes of action: (i) oxidation of free radicals [71], (ii) electron transfer between a photoexcited molecule and an onium salt [23, 63], and (iii) excitation of charge transfer complexes of onium salts [72]. Among these, radical promoted cationic polymerization involving the oxidation of photochemically formed electron donor radicals by oxidants such as iodonium [73-75] and alkoxy pyridinium salts [76, 77] has strongly influenced research strategies. This is due to the wavelength flexibility offered by the availability of a wide range of free radical photoinitiators. This route also gives the possibility to fabricate complex macromolecular architectures such as block and graft copolymers [10, 78, 79]. Group-transfer addition reactions of organotellurium compounds (R-TeR′) to alkenes and alkynes [80, 81] is a well-established process in organic

[2] This chapter is based on the paper "Visible Light-Initiated Free Radical Promoted Cationic Polymerization Using Organotellurium Compounds", Kaya K., Seba M., Fujita T., Yamago S., Yagci Y., Polymer Chemistry, 2018,**9**, 5639-5643 .

synthesis. Adaptation of this process to synthetic polymer chemistry has led to the development of organotellurium-mediated living radical polymerization (TERP) with several advantages over the other controlled/living radical polymerizations [82-84], such as applicability to structurally different monomers, and tolerance to functional groups and solvents [85, 86]. Moreover, block copolymers and functional polymers with well-defined structures can be readily prepared by TERP [87-89]. The overall process based on the addition reactions of organotellurium compounds to alkenes is presented in Figure 3.1.

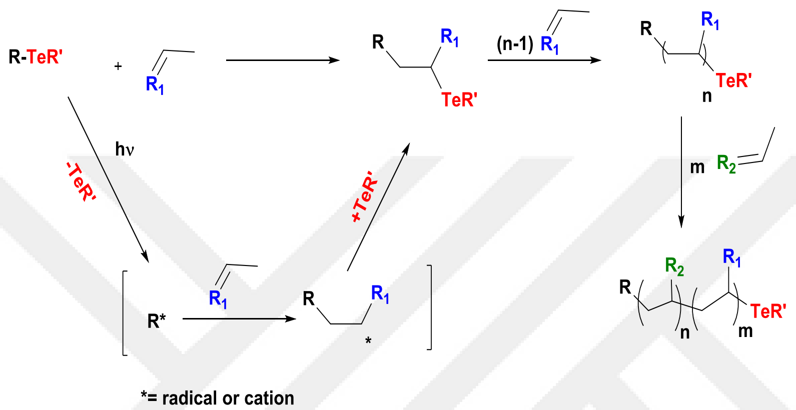


Figure 3.1 : Photoinduced addition of organotellurium compounds to alkenes.

This process can be externally stimulated by photochemical, thermal and chemical means [90]. It has also been shown that TERP can be photochemically switched to other processes including coupling reactions [91] and cobalt mediated living radical polymerization [92]. However, the use of organotellurium compounds for photoinduced cationic polymerization has been scarcely investigated. Mishima et al. showed that the combination of organotellurium compounds with certain Lewis acids can photochemically initiate cationic polymerization of different vinyl ethers under controlled conditions (−40 to 0 °C using a glovebox). The present article describes the use of visible light sensitive organotellurium derivatives in conjunction with diphenyliodonium salt (DPI) as a new and efficient visible light cationic photoinitiator system for the polymerization of several types of cationically polymerizable monomer. As it will be shown below, the described system is also useful for dual polymerization since both radical and cationic species are formed concomitantly.

3.2 Results and Discussion

In light of the competent role of organotellurium compounds in visible light-induced free radical polymerizations, a series of experiments were carried out to extend the process to cationic systems. For these investigations, we selected the following low molar mass and polymeric organotellurium photoinitiators and cationic monomers representing cyclic ethers, vinyl ethers, and bi- and dual-functional monomers (Figure 3.2).

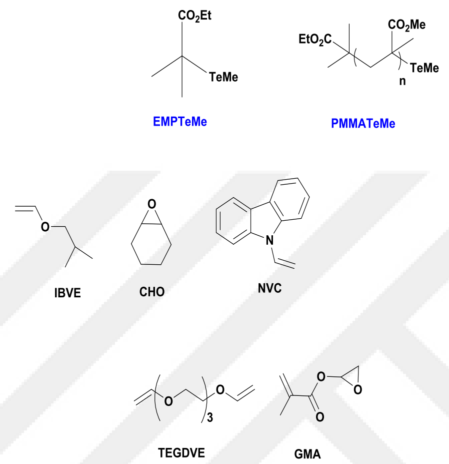


Figure 3.2 : Structure of the photoinitiators and monomers used.

Dichloromethane solutions of monomers containing the organotellurium compound and DPI were irradiated at 450 nm or under sunlight. At the irradiation wavelength diphenyliodonium salt is transparent, and all the light is absorbed only by the organotellurium compounds (Figure 3.3).

