NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS

By

Neslihan Karıksız

B.S., Chemistry, Boğaziçi University, 2020

Submitted to the Institute for Graduate Studies in
Science and Engineering in partial fulfillment of
the requirements for the degree of
Master of Science

Graduate Program in Chemistry

Boğaziçi University

2023

Dedicated to my extented family…

ACKNOWLEDGEMENTS

I would like to sincerely thank to Prof. Duygu Avcı Semiz for her help, polite approach and valuable suggestions throughout my graduate life.

I would like to express my thanks to my committee members Asist. Prof. Funda Oğuz and Prof. Ersin Acar for politely sparing their valuable time for reviewing the final manuscript and for their constructive comments and recommendations.

I would like to extend my great thanks to Tuğçe Nur, Seçkin, Melek and Türkan due to their assistance and advice in the laboratory. I also thank to my dear group friends Burcu and Simay for their help, friendship, support and encouragement.

I would like to thank also my dear extented family for their love, encouragement and support through my entire life.

This research was financed supported by The Scientific and Technological Research Council of Turkey (TÜBİTAK) [120Z729] and Bogazici University Research Fund (19366).

ABSTRACT

NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS

The aim of this thesis is to improve the "green" aspects of photopolymerization processes. So novel photoinitiators with high reactivity, low migration, water solubility and biocompatibility were designed, synthesized and evaluated. In the first part of this work, a new cyclopolymerizable, doubly I2959 functionalized allyl-acrylate quaternary ammonium salt (2xI2959-QS) and its copolymer with diallyldimethylammonium chloride (DADMAC) were synthesized and their characterizations were done. Also, their photochemical properties, migration stabilities and photopolymerization behaviours were examined. The water soluble polymer, p-DADMAC-*co*-2xI2959-QS has five-membered pyrrolidine rings in the backbone and showed excellent thermal stability. These photoinitiators (PIs) have similar λ_{max} (271 and 272 nm in ethanol) to I2959, the ε value of 2xI2959-QS is twice that of I2959. The photochemical mechanisms studied by electron spin resonance (ESR) and photolysis indicated formation of isopropyl ketyl radicals. Photopolymerization of 2-hydroxyethylmethacrylate (HEMA) initiated by both PIs shows higher efficiency than via I2959. The synthesized photoinitiators showed higher migration stability compared to I2959 as reference. In the second part of this work, a new facile route to prepare highly water-soluble and migration stable photoinitiator was reported. A doubly Irgacure 2959 (I2959) functionalized meso-2,3-dimercaptosuccinic acid (DMSA) salt (DMSA-I2959-DBU) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) counterion was synthesized in one-pot thiol-Michael addition reaction. It has excellent water solubility. DMSA-I2959-DBU has similar λ_{max} (272 nm in ethanol) but slightly lower ε value (~11000) compared to I2959. Its decomposition mechanism was investigated by steady state photolysis. It showed reasonable photoinitiating reactivity towards (meth)acrylic double bonds.

ÖZET

DÜŞÜK MİGRASYON ÖZELLİKLİ ÜRÜNLER İÇİN I2959 TABANLI YENİ FOTOBAŞLATICI TUZLARI

Bu tezin amacı fotopolimerizasyon sürecinin "yeşil" özelliklerini iyileştirmektir. Bu amaçla, yüksek reaktiflik, düşük sızma, suda çözünürlük ve biyouyumluluk özellikli yeni fotobaşlatıcılar tasarlandı, sentezlendi ve değerlendirildi. Bu çalışmanın ilk bölümünde, yeni bir siklopolimerize edilebilir, çift I2959 ile fonksiyonlandırılmış alil-akrilat kuaterner amonyum tuzu (2xI2959-QS) ve bunun dialildimetilamonyum klorür (DADMAC) ile kopolimeri sentezlendi ve karakterizasyonları yapıldı. Ayrıca fotokimyasal özellikleri, migrasyon kararlılıkları ve fotopolimerizasyon davranışları incelendi. Suda çözünen polimer (p-DADMAC-*co*-2xI2959-QS), ana zincirinde beş üyeli pirolidin halkalarına sahiptir ve termal kararlılığı çok yüksektir. Bu fotobaşlatıcılar I2959'a benzer λ_{max} değerine (etanolde 271 ve 272 nm) sahip ve 2xI2959-QS'nin absorpsiyon katsayısı değeri (ε) I2959'un iki katıdır. Elektron spin rezonansı (ESR) ve kararlı durum fotolizi ile incelenen fotokimyasal mekanizmalar, izopropil ketil radikallerinin oluşumunu göstermektedir. Her iki fotobaşlatıcının, 2-hidroksietilmetakrilatın (HEMA) fotopolimerizasyonunu başlatma verimliliği, I2959'unkinden daha yüksektir. Ayrıca, sentezlenen fotobaşlatıcılar, referans I2959'a kıyasla daha yüksek migrasyon stabilitesi göstermektedir. Bu çalışmanın ikinci bölümünde, suda yüksek oranda çözünür ve migrasyon kararlı fotobaşlatıcı hazırlamak için yeni kolay bir yol rapor edildi. 1,8-diazabisiklo[5.4.0]undek-7-en (DBU) karşı iyonlu çift Irgacure 2959 (I2959) ile fonksiyonlandırılmış mezo-2,3-dimerkaptosüksinik asit (DMSA) tuzu (DMSA-I2959-DBU) tek adımlı tiol-Michael katılma reaksiyonu ile sentezlendi. Bu fotobaşlatıcının suda çözünürlüğü I2959'dan çok daha iyidir. DMSA-I2959-DBU, I2959 ile karşılaştırıldığında benzer λ_{max} (etanolde 272 nm) değerine, ancak biraz daha düşük ε değerine (~11000) sahiptir. Bu fotobaşlatıcının ayrışma mekanizması, fotoliz ile araştırıldı; (met)akrilik çift bağlara karşı makul bir fotobaşlatıcı reaktivite gösterdiği bulundu.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS iv
ABSTRACT v
ÖZET vi
LIST OF FIGURES x
LIST OF TABLES xvii
LIST OF SYMBOLS xviii
LIST OF ACRONYMS/ABBREVIATIONS xx
1. INTRODUCTION 1
1.1. Free Radical Photopolymerization 2
1.2. Free Radical Photoinitiators 4
1.2.1. Type I Photoinitiators 5
1.2.2. Type II Photoinitiators 6
1.3. Monomeric and Polymeric Photoinitiators. 7
1.4. Water-Soluble Photoinitiators 12
1.5. Cyclopolymerization. 13
1.5.1. Cyclopolymerizable and Cyclopolymeric Photoinitiators 15
2. OBJECTIVES 17
3. CYCLOPOLYMERIZABLE AND CYCLOPOLYMERIC PHOTOINITIATORS FROM *tert*-BUTYL a-HYDROXYMETHACRYLATE 18
3.1. Introduction. 18
3.2. Experimental. 19
3.2.1. Materials and Characterization 19
3.2.2. Synthesis of Starting Materials 20
3.2.2.1. Synthesis of I2959-AC 20
3.2.2.2. Synthesis of I2959-Ts 20
3.2.2.3. Synthesis of I2959-AA 21

3.2.2.4. Synthesis of 2xI2959-AA 21
3.2.3. Synthesis of Monomeric Photoinitiator 22
3.2.4. Synthesis of Polymeric Photoinitiator 23
3.2.5. ESR Spin Trapping (ESR-ST) Experiments 23
3.2.6. UV–Vis Spectroscopy and Photolysis 23
3.2.7. Photoinitiating Activity Measurements 23
3.2.8. Migration Studies 24
3.3. Results and Discussion. 24
3.3.1. Synthesis and Characterization of Monomeric Photoinitiator 24
3.3.2. Synthesis and Characterization of Polymeric Photoinitiator 29
3.3.3. Light Absorption Properties 31
3.3.4. Electron Spin Resonance (ESR) Experiments 33
3.3.5. Photopolymerization Results 34
3.3.6. Migration Stability 37
3.4. Conclusion. 38
4. A WATER-SOLUBLE PHOTOINITIATOR FROM 2,3-DIMERCAPTOSUCCINIC ACID…… 39
4.1. Introduction. 39
4.2. Experimental. 40
4.2.1. Materials and Characterization 40
4.2.2. Synthesis of DMSA-I2959-DBU 41
4.2.3. UV–Vis Spectroscopy and Photolysis 41
4.2.4. Photoinitiating Activity Measurements 42
4.2.5. Migration Study 42
4.3. Results and Discussion. 42
4.3.1. Synthesis and Characterization of Water Soluble Photoinitiator 42
4.3.2. Light Absorption Properties 46

4.3.3. Photopolymerization Results 48
4.3.4. Migration Stability 49
4.4. Conclusion. 50
5. CONCLUDING REMARKS 51
REFERENCES. 52
APPENDIX A: COPYRIGHT LICENCES 62

LIST OF FIGURES

Figure 1.1. Photopolymerization reaction process. Permission from [12] John Wiley and Sons, Copyright (2008)..... 1

Figure 1.2. Chemical reaction steps of photopolymerization. Permission from [14] American Chemical Society, Copyright (2015). 2

Figure 1.3. Formation of radical from photoinitiator and photosensitizer molecules. [3] published under an open access. 2

Figure 1.4. Oxygen inhibition on free radical photopolymerization. Permission from [11] American Chemical Society, Copyright (2010). 4

Figure 1.5. Jablonski diagram where S_0 is the ground singlet state, S_1, S_2 and S_n are the excited singlet states and T_1 and T_2 are the excited triplet states. [20] published under an open access. 5

Figure 1.6. Photocleavage reaction from triplet state of Type I photoinitiators. Permission from [13] John Wiley and Sons, Copyright (2013). 6

Figure 1.7. Examples of commercially available Type I photoinitiators. Permission from [13] John Wiley and Sons, Copyright (2013)..... 6

Figure 1.8. Type II photoinitiation mechanism with benzophenone and hydrogen donors. Permission from [11] American Chemical Society, Copyright (2010)..... 7

Figure 1.9. Examples of commercially available Type II photoinitiators. Permission from [13] John Wiley and Sons, Copyright (2013)..... 7

Figure 1.10. Examples of further rearrangements of photoinitiators. Permission from [21] Elsevier, Copyright (2019). 8

Figure 1.11. Structures of polymeric photoinitiators. Permission from [21] Elsevier, Copyright (2019). 9

Figure 1.12. Syntheses scheme of polymeric photoinitiators [38]. 10

Figure 1.13. Structure of a polymeric photoinitiator. Permission from [39] Springer Nature, Copyright (2019). 10

Figure 1.14. Structure of monomeric and polymeric photoinitiators. Permission from [28] Elsevier, Copyright (2015). 11

Figure 1.15. Structure of polymeric photoinitiators. Permission from [40] Elsevier, Copyright (2017). 11

Figure 1.16. Structures of a water-insoluble photoinitiator (MAPO-1) and its water-soluble derivatives (MAPO-2 and MAPO-3) and other water soluble photoinitiators. Permission from [42] John Wiley and Sons, Copyright (2021), [43] Elsevier, Copyright (2009), [44] Elsevier, Copyright (2018), [46] Elsevier, Copyright (2009) and [47] Elsevier, Copyright (2015). 13

Figure 1.17. Mechanism of cycle-formation of an unspecific unsubstituted diene during cyclopolymerization. Permission from [52] John Wiley and Sons, Copyright (2021). 14

Figure 1.18. Schematic representation of volumetric shrinkage during polymerization. Permission from [52] John Wiley and Sons, Copyright (2021). 14

Figure 1.19. Structure of cyclopolymerizable photoinitiator. Permission from [17] Elsevier, Copyright (2019). 15

Figure 1.20. Structure of cyclopolymerizable photoinitiators. Permission from [53] Elsevier, Copyright (2022). 16

Figure 1.21. Structure of cyclopolymerizable and cyclopolymeric photoinitiators [54] 16

Figure 3.1. Structures of the novel monomeric (2xI2959-QS) and polymeric (p-DADMAC-*co*-2xI2959-QS) photoinitiator. 19

Figure 3.2. Synthesis of the monomeric PI, 2xI2959-QS. 25

Figure 3.3. ^{1}H-NMR spectra of I2959-AC, I2959-AA and 2xI2959-AA 26

Figure 3.4. ^{1}H-NMR spectra of 2xI2959-QS and p-DADMAC-*co*-2xI2959-QS 27

Figure 3.5. ^{13}C-NMR spectrum of 2xI2959-QS 27

Figure 3.6. FTIR spectra of 2xI2959-QS and its copolymer with DADMAC. 28

Figure 3.7. Synthesis of PPI. 30

Figure 3.8. TGA spectrum of p-DADMAC-*co*-2xI2959-QS. 30

Figure 3.9. UV–vis absorption spectra of 2xI2959-QS in ethanol. 32

Figure 3.10. UV–vis absorption spectra of p-DADMAC-*co*-2xI2959-QS in ethanol. 32

Figure 3.11. Photolysis of (a) 2xI2959-QS in ethanol ($8.8x10^{-5}$ M) and (b) p-DADMAC-*co*-2xI2959-QS in ethanol ($5.76x10^{-6}$ M) using 320-500 nm (intensity = 50 W) light source. 33

Figure 3.12. The fluorescence spectrum of p-DADMAC-*co*-2xI2959-QS in CH_3CN:H_2O (3:7 v/v). 33

Figure 3.13. ESR spectra of I2959 (a) and 2xI2959-QS (c) before and after irradiation; simulation of their EPR spectrum (b and d) after irradiation. 34

Figure 3.14. (a) Rate-time and (b) Conversion-time plots for HEMA containing 2xI2959-QS and I2959 at 25 °C under nitrogen irradiated by 320-500 nm. 35

Figure 3.15. (a) Rate-time and (b) Conversion-time plots for PEGDA containing 2xI2959-QS and I2959 at 25 °C under nitrogen irradiated by 320-500 nm. 35

Figure 3.16. (a) Rate-time and (b) Conversion-time plots for HEMA containing p-DADMAC-*co*-2xI2959-QS and I2959 at 25 °C under nitrogen irradiated by 320-500 nm. 36

Figure 3.17. (a) Rate-time and (b) Conversion-time plots for PEGDA containing p-DADMAC-*co*-2xI2959-QS and I2959 at 25 °C under nitrogen irradiated by 320-500 nm. 36

Figure 3.18. Heat flow-time plot for 2xI2959-QS at 40 °C under nitrogen irradiated by 320-500 nm. 37

Figure 3.19. UV-Visible absorption spectra of I2959, 2xI2959-QS and p-DADMAC-*co*-2xI2959-QS extracted with methanol from the HEMA/PEGDA/water (3/3/1 wt%) polymer samples. 38

Figure 4.1. Structure of the novel (DMSA-I2959-DBU) photoinitiator. 40

Figure 4.2. Synthesis of the PI, DMSA-I2959-DBU. 43

Figure 4.3. ^{1}H-NMR spectrum of DMSA-I2959-DBU. 44

Figure 4.4. ^{13}C-NMR spectrum of DMSA-I2959-DBU. 45

Figure 4.5. FTIR spectrum of DMSA-I2959-DBU. 45

Figure 4.6. Raman spectra of (a) DMSA and (b) DMSA-I2959-DBU. 46

Figure 4.7. UV–vis absorption spectra of DMSA-I2959-DBU in (a) water and (b) ethanol. 47

Figure 4.8. Photolysis of DMSA-I2959-DBU (a) in water (3.52×10^{-5} M) and (b) in ethanol (2×10^{-4} M). 47

Figure 4.9. (a) Rate-time and (b) Conversion-time plots for HEMA containing DMSA-I2959-DBU (1 wt%) and I2959 (1 wt%) at 25 °C under nitrogen irradiated by 320-500 nm. 48

Figure 4.10. (a) Rate-time and (b) Conversion-time plots for PEGDA/water (95/5 wt%) containing DMSA-I2959-DBU and I2959 at 25 °C under nitrogen irradiated by 320-500 nm. 49

Figure 4.11. UV-Visible absorption spectra of I2959 and DMSA-I2959-DBU extracted with methanol from the HEMA/PEGDA (50/50 mmol%) polymer samples..... 50

Figure A.1. Permission from [12] John Wiley and Sons, Copyright (2008)..... 62

Figure A.2. Permission from [14] American Chemical Society, Copyright (2015)..... 62

Figure A.3. Permission from [11] American Chemical Society, Copyright (2010)..... 63

Figure A.4. Permission from [13] John Wiley and Sons, Copyright (2013)..... 63

Figure A.5. Permission from [21] Elsevier, Copyright (2019)..... 64

Figure A.6. Permission from [39] Springer Nature, Copyright (2019)..... 64

Figure A.7. Permission from [28] Elsevier, Copyright (2015)..... 65

Figure A.8. Permission from [40] Elsevier, Copyright (2017)..... 65

Figure A.9. Permission from [42] John Wiley and Sons, Copyright (2021)..... 66

Figure A.10. Permission from [43] Elsevier, Copyright (2009)..... 66

Figure A.11. Permission from [44] Elsevier, Copyright (2018)..... 67

Figure A.12. Permission from [46] Elsevier, Copyright (2009)..... 67

Figure A.13. Permission from [47] Elsevier, Copyright (2015)..... 68

Figure A.14. Permission from [52] John Wiley and Sons, Copyright (2021). 68

Figure A.15. Permission from [17] Elsevier, Copyright (2019). 69

Figure A.16. Permission from [53] Elsevier, Copyright (2022). 69

LIST OF TABLES

Table 3.1. Solubilities of the synthesized PIs and I2959. 28

Table 3.2. Absorption characteristics of 2xI2959-QS and I2959 in methanol and ethanol. 31

Table 4.1. Solubilities of the synthesized PI and I2959. 43

Table 4.2. Absorption characteristics of DMSA-I2959-DBU and I2959 in water and ethanol. 46

LIST OF SYMBOLS

DAA-I184	I184 functionalized diallyl amine
DAA-I2959	I2959 functionalized dially lamine
f	Efficiency of initiator
[I]	Initiator concentration
I_0	Light intensity
I2959-AA	I2959 functionalized allylamine
I2959-AC	I2959 functionalized acrylate
I2959-Ts	I2959 functionalized tosylate
k_p	Propagation rate constant
k_t	The termination rate constant
m	The mass of monomer in the sample
M	The molar mass of the monomer
[M]	The double bond concentration
M_1·	The first chain radical
[M_n·]	Total propagating radical concentration
n	The number of double bonds per monomer molecule
p-DADMAC-co-2x-I2959-QS	PolyDADMAC copolymer with doubly I2959 functionalized quaternary ammonium salt
p-DADMAC-co-DAA-I2959-QS	PolyDADMAC copolymer with I2959 functionalized diallyl amine quaternary ammonium salt
PEI-I2959	I2959 functionalized poly(ethylene imine)
PEI-I2959-Ts	I2959 and tosylate counteranion functionalized poly(ethylene imine)
PI	Photoinitiator
PPI	Polymeric photoinitiator
Q/s	The heat flow per second
QS	Quaternary ammonium salt
R_i	The rate of initiation
R_p	The rate of propagation

R_{pmax}	The maximum rate of polymerization
R_t	The rate of termination
TA	Thermal Analyzer
t_{max}	Time to reach the maximum heat of polymerization
TXdMA	2,2′-(((9-oxo-9H-thioxanthen-2-yl)azanediyl)bis(methylene))diactylic acid
ΔH_p	The heat of reaction
ε	Initiator molar absorptivity
λ_{max}	The wavelengths for maximum absorption
ϕ	Initiator quantum yield
2xI2959-AA	I2959 functionalized allyl-acrylate
2xI2959-QS	I2959 functionalized allyl-acrylate quaternary ammonium salt

LIST OF ACRONYMS / ABBREVIATIONS

AA	Allylamine
AC	Acrylate
bPEI	Branched poly(ethyleneimine)
DAA	Diallylamine
DABPO	4-Diallyl amino benzoyl diphenyl phosphine oxide
DADMAC	Diallyldimethyl ammonium chloride
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCM	Dichloromethane
DMF	N,N-Dimethylformamide
DMSA	Meso-2,3-dimercaptosuccinic acid
DSC	Differential Scanning Calorimetry
ESR-ST	Electron Spin Resonance Spin Trapping
Et_3N	Triethylamine
FT-IR	Fourier Transform Infrared Spectroscopy
HCPPIs	Hyperbranched or cross-linked polymeric photoinitiators
HDDA	Hexanediol diacrylate
HEMA	2-Hydroxyethyl methacrylate
I2959	2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone
Irgacure 184	1-Hydroxycyclohexyl phenyl ketone
LPPIs	Linear polymeric photoinitiators
$M_1\cdot$	The first chain radical
MAPO	Monoacylphosphine oxide
MeOH	Methanol
MFPIs	Multifunctional photoinitiators
NMR	Nuclear Magnetic Resonance spectroscopy
PBN	Phenyl-N-*tert*-butylnitrone
PEG	Polyethylene glycol
PEGDA	Poly(ethylene glycol) diacrylate
QS	Quaternary ammonium salt
TBBr	*Tert*-butyl α-bromomethacrylate

TGA	Thermal Gravimetric Analysis
THF	Tetrahydrofuran
TMPTA	Trimethylolpropane triacrylate
TPGDA	Tripropylene glycol diacrylate
TPO	2,4,6-Trimethyl(phenyl)diphenyl oxide
Ts	Tosylate
TsCl	P-toluenesulfonyl chloride
TX	Thioxanthone
TX-PPO	Thioxanthone-poly(propylene oxide)
V-50	2,2'-Azobis(2-methylpropionamidine) dihydrochloride

1. INTRODUCTION

Light-induced polymerization has attracted great interest in recent years. This is because it has some fundamental advantages over traditional thermal polymerization. Light-induced polymerization has fast polymerization rates, it can operate at low temperature with low energy consumption, and also it can operate without solvent (no volatile organic compounds emission) [1]. Thanks to these advantages of photopolymerization, it has seen extensive use in numerous applications such as coatings, varnishes, paints, adhesives, graphic arts, stereolithography, 3D printing, microelectronics and dental restoration [2,3]. In addition to these areas, photopolymerization technique can be used in also biochemistry such as drug delivery [4,5] and tissue engineering [6-9].