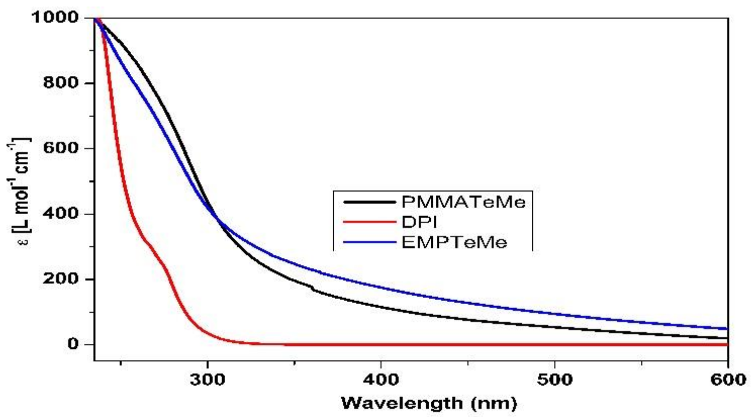


Figure 3.3 : Uv-vis absorption spectra of 1×10^{-3} M organotellurium compounds and diphenyliodonium hexafluorophosphate in dichloromethane.

Table 3.1 depicts conversions and the molecular weight characteristics of the polymers obtained in this process.

Table 3.1 : Light-induced free radical promoted cationic polymerization results using organotellurium compounds and diphenyl iodonium salt.

Initiator	Monomer	Wavelength (nm)	Conversion[b] (%)	M_n[c] (kg/mol)	$Đ$[c]
EMPTeMe	IBVE	450	90	21.16	2.51
PMMATeMe	IBVE	450	92	14.23	2.36
EMPTeMe	CHO	450	81	28.26	1.63
PMMATeMe	CHO	450	85	14.08	1.50
EMPTeMe	NVC	450	72	25.13	2.42
EMPTeMe	NVC	sunlight	39	18.90	2.89
EMPTeMe	IBVE	sunlight	49	27.32	2.51
EMPTeMe	CHO	sunlight	41	16.19	1.90
EMPTeMe	GMA	450	90	∞	-
PMMATeMe[d]	TEGDVE	320-500	79[e]	∞	-

We observed that all of the monomers were polymerized with high conversions using both EMPTeMe and PMMATeMe as free radical sources. In the absence of these compounds, irradiation under identical conditions failed to produce any precipitated polymer. Notably, polymerizations under sunlight resulted in relatively lower yields, probably due to the formation of elemental tellurium by broader wavelength irradiation, as evidenced by black precipitates. Depending upon the structural characteristics of the monomers, two different mechanisms are feasible. In the case of cyclohexene oxide (CHO), electron donor radicals, formed by a hydrogen abstraction reaction of photochemically generated radicals from the monomer, are responsible for generating reactive cations by an electron transfer reaction with the iodonium ions [93, 94]. (Figure 3.4)

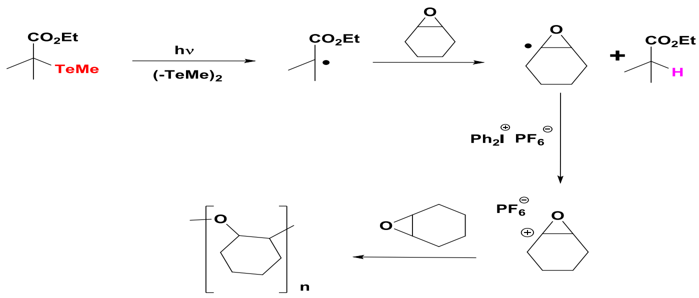


Figure 3.4 : Mechanism of the visible light-induced cationic polymerization of cyclohexene oxide using EMPTeMe and DPI.

Although the initially generated ester-substituted radical is more stable than the CHO-derived radical, direct oxidation of the former is not likely to occur as it possesses a strongly electron withdrawing ester group in the structure. Chemically induced dynamic nuclear polarization studies (CIDNP) showed that the radicals with carbonyl groups did not undergo electron transfer reactions with iodonium salts [95]. In the present study, ^{1}H-NMR and ^{13}C-NMR analyses of the photolysis products of the initiating system in the absence and presence of monomer revealed that various abstraction and coupling compounds were formed. The effect of light on the process was demonstrated by light on–off experiments. (Figure 3.5).

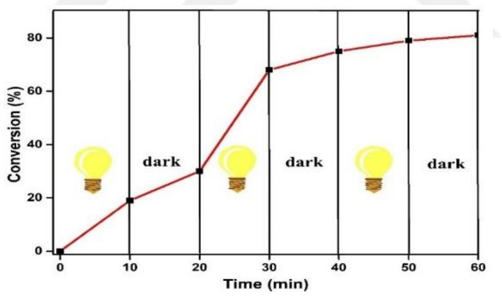


Figure 3.5 : Monomer (CHO) conversion (%) vs. time, demonstrating the dependency of the polymerization on irradiation.

The polymerization mixture was subjected to repeated cycles of light exposure (λ = 450 nm), 10 min illumination followed by 10 min of dark time, respectively. At the end of each step, equivalent volumes of the solutions were precipitated into excess methanol and analyzed gravimetrically to determine the conversions. The results revealed that the polymerization was accelerated by light illumination. Significant polymerization observed even in the dark period was attributed to the quasi-living character of the polymerization through propagating oxonium ions favored by the non-nucleophilic PF_6^- ions. However, in the case of vinyl monomers such as IBVE and NVC, a different mechanism was encountered as supported by GPC and NMR analyses. The proposed mechanism presented in Figure 3.6 is consistent with the reaction of free radicals with vinyl monomers in a living radical polymerization, and oxidation of the electron donor radicals.

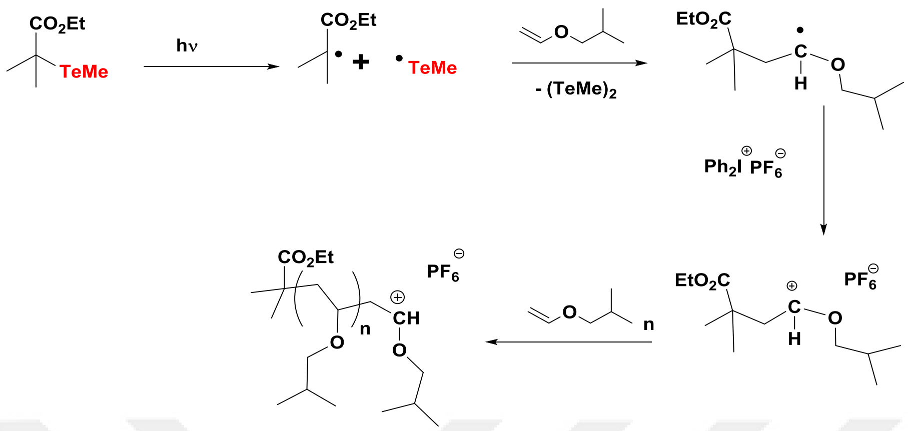


Figure 3.6 : Mechanism of visible light-induced cationic polymerization of isobutyl vinylether using EMPTeMe and DPI.

In this case, EMPTeMe absorbs visible light and forms a carbon-centered radical that adds to the monomer. The resulting electron donor adduct radical is readily oxidized to the corresponding cation by the iodonium salt to initiate the cationic polymerization. The mechanism was further supported by using PMMATeMe as the initiator for the polymerization. Chromatographic studies revealed that block copolymers with PMMA and PIBVE segments were formed as a consequence of the polymeric radical addition and oxidation processes. (Figure 3.7).

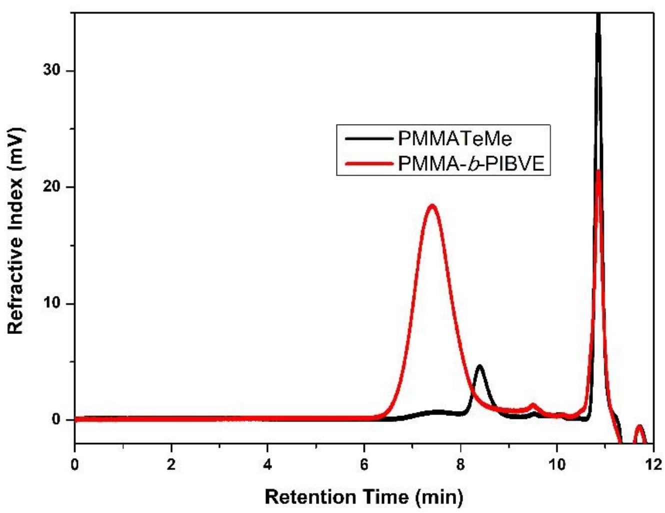


Figure 3.7 : GPC Chromatogram of PMMATeMe and PMMA-*b*-PIBVE.

The possibility of the initiation of concomitant radical and cationic polymerizations was also demonstrated. Glycidyl methacrylate possessing both methacrylate and epoxy groups in the structure underwent complete gelation, since radical and cationic species are formed upon photolysis of solutions containing EMPTeMe and DPI (see Table 3.1). The efficiency of the photoinitiating system in the photocuring of formulations containing multifunctional monomers was also studied. The heat released during the photocuring of the formulations was followed by Photo-DSC. The kinetic profile referring to the polymerization of triethyleneglycol divinylether (TEGDVE) under UV-visible light emitting at λ = 320–500 nm is shown in Figure 3.8. A rapid gelation occurred upon irradiation.