Photopolymerization is a polymerization process which is initiated by light [10] (Figure 1.1). For photopolymerization reaction; a polymerizable monomer/oligomer, a photoinitiating system and a light source are required. A photoinitiating system consists of a photoinitiator and/or a photosensitizer and it induces polymerization by absorption of light. Photopolymerization reactions can be categorized as free radical photopolymerization and cationic photopolymerization according to the polymerization mechanism [2,11].

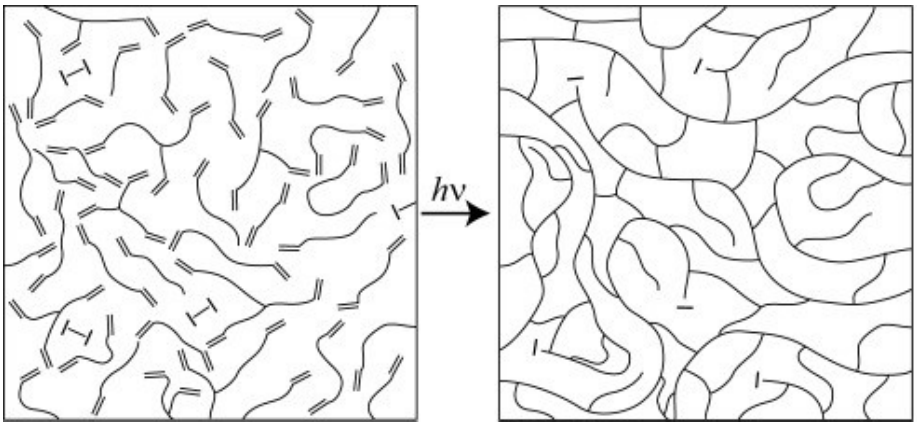


Figure 1.1. Photopolymerization reaction process. Permission from [12] John Wiley and Sons, Copyright (2008).

1.1. Free Radical Photopolymerization

Free radical polymerization is more extensively used compared to cationic photopolymerization. Although it has two problems which are oxygen inhibition and volume shrinkage, free radical polymerization technique is still preferred due to its advantages. It provides usage of wide variety of monomers, oligomers and possible photoinitiating systems [2,3,13]. Free radical photopolymerization reactions involve photoinitiation, propagation, termination and chain transfer steps as shown in Figure 1.2 [12].

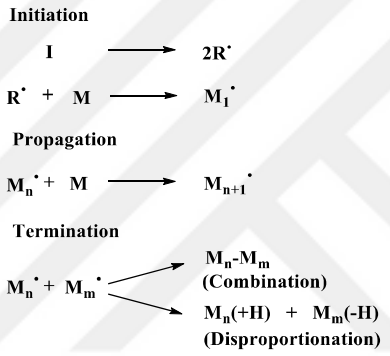


Figure 1.2. Chemical reaction steps of photopolymerization. Permission from [14] American Chemical Society, Copyright (2015).

In the first step, which is photoinitiation, the photoinitiator system becomes excited by absorbing light, goes to a higher electronic state; and produces radicals. In the presence of a photosensitizer, the photosensitizer molecule is excited by absorption of light and transfers energy to the photoinitiator molecule. The excitation of the photoinitator molecule generates a radical (Figure 1.3.) [3,10]. These radicals react with carbon-carbon double bonds of monomers, initiating polymer formation [12].

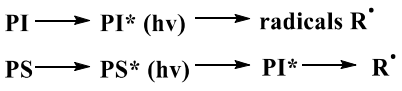


Figure 1.3. Formation of radical from photoinitiator and photosensitizer molecules. [3] published under an open access.

The rate of initiation, R_i, within the polymerizing film is expressed as

$$R_i = 2f\phi\,\varepsilon[I]I_0 \quad (1.1)$$

where I_0 is light intensity, $[I]$ is initiator concentration, ε is initiator molar absorptivity, f is efficiency of initiator and ϕ is initiator quantum yield. The values of I_0 and $[I]$ may depend on the position within the film. The second step in free radical photopolymerization is propagation. In this step, the first chain radical ($M_1\cdot$) reacts with carbon-carbon double bond of another monomer to give longer polymer chain which has radical end. The rate of propagation, R_p, is given by

$$R_p = k_p[M][M_n\cdot] \quad (1.2)$$

where k_p is propagation rate constant, $[M]$ is the double bond concentration and $[M_n\cdot]$ is total propagating radical concentration. Although there are arguments for dependence of degrees of polymerization to polymer chain length; the propagation rate constant k_p is generally assumed to be the same for all propagation steps. By the chain transfer reaction, a chain radical is terminated meanwhile a new chain is initiated at the same time [10,12].

The last step is termination. Chains are propagated until termination occurs. Termination takes place when the growing chain radicals react with each other, producing an inactive polymer molecule. Also, disproportion may occur in the termination step, one radical chain may act as a hydrogen donor and the other as a hydrogen acceptor, forming two inactive polymer chains. This hydrogen transfer causes olefinic bond formation on radical chain which act as hydrogen donor. The rate of termination, R_t, is expressed by the assumption of chain-length independence, no effects of the polymer heterogeneity and no radical trapping as

$$R_t = 2k_t[M_n\cdot]^2 \quad (1.3)$$

where k_t is the termination rate constant [12,15].

Overall, the rate of polymerization, R_p, is written as

$$R_p = k_p\,[M](R_i/2k_t)^{1/2} \quad (1.4)$$

where k_p is propagation rate constant, [M] is the double bond concentration, R_i is the initiaton rate and k_t is the termination rate constant [12].

One of the main problems of free radical photopolymerization is oxygen inhibition. Peroxyl radicals are formed as a result of reactions between oxygen and initiator, primary or

growing polymer radicals (Figure 1.4). Because of high stability of peroxyl radicals, they are completely unreactive towards propagation which means that they quench the polymerization process. Therefore, only when oxygen is consumed, polymerization can start properly [12,16]. By using high-intensity lamps, high cure dosage, inert atmosphere and additives such as amine and thiols, the effect of oxygen inhibition can be reduced [11].

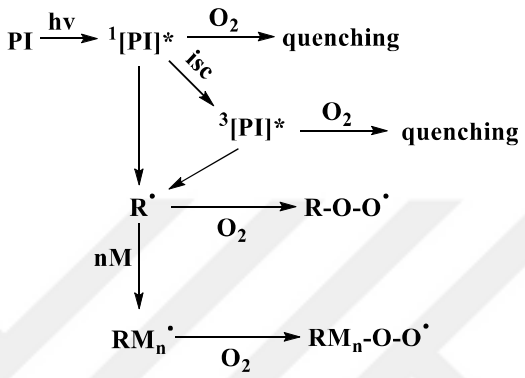


Figure 1.4. Oxygen inhibition on free radical photopolymerization. Permission from [11] American Chemical Society, Copyright (2010).

1.2. Free Radical Photoinitiators

In the photopolymerization process, one of the most crucial elements is the photoinitiator. The efficiency of the photopolymerization reaction and the final characteristics of the product can vary depending on the photoinitiator used. Photoinitiators also have influence on cure speed, yellowing and cost of photopolymerization process. They should be commercially available or easily synthesized, soluble in the monomer to be polymerized and stable for a long time. Also, they should have low odor, nonyellowing and low migration property so that they can be used in coatings industry. Of course, for successful photopolymerization, the light absorption properties of photoinitiators and emission wavelength of the light source should be in accordance with each other [11,17].

As shown in Jablonski diagram (Figure 1.5), a photon is absorbed by the molecule in the ground state and the molecule is excited to singlet state which has higher energy. The

singlet excited state may lose energy by emitting light (fluorescence, $S_1 \rightarrow S_0$) or it may lose energy by heat (internal conversion (S→S) or intersystem crossing (S→T)). The triplet excited state may lose energy by light (phosphorescence ($T_1 \rightarrow S_0$) and it may lose energy by heat (internal conversion (T→T)) [18,19].

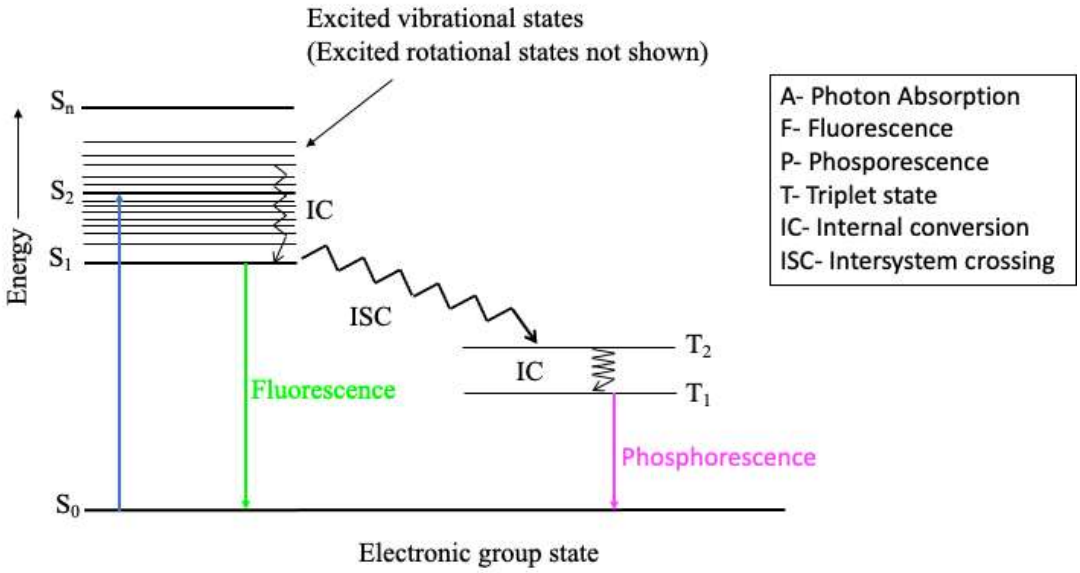


Figure 1.5. Jablonski diagram where S_0 is the ground singlet state, S_1, S_2 and S_n are the excited singlet states and T_1 and T_2 are the excited triplet states. [20] published under an open access.

There are three possibilities for the photoinitiator molecule, excited by absorbing a photon. It may emit light and/or heat. It may react with another substance to create a radical or it may break down itself into radicals [10]. Photoinitiators are categorized into two as Type I photoinitiator and Type II photoinitiator according to the mechanism of free radical formation [21].

1.2.1. Type I Photoinitiators

Via a Norrish I photoreaction (Type I), homolytic cleavage of photoinitiator molecule happens to create two radicals which are both capable of reacting toward double bonds (Figure 1.6). Benzoin ether derivatives, benzylketals, α-aminoketones, hydroxylalkyl phenones and acylphosphine oxides are used as Type I photoinitiators (Figure 1.7). Most of

the Type I photoinitiators are used only under UV irradiation because most of them are only reactive under UV light whereas there are only a few Type I photoinitiators which can be reactive in the blue or green region [13].

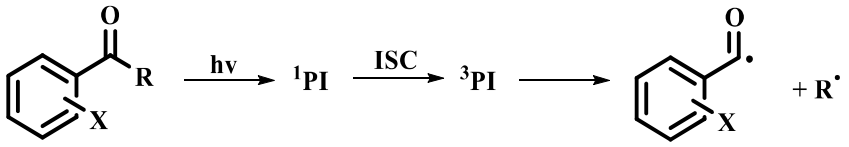


Figure 1.6. Photocleavage reaction from triplet state of Type I photoinitiators. Permission from [13] John Wiley and Sons, Copyright (2013).

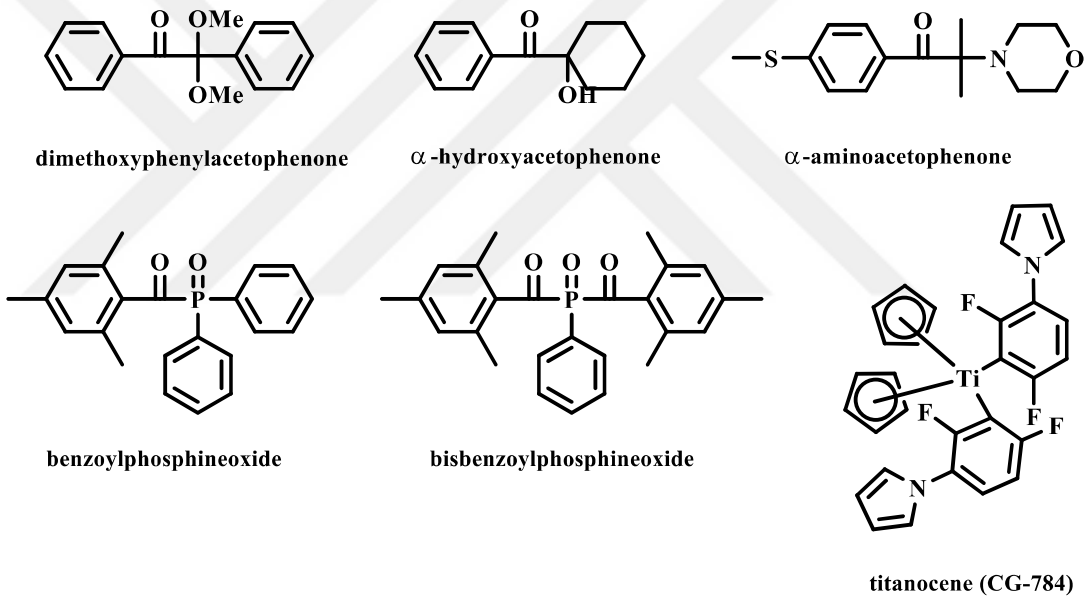


Figure 1.7. Examples of commercially available Type I photoinitiators. Permission from [13] John Wiley and Sons, Copyright (2013).

1.2.2. Type II Photoinitiators

For the formation of initiating radical from Type II photoinitiators, there should be a coinitiator. Triplet state of photoinitiator reacts with coinitiator to create initiating radical (Figure 1.8). Usually the coinitiator is a hydrogen donor which can be amine, ether, sulfide or thiol. After photoreaction, two radicals are formed. One is created from the hydrogen donor and this radical initiates the photopolymerization process. The other one is a ketyl

radical which is formed from the carbonyl compound and this radical is relatively stable because of steric hindrance and delocalized unpaired electron. Due to this stability, ketyl radicals are not reactive toward double bonds [11,13].

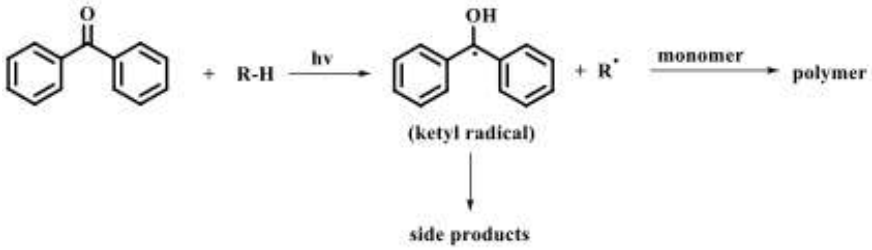


Figure 1.8. Type II photoinitiation mechanism with benzophenone and hydrogen donors. Permission from [11] American Chemical Society, Copyright (2010).

Benzophenone, thioxanthone, camphorquinone and benzyl derivatives are the example of Type II photoinitiators (Figure 1.9) which are active in the UV-blue region whereas coumarins, xanthenic dyes, cyanine dyes, thiazine dyes and pyrromethene dyes are used as Type II photoinitiators which are active in visible light [13].

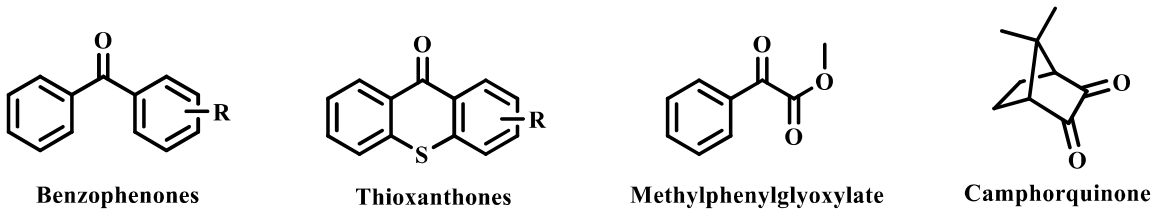


Figure 1.9. Examples of commercially available Type II photoinitiators. Permission from [13] John Wiley and Sons, Copyright (2013).

1.3. Monomeric and Polymeric Photoinitiators

In the photopolymerization process, the higher reactive radicals which are formed by Type I or Type II photoinitiators initiate polymerization. Radicals from initiators can become incorporated into the polymer chains, while residual photoinitiators, the products of their

photodissociation, and/or coinitiators might have the potential to leach out. Also, further rearrangement, combination, oxidation and decomposition of these unreacted molecules may happen as shown in Figure 1.10. Unreacted radicals and their derivatives may show different physical and chemical properties which harm the environment and/or products. These small molecules may be colored or odorous and have tendency to migrate out of the polymer networks. If they are colored, they may cause yellowing of the material. They may cause odor due to migration of them in the polymer networks [17,21].

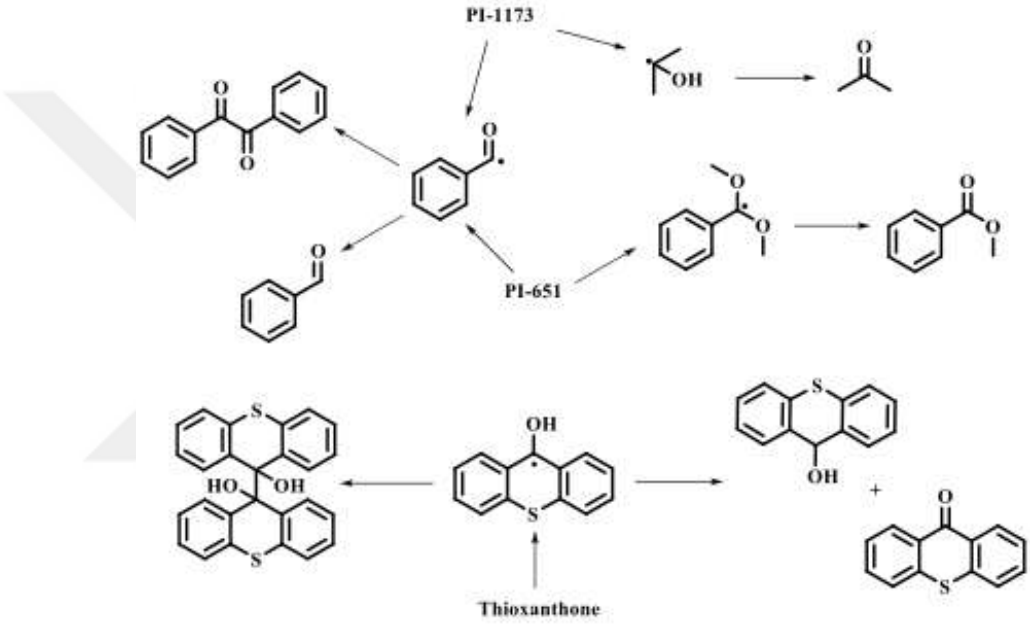


Figure 1.10. Examples of further rearrangements of photoinitiators. Permission from [21] Elsevier, Copyright (2019).

To eliminate these problems, monomeric or polymeric photoinitiators can be used. Monomeric photoinitiators are polymerizable, hence can form covalent bond with the product; polymeric photoititiators are large molecules which cannot diffuse appreciably. According to molecular structure, polymeric photoinitiators can be classified into three categories which are linear polymeric photoinitiators (LPPI), hyperbranched and cross-linked polymeric photoinitiators (HCPPI) and multifunctional photoinitiators (Figure 1.11) [17,21].

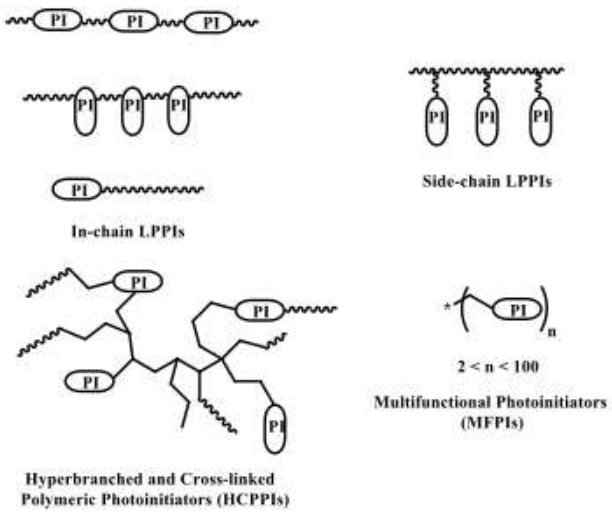


Figure 1.11. Structures of polymeric photoinitiators. Permission from [21] Elsevier, Copyright (2019).

There are many examples for monomeric and polymeric photoinitiators containing α-hydroxy ketones [22-25], acyl phosphine oxides [26,27], benzophenone [28-32] and thioxanthone [33-37] in literature. For example, two polymeric photoinitiators were synthesized, PEI-I2959-Ts and PEI-I2959, by functionalization of branched poly(ethyleneimine) with Irgacure 2959 (Figure 1.12). Branched poly(ethyleneimine) is a water soluble cationic polymer and it can undergo numerous substitution reactions with Irgacure 2959 which is an electrophile due to presence of primary, secondary and tertiary amines in its structure. The synthesized polymeric photoinitiators have superior water solubility compared to Irgacure 2959 due to existence of branched poly(ethyleneimine) in their structures. PEI-I2959-Ts shows higher migration stability than Irgacure 2959. This is because PEI-I2959-Ts has higher molecular weight, branched core and it can incorporate into the polymer network [38].