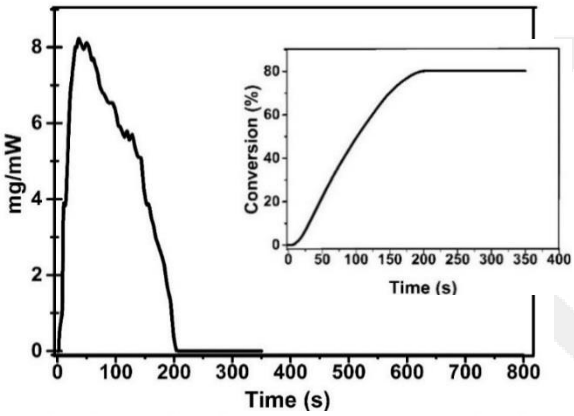


Figure 3.8 : Photo-DSC profiles for the photopolymerization of TEGDVE.

3.3 Conclusion

In conclusion, we demonstrated for the first time that organotellurium compounds in conjunction with iodonium salt are highly efficient visible light photoinitiators for the free radical promoted cationic polymerization of various monomers. Upon visible light irradiation, carbon-centered radicals are formed in a similar manner to that described for living radical polymerization [96] and react with the monomers in two pathways. In the case of cyclic ethers, these radicals undergo hydrogen abstraction while the addition reaction is responsible for generating oxidizable radicals for vinyl-type monomers. Electron donor radicals formed either way are readily oxidized by the iodonium salt, producing cations capable of initiating the polymerization. As demonstrated for the bifunctional monomer TEGDVE, such a visible light-induced radical to cation transformation is of great importance in the design of photocurable cationic systems required for surface coatings and printing plate manufacture.

Initiation of both cationic and radical polymerizations by integration of the photoinduced electron transfer process into these systems suggests that this organotellurium based photoinitiating approach can be used for practical applications.

4. CHARGE TRANSFER COMPLEX OF THIOXANTHONEPHENACYL SULFONIUM SALT AS VISIBLE LIGHT PHOTOINITIATOR FOR FREE RADICAL AND CATIONIC POLYMERIZATIONS[3]

4.1 Introduction

Photoinduced polymerization processes have attracted considerable attention and have provided green, efficient route to synthesize complex macromolecular structures such as block [77, 97] and graft [98, 99] copolymers, nano composites [100, 101] as well as hyperbranched [102, 103] and networked polymers [104, 105] at low or mild temperatures without significant emissions. Compared with conventional thermal polymerization, corresponding photopolymerizations have several advantages such as low energy consumption, low environmental pollution, fast polymerization rate, low polymerization temperature, and wide adaptability [106, 107]. Therefore, photopolymerization technologies have been widely applied in coatings, printing inks [108], electronic circuits [109], digital storage [110], solar cells [111] and 3D printing [112]. However, it is important to note that UV induced photopolymerization reactions cause several concerns for the environment such as ozone generation and radiation safety [113]. To overcome these issues visible-light photopolymerization reactions were proposed. More recently, interest has also been directed towards photoinduced processes that facilitate polymerizations in the near-IR region [107, 114-116]. The visible light initiating systems can generate active species under visible light irradiation [60]. Various visible light initiating systems for free radical and cationic polymerizations have been developed by us and others [117, 118]. Recently, attention has been drawn to the adaptation of visible light-mediated processes with controlled/living radical polymerization processes [119-121]. Thioxanthone (TX) based compounds are an efficient class of hydrogen abstraction type photoinitiators widely used in many free radical and cationic polymerization processes [122-125]. The characteristics and optical behavior of TX photoinitiators can be modified through various synthetic approaches resulting in the extension of the absorption band to higher

[3] This chapter is based on the paper "Charge-Transfer Complex of Thioxanthonephenacyl Sulfonium Salt as Visible Light Photoinitiator for Radical and Cationic Polymerizations", Kaya K., Kreutzer J., Yagci Y., ChemPhotoChem, 2019, 3, 1-7

wavelengths [6], applicability in different media and for various purposes [126, 127] and enhancement of the photoactivity [128]. Thermally stable diaryliodonium and triarylsulfonium salts with non-nucleophilic counter anions are the well-established and widely used photoinitiators for cationic polymerization [21]. However, the low absorptivity of these salts above 300 nm limits their efficiency [129]. Several approaches to extend their spectral activity have been proposed and successfully applied [130]. Recently, Lalevee and coworkers introduced specially designed CTC system consisting of iodonium salt (acceptor) and an amine compound (donor) for radical and cationic polymerizations [131]. These authors also showed that a series of iodonium salts formed strong CTCs with aniline derivatives and N-phenylglycine which enabled deep photopolymerization for 3D-printing. Several other examples of visible light absorbing CTCs morpholine/bromine [132], morpholine/sulfur dioxide [133], amine/iodine [134] have been reported. Despite these remarkable attempts made to form onium salt-based CTCs, progress is very limited to adjust the wavelength as photoinitiating systems for specific applications. We reasoned that the corresponding sulfonium salt analogous would be a good candidate to form highly efficient CTCs with adjustable absorption characteristics. Although conventional sulfonium salts do not represent strong acceptor power, they have several advantages over iodonium salts such as higher thermal stability, straightforward syntheses and lower hazardous properties. Therefore, we investigated whether the introduction of electron withdrawing groups on specially designed sulfonium salt could lead to a better acceptor property.

4.2 Results and Discussion

A new sulfonium salt, namely 2-isopropylthioxanthonium phenacyl hexafluoroantimonate (ITXPhenS), possessing both thioxanthone and phenacyl chromophoric moieties was synthesized according to the previously described procedure (Figure 4.1) and characterized using NMR and infrared spectroscopy together with matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF/MS).

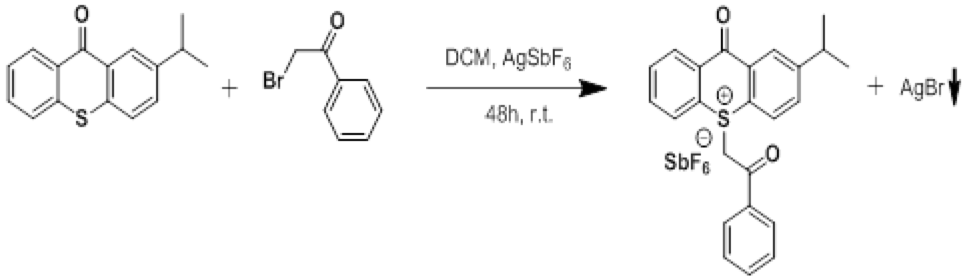
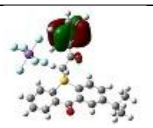
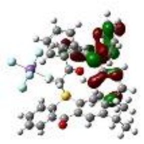


Figure 4.1 : Synthesis of ITXPhenS.

This structural transition can be directly verified for ITXPhenS by analyzing UV-vis and ^{1}H-NMR spectra as well as redox potential. Although absorption features did not significantly change. (Figure 7) We started screening several commercially available amines (triethylamine (TEA), triphenylamine (TPA)) and pyridine to form CTCs with ITXPhenS. These studies, however, failed and we could not find a system which could provide both, high absorbance and a sufficiently strong shift of the absorption band to the visible range. The most promising results were obtained with *N*, *N*-dimethylaniline (DMA) (Table 4.1).

Table 4.1 : Acceptor (ITXPhenS) Molecular Orbital, properties (Calculated at the UB3LYP/ LANL2DZ Level) and the CTC, character ([Donor−Acceptor]) observed in DCM.

Donor	**HOMO visualization**	**Theoretical HOMO energy (eV)[a]**	**CTC observed[b]**
DMA		-5.37	Strong
TEA		-7.06	None
TPA		- 6.44	None
Pyr		- 8.72	None

The absorption shift to the visible range by the addition of DMA (*N*, *N*-dimethylaniline) to the solutions of ITXPhenS, as a consequence of the formation of CTC, is illustrated in Figure 4.2.a. Interestingly, this spectral change was even more pronounced when the mole ratio donor to acceptor was increased. Expectedly, photolysis of a degassed solution of CTC for different time intervals resulted in a significant decrease of the absorption in an exposure window region indicating successful bleaching of the complex (Figure 4.2.b).

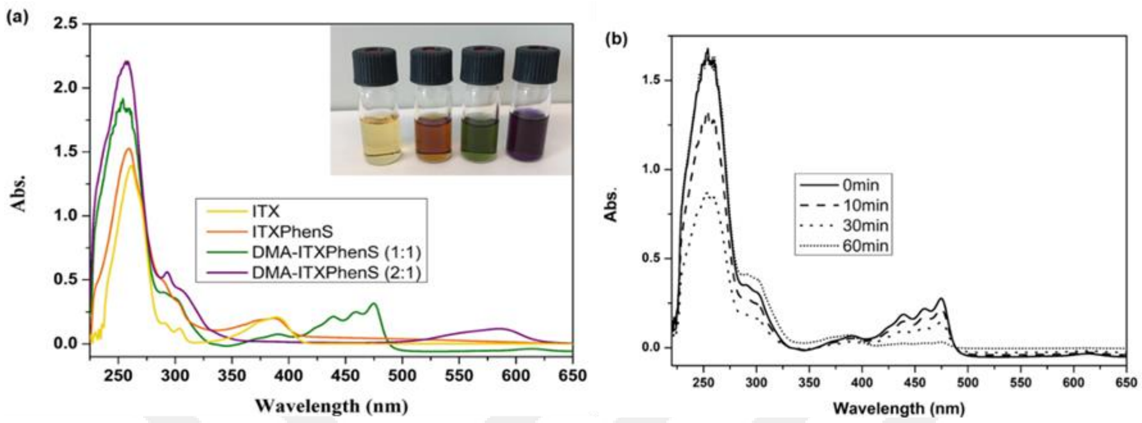


Figure 4.2 : (a) UV-vis absorption spectra of $5x10^{-3}$ mol/L ITX, ITXPhenS, DMA-ITXPhenS(1:1), DMA-ITXPhenS(2:1) and visual observation (inner photo) at different mol ratios in DCM; (b) UV-vis optical change under 450nm irradiation of DMA-ITXPhenS ($5x10^{-3}$ mol/L) in DCM.