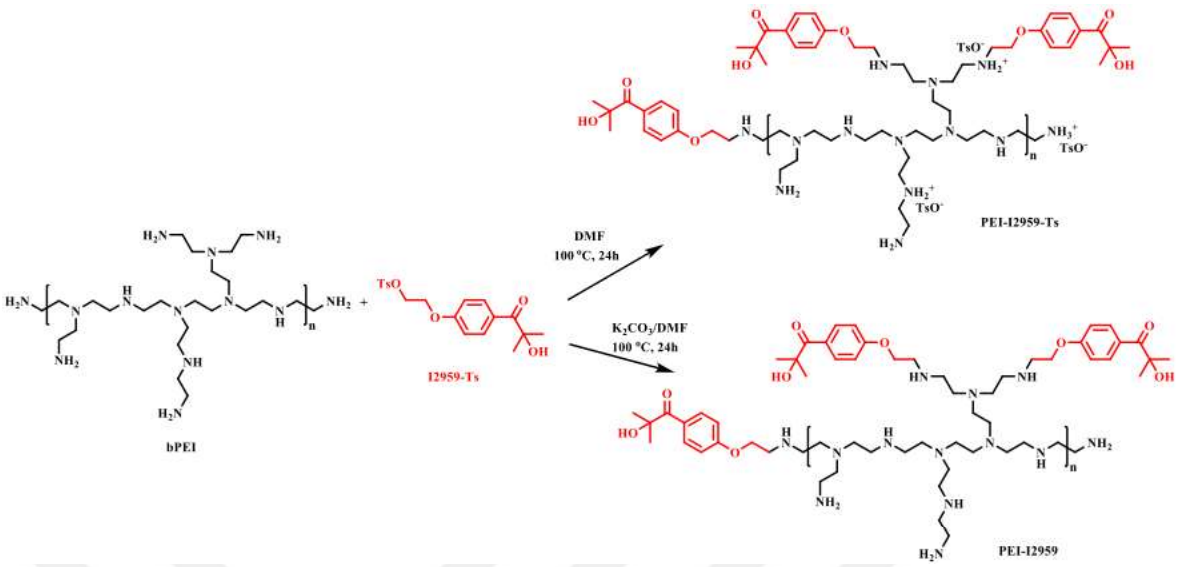


Figure 1.12. Syntheses scheme of polymeric photoinitiators [38].

Another example from the literature is two different polymeric photoinitiators, with two thioxanthone initiating groups at the two ends (Figure 1.13). They found that the higher molecular weight one has higher migration stability, high enough to be used in food packaging applications [39].

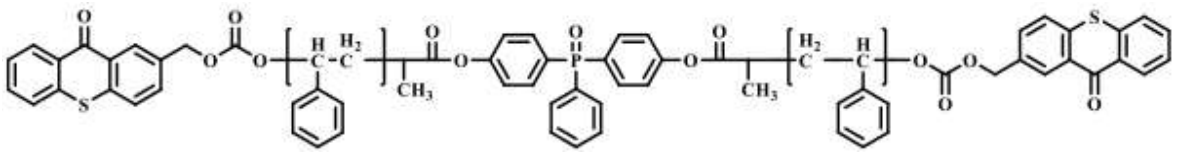


Figure 1.13. Structure of a polymeric photoinitiator. Permission from [39] Springer Nature, Copyright (2019).

In the literature, two monomeric photoinitiators (PI-1 and PI-2) and their polymeric photoinitiators (PPI-1 and PPI-2) based on the photosensitive benzophenone group were synthesized (Figure 1.14). Polymeric ones have higher maximum rate of polymerization (R_{pmax}) than monomeric ones [28].

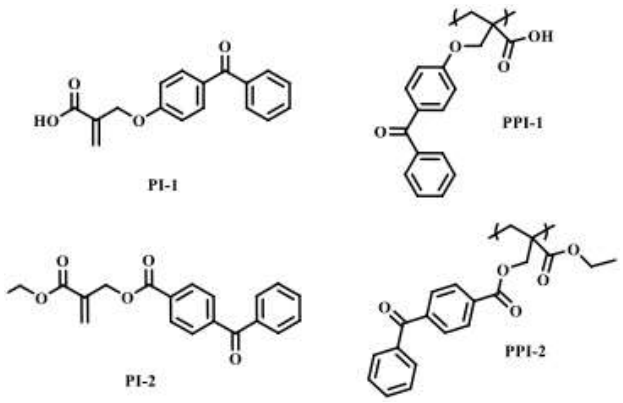


Figure 1.14. Structure of monomeric and polymeric photoinitiators. Permission from [28] Elsevier, Copyright (2015).

Polymeric photoinitiators (TX-PPO_4 and TX-PPO_5K) were synthesized based on thioxanthone with two different molecular weights (Figure 1.15) in the literature, and found that solubility of the polymeric photoinitiators improve with higher molecular weight of amine functional poly(propylene oxide) used in synthesis. These initiators are considered to be one-component polymeric photoinitiators because thioxanthone molecules are covalently bonded to poly(propylene oxide) backbone and this gives opportunity to create radicals even without addition of a coinitiator. Also, low migration behavior was obtained for these polymeric photoinitiators [40].

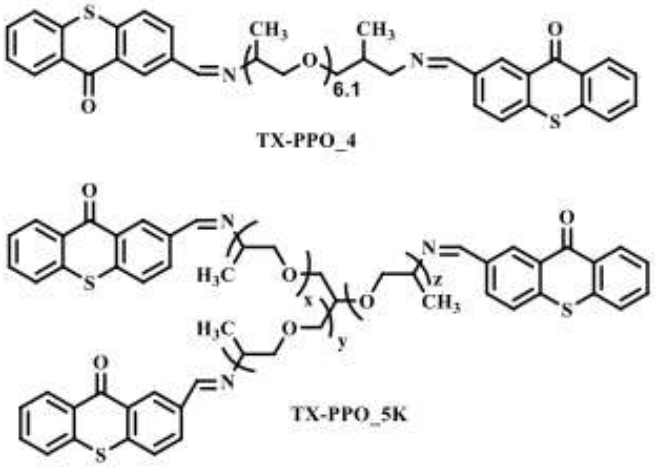


Figure 1.15. Structure of polymeric photoinitiators. Permission from [40] Elsevier, Copyright (2017).

1.4. Water-Soluble Photoinitiators

Water-based photocuring systems are important for “greener” photopolymerization because water is a non-toxic and cheap solvent which avoids many problems of organic solvents. These systems have found applications in many fields such as dental materials, biological and medical applications, and fabrication of 3D scaffolds for tissue engineering. For biomedical applications in particular, total or partial water solubility is necessary. Also, it was reported that the oxygen concentration in aqueous systems is lower than in organic systems, which serves to decrease oxygen’s negative effect on free radical photopolymerization [38,41]. However, the number of water soluble photoinitiators which are reported in literature is low and only few of them are commercially available [42]. The most commonly used commercially available water soluble Type I photoinitator is Irgacure 2959 due to its high reactivity, biocompatibility and water solubility. However, its solubility in water is limited [38]. For improvement in water solubility of photoinitiators, hydrophilic ionic groups such as lithium salts [43], carboxylic acids [44], quaternary ammonium salts [45] and sulfonates [46] or hydrophilic non-ionic groups [47] are affixed onto the photoinitiator molecules (Figure 1.16) [48].

In the literature, two different water-soluble Type I diphenylphosphine oxide photoinitiators (MAPO-2 and MAPO-3) from water-insoluble photoinitiator (MAPO-1) were synthesized (Figure 1.16). These photoinitiators are not cytotoxic and they have good storage stability [42]. From the literature, another example is modified thioxanthone with highly polar bisphosphonate group to make it water soluble. Water solubility of this photoinitiator is very high compared to the commercially available photoinitiator (Irgacure2959) [49]. Also, there are water soluble macro-photoinitiators based on Irgacure 2959 in the literature. They were synthesized by the esterification of linear poly(styrene-*alt*-maleic anhydride) with Irgacure 2959 and they show great water solubility and unique photoinitiating efficiency [50].

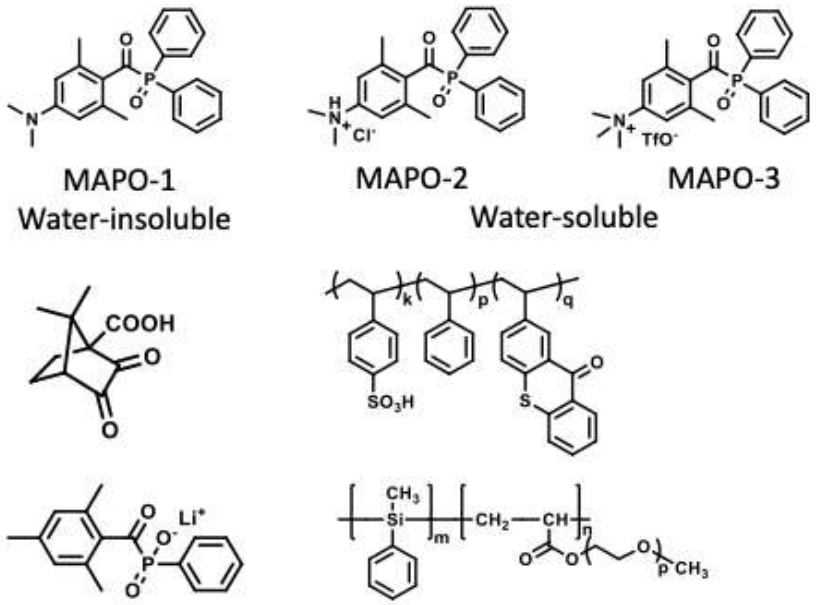


Figure 1.16. Structures of a water-insoluble photoinitiator (MAPO-1) and its water-soluble derivatives (MAPO-2 and MAPO-3) and other water soluble photoinitiators. Permission from [42] John Wiley and Sons, Copyright (2021), [43] Elsevier, Copyright (2009), [44] Elsevier, Copyright (2018), [46] Elsevier, Copyright (2009) and [47] Elsevier, Copyright (2015).

1.5. Cyclopolymerization

Through cyclopolymerization process, polymers are made efficiently and at the same time cyclic units are formed in the polymer backbone as shown in Figure 1.17. Within this scope, polymer rigidity, packing and solubility can be controlled by using cyclopolymerization process [51]. From non-conjugated diene monomers, polymer backbone with cyclic units is formed by radical cyclopolymerization. An intramolecular radical cyclization is followed by an intermolecular polymerization during copolymerization, which induces polymer backbone with cyclic units during the propagation [52].

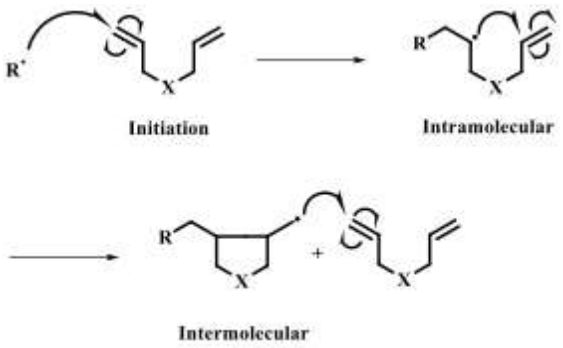


Figure 1.17. Mechanism of cycle-formation of an unspecific unsubstituted diene during cyclopolymerization. Permission from [52] John Wiley and Sons, Copyright (2021).

Cyclopolymers have advantages over noncyclic linear analogues. Cyclopolymers possess high glass transition temperatures, good thermal stabilities, and reduced shrinkage stress throughout polymerization process [17]. Cyclopolymerization process can be used in various areas such as dental industry and 3D-printing because it provides good mechanical properties to materials [52].

Monomers used in cyclopolymerization process are generally non-conjugated dienes. Low shrinkage stress is one of the most important benefits of these cyclopolymerizable monomers. During polymerization process, the distance between monomers is reduced as illustrated in Figure 1.18, compared with distance of monomers which are not polymerized. This phenomenon causes volumetric shrinkage. However, formation of cyclic units in the polymer backbone can reduce this volumetric shrinkage [52].

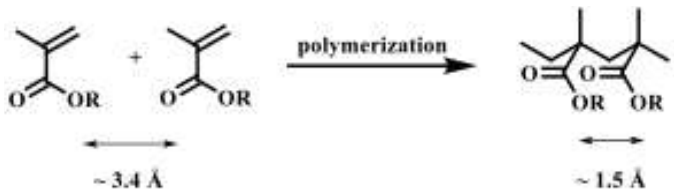


Figure 1.18. Schematic representation of volumetric shrinkage during polymerization. Permission from [52] John Wiley and Sons, Copyright (2021).

1.5.1. Cyclopolymerizable and Cyclopolymeric Photoinitiators

There are only few cyclopolymerizable photoinitiators and there is only one cyclopolymeric photoinitiator in literature. One is modified thioxanthone with 1,6-heptadiene structure as shown in Figure 1.19. During polymerization, the 1,6-heptadiene structure can facilitate the creation of cyclopolymers or crosslinked formations, depending on the concentration and/or temperature factors. Photoinitiating efficiency of this monomeric photoinitiator shows similarity with thioxanthone, however its migration stability is much better than thioxanthone [17].

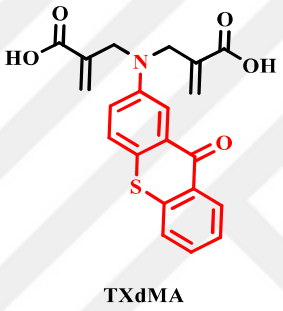


Figure 1.19. Structure of cyclopolymerizable photoinitiator. Permission from [17] Elsevier, Copyright (2019).

Other examples are three different cyclopolymerizable photoinitiators (DABPO-1, DABPO-2 and DABPO-3) shown in Figure 1.20, based on the commercial photoinitiator 2,4,6-trimethyl(phenyl)diphenyl oxide (TPO). These photoinitiators have diallyl amino groups in their structures, which allow cyclopolymerization. They show low migration behaviors compared to TPO due to their higher molecular weights and they have C=C double bonds in their structures which allow connection between polymer and photoinitiators [53].

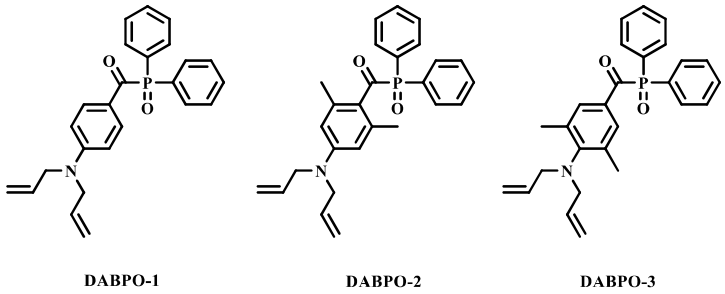


Figure 1.20. Structure of cyclopolymerizable photoinitiators. Permission from [53] Elsevier, Copyright (2022).

Also, two cyclopolymerizable (DAA-I2959 and DAA-I184) and one cyclopolymeric (p-DADMAC-*co*-DAA-I2959-QS) photoinitiators based on Irgacure 2959 and 1-hydroxycyclohexyl phenyl ketone (Irgacure 184) were synthesized (Figure 1.21). DAA-I2959 copolymerized with diallyldimethylammonium chloride (DADMAC) to increase water solubility and cyclization efficiency of the polymeric photoinitiator. DAA-I2959 shows better migration stability compared to Irgacure2959 due to its fusion into polymer network. However, p-DADMAC-*co*-DAA-I2959-QS shows better migration stability compared to DAA-I2959 due to its macromolecular nature and incorporation into polymer network [54].

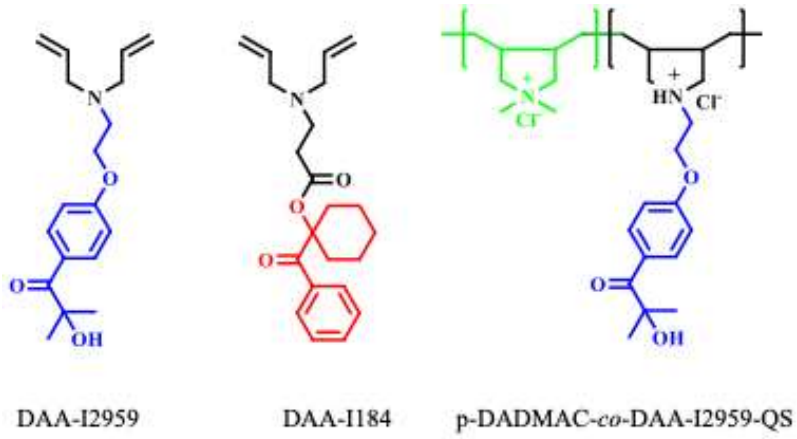


Figure 1.21. Structure of cyclopolymerizable and cyclopolymeric photoinitiators [54].

2. OBJECTIVES

The goal of this study is to design and synthesize novel photoinitiators with high reactivity and “greener” properties: water solubility, biocompatibility and low migration. For this purpose, a doubly I2959 functionalized cyclopolymerizable allyl-acrylate quaternary ammonium salt, its water soluble cyclic copolymer with DADMAC and a doubly I2959 functionalized water soluble DMSA salt with DBU counterion are synthesized and characterized. High migration stability is expected qualification due to the polymerizable, polymeric, and macromolecular structures of the synthesized photoinitiators. Their photophysical and photochemical properties were investigated.

3. CYCLOPOLYMERIZABLE AND CYCLOPOLYMERIC PHOTOINITIATORS FROM *tert*-BUTYL α-HYDROXYMETHACRYLATE

This chapter is published as: Kariksiz N., B. Balaban, T. Gencoglu, F. Morlet-Savary, J. Lalevee, D. Avci, "A Cyclopolymerizable, Doubly Irgacure 2959 Functionalized Quaternary Ammonium Salt Photoinitiator and Its Water-Soluble Copolymer with Diallyldimethylammonium Chloride", Polymer Chemistry, Vol. 14, No. 11, pp. 1195-1205, 2023.

3.1. Introduction

This chapter describes synthesis, characterization, photochemical and migration stability and photopolymerizations of a novel doubly I2959 and quaternary ammonium functionalized, cyclopolymerizable photoinitiator (2xI2959-QS) and its cyclic copolymer (p-DADMAC-*co*-2xI2959-QS) with DADMAC (Figure 3.1). 1,6-heptadiene structure of the monomeric PI makes it polymerizable to give either or both of cyclopolymers or crosslinked polymers during photopolymerization, hence it possesses the advantages coming with being polymerizable. Its thermal copolymerization with DADMAC enables excellent cyclization performance [55, 56] to provide polymeric PIs (PPIs) with good thermal stability and water solubility, thus to overcome the limited solubility of commercial I2959. The reactivity of the new PIs was examined under UV light exposure during the photopolymerization of HEMA and poly(ethylene glycol) diacrylate (PEGDA, Mn = 575 D) using differential scanning photocalorimetry. The solubility, thermal stability, UV-visible absorption properties and migration stability were investigated.

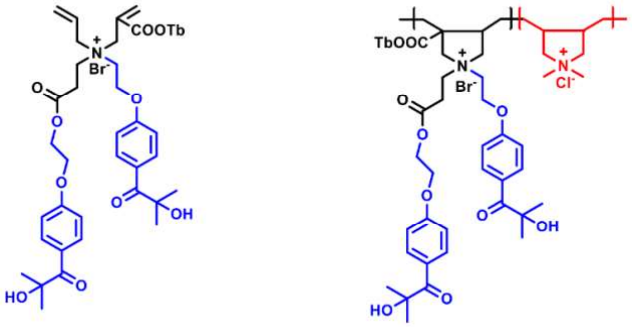


Figure 3.1. Structures of the novel monomeric (2xI2959-QS) and polymeric (p-DADMAC-*co*-2xI2959-QS) photoinitiator.

3.2. Experimental

3.2.1. Materials and Characterization

tert-Butyl α-bromomethacrylate (TBBr) was synthesized according to literature procedures [57,58].

Irgacure 2959 (I2959), allylamine, acryloyl chloride, p-toluenesulfonyl chloride (tosyl chloride, TsCl), sodium hydroxide, anhydrous sodium sulfate (Na_2SO_4), 2-hydroxyethyl methacrylate (HEMA), poly(ethylene glycol) diacrylate (PEGDA, M_n = 575 D), diallyldimethyl ammoniumchloride (DADMAC, 65 wt % aqueous solution) and the additional reagents and solvents were purchased from Sigma-Aldrich or Alfa Aesar and used as received without further purification. 2,2'-Azobis(2-methylpropionamidine) dihydrochloride (V-50) is a product of Polysciences. Dichloromethane (DCM) was dried over molecular sieves.

^{1}H and ^{13}C-NMR spectra were recorded on Varian Gemini (400 MHz) spectrometer in solvents as indicated. IR spectra were obtained by using a Nicolet 6700 FT-IR spectrophotometer. TGA analysis was performed on a TGA instrument (Mettler Toledo)

under nitrogen atmosphere at a heating rate of 10 °C min^{-1} (25 to 600 °C). The molecular weights of the polymers were analyzed by GPC/SEC System (Agilent 1260 Infinity II) with a PL1120-6830 column using a refractive index detector. Fluorescence characteristics of the PIs were investigated in CH_3CN:H_2O (3:7 v/v) with a JASCO FP-6200 spectrofluorometer.

3.2.2. Synthesis of Starting Materials

3.2.2.1. Synthesis of I2959-AC. 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (I2959) (1.0 g, 4.46 mmol), Et_3N (1.85 ml, 13.27 mmol) and dry CH_2Cl_2 (5 mL) were added into a three-necked round-bottom flask equipped with a condenser . The mixture was stirred in an ice bath under nitrogen gas. Under cooling, acryloyl chloride (0.425 ml, 5.26 mmol) and dry CH_2Cl_2 (2.5 mL) mixture was added dropwise into the flask and the mixture was stirred at room temperature for 2 hours. After 2 hours the crude product was extracted three times with saturated $NaHCO_3$ (5 mL), saturated NaCl (brine) (5 mL) and distilled water (5 mL), respectively. The organic layer was dried over Na_2SO_4. The solvent was removed by rotary evaporation. The residue was purified by column chromatography (hexane:ethyl acetate, 4:1). I2959-AC was obtained as a white solid in 13% yield [59].