The formation of the CTC was also supported by ^{1}H-NMR analysis. Addition of DMA caused upfield shift of the protons of the sulfonium salt. Sunlight and visible irradiation for 1h resulted in significant changes in the spectra. The increase of the proton peaks near 4.5 ppm can be attributed to the formation of products from the phenacyl based radical and cationic species. Moreover, the excited state emission characteristics of the CTC were investigated by means of fluorescence measurements. The excitation and emission spectra of ITXPhenS-DMA exhibit mirror image behavior in agreement with the reported CTC's [134-137]. Introduction of phenacyl unit to the ITX structure increased the reduction potential from usually observed value of -1.7V to -1.25V which is the average value for most of the phenacyl salts [39] (Figure 4.3).

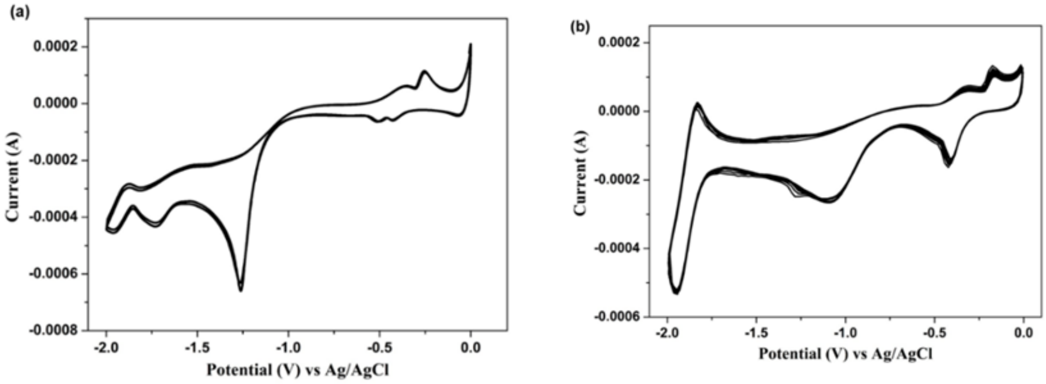


Figure 4.3 : Cyclic Voltammograms of 5x10^{-2} M: (a) ITXPhenS; (b) DMA ITXPhenS (2:1) in dry acetonitrile at 25^{o}C.

It is also noted that the reduction potential of the salt related to the phenacyl moiety raised to the value of -0.36V indicating the reduction occurs more favorably on the phenacyl-sulfur bond (Figure 4.3b). Formation of CTC was further supported by theoretical calculations. The calculated IR spectrum perfectly matched with the experimental IR spectrum. The calculated absorption spectra show an intensive band in the region of 250 nm, 400 nm, 450nm and 600 nm for ITXPhenS, DMA-ITXPhenS (1:1) and DMA-ITXPhenS (2:1), respectively. As demonstrated before [128], the absorption band in the long wavelength region for TX derivatives typically corresponds to pure HOMO-LUMO excitation that can be found for the DMAITXPhenS complex as well, where the HOMO the LUMO orbitals are located at the DMA moiety and on the aromatic system of the ITXPhenS moiety, respectively (Figure 4.3). For the ITXPhenS compound in the absence of DMA, the assignment of the orbitals which are involved in the transitions are different. The first transition of the calculated UV-vis spectrum of the DMA-ITXPhenS which corresponds to the long wavelength band at 390 nm in the experimental spectrum, stems mainly from HOMO-5 to LUMO and HOMO-4 to LUMO excitations.

However, despite the fact that its spectral sensitivity is extended to the near UV region due to the ITX moiety, it is transparent in the visible range. The ability of the CTC to efficiently initiate free radical as well as cationic visible light phopolymeriztion was demonstrated by using mono and bifunctional monomers with respective polymerizable functions (groups), namely isobutyl vinylether (IBVE), cyclohexene oxide (CHO), methyl methacrylate (MMA), styrene (St), triethylene glycol divinylether (TEGDVE) and triethyleneglycol dimethacrylate (TEGDMA). Their chemical structures are presented in Figure 4.4.

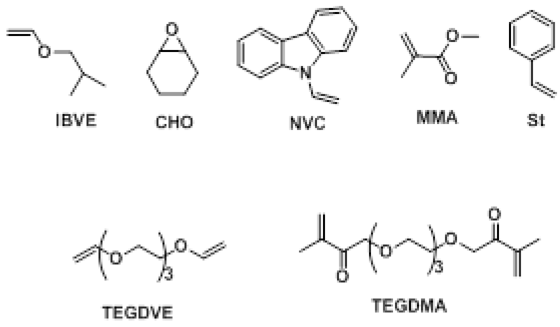


Figure 4.4 : Chemical structures of the monomers used.

On the other hand, during visible light irradiation at 450 nm, the light emission is well matched with the absorbance of ITXPhenS/DMA CTC and polymerization reactions were successfully initiated with all monomers. (Table 4.2).

Table 4.2 : Light-induced radical and cationic polymerization results using CTC's.

Initiator[a]	Monomer	Wavelength (nm)	Conversion[b] (%)	M_n[c] (kg/mol)	$Đ$[c]
ITXPhenS	IBVE	350	63	33.73	2.94
ITXPhenS	CHO	350	68	17.57	2.24
ITXPhenS	NVC	350	54	10.42	4.28
ITXPhenS	MMA	350	75	29.31	2.28
ITXPhenS	St	350	64	6.62	1.82
DMA-ITXPhenS (1:1)	IBVE	450	60	21.15	2.52
DMA-ITXPhenS (1:1)	CHO	450	65	74.94	2.13
DMA-ITXPhenS (1:1)	NVC	450	48	14.98	4.13
DMA-ITXPhenS (1:1)	MMA	450	72	14.99	2.52
DMA-ITXPhenS (1:1)	St	450	62	2.54	3.24
DMA-ITXPhenS (1:1)	MMA	sunlight	32	37.92	1.49
DMA-ITXPhenS (2:1)	MMA	sunlight	45	96.55	1.88
DMA-ITXPhenS (1:1)	IBVE	sunlight	75	12.40	1.91
DMA-ITXPhenS (2:1)	IBVE	sunlight	42	19.81	2.46

The polymerization reactions can also be initiated under sunlight. In fact, upon addition of the dichloromethane solution of CTC to the monomer, the polymerization was initiated quite vigorously. It is interesting to note that the higher conversions were attained with MMA arising from the stronger absorption of the CTC formed with the higher molar ratio of the donor DMA in the near visible range (vide ante) matching with the emission of sunlight. A different situation was encountered with the cationic polymerizable monomer IBVE. Although IBVE conversions found by gravimetric determination was lower than those of MMA Photo-DSC studies showed that

TEGDVE polymerization was much faster than TEGDMA polymerization. The relatively lower conversion of IBVE observed by gravimetric analysis can be attributed to the transfer reactions and terminating effect the excess DMA with strong nucleophilic character causing oligomers. However, with PhotoDSC of the polymerization of bifunctional monomers, conversions are determined by the heat released. As an illustration of the possible value of this approach in coating applications, photo-DSC studies of the polymerizations of vinyl ether and methacrylate type cross-linkable monomers, initiated by CTC were performed. In Figure 4.5.a, photo-DSC profiles referring to the polymerization of TEGDVE and TEGDMA in the presence of ITXPhenS/DMA (1:1) under 320-500 nm are shown. Figure 4.5.b displays plots of the conversion versus irradiation time derived from Figure 4.5.a.

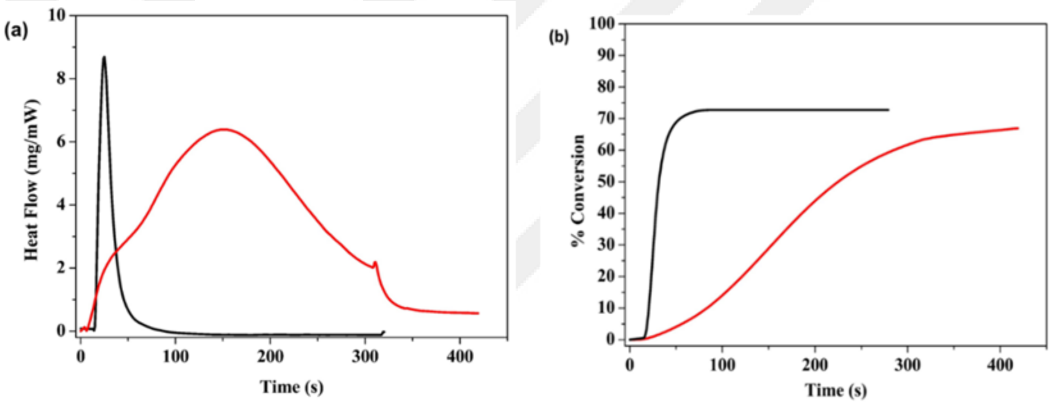


Figure 4.5 : Photo-DSC profiles for the photopolymerization of TEGDVE (black) and TEGDMA (red) irradiated at 30ºC by polychromatic UV-light (320-500nm); (a) Monomer conversions for TEGDVE(black) and (b) TEGDMA (red) derived from Photo-DSC profiles.

It can be seen that much faster polymerization takes place with cationic monomer TEGDVE. Photo-DSC study of oxirane type of monomer, CHO was also performed. The rate of polymerization was faster than TEGDMA but slower than TEGDVE. The initiation mechanism of CTC is presumably based on the homolytic and heterolytic cleavage of phenacyl moiety in the excited state CTC followed by the electron transfer, in analogy to the usual behavior of phenacylium [138] and sulfonium salts as photocatalyst (Figure 4.6). The sulfinium radical cations thus formed can contribute to the formation of Brönsted acids by hydrogen abstraction and proton release. The mechanism proposed by Neckers [139] involving direct hydrogen abstraction from DMA and subsequent oxidation can be discarded as the TX moiety is initiatially in the salt form.