^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 1.61 (s, 6H, CH_3), 4.27 (m, 2H, CH_2-O-Ar), 4.52 (m, 2H, CH_2-O-C=O), 5.84 (d, 1H, CH_2=), 6.13 (m, 1H, CH=), 6.43 (d, 1H, CH_2=), 6.95 (d, 2H, Ar-CH), 8.03 (d, 2H, Ar-CH).

FTIR (ATR): 3419 (O-H), 2995, 2962, 2935 (C-H), 1721 (C=O, ester), 1643 (C=O, ketone), 1599 (C=C), 1167,1251 (C-O) cm^{-1}.

3.2.2.2. Synthesis of I2959-Ts. A mixture of I2959 (0.8 g, 3.57 mmol), KOH (0.66 g, 11.76 mmol) and 4-toluenesulfonyl chloride (0.57 g, 2.99 mmol) in CH_2Cl_2 (9 mL) was stirred at room temperature for 2 hours under nitrogen gas. After 2 hours, the reaction mixture was washed three times with distilled water (5 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed by rotary evaporation. The residue was purified by column chromatography (methylene chloride:ethyl acetate, 20:1). I2959-Ts was obtained as a white solid [60].

^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 1.60 (s, 6H, CH_3-C-OH), 2.43 (s, 3H, CH_3-Ar), 4.19 (m, 2H, CH_2-O-SO_2), 4.37 (m, 2H, CH_2-O-Ar), 6.80 (d, 2H, Ar-CH-C-O), 7.32 (d, 2H, Ar-CH-C-CH_3), 7.80 (d, 2H, Ar-CH-C-SO_3), 7.99 (d, 2H, Ar-CH-C-C=O).

FTIR (ATR): 3558 (O-H), 2970 (C-H), 1660 (C=O, ketone), 1604, 1443 (C=C), 1354 (S=O), 1258 (C-O) cm^{-1}.

3.2.2.3. Synthesis of I2959-AA. I2959-AA was synthesized according to a modified procedure described in the literature [61]. A mixture of I2959-Ts (0.2004 g, 0.5295 mmol), allylamine (0.4480 g, 4.6110 mmol), 0.5 mL ethanol and 0.1 mL water was stirred at 80 ºC for 3 hours. Then, the temperature was decreased to 40 ºC, 30 wt % NaOH solution (0.8 mL) was added and the mixture was stirred for 3 h. The aqueous phase was extracted with dichloromethane (DCM) (5x5 mL). The organic phases were combined and extracted with water (5x5 mL). Organic phase was stirred with 5 mL 2M HCl for 30 minutes. Organic and aqueous phases were separated and organic phase was extracted with 2M HCl (5x5 mL). To the aqueous phase 2 M NaOH was added until the pH was reached to 11 and was extracted with DCM for several times. The extracts were washed with water (5x5 mL), dried over anhydrous sodium sulfate and the solvent was taken away under reduced pressure. The product was obtained as a white solid in 52% yield.

^{1}H-NMR (MeOD, 400 MHz, δ): 1.44 (s, 6H, CH_3), 2.93 (m, 2H, CH_2-N), 3.25 (d, 2H, CH_2-N), 4.10 (m, 2H, CH_2-O), 5.13 (m, 2H, CH_2=), 5.86 (m, 1H, CH=), 6.94 (d, 2H, Ar-CH), 8.15 (d, 2H, Ar-CH).

FTIR (ATR): 3292 (OH, NH), 3082, 2981 (CH), 1658 (C=O), 1597 (C=C, NH) cm^{-1}.

3.2.2.4. Synthesis of 2xI2959-AA. A mixture of I2959-AC (41.7 mg, 0.15 mmol) and I2959-AA (39 mg, 0.15 mmol) in 0.8 mL of methanol was stirred at 60 °C for 48 h under nitrogen. The solvent was removed under reduced pressure to give 2xI2959-AA as a pale orange oil.

^{1}H-NMR ($CDCl_3$, 400 MHz, δ): 1.60 (s, 12H, CH_3), 2.49 (m, 2H, CH_2-C=O), 2.89 (m, 4H, CH_2-N), 3.19 (d, 2H, CH_2-N), 3.98 (m, 2H, CH_2-O), 4.06 (m, 2H, CH_2-O), 4.14 (m, 2H,

CH_2-O), 5.16 (m, 2H, CH_2=), 5.85 (m, 1H, CH=), 6.92 (m, 4H, Ar-CH), 8.02 (m, 4H, Ar-CH).

FTIR (ATR): 3411 (OH), 2932 (CH), 1733 (C=O, ester), 1661 (C=O, ketone), 1597, 1571 (C=C, Ar) cm^{-1}.

Q-Tof-MS (m/z): Calcd for $C_{30}H_{39}O_8N$, 541.265. Found: 541.2676 [M+H]+.

3.2.3. Synthesis of Monomeric Photoinitiator

2xI2959-AA (81.0 mg, 0.15 mmol) was dissolved in 5 ml diethyl ether. The mixture was stirred in an ice bath. After 10 min., TBBr (46.3 mg, 0.21 mmol) and 1 ml diethyl ether mixture was added. The reaction mixture was stirred for 1 h under cooling. The solvent was removed under reduced pressure. The product was washed with diethyl ether and it was obtained as a pale yellow oil in 73% yield.

^{1}H-NMR (MeOD, 400 MHz, δ): 1.40 (s, 12H, CH_3-C-OH), 1.44 (s, 9H, CH_3-C), 3.04 (m, 2H, CH_2-C=O), 3.60 (d, 2H, CH_2-N), 3.77 (m, 4H, CH_2-N), 4.04 (m, 4H, CH_2-O), 4.37 (s, 2H, CH_2-N), 4.55 (m, 2H, CH_2-O), 5.68 (m, 2H, CH_2=), 6.15 (m, 1H, CH=), 6.37 (s, 1H, CH_2=), 6.80 (s, 1H, CH_2=), 6.94 (m, 4H, Ar-CH), 8.15 (m, 4H, Ar-CH).

^{13}C-NMR (MeOD, 101 MHz, δ): 28.28 (*C*H_3-C-OH), 28.68 (*C*H_3-C), 30.86 (*C*H_2-C=O), 53.00 (*C*H_2-N), 56.51 (*C*H_2-O-C=O), 59.51 (*C*H_2-O), 60.14 (*C*H_2-N), 61.63 (*C*H_2-O), 63.13 (*C*H_2-N), 63.95 (*C*H_2-N), 78.58 (*C*-$(CH_3)_2$), 84.49 (*C*-$(CH_3)_3$), 115.15 (*C*H_2=CH), 126.25 (*C*H_2=C), 129.60 (Ar-*C*), 130.28 (Ar-*C*H), 131.80 (Ar-*C*H), 133.92 (*C*H=CH_2), 141.19 (*C*=CH_2), 162.16 (Ar-*C*-O), 164.14 (Ar-*C*-O), 166.31 (O-*C*=O), 171.30 (O-*C*=O), 204.53 (Ar-*C*=O).

FTIR (ATR): 3324 (OH), 2977 (CH), 1733 (C=O, ester), 1708 (C=O, ester), 1666 (C=O, ketone), 1598 (C=C, Ar), 1247, 1149 (C-O) cm^{-1}.

Q-Tof-MS (m/z): Calcd for : $C_{38}H_{52}O_{10}NBr$, 762.3466. Found: 761.3543.

3.2.4. Synthesis of Polymeric Photoinitiator

In a typical copolymerization, DADMAC (84.3 mg of a 65 wt % aqueous solution, 0.339 mmol), 2xI2959-QS (28.8 mg, 0.038 mmol), V-50 (0.91 mg) as initiator and 24.4 mg of methanol were mixed in a test tube, and the tube was subjected to repeated freeze–thaw cycles. The tube was placed in an oil bath and kept at 70 °C for 3-5 h. The copolymer was precipitated into hot acetone and dried under vacuum to give the polymer as a colorless oil in 15% yield.

3.2.5. ESR Spin Trapping (ESR-ST) Experiments

ESR-ST experiments were performed utilizing a Bruker EMX-plus spectrometer (X-band). Toluene solutions of I2959 and 2xI2959-QS were deoxygenated with nitrogen 15 min prior to measurements. The irradiation was carried out with UV-vis light (Omnicure 1000, 150 W, 50% intensity) at 320-500 nm. The radicals formed at room temperature were captured by phenyl-N-*tert*-butylnitrone (PBN). The ESR spectra simulations were carried out with the WINSIM program [62].

3.2.6. UV–Vis Spectroscopy and Photolysis

UV–vis spectra of PIs were recorded in different solvents with a Carry 3 UV/Vis spectrophotometer from Varian in methanol solution. For the photolysis experiments, ethanol solutions of the PIs were irradiated with UV light (Omnicure 1000, 150 W, 50% intensity) at 320-500 nm and the UV–vis spectra at different irradiation times were recorded.

3.2.7. Photoinitiating Activity Measurements

Photopolymerization experiments were carried out using a TA Instruments DSC 250 differential photocalorimeter with an Omnicure 2000 mercury lamp light source equipped with a 320-500 nm filter. HEMA or PEGDA monomer (3-4 mg) containing PIs or the reference (I2959) were subjected to irradiation at 25 °C under nitrogen for 5 minutes. The heat flow was observed as a function of time, and the polymerization rate was determined using equation 3.1.

$$\text{Rate} = \frac{(Q/s)M}{n(\Delta H_p)m} \quad (3.1)$$

where *Q/s* represents heat flow per second, *M* the molar mass of the monomer, *n* the number of double bonds per monomer molecule, ΔH_p the heat of reaction and *m* the mass of monomer in the sample. The theoretical heats for the complete conversion of an acrylate and methcarylate double bond are 86 kJ/mol and 55 kJ/mol, respectively.

3.2.8. Migration Studies

The mixture of HEMA/PEGDA/water (3/3/1 wt%) containing I2959, 2xI2959-QS or p-DADMAC-*co*-2xI2959-QS (0.2 wt%) underwent photopolymerization under air for 1 h in glass vials using 365 nm irradiation. The crosslinked polymers were immersed in 25 mL of methanol for 3 days. The quantity of extracted photoinitiators was determined by using UV-visible spectroscopy.

3.3. Results and Discussion

3.3.1. Synthesis and Characterization of Monomeric Photoinitiator

A novel I2959-functionalized 1,6-heptadiene was synthesized using a four step procedure (Figure 3.2). In the first step, I2959-Ts was synthesized by the reaction of I2959 and tosyl chloride [60]. Then, nucleophilic substitution reaction of allylamine with I2959-Ts provided a secondary amine (I2959-AA) which underwent an aza-Michael addition reaction with I2959-acrylate in the third step to give a tertiary amine with two Irgacure 2959 functionalities (2xI2959-AA) (Figure 3.2). The last step involved a quaternization reaction between 2xI2959-AA and TBBr in diethyl ether to give the pure product (2xI2959-QS) as a pale orange oil in 73% yield.

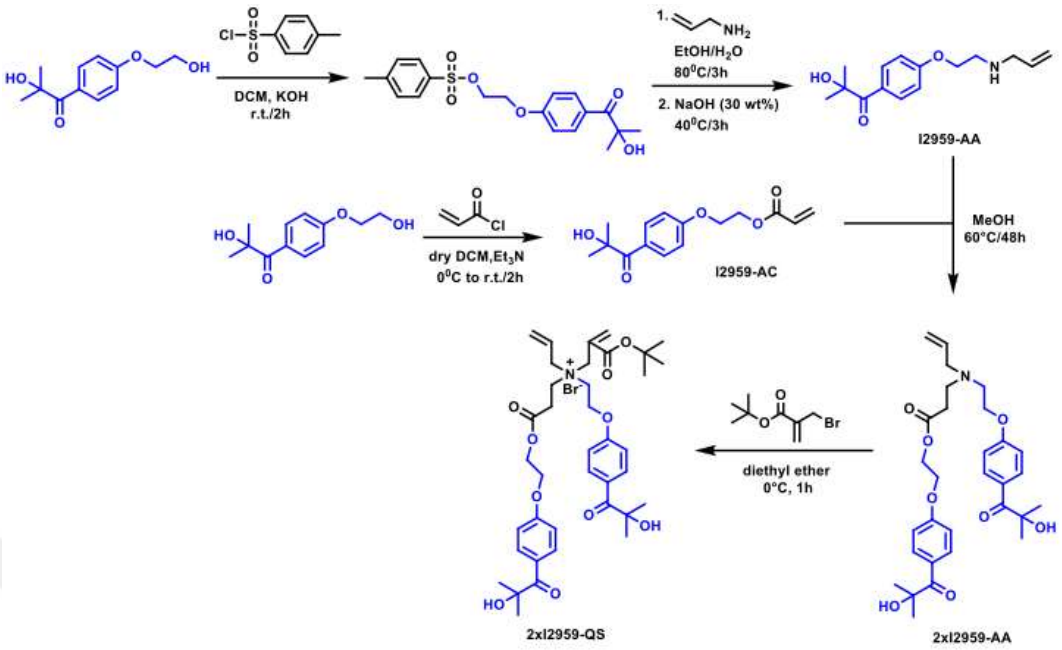


Figure 3.2. Synthesis of the monomeric PI, 2xI2959-QS.

Structural characterization of the intermediates and PIs have been carried out using ^{1}H, ^{13}C and FTIR spectroscopy and mass spectrometry. In the ^{1}H NMR of I2959-AA the peaks at 5.13 and 5.86 ppm were assigned to the characteristic allyl proton peaks. The aromatic proton peaks appear as two doublets at 6.94 and 8.15 ppm (Figure 3.3). The ^{1}H NMR of 2xI2959-AA showed four new methylene peaks at 2.49, 2.89, 4.06 and 4.14 ppm due to addition of the second I2959 unit. The structure of this amine was further confirmed using mass spectroscopy. After quaternization, we observed deshielding of about 0.4-0.9 ppm for the methylene groups directly attached to the positively charged nitrogen atoms (Figure 3.4). In the ^{1}H NMR of 2xI2959-QS, two singlets observed at 1.40 and 1.44 ppm were assigned to the methyl protons of *tert*-butyl and I2959 and the other two at 6.37 and 6.80 ppm to methacrylate double bond. One of the two sets of aromatic protons due to two I2959 units appears as two different doublets at 6.94 ppm, whereas the other set appears as overlapping doublets at 8.15 ppm. The ^{13}C-NMR showed three different carbonyl groups at 166.31, 171.30 and 204.53 ppm which are two ester groups and a ketone, respectively (Figure 3.5). Also, the FT-IR showed three different C=O group stretchings due to a ketone (1666 cm^{-1}) and two ester (1733 and 1708 cm^{-1}) groups (Figure 3.6).

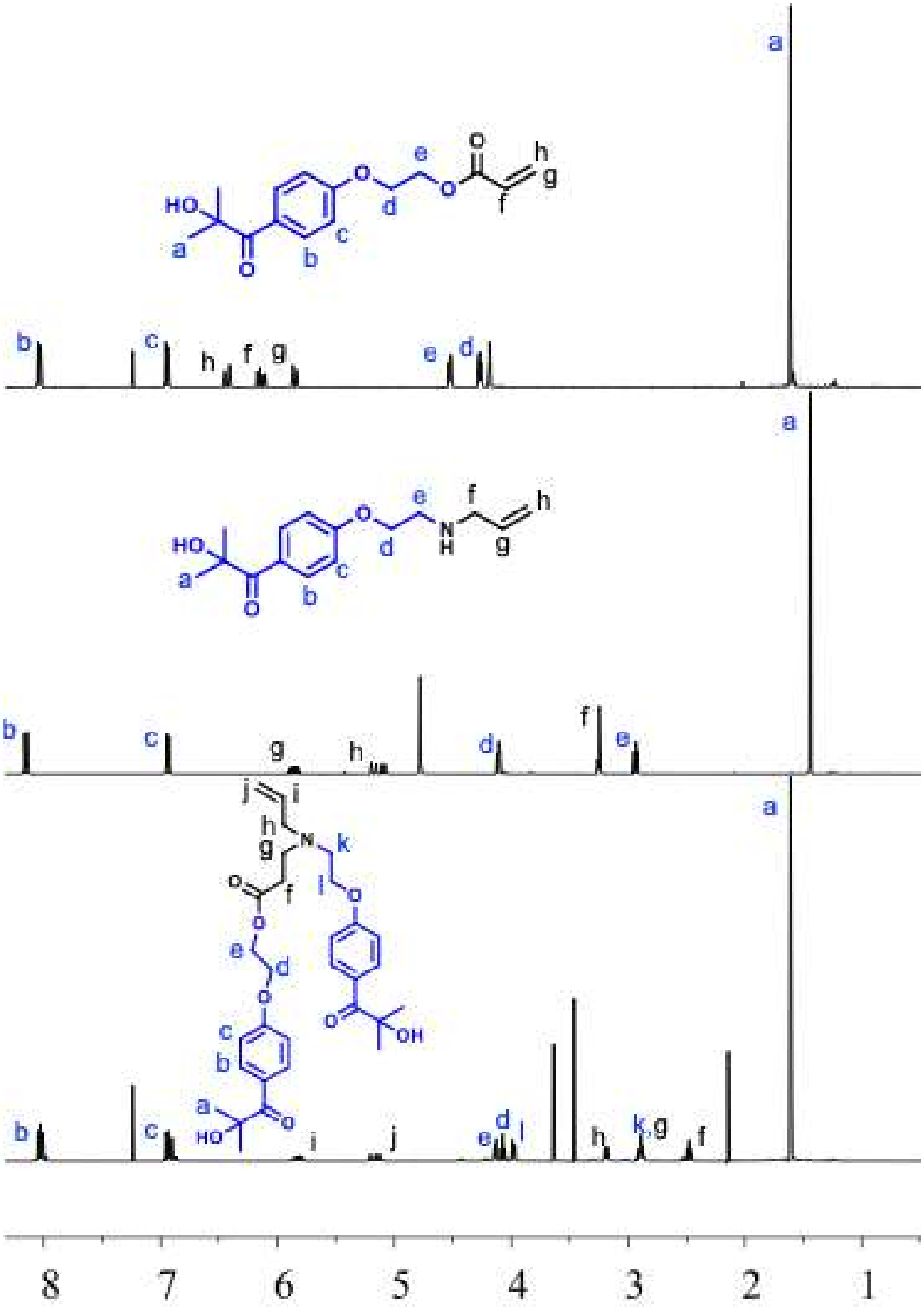


Figure 3.3. [1]H-NMR spectra of I2959-AC, I2959-AA and 2xI2959-AA.

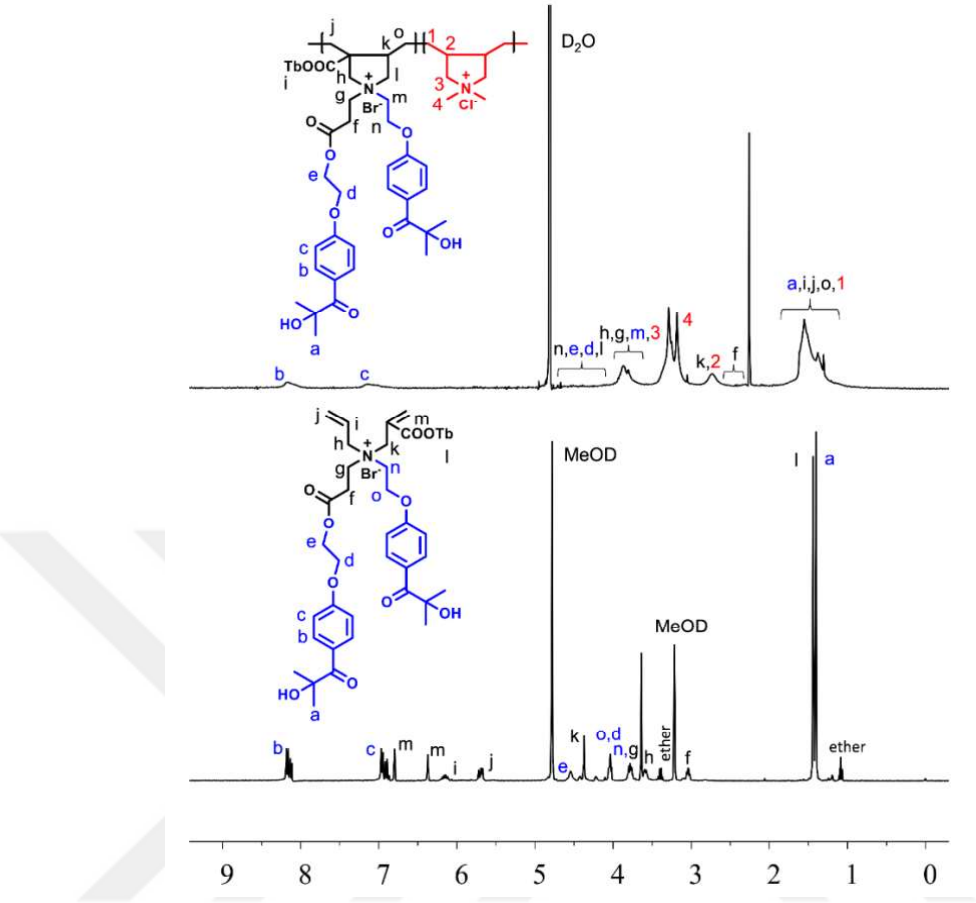


Figure 3.4. [1]H-NMR spectra of 2xI2959-QS and p-DADMAC-*co*-2xI2959-QS.

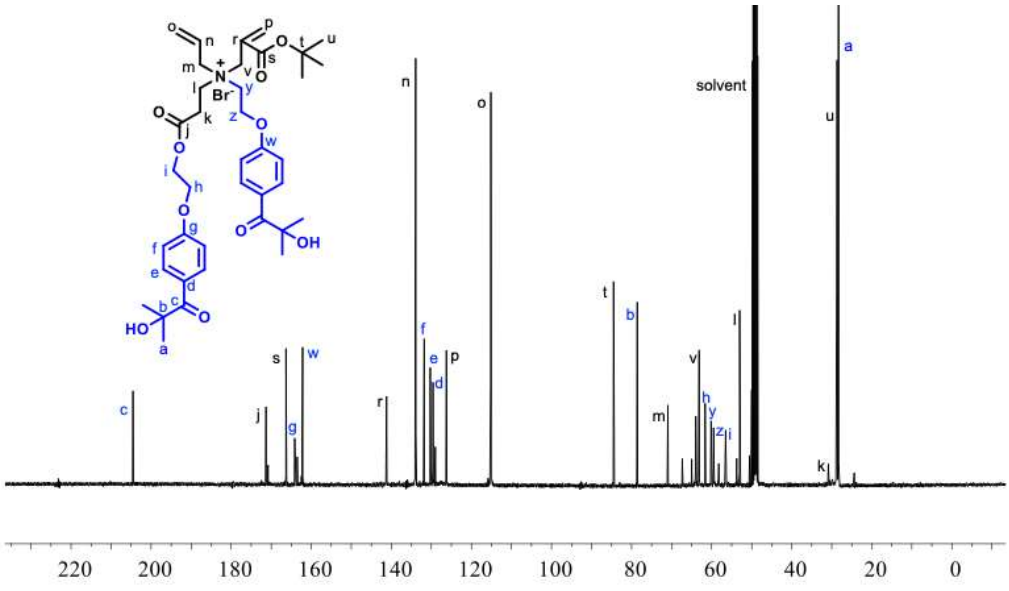


Figure 3.5. [13]C-NMR spectrum of 2xI2959-QS.

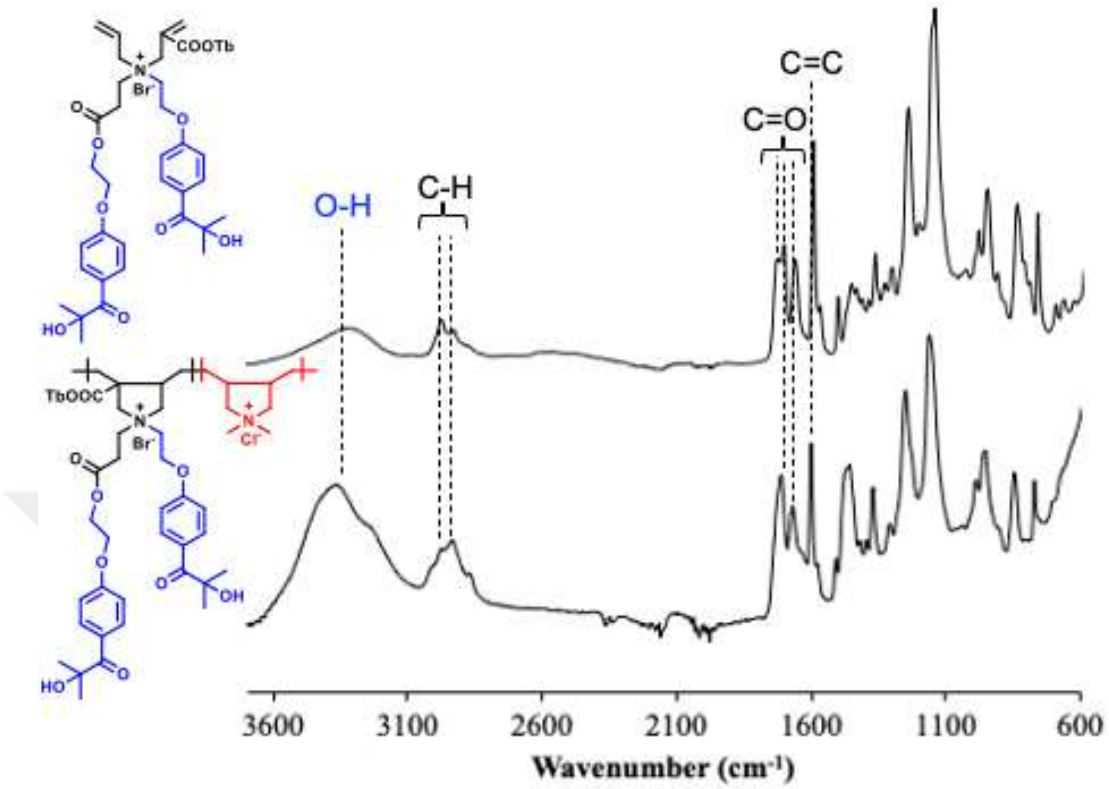


Figure 3.6. FTIR spectra of 2xI2959-QS and its copolymer with DADMAC.

Table 3.1 summarizes the solubility of PIs and I2959 as reference. Quaternary ammonium salts are generally highly soluble in polar and protic solvents such as water and alcohols due to their ionic nature. However, 2xI2959-QS is insoluble in water probably due to two hydrophobic-tailed quaternary ammonium structure forming micelles. It is soluble in low polarity solvents such as DCM and tetrahydrofuran. Additionally, the novel PI has a good compatibility with HEMA and PEGDA.

Table 3.1. Solubilities of the synthesized PIs and I2959.

PI	H_2O	Methanol	Diethyl ether	CH_2Cl_2	THF	DMF
I2959	+	+	+	+	+	+
2xI2959-QS	-	+	-	+	+	+
p-DADMAC-co-I2959-QS	+	+	-	-	-	-

3.3.2. Synthesis and Characterization of Polymeric Photoinitiator

The copolymer of 2xI2959-QS with DADMAC (10:90 mol% in feed) was prepared in water/methanol (6/5 wt/wt) mixture at 70 °C with V-50 as thermal initiator (Figure 3.7). The polymer is soluble in polar solvents such as water and methanol, suggesting the formation of a highly cyclized polymer despite the monomer has an unsymmetrical structure (Table 3.1). In general, when the reactivities of double bonds are different there is a possibility of unfavorable cyclopolymerization. The high cyclization tendency of the monomeric PI was also confirmed by ^{1}H NMR spectrum of the polymer, where no pendant double bonds could be detected (Figure 3.4). In the literature, the cyclization efficiency was found to be affected by the size of the alkyl groups both on the vinyl groups and on the linkage group [63-65]. The bulky groups prevent intermolecular reaction, thus favoring cyclization. Therefore, we can say that due to a *tert*-butyl group on the methacrylate side and two I2959 substituents on the linkage, 2xI2959-QS is a favorable monomer for cyclocopolymerization. ^{1}H NMR also shows two methyl protons of DADMAC at 3.22 ppm, methylene protons attached to oxygen at 4.38 ppm, aromatic protons at 7.12 and 8.17 ppm while backbone methylenes show peaks at 1.45 ppm. The experimentally measured copolymer compositions calculated from the ratio of peak areas of aromatic CH groups of 2xI2959-QS units to methyl groups attached to nitrogen of DADMAC (3.22 ppm) were similar (88.3:11.7 mol% DADMAC:2xI2959-QS) to feed compositions. The FTIR spectrum of the copolymer exhibited a broad absorption at 3367 cm^{-1} due to the presence of OH groups and two intense peaks at 1711 and 1667 cm^{-1} due to stretching of the ester and ketone carbonyl groups (Figure 3.5). M_n value of this polymer was around 25,000 D and has a five-membered ring structure at the backbone, expected because both DADMAC and allyl-acrylate also give similar backbones upon homopolymerization [55,56,64,65].

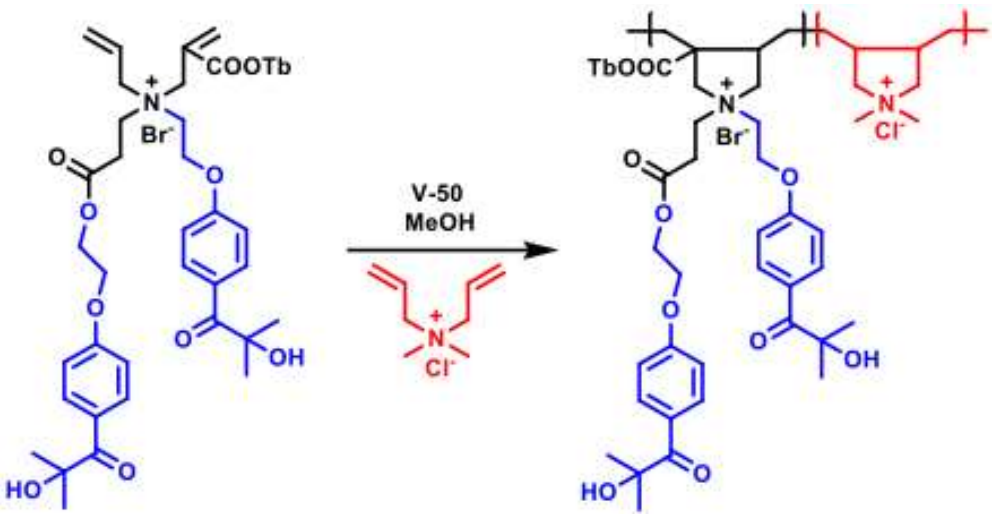


Figure 3.7. Synthesis of PPI.

Thermal stability of I2959 was studied using TGA [66]. It shows an initial weight loss at 151 °C and was completed at 269 °C [66]. Thermogravimetric analysis of the PPI showed a multistep weight loss similar to the homopolymer of poly-DADMAC (Figure 3.8) [66]. The initial weight loss was 9 wt % at 100 °C due to the loss of moisture from the sample. Then two step degradation was observed, ~ 35 wt % loss at 250-385 °C (formation of methyl chloride and tertiary amine) and 53 wt% loss at 385-485 °C (involves a number of reactions) [66]. As a result, PPI exhibited excellent thermal stability compared to I2959, attributed to quaternary ammonium groups of poly-DADMAC segments.

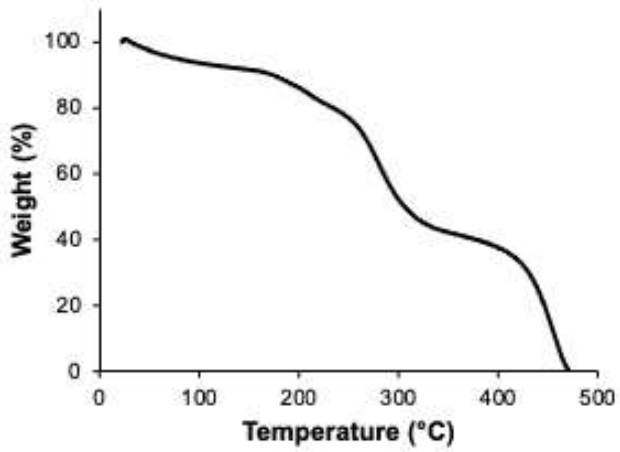


Figure 3.8. TGA spectrum of p-DADMAC-*co*-2xI2959-QS.

3.3.3. Light Absorption Properties

Absorption properties of the monomeric and polymeric PIs were determined by UV-vis spectroscopy. 2xI2959-QS and p-DADMAC-*co*-2xI2959-QS have a maximum UV absorption wavelength at 271 and 272 nm in ethanol due to π-π∗ transition, similar to I2959 (Figure 3.9, Figure 3.10 and Table 3.2). The photodissociation of I2959 involves the following transitions: $^{1}\pi\pi^{*} \rightarrow {}^{1}n\pi^{*} \rightarrow {}^{3}\pi\pi^{*} \rightarrow {}^{3}n\pi^{*}$ which result in formation of benzoyl and ketyl radicals [67]. A shoulder peak observed around 330 nm corresponds to the direct n-π∗ transition. The molar absorption coefficient of 2xI2959-QS (ε = 32237 M^{-1} cm^{-1}) is stronger than that of I2959 (ε = 16538 M^{-1} cm^{-1}) which can be explained by the two aromatic rings in the structure of 2xI2959-QS (Table 3.2). Actually, this 2-fold increase in ε value and almost no change in the maximum absorption compared to I2959 indicate the independence of the two PI units. Therefore they can be considered as isolated chromophoric groups [68]. The approximate extinction coefficient of PPI was also calculated using the amount of 2xI2959-QS unit in the copolymer and found to be around 40000, again consistent with the double substitution of the chromophoric group.

Table 3.2. Absorption characteristics of 2xI2959-QS and I2959 in methanol and ethanol.

PI	Solvents	λ_{max} (nm)	ε (M^{-1} cm^{-1})
2xI2959-QS	MeOH	268	32237
2xI2959-QS	EtOH	271	26038
I2959	MeOH	272	16538

When 2xI2959-QS was irradiated using a 320-500 nm light source, the intensity of the peak at 271 nm decreased very fast in only 5-10 sec, indicating very fast photolysis rate (Figure 3.11A). We also observed a new peak at 251 nm, reaching a maximum absorbance in 35 sec. The presence of two isobestic points suggests clean photolysis without other side reactions. A similar peak was indicated during photolysis of a PEG based alpha-hydroxyalkylphenone photoinitiator and assigned it to acetone generated by the cleavage of hydroxyketone [69]. The photolysis of the PPI was also carried out under the same conditions (Figure 3.11B). The decrease of the intensity of absorption peak at 272 nm also confirmed decomposition of the PPI. Fluorescence spectra of the photoinitiators were taken to get information on the nature of their excited states. Although 2xI2959-QS did not show

any fluorescence property, p-DADMAC-*co*-2xI2959-QS showed a weak fluorescence emission (Figure 3.12).

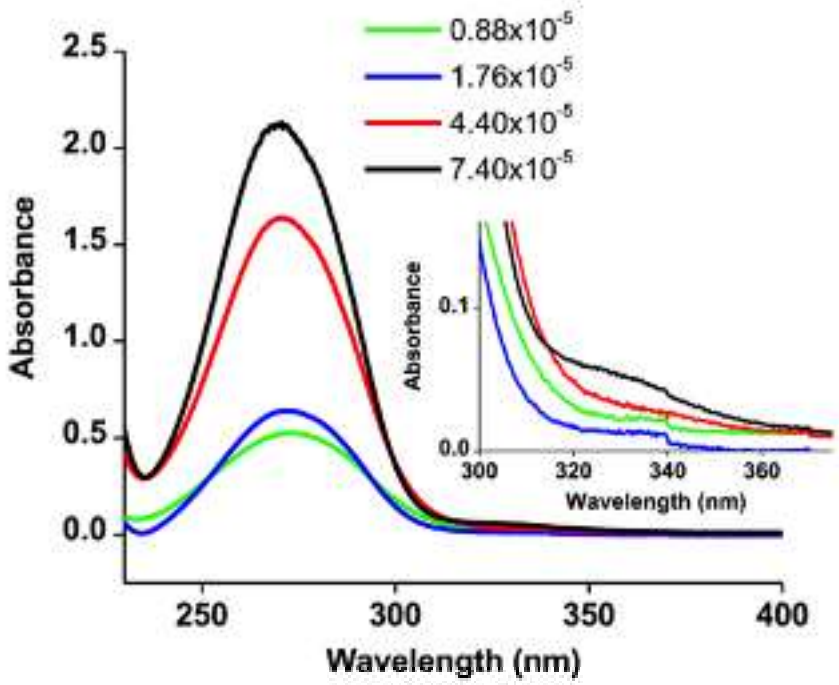


Figure 3.9. UV–vis absorption spectra of 2xI2959-QS in ethanol.

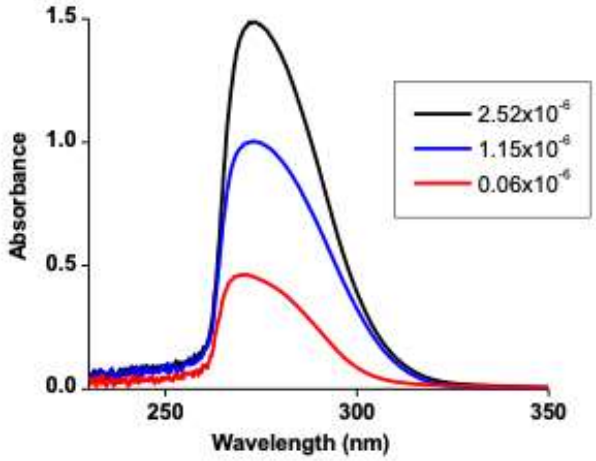


Figure 3.10. UV–vis absorption spectra of p-DADMAC-*co*-2xI2959-QS in ethanol.

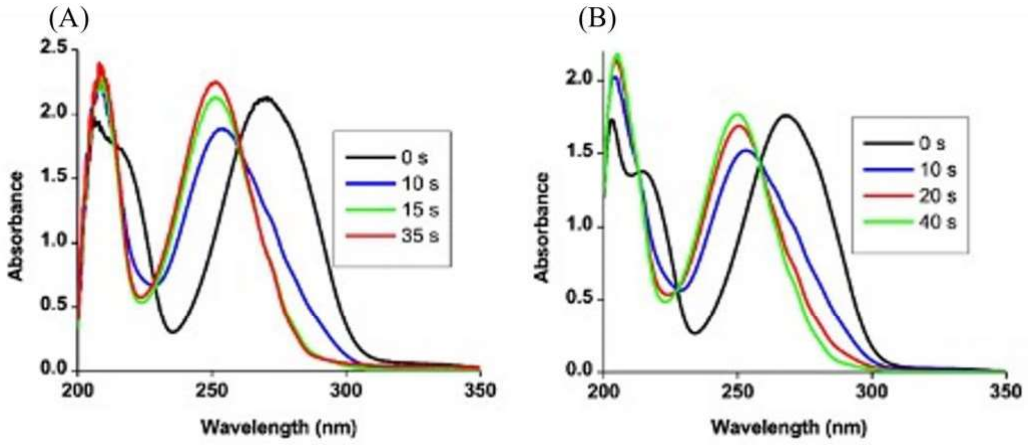


Figure 3.11. Photolysis of (a) 2xI2959-QS in ethanol ($8.8x10^{-5}$ M) and (b) p-DADMAC-*co*-2xI2959-QS in ethanol ($5.76x10^{-6}$ M) using 320-500 nm (intensity = 50 W) light source.

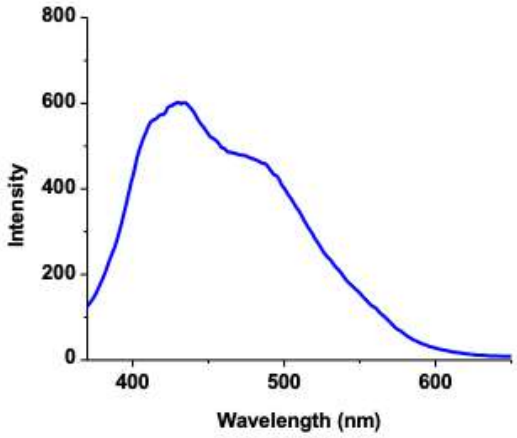


Figure 3.12. The fluorescence spectrum of p-DADMAC-*co*-2xI2959-QS in CH_3CN:H_2O (3:7 v/v).

3.3.4. Electron Spin Resonance (ESR) Experiments

ESR-spin trapping experiments were carried out on 2xI2959-QS, p-DADMAC-*co*-2xI2959-QS and I2959 as reference. The I2959 solution leads to two PBN radical adducts which correspond to substituted benzoyl (a_H ~ 4.3 G) and alkyl radicals (a_H ~ 1.5 G) in agreement with Type I behavior (Figure 3.12) [70]. A similar behavior is observed for 2xI2959-QS, p-DADMAC-*co*-2xI2959-QS (Figure 3.13).

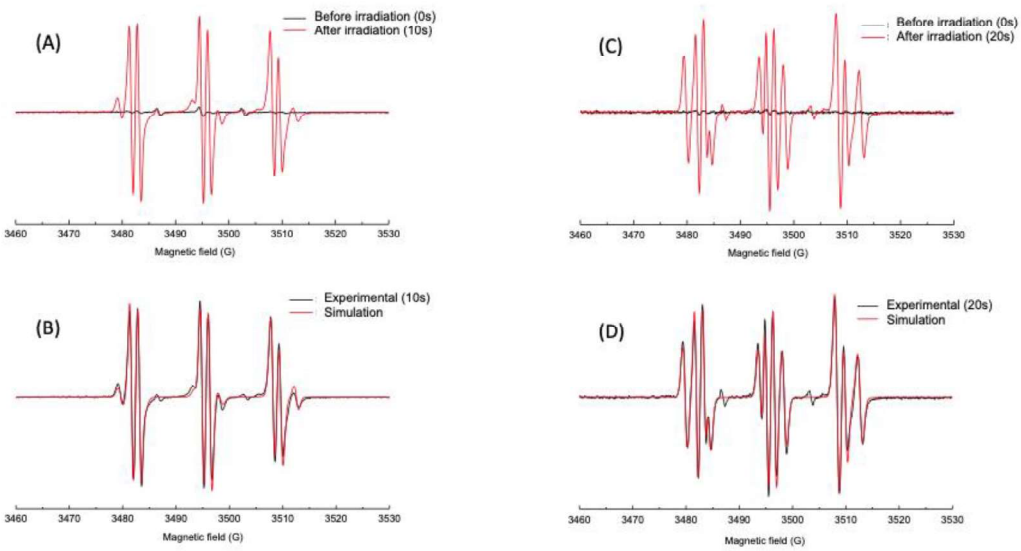


Figure 3.13. ESR spectra of I2959 (a) and 2xI2959-QS (c) before and after irradiation; simulation of their EPR spectrum (b and d) after irradiation.