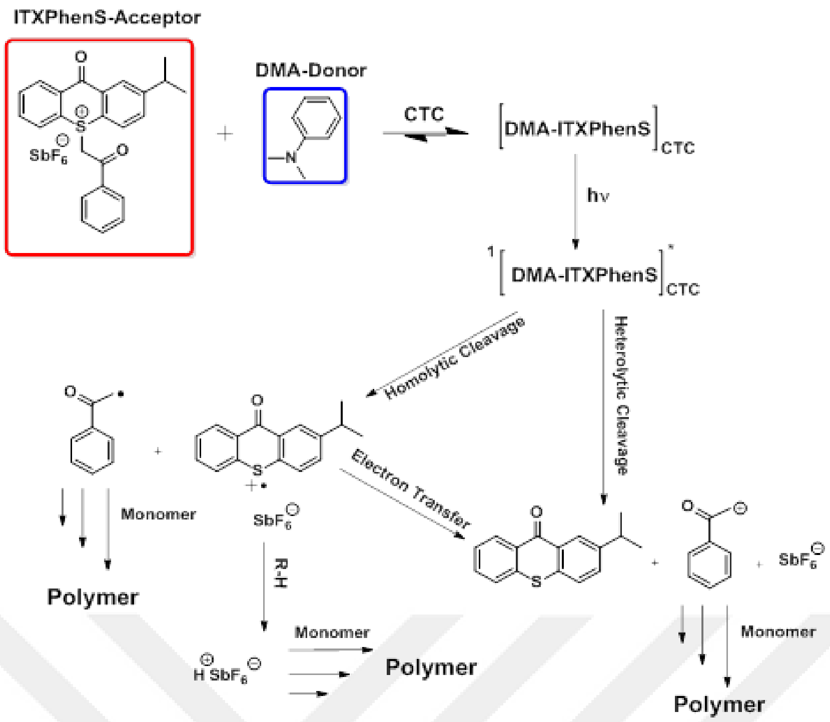


Figure 4.6 : Proposed initiation mechanism for visible light free radical and cationic photopolymerizations by CTC’s.

4.3 Conclusion

In conclusion, a new thioxanthone based phenacyl sulfonium salt was synthesized and used as a photoinitiator for free radical and cationic polymerization of appropriate monomers in the near UV region. This salt can form CTCs with DMA as donor and shows excellent optical properties in the visible range as evidenced by UV-Vis and fluorescence spectroscopy. The initiator was fully characterized by ^{1}H-NMR, MS and IR spectroscopy as well as CV studies. DFT studies confirmed the formation of a CTC and were used for the interpretation of the absorption bands. It is demonstrated that the absorption band can be shifted by adjusting the mole ratio of donor molecules. The CTC’s possess excellent photophysical properties for initiation of polymerization reactions of both, radical and cationic polymerizations in the visible region, which may find use in many specific applications. A mechanism was proposed, in which the phenacyl moiety of the CTC undergoes photoinduced cleavage to yield radical and ionic species, which are responsible for the initiation of the respective polymerization reactions. Due to the possibility of the initiation of two different polymerization modes, the described system may be used for the simultaneous fabrication of interpenetrating networks under visible light.

5. CONCLUSION

The first conclusion concerning the first and third articles (Chapter 2 and Chapter 4) reflects the importance of phenacyl unit in decreasing reduction potentials of the sulfonium salts. Cyclic voltammetry studies for both work showed that the reduction potentials were closer to 0 V compared with the reduction potentials of their analogues. Another important conclusion is the role of electron donor molecules which can form charge-transfer complexes with electron acceptor (or electron deficient) sulfonium salts. The reduction potential of the CTC's mentioned in Chapter 4 were comparable to those of iodonium salts which are known to be the best oxidants available for the cationic polymerization reactions. This change in the reduction potential makes the phenacyl bond (methylene-sulphur bond) more prone to cleave, forming reactive species. (both radical and cationic). It was shown in the second article (Chapter 3) that it is possible to form polymers of monomers that can polymerize with only cationic mechanism. The described process also facilitates formation of block copolymers of vinyl ethers using organotellurium initiators and macrophotoinitiators like PMMATeMe in conjunction with iodonium salts. These photoinitiators in the presence of iodonium salts can also be used for industrial purposes due to the generation of both radical and cationic species, thus monomers with dual functionality like glycidyl methacrylate can readily undergo photoinduced crosslinking. Future works concern the syntheses of new phenacyl salts that contain both electron acceptor and electron donor groups in the structure which can form intramolecular charge-transfer complex: This will eliminate the necessity of the additional electron donor molecules. The electronic interactions within these charge-transfer complexes can be more precisely characterized using single crystal X-Ray diffraction method. These new CTC's will be able to polymerize both radically and cationically various monomers under visible light irradiation.

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