3.3.5. Photopolymerization Results

The photopolymerization performance of the synthesized PIs in the polymerization of HEMA and PEGDA was investigated and compared to commercial I2959, using photo-DSC with UV-vis irradiation (320-500 nm) at 25 °C (Figure 3.14-Figure 3.17). In photopolymerization of HEMA, 2xI2959-QS showed higher R_{pmax} and lower t_{max} (time to reach the maximum heat of polymerization) values compared to I2959. The higher reactivity of 2xI2959-QS can be explained by two I2959 functional groups per molecule while I2959 is monofunctional (Figure 3.14). However, the same PI showed much slower kinetics in photopolymerizing PEGDA compared to I2959 (Figure 3.15). The higher photoinitiating reactivity of 2xI2959-QS with HEMA compared to with PEGDA can be explained by hydrogen bonding in the former.

In Figure 3.16, the rate-time and conversion-time graphs for the polymerization of HEMA, which contains two different mol% of PPI and I2959 under the same conditions, mentioned above. Increasing I2959 concentration from 0.13 to 2.13 mmol% resulted in a shorter induction time without changing R_{pmax} and conversion values significantly. However, increasing 2xI2959-QS concentration resulted in approximately two times higher

R_{pmax} values in addition to lower t_{max} values. Actually, the formulation with the high PPI concentration gives the shortest t_{max} and highest R_{pmax} (t_{max} = 0.27 min, R_{pmax}= 0.0385 s^{-1}) values among the four, but also the lowest double bond conversion (69.9%). This can be attributed to the high viscosity of the system obtained as a result of faster gelation which decreases the initiation, propagation and termination reactions; thus decreasing both the rate of polymerization and conversion [71]. The photopolymerization performance of p-DADMAC-*co*-2xI2959-QS was also examined in the polymerization of PEGDA using photo-DSC (Figure 3.17). A formulation containing 4.3 I2959 equivalent mmol% of PPI was used. Since this amount of PPI was not completely soluble in PEGDA, a small amount of water (34 wt% of PEGDA) was added to the formulation and the polymerization was carried out at 25 °C. The PPI showed slower photopolymerization kinetics compared to I2959, as observed for 2xI2959-QS.

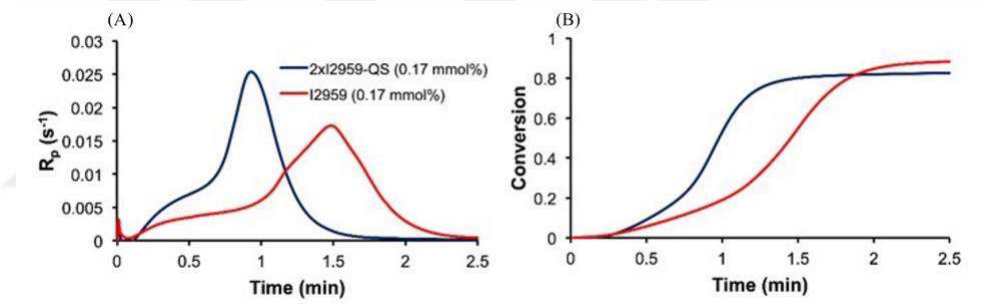


Figure 3.14. (a) Rate-time and (b) Conversion-time plots for HEMA containing 2xI2959-QS and I2959 at 25 °C under nitrogen irradiated by 320-500 nm.

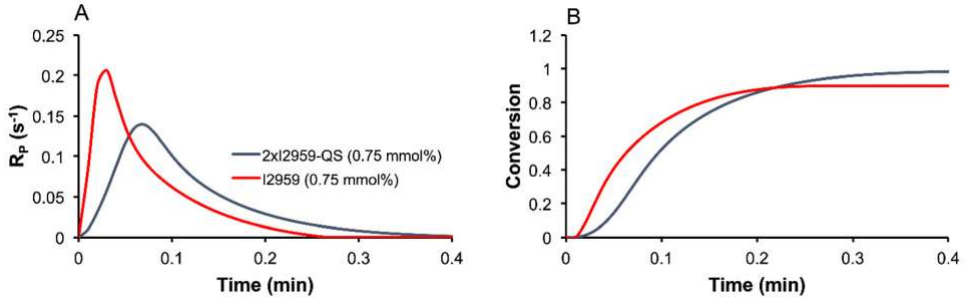


Figure 3.15. (a) Rate-time and (b) Conversion-time plots for PEGDA containing 2xI2959-QS and I2959 at 25 °C under nitrogen irradiated by 320-500 nm.

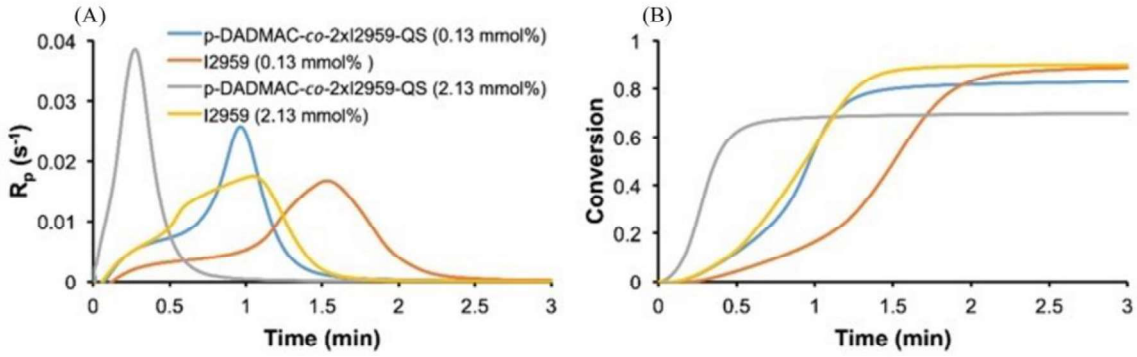


Figure 3.16. (a) Rate-time and (b) Conversion-time plots for HEMA containing p-DADMAC-*co*-2xI2959-QS and I2959 at 25 °C under nitrogen irradiated by 320-500 nm.

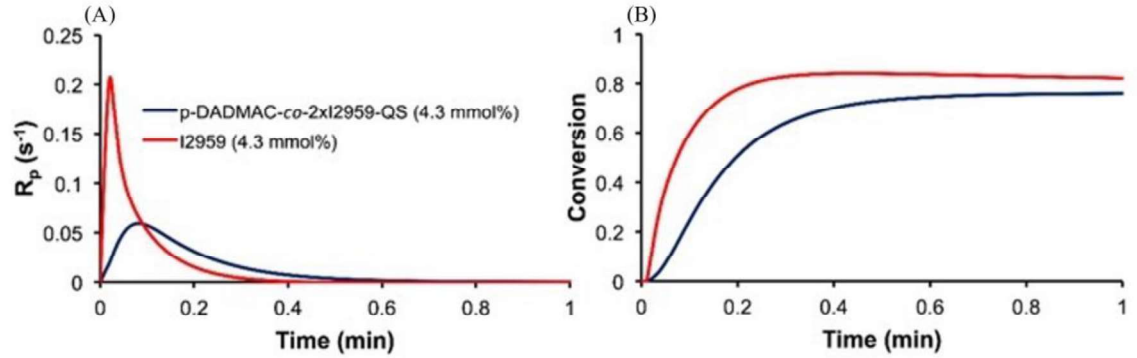


Figure 3.17. (a) Rate-time and (b) Conversion-time plots for PEGDA containing p-DADMAC-*co*-2xI2959-QS and I2959 at 25 °C under nitrogen irradiated by 320-500 nm.

2xI2959-QS is expected to have high polymerization reactivity as a monomer due to its allyl-acrylate structure [64,65]. In order to test, it was photopolymerized with photo-DSC under UV-vis (320-500 nm) irradiation. Figure 3.18 shows the exotherm recorded during the photopolymerization. The high rate of polymerization upon irradiation indicates that the degradative chain transfer reaction observed for N,N-diallylamine monomers is not occuring.

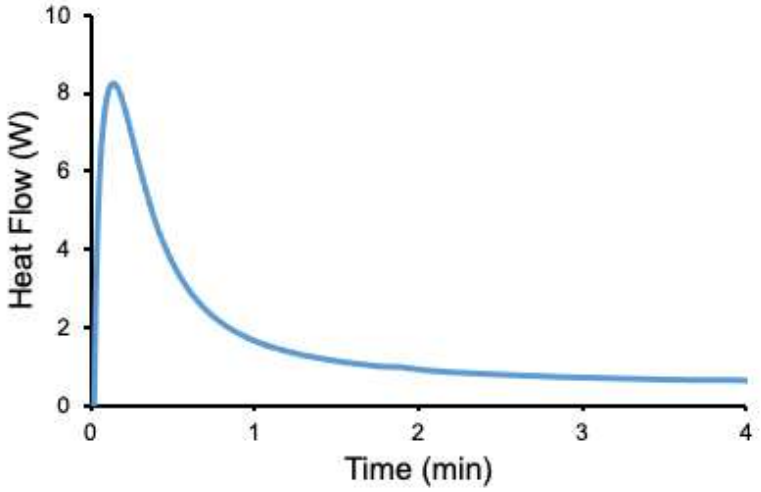


Figure 3.18. Heat flow-time plot for 2xI2959-QS at 40 °C under nitrogen irradiated by 320-500 nm.

3.3.6. Migration Stability

Migration stabilities of 2xI2959-QS and p-DADMAC-*co*-2xI2959-QS were investigated and compared with commercial I2959 (Figure 3.19). Amounts of the extracted photoinitiators into methanol from HEMA/PEGDA hydrogel samples were determined by using UV-Visible spectroscopy. To compare migration stability of crosslinked polymer systems, the photoinitiator contents of I2959, 2xI2959-QS and p-DADMAC-*co*-2xI2959-QS polymer samples were fixed to 0.2 wt%. It was found that the migrations of 2xI2959-QS (6%) and p-DADMAC-*co*-2xI2959-QS (9%) are lower than I2959 (51%). This indicates much better incorporation of 2xI2959-QS and copolymer into polymer samples.

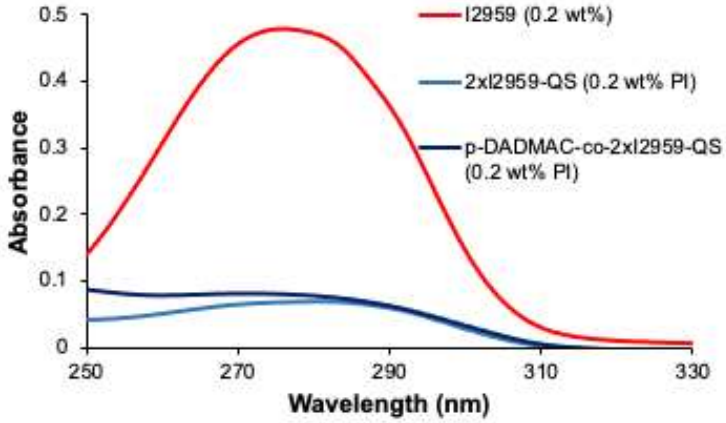


Figure 3.19. UV-Visible absorption spectra of I2959, 2xI2959-QS and p-DADMAC-*co*-2xI2959-QS extracted with methanol from the HEMA/PEGDA/water (3/3/1 wt%) polymer samples.

3.4. Conclusion

In summary, one cyclopolymerizable and one cyclopolymeric Type I PI with quaternary ammonium functionality were synthesized and their structures were confirmed by NMR, FTIR and mass spectroscopies. These PIs show an absorption at 271, 272 nm similar to I2959 but have about twice the extinction coefficient of I2959 due to double substitution. PPI has higher water solubility than I2959 due to DADMAC units and high cyclization efficiency, makes it useful for photopolymerizations in aqueous solutions. It also has good thermal stability compared to I2959 provided by quaternary ammonium functionalities. Both PIs generate benzoyl and isopropyl ketyl radicals under UV light. They can initiate the photopolymerization of PEGDA and HEMA, their photoinitiating efficiency of HEMA was found to be higher compared to I2959 however lower than I2959 in PEGDA. The migration stability of the synthesized PIs from the photocured materials were much higher than I2959, consistent with high reactivity of monomeric and high molecular weight of PPI and incorporation of both into the network structure. These PIs may also improve the properties (mechanical and antibacterial) of the final materials they get incorporated into.

4. WATER-SOLUBLE PHOTOINITIATOR FROM 2,3-DIMERCAPTOSUCCINIC ACID

4.1. Introduction

2,3-Dimercaptosuccinic acid (DMSA) contains two carboxylic acid and two thiol groups and can exist as three different stereoisomers (2S,3S and 2R,3R isomers as enantiomers and 2R,3S isomer is a meso compound). meso 2, 3-dimercaptosuccinic acid, commercially sold as Chemet®, is used in the chelation of heavy metals for therapy [72]. DMSA has a multiple functionalization capacity due to its thiol and carboxylic acid groups. It can be used in Michael type thiol-ene addition reactions as a non-enolate nucleophile. These thiol-Michael additon reactions requires thiolate anions which can be obtained with either the base or the nucleophile catalyst [73,74]. Then the thiolate anion attacks the double bond carbon, forming carbon-centered anion as an intermediate which is then protonated using the conjugate acid to generate thioether products. In general, reactions take place in mild conditions and have no byproducts.

In this chapter, thiol-Michael addition capability of DMSA was utilized to synthesize a novel double I2959 functionalized PI using DBU (Figure 4.1). After formation of the thioether products, regenered base catalyst was also used to neutralize carboxylic acid groups of the products to obtain a water soluble PI. It provides high water solubility and thermal stability compared to I2959 due to its quaternary ammonium functionality. It is expected to have high reactivity due to two α-hydroxyketone units in its structure. It has migration stability coming with its reasonably high molecular weight, overcome the limited migration stability of I2959. The photoinitiating ability, migration stability and photochemical mechanisms of the of the novel PI were investigated.

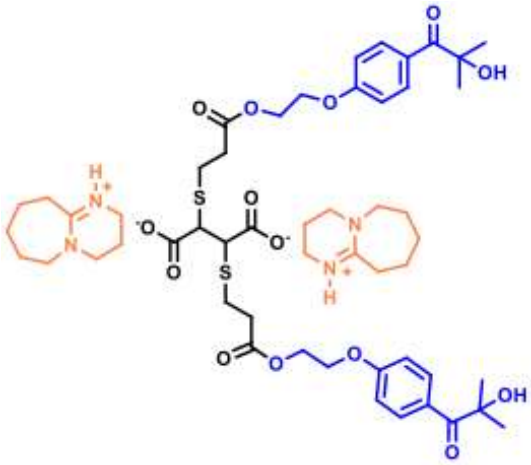


Figure 4.1. Structure of the novel (DMSA-I2959-DBU) photoinitiator.

4.2. Experimental

4.2.1. Materials and Characterization

Acrylate ester of I2959 (I2959-AC) was synthesized according to a literature procedure [59]. Irgacure 2959 (I2959), acryloyl chloride, anhydrous sodium sulfate (Na_2SO_4), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), meso-2,3-dimercaptosuccinic acid (DMSA), 2-hydroxyethyl methacrylate (HEMA), poly(ethylene glycol) diacrylate (PEGDA, M_n= 575 D) and the other reagents and solvents purchased from Sigma-Aldrich and used as received without further purification. Dichloromethane (DCM) was dried over molecular sieves.

^{1}H and ^{13}C-NMR spectra were acquired using Varian Gemini (400 MHz) spectrometer in deuterated water (D_2O). IR spectra were obtained with a Nicolet 6700 FT-IR spectrophotometer. Raman spectroscopic measurements were performed on a Renishaw InVia Raman microscope.

4.2.2. Synthesis of DMSA-I2959-DBU

DMSA (19.3 mg, 0.106 mmol) was dissolved in distilled water (6.4 ml) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (32.2 mg, 0.212 mmol) mixture. The mixture was added into round bottom flask which contains I2959-AC (58.9 mg, 0.212 mmol) and 0.3 mL MeOH. The mixture was stirred at 45^0C for 48h. The solvent was removed under reduced pressure. The residue was washed with THF to remove unreacted DBU and Irgacure 2959-AC. The product was obtained as a pale yellow oil in 40-50% yield.

^{1}H-NMR (D_2O, 400 MHz, δ): 1.60 (s, 12H, CH_3-C-OH), 1.72 (m, 16H, CH_2-CH_2), 2.63 (t, 4H, CH_2-C), 2.77 (t, 4H, CH_2-C=O), 2.92 (t, 4H, CH_2-S), 3.34 (m, 6H, CH-S and CH_2-N^+H), 3.57 (m, 8H, CH_2-N), 4.42 (t, 4H, CH_2-O), 4.52 (t, 4H, CH_2-O), 7.12 (d, 4H, Ar-CH), 8.14 (d, 4H, Ar-CH).

^{13}C-NMR (D_2O, 101 MHz, δ): 18.84 (CH_2-CH_2), 23.24 (CH_2-S), 24.95 (CH_2-CH_2), 27.24 (*C*H_2-CH_2), 28.35 (*C*H_3-C and CH_2-C), 32.68 (*C*H_2-CH_2-N), 37.89 (*C*H_2-C=O), 48.11 (CH_2-N and CH_2-N^+H), 54.03 (CH-S), 63.25 (*C*H_2-O-C=O), 66.10 (*C*H_2-O-Ar), 77.39 (*C*$(CH_3)_2$-OH), 127.54 (Ar-*C*), 132.35 (Ar-*C*H), 161.80 (C=N^+H), 165.82 (O-*C*-Ar), 174.09 (O-C=O), 177.12 (O^--C=O), 206.10 (O=*C*-Ar).

FT-IR (ATR): 3232, 3100, 2929 (O-H,N-H,C-H), 1732 (C=O, ester), 1644 (C=O (ketone) and C=N), 1596 (C=C), 1158 (C-O) cm^{-1}.

Q-Tof-MS (m/z): Calcd for : $C_{52}H_{74}O_{14}N_4S_2$, 1042.4578. Found: 1043.4658 [M+H]+.

4.2.3. UV–Vis Spectroscopy and Photolysis

UV–vis spectra of PI were obtained in various solvents with a Carry 3 UV/Vis spectrophotometer from Varian in methanol solution. For the photolysis experiments, ethanol solution of the PIs was irradiated with UV light (Omnicure 1000, 150 W, 50% intensity) at 320-500 nm and the UV–vis spectra at different irradiation times were recorded.

4.2.4. Photoinitiating Activity Measurements

A TA Instruments DSC 250 differential photocalorimeter using an Omnicure 2000 mercury lamp light source with a 320-500 nm filter was used for photopolymerization experiments. HEMA or PEGDA monomer (3-4 mg) containing 1 wt% of DMSA-I2959 DBU or the reference (I2959) were exposed to irradiation at 25 °C under nitrogen for 5 min. The heat flow was monitored as a function of time, and the polymerization rate was calculated as

$$\text{Rate} = \frac{(Q/s)M}{n(\Delta H_p)m} \ , \tag{4.1}$$

where *Q/s* is the heat flow per second, *M* the molar mass of the monomer, *n* the number of double bonds per monomer molecule, ΔH_p the heat of reaction evolved and *m* the mass of monomer in the sample. The theoretical heats for the total conversion of an acrylate and methcarylate double bond are 86 kJ/mol and 55 kJ/mol, respectively.

4.2.5. Migration Study

In the presence of I2959 and DMSA-I2959-DBU (0.5 mmol% PI), the HEMA/PEGDA (50/50 mmol%) mixture was photopolymerized under air for 1 h in glass vials via 365 nm irradiation. The crosslinked polymers were immersed in 25 mL of methanol for 3 days. The amount of extracted photoinitiators was calculated by using UV-visible spectroscopy.

4.3. Results and Discussion

4.3.1. Synthesis and Characterization of Water Soluble Photoinitiator

A I2959-functionalized DMSA was synthesized as a novel photoinitiator in two steps (Figure 4.2). In the first step, I2959-AC was synthesized by the reaction of I2959 and acryloyl chloride [59]. In the second step, DMSA-I2959-DBU was synthesized by thiol-Michael addition reaction of I2959-AC and DMSA in the presence of DBU as a base catalyst. DMSA-I2959-DBU was obtained as a pale yellow oil in the range of 40-50% yield.

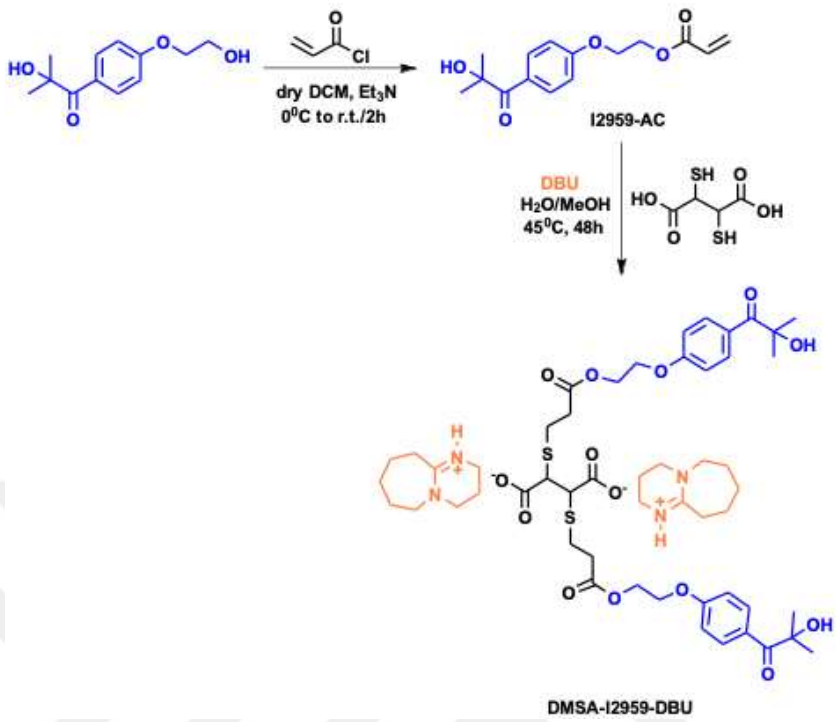


Figure 4.2. Synthesis of the PI, DMSA-I2959-DBU.

Table 4.1 shows the solubilities of the novel PI and I2959 as reference. The synthesized photoinitiator is soluble in polar protic solvents such as water and methanol due to its ionic nature. It is insoluble in nonpolar solvents such as diethyl ether; however, it is soluble in CH_2Cl_2. Furthermore, the novel PI has a good compatibility with HEMA.

Table 4.1. Solubilities of the synthesized PI and I2959.

PI	H_2O	Methanol	Diethyl ether	CH_2Cl_2	THF	DMF
I2959	+	+	+	+	+	+
DMSA-I2959-DBU	+	+	-	+	-	+

The structure of the novel photoinitiator was confirmed by ^{1}H-NMR, ^{13}C-NMR, Raman and FTIR spectra and mass spectrometry. The ^{1}H NMR spectrum shows peaks for methylene groups of I2959 at 4.42, 4.52 ppm and methylene groups of DBU at 1.72, 2.63, 3.34 and 3.57 ppm and also specific signals of the I2959 aromatic ring at 7.12 and 8.14 ppm as doublets (Figure 4.3). The ^{13}C-NMR showed three different carbonyl groups at 174.09, 177.12 and 206.10 ppm which are ester, carboxylate and ketone groups, respectively (Figure

4.4). The FT-IR spectrum shows two different C=O peaks due to ketone, ester and carboxylate groups (Figure 4.5). Raman spectrum shows C-S rooting at 693 cm^{-1} and no peaks at 2563 cm^{-1} which is specific for S-H in mercapto group of pure DMSA (Figure 4.6). This proves that the novel photoinitiator has two I2959 units. The structure of the photoinitiator was further confirmed by using mass spectroscopy.

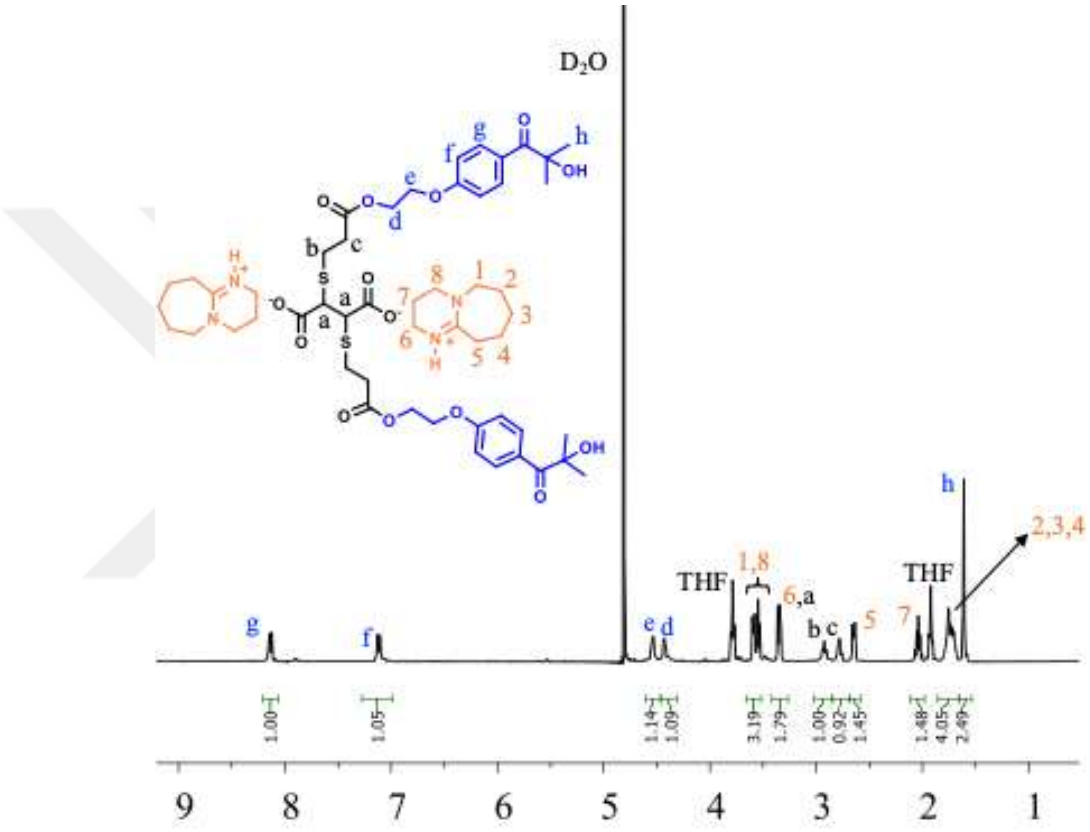


Figure 4.3. ^{1}H-NMR spectrum of DMSA-I2959-DBU.

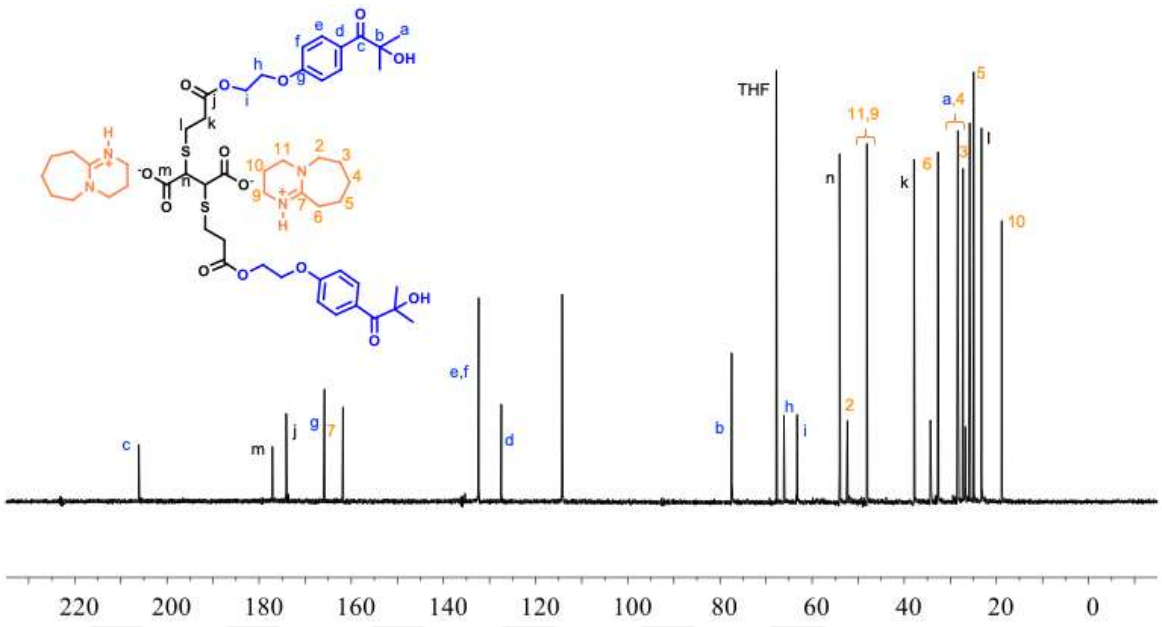


Figure 4.4. ^{13}C-NMR spectrum of DMSA-I2959-DBU.

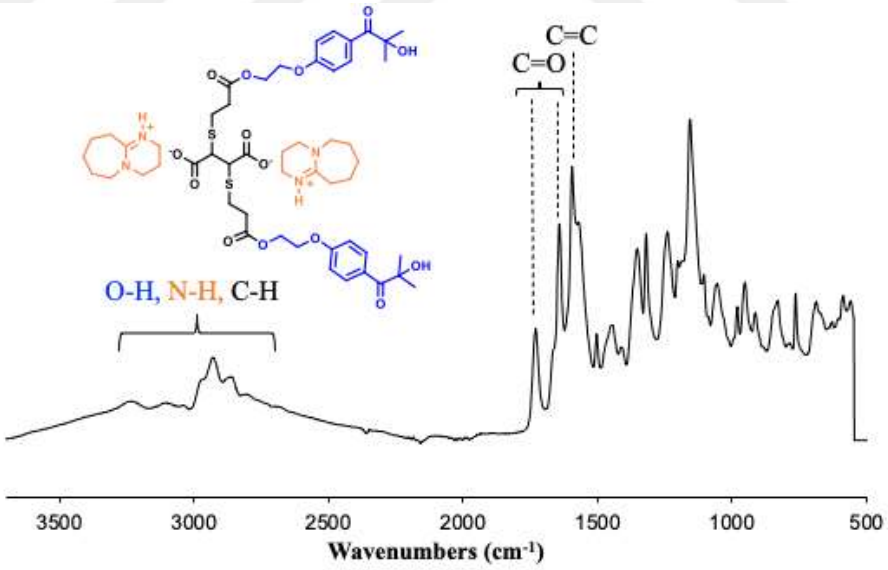


Figure 4.5. FTIR spectrum of DMSA-I2959-DBU.

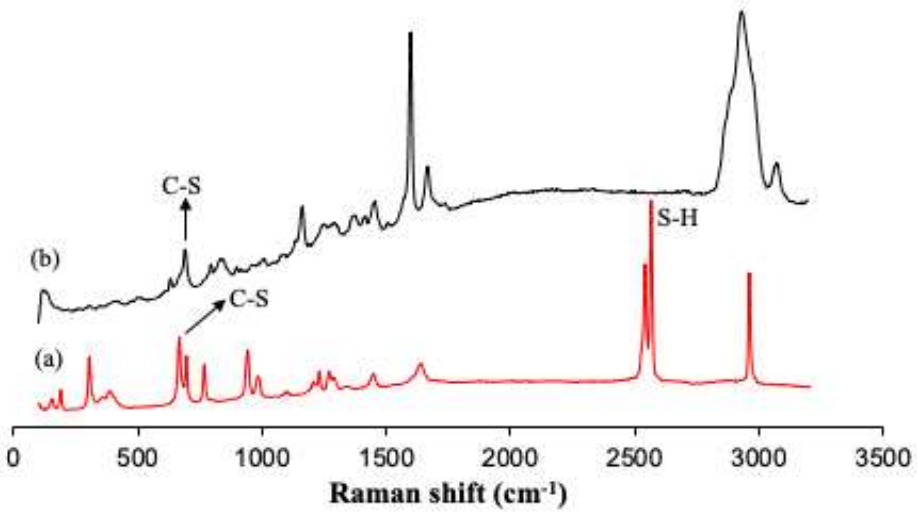


Figure 4.6. Raman spectra of (a) DMSA and (b) DMSA-I2959-DBU.

4.3.2. Light Absorption Properties

Absorption characteristics of DMSA-I2959-DBU was examined by UV-vis spectroscopy. It has a maximum UV absorption wavelength at 278 nm in water and 272 nm in ethanol due to π-π∗ transition, similar to I2959 (λ_{max}= 276 nm in water) (Figure 4.7) [62]. The molar absorption coefficients of DMSA-I2959-DBU (ε = 11716 M^{-1} cm^{-1} in water and 10784 M^{-1} cm^{-1} in ethanol) are slightly lower than that of I2959 (ε = 15150 M^{-1} cm^{-1} in water) (Table 4.2).

Table 4.2. Absorption characteristics of DMSA-I2959-DBU and I2959 in water and ethanol.

PI	Solvents	λ_{max} (nm)	ε (M^{-1} cm^{-1})
DMSA-I2959-DBU	H_2O	278	11716
DMSA-I2959-DBU	EtOH	272	10784
I2959	H_2O	276	15150

The photolysis of DMSA-I2959-DBU in water and ethanol was investigated. When DMSA-I2959-DBU in water was irradiated using a 320-500 nm light source, the intensity of the peak at 274 nm decreased and also a new peak at 248 nm was observed, reaching a

maximum absorbance in 120 s (Figure 4.8A). During the investigation of photolysis of PEG-based alpha-hydroxyalkylphenone photoinitiators, a similar peak was reported, which they linked to the production of acetone resulting from the cleavage of the C-C bond within the hydroxyketone structure [69]. Also, photolysis spectrum of DMSA-I2959-DBU in ethanol shows decrease in the intensity of the peak at 272 nm and a new peak at 250 nm due to the formation of acetone after cleavage of hydroxyketone (Figure 4.8B).

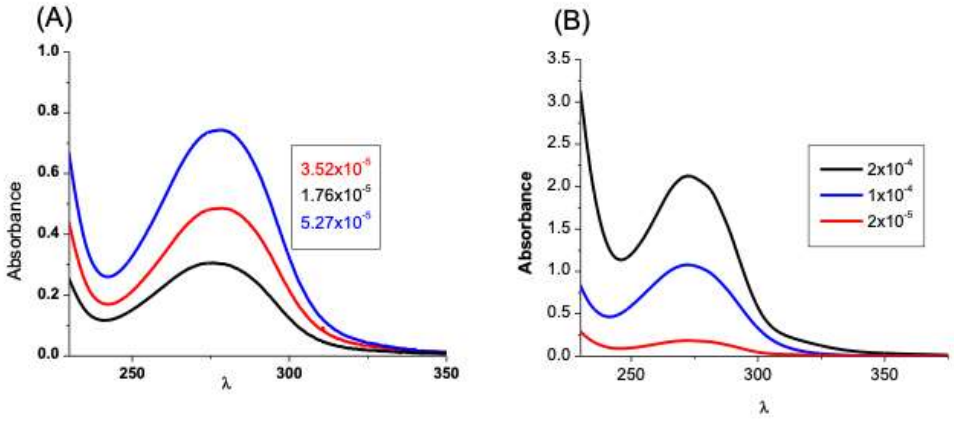


Figure 4.7. UV–vis absorption spectra of DMSA-I2959-DBU in (a) water and (b) ethanol.

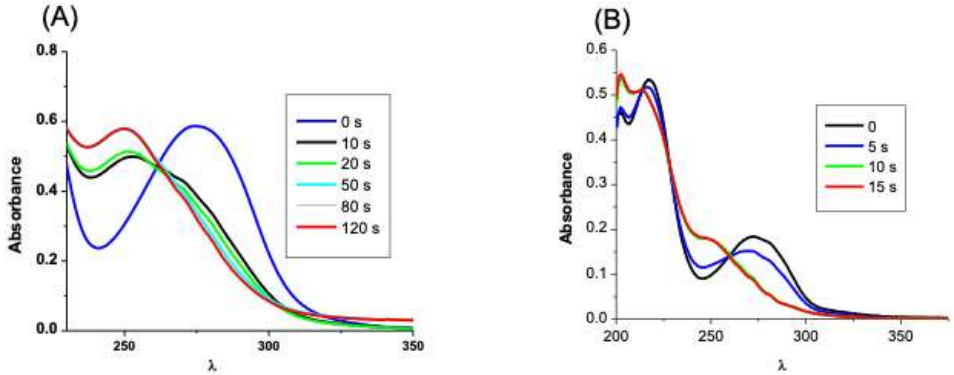


Figure 4.8. Photolysis of DMSA-I2959-DBU (a) in water ($3.52x10^{-5}$ M) and (b) in ethanol ($2x10^{-4}$ M).

4.3.3. Photopolymerization Results

The photopolymerization efficiency of the synthesized PI in the polymerization of HEMA and PEGDA was tested and commercial I2959 was used for comparison. DMSA-I2959-DBU (1 wt%) was soluble in HEMA, but not in PEGDA at the same concentration. Therefore PI/PEGDA/water (1/95/5 wt%) system was used. Photo-DSC with UV-vis irradiation (320-500 nm) at 25 ºC was used for analysis. Figure 4.9 displays the rate-time and conversion-time plots for the polymerization of HEMA containing DMSA-I2959-DBU (1 wt%) and I2959 (1 wt%). It was observed that, DMSA-I2959-DBU (R_{pmax} = 0.0180 s−1, t_{max} = 1.52 min, conversion = 92.4%) has a lower maximum rate of polymerization, longer induction time and slightly higher conversion than I2959 (R_{pmax} = 0.0252 s^{-1}, t_{max} = 0.79 min, conversion = 86.3%). In Figure 4.10, photopolymerization profiles of PEGDA/water (95/5 wt%) mixture using DMSA-I2959-DBU and I2959 are given. DMSA-I2959-DBU showed slower kinetics compared to I2959; DMSA-I2959-DBU (R_{pmax} = 0.125 s^{-1}, t_{max} = 0.07 min) and I2959 (R_{pmax} = 0.170 s^{-1}, t_{max} = 0.04 min). However, DMSA-I2959-DBU has higher conversion than I2959. The lower polymerization rates can be explained by the steric hinderance of this PI and also residual unreacted thiol groups in the PI structure (although they were not observed in Raman) which may cause degradative chain transfer reactions.

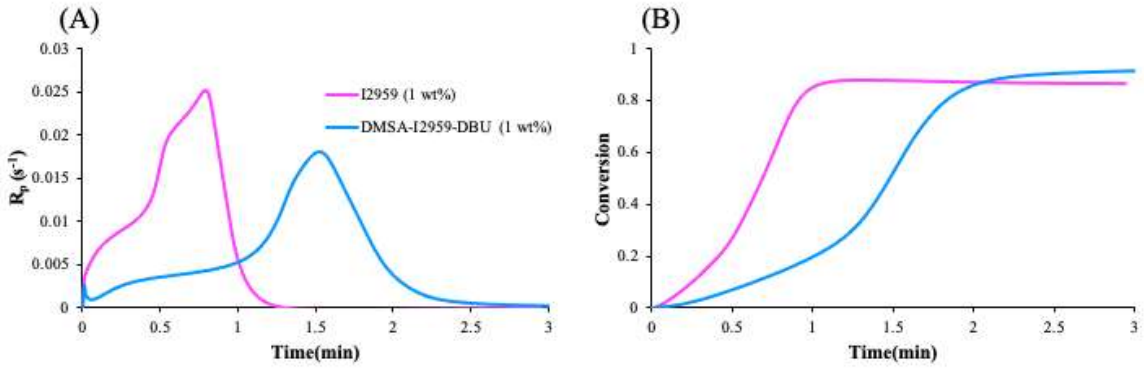


Figure 4.9. (a) Rate-time and (b) Conversion-time plots for HEMA containing DMSA-I2959-DBU (1 wt%) and I2959 (1 wt%) at 25 °C under nitrogen irradiated by 320-500 nm.

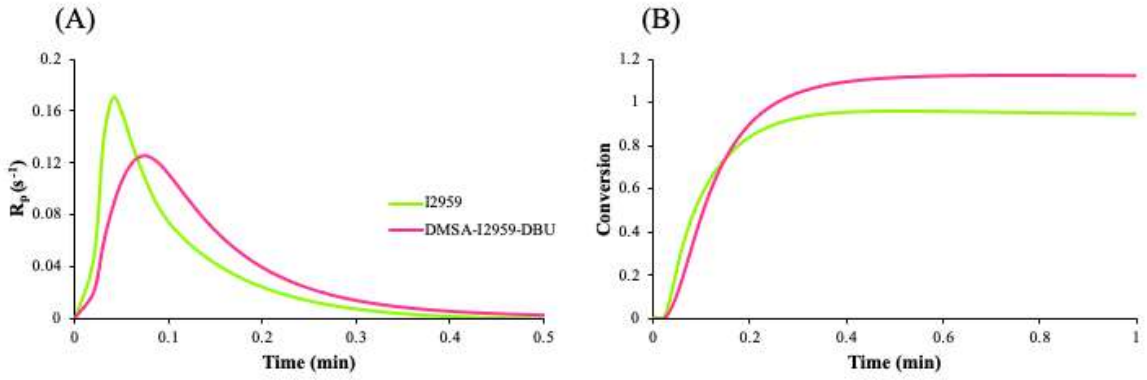


Figure 4.10. (a) Rate-time and (b) Conversion-time plots for PEGDA/water (95/5 wt%) containing DMSA-I2959-DBU and I2959 at 25 °C under nitrogen irradiated by 320-500 nm.

4.3.4. Migration Stability

The properties of the PIs such as molecular weight, volatility, polarity and lipophilicity are found to be important factors affecting migration [75]. In a literature experiment, the concentration of main photodecomposition products of I2959, (2-hydroxyethoxy)-2-methylpropiophenone, 3-(4-methoxyphenyl)-1-propanol, 1-phenylethenol was found to be low compared to the unreacted PI in the absence of monomer [76].

The migration stability of DMSA-I2959-DBU was investigated and compared with commercial I2959 as a reference. The amount of extracted PIs from HEMA/PEGDA gel samples into methanol was determined by using UV-Vis spectroscopy. The photoinitiator contents of I2959 and DMSA-I2959-DBU crosslinked polymer samples were fixed into 0.5 mmol% to compare migration stability of DMSA-I2959-DBU with I2959. As shown in Figure 4.11, the amount of extracted PIs from DMSA-I2959-DBU sample (14%) was lower than I2959 sample (53%) due to better incorporation and macromolecular structure of DMSA-I2959-DBU or its higher molecular weight.

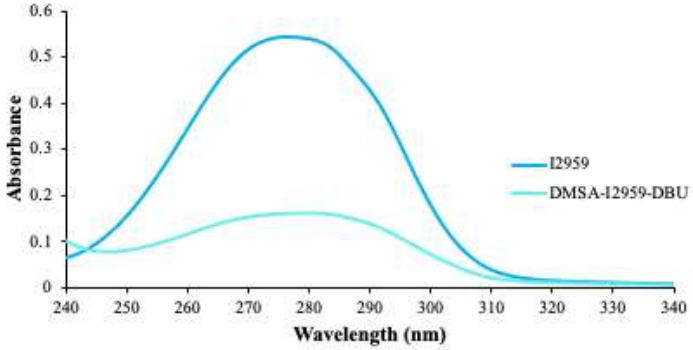


Figure 4.11. UV-Visible absorption spectra of I2959 and DMSA-I2959-DBU extracted with methanol from the HEMA/PEGDA (50/50 mmol%) polymer samples.

4.4. Conclusion

In summary, a novel highly water-soluble Type I PI with DBU counterion was synthesized and their structures were confirmed by NMR, FTIR, Raman and mass spectroscopies. PI has higher water solubility than I2959 due to presence of two carboxylate salt units. This PI shows an absorption at 272 nm similar to I2959 but has lower extinction coefficient compared to I2959. It can initiate the photopolymerization of PEGDA and HEMA. The migration stability of the synthesized PI is about 4 times higher than that of I2959 because of high molecular weight of it and unreactive photodecomposition byproducts.

5. CONCLUDING REMARKS

In this thesis, novel photoinitiators based on I2959 were synthesized with diverse purposes of water solubility, UV-vis light reactivity and high migration stability. Their structures were proven by ^{1}H-NMR, ^{13}C-NMR, FT-IR, Raman and mass spectroscopies. Also, their photophysical and photochemical properties were investigated.

A novel doubly Irgacure 2959 functionalized allyl-acrylate quaternary ammonium salt (2xI2959-QS) as cyclopolymerizable monomer/photoinitiator and its cyclocopolymer with DADMAC (p-DADMAC-*co*-2xI2959-QS) as a water-soluble polymeric photoinitiator were synthesized. There is no cylopolymerizable quaternary ammonium salt photoinitiator in the literature. A Irgacure 2959 functionalized 2,3-dimercaptosuccinic acid DBU salt was synthesized as a high molecular weight photoinitiator.

The advantageous properties of these monomeric/polymeric and high molecular weight photoinitiators include high reactivity (due to two I2959 and acrylate functionalities), water solubility (polymeric and high molecular weight one, due to salt structures), migration stability (monomeric/polymeric, high molecular weight nature), excellent thermal stabilities (monomeric/polymeric, quaternary ammonium functionality and cyclopolymerizable and/or cyclic structures).

REFERENCES

1. Xu, Y., Z. Ding, H. Zhu, B. Graff, S. Knopf, P. Xiao, F. Dumur, and J. Lalevée, "Design of Ketone Derivatives as Highly Efficient Photoinitiators for Free Radical and Cationic Photopolymerizations and Application in 3D Printing of Composites", *Journal of Polymer Science*, Vol. 58, No. 24, pp. 3432–3445, 2020.

2. Tang, L., J. Nie, and X. Zhu, "A High Performance Phenyl-Free Led Photoinitiator for Cationic or Hybrid Photopolymerization and Its Application in Led Cationic 3D Printing", *Polymer Chemistry*, Vol. 11, No. 16, pp. 2855–2863, 2020.

3. Tehfe, M., F. Louradour, J. Lalevée, and J.-P. Fouassier, "Photopolymerization Reactions: On the Way to a Green and sustainable Chemistry", *Applied Sciences*, Vol. 3, No. 2, pp. 490–514, 2013.

4. Mellott, M. B., K. Searcy, and M. V. Pishko, "Release of Protein from Highly Cross-Linked Hydrogels of Poly(ethylene Glycol) Diacrylate Fabricated by UV Polymerization", *Biomaterials*, Vol. 22, No. 9, pp. 929–941, 2001.

5. Quick, D. J., and K. S. Anseth, "DNA delivery from photocrosslinked Peg Hydrogels: Encapsulation efficiency, release profiles, and DNA quality", *Journal of Controlled Release*, Vol. 96, No. 2, pp. 341–351, 2004.

6. Burkoth, A. K., J. Burdick, and K. S. Anseth, "Surface and Bulk Modifications to Photocrosslinked Polyanhydrides to Control Degradation Behavior", *Journal of Biomedical Materials Research*, Vol. 51, No. 3, pp. 352–359, 2000.

7. Davis, K. A., J. A. Burdick, and K. S. Anseth, "Photoinitiated Crosslinked Degradable Copolymer Networks for Tissue Engineering Applications" *Biomaterials*, Vol. 24, No. 14, pp. 2485–2495, 2003.

8. Chan-Park, M. B., A. P. Zhu, J. Y. Shen, and A. L. Fan, "Novel Photopolymerizable Biodegradable Triblock Polymers for Tissue Engineering Scaffolds: Synthesis and Characterization", *Macromolecular Bioscience*, Vol. 4, No. 7, pp. 665–673, 2004.

9. Watkins, A. W., and K. S. Anseth, "Copolymerization of Photocrosslinkable Anhydride Monomers for Use as a Biodegradable Bone Cement", *Journal of Biomaterials Science, Polymer Edition*, Vol. 14, No. 3, pp. 267–278, 2003.

10. Oster, G., and N.-L. Yang,"Photopolymerization of Vinyl Monomers", *Chemical Reviews*, Vol. 68, No. 2, pp. 125–151, 1968.

11. Yagci, Y., S. Jockusch, and N. J. Turro, "Photoinitiated Polymerization: Advances, Challenges, and Opportunities", *Macromolecules*, Vol. 43, No. 15, pp. 6245–6260, 2010.

12. Bowman, C. N., and C. J. Kloxin, "Toward an Enhanced Understanding and Implementation of Photopolymerization Reactions", *AIChE Journal*, Vol. 54, No. 11, pp. 2775–2795, 2008.

13. Ibrahim, A., L. D. Stefano, O. Tarzi, H. Tar, C. Ley, and X. Allonas, "High-Performance Photoinitiating Systems for Free Radical Photopolymerization. Application to Holographic Recording", *Photochemistry and Photobiology*, Vol. 89, No. 6, pp. 1283–1290, 2013.

14. Nakamura, Y., and S. Yamago, "Termination Mechanism in the Radical Polymerization of Methyl Methacrylate and Styrene Determined by the Reaction of Structurally Well-Defined Polymer End Radicals", *Macromolecules*, Vol. 48, No. 18, pp. 6450–6456, 2015.

15. Kelley, R. D., and R. Klein, "Cross Disproportionation of Alkyl Radicals", *The Journal of Physical Chemistry*, Vol. 78, No. 16, pp. 1586–1595, 1974.

16. O'Brien, A. K., and C. N. Bowman, “Impact of Oxygen on Photopolymerization Kinetics and Polymer Structure”, *Macromolecules*, Vol. 39, No. 7, pp. 2501–2506, 2006.

17. Eren, T. N., B. Graff, J. Lalevee, and D. Avci, “Thioxanthone-Functionalized 1,6-Heptadiene as Monomeric Photoinitiator”, *Progress in Organic Coatings*, Vol. 128, pp. 148–156, 2019.

18. Chatani, S., C. J. Kloxin, and C. N. Bowman, “The Power of Light in Polymer Science: Photochemical Processes to Manipulate Polymer Formation, Structure, and Properties”, *Polymer Chemistry*, Vol. 5, No. 7, pp. 2187–2201, 2014.

19. Vaidyanathan, T. K., J. Vaidyanathan, P. P. Lizymol, S. Ariya, and K. V. Krishnan, “Study of Visible Light Activated Polymerization in Bisgma-TEGDMA Monomers with Type 1 and Type 2 Photoinitiators Using Raman Spectroscopy”, *Dental Materials*, Vol. 33, No. 1, pp. 1–11, 2017.

20. Iyer, S. N., N. Behary, V. Nierstrasz, J. Guan, and G. Chen, “Study of Photoluminescence Property on Cellulosic Fabric Using Multifunctional Biomaterials Riboflavin and Its Derivative Flavin Mononucleotide”, *Scientific Reports*, Vol. 9, No. 1, pp. 1–16, 2019.

21. Zhou, J., X. Allonas, A. Ibrahim, and X. Liu, “Progress in the Development of Polymeric and Multifunctional Photoinitiators”, *Progress in Polymer Science*, Vol. 99, p. 101165, 2019.

22. Cesur, B., O. Karahan, S. Agopcan, T. N. Eren, N. Okte and D. Avci, “Difunctional Monomeric and Polymeric Photoinitiators: Synthesis and Photoinitiating Behaviors”, *Progress in Organic Coatings*, Vol. 86, pp. 71–78, 2015.

23. Sun, F., Y. Li, N. Zhang and J. Nie, “Initiating Gradient Photopolymerization and Migration of a Novel Polymerizable Polysiloxane α-Hydroxy Alkylphenones Photoinitiator”, *Polymer*, Vol. 55, No. 16, pp. 3656–3665, 2014.

24. Zhang, G., S. Jiang, Y. Gao and F. Sun, “Regulating Photochemical Behavior and Property of Imidazolium-Based Water Soluble Polysiloxane Macromolecular Photoinitiators by Anions”, *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 364, pp. 363–372, 2018.

25. Liu, Y., X. Huang, K. Han, Y. Dai, X. Zhang and Y. Zhao, “High-Performance Ligninbased Water-Soluble Macromolecular Photoinitiator For The Fabrication of Hybrid Hydrogel”, *ACS Sustainable Chemistry and Engineering*, Vol. 7, No. 4, pp. 4004–4011, 2019.

26. Oesterreicher, A., M. Roth, D. Hennen, F. H. Mostegel, M. Edler, S. Kappaun and T. Griesser, “Low Migration Type I Photoinitiators for Biocompatible Thiol-ene Formulations”, *European Polymer Journal*, Vol. 88, pp. 393–402, 2017.

27. De Groot, J. H., K. Dillingham, H. Deuring, H. J. Haitjema, F. J. Van Beijma, K. Hodd and S. Norrby, “Hydrophilic Polymeric Acylphospine Oxide Photoinitiators/Crosslinkers for in Vivo Blue-Light Photopolymerization”, *Biomacromolecules*, Vol. 2, No. 4, pp. 1271–1278, 2001.

28. Karaca Balta, D., Ö. Karahan, D. Avci, and N. Arsu, “Synthesis, Photophysical and Photochemical Studies of Benzophenone Based Novel Monomeric and Polymeric Photoinitiators”, *Progress in Organic Coatings*, Vol. 78, pp. 200–207, 2015.

29. Wei, J., and B. Wang, “A Highly Efficient Polymerizable Photoinitiator Comprising Benzophenone, Thio Moieties, And N-Arylmaleimide”, *Macromolecular Chemistry and Physics*, Vol. 212, No. 1, pp. 88–95, 2011.

30. Jiang, B., T. Zhang, L. Zhao, Z. Xu and Y. Huang, “Effect of Polymerizable Photoinitiators on the UV-Polymerization Behaviors of Photosensitive Polysiloxane”, *Journal of Polymer Science*, *Part A: Polymer Chemistry*, Vol. 55, No. 10, pp. 1696–1705, 2017.

31. Wang, K., Y. Lu, P. Chen, J. Shi, H. Wang and Q. Yu, "Novel One-Component Polymeric Benzophenone Photoinitiator Containing Poly (Ethylene Glycol) as Hydrogen Donor", *Materials Chemistry and Physics*, Vol. 143, No. 3, pp. 1391–1395, 2014.

32. Shi, J., P. Chen, K. Wang, J. Lu and J. Nie, "A Novel High Efficiency Benzophenone Based Polymeric Photoinitiator from Ring-Opening Polymerization of Benzoxazine", *Polymer Science Series B*, Vol. 56, No. 5, pp. 632–638, 2014.

33. Wu, Q., Y. Xiong, Q. Liang and H. Tang, "Developing Thioxanthone Based Visible Photoinitiators for Radical Polymerization", *RSC Advances*, Vol. 4, No. 94, pp. 52324–52331, 2014.

34. Eren, T. N., N. Yasar, V. Aviyente, F. Morlet-Savary, B. Graff, J. P. Fouassier, J. Lalevee and D. Avci, "Photophysical and Photochemical Studies of Novel Thioxanthone-Functionalized Methacrylates Through LED Excitation", *Macromolecular Chemistry and Physics*, Vol. 217, No. 13, pp. 1501–1512, 2016.

35. Eren, T. N., J. Lalevée and D. Avci, "Water Soluble Polymeric Photoinitiator for Dualcuring of Acrylates and Methacrylates", *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 389, pp. 112288–112298, 2020.

36. Luo, A., X. Jiang and J. Yin, "Thioxanthone-Containing Renewable Vegetable Oil as Photoinitiators", *Polymer*, Vol. 53, No. 11, pp. 2183–2189, 2012.

37. Jiang, X., J. Luo and J. Yin, "A Novel Amphipathic Polymeric Thioxanthone Photoinitiator", *Polymer*, Vol. 50, No. 1 pp. 37–41, 2009.

38. Eren, T. N., N. Kariksiz, G. Demirci, D. Tuncel, N. Okte, H. Yagci Acar, and D. Avci, "Irgacure 2959-Functionalized Poly(Ethyleneimine)s as Improved Photoinitiators: Enhanced Water Solubility, Migration Stability and Visible-Light Operation", *Polymer Chemistry*, Vol. 12, No. 18, pp. 2772–2785, 2021.

39. Kandirmaz, E. A., E. N. Gençoğlu, and N. Kayaman Apohan, "The Synthesis of New Type II Polymeric Photoinitiator (Thioxantone) via Atom Transfer Radical Polymerization and Their Curing and Migration Studies", *Macromolecular Research*, Vol. 27, No. 8, pp. 756–763, 2019.

40. Kreutzer, J., K. Kaya, and Y. Yagci, "Poly(Propylene Oxide)-Thioxanthone as One-Component Type II Polymeric Photoinitiator for Free Radical Polymerization with Low Migration Behavior", *European Polymer Journal*, Vol. 95, pp. 71–81, 2017.

41. Tomal, W., and J. Ortyl, "Water-Soluble Photoinitiators in Biomedical Applications", *Polymers*, Vol. 12, No. 5, p. 1073, 2020.

42. Le, C. M. Q., T. Petitory, X. Wu, A. Spangenberg, J. Ortyl, M. Galek, L. Infante, H. Thérien-Aubin, and A. Chemtob, "Water-Soluble Photoinitiators from Dimethylamino-Substituted Monoacylphosphine Oxide for Hydrogel and Latex Preparation", *Macromolecular Chemistry and Physics*, Vol. 222, No. 19, p. 2100217, 2021.

43. Fairbanks, B. D., M. P. Schwartz, C. N. Bowman, and K. S. Anseth, "Photoinitiated Polymerization of PEG-Diacrylate with Lithium Phenyl-2,4,6-Trimethylbenzoylphosphinate: Polymerization Rate and Cytocompatibility", *Biomaterials*, Vol. 30, No. 35, pp. 6702–6707, 2009.

44. Kamoun, E. A., A. El-Betany, H. Menzel, and X. Chen, "Influence of Photoinitiator Concentration and Irradiation Time on the Crosslinking Performance of Visible-Light Activated Pullulan-Hema Hydrogels", *International Journal of Biological Macromolecules*, Vol. 120, pp. 1884–1892, 2018.

45. Zhong, R., and C. Cao, "Synthesis and Photo-Initiating Properties of a Quaternary Ammonium Salts Photoinitiator with Ionic Liquids Structure", *Advanced Materials Research*, Vol. 557-559, pp. 798–801, 2012.

46. Temel, G., and N. Arsu, "One-Pot Synthesis of Water-Soluble Polymeric Photoinitiator via Thioxanthonation and Sulfonation Process", *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 202, No. 1, pp. 63–66, 2009.

47. Liang, Q., L. Zhang, Y. Xiong, Q. Wu, and H. Tang, “A Facile Method to Prepare a Polyethylene Glycol Modified Polysilane as a Waterborne Photoinitiator”, *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 299, pp. 9–17, 2015.

48. Wei, M., Y. Gao, S. Jiang, J. Nie, and F. Sun, “Design of Photoinitiator-Functionalized Hydrophilic Nanogels with Uniform Size and Excellent Biocompatibility”, *Polymer Chemistry*, Vol. 10, No. 22, pp. 2812–2821, 2019.

49. Eren, T. N., T. Gencoglu, M. Abdallah, J. Lalevée, and D. Avci, “A Water Soluble and Highly Reactive Bisphosphonate Functionalized Thioxanthone-Based Photoinitiator”, *European Polymer Journal*, Vol. 135, p. 109906, 2020.

50. Wu, Y., X. Zhang, D. Chen, Y. Ma, Q. Wang, J. Wang, and W. Yang, “Synthesis and Characterization of a Novel Kind of Water-Soluble Macromolecular Photoinitiators and Their Application for the Preparation of Water-Soluble Branched Polymers”, *Industrial & Engineering Chemistry Research*, Vol. 60, No. 21, pp. 7755–7763, 2021.

51. Pasini, D., and D. Takeuchi, “Cyclopolymerizations: Synthetic Tools for the Precision Synthesis of Macromolecular Architectures”, *Chemical Reviews*, Vol. 118, No. 18, pp. 8983–9057, 2018.

52. Ruppitsch, L. A., G. Peer, K. Ehrmann, T. Koch, and R. Liska, “Photopolymerization of Difunctional Cyclopolymerizable Monomers with Low Shrinkage Behavior”, *Journal of Polymer Science*, Vol. 59, No. 6, pp. 519–531, 2021.

53. Wu, Y. P., R. Li, J. Ke, X. Cheng, R. Tang, Y. Situ, and H. Huang, “Study on Bifunctional Acyldiphenylphosphine Oxides Photoinitiator for Free Radical Polymerization”, *European Polymer Journal*, Vol. 168, p. 111093, 2022.

54. Balaban, B., N. Kariksiz, T. N. Eren, and D. Avci, “Cyclopolymerizable and Cyclopolymeric Photoinitiators from Diallyl Amine and α-Hydroxy Ketones”, *Polymer Chemistry*, Vol. 13, No. 35, pp. 5094–5104, 2022.

55. Butler, G. B., and R. J. Angelo, “Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds. VIII. A Proposed Alternating Intramolecular-Intermolecular Chain Propagation”, *Journal of the American Chemical Society*, Vol. 79, No. 12, pp. 3128–3131, 1957.

56. Butler, G. B., “Cyclopolymerization”, *Journal of Polymer Science Part A: Polymer Chemistry*, Vol. 38, No. 19, pp. 3451-3461, 2000.

57. Warren, S. C., and L. J. Mathias, “Synthesis and Polymerization of Ethyl α-Chloromethylacrylate and Related Derivatives”, *Journal of Polymer Science Part A: Polymer Chemistry,* Vol. 28, No. 6, pp. 1637-1648, 1990.

58. Mathias, L. J., R. M. Warren, and S. Huang, “tert-Butyl α-Hydroxymethylacrylate and Its Dimer: Multifunctional Monomers Giving Polymers with Easily Cleaved Ester Groups” *Macromolecules,* Vol. 24, No. 8, pp. 2036-2042, 1991.

59. Wissing, M., M. Niehues, B. J. Ravoo, and A. Studer, “Mixed AuPd Nanoparticles as Highly Active Catalysts for Alkyne z-Semihydrogenation”, *European Journal of Organic Chemistry*, Vol. 2018 , No. 26, pp. 3403–3409, 2018.

60. Sun, F., Y. Li, N. Zhang, and J. Nie, “Initiating Gradient Photopolymerization and Migration of a Novel Polymerizable Polysiloxane α-Hydroxy Alkylphenones Photoinitiator”, *Polymer*, Vol. 55, No. 16, pp. 3656–3665, 2014.

61. Knaus, S., and H. F. Gruber, “Photoinitiators with Functional Groups. III. Water-Soluble Photoinitiators Containing Carbohydrate Residues”, *Journal of Polymer Science Part A: Polymer Chemistry*, 1995, **33**, 929-939.

62. Duling, D. R., “Simulation of Multiple Isotropic Spin-trap EPR Spectra”, *Journal of Magnetic Resonance, Series B*, Vol. 104, No. 2, pp. 105–110, 1994.

63. Tsuda, T., and L. J. Mathias, “Cyclopolymerization of Ether Dimers of α-(Hydroxymethyl)acrylic Acid and Its Alkyl Esters: Substituent Effect an Cyclization Efficiency and Microstructures”, *Polymer*, Vol. 35, No. 15, pp. 3317-3328, 1994.

64. Avci, D., and L. J. Mathias, "Synthesis and Cyclopolymerization of Novel Allyl-Acrylate Quaternary Ammonium Salts", *Journal of Polymer Science Part A: Polymer Chemistry*, Vol. 37, No. 7, pp. 901-907, 1999.

65. Avci, D., K. Lemopulo, and L. J. Mathias, "Cyclocopolymerization of Allyl-Acrylate Quaternary Ammonium Salts with Diallyldimethylammonium Chloride", *Journal of Polymer Science Part A: Polymer Chemistry*, Vol. 39, No. 5, pp. 640-649, 2001.

66. Francis, S., L. Varshney, and S. Sabharwal, "Thermal Degradation Behavior of Radiation Synthesized Polydiallyldimethylammonium Chloride", *European Polymer Journal,* Vol. 43, No. 6, pp. 2525-2531, 2007.

67. Marlton, S. J. P., B. I. McKinnon, N. S. Hill, M. L. Coote, and A. J. Trevitt, "Electrostatically Tuning the Photodissociation of the Irgacure 2959 Photoinitiator in the Gas Phase by Cation Binding", *Journal of American Chemical Society*, Vol. 143, No. 5, pp. 2331-2339, 2021.

68. Dietlin, C., J. Lalevee, X. Allonas, J. P. Fouassier, M. Visconti, G. Li Bassi, and G. Norcini, "Reactivity and Efficiency of Difunctional Radical Photoinitiators", *Journal of Applied Polymer Science*, Vol. 107, No. 1, pp. 246-252, 2008.

69. Huo, S., H. Y. Zhou, and J. X. Wang, "Preparation and Photochemical Properties of PEG Based Alpha-Hydroxyalkylphenone Photoinitiator", *Reactive and Functional Polymers*, Vol. 163, 104892, 2021.

70. Criqui, A., J. Lalevee, X. Allonas, and J-P. Fouassier, "Electron Spin Resonance Spin Trapping Technique: Application to the Cleavage Process of Photoinitiators", *Macromolecular Chemistry and Physics*, Vol. 209, No. 21, pp. 2223–2231, 2008.

71. Skliutas, E., M. Lebedevaite, E. Kabouraki, T. Baldacchini, J. Ostrauskaite, M. Vamvakaki, M. Farsari, S. Juodkazis, and M. Malinauskas, "Polymerization Mechanisms Initiated by Spatio-Temporally Confined Light", *Nanophotonics*, Vol. 10, No. 4, pp. 1211-1242, 2021.

72. Bemowsky, S., A. Rother, W. Willmann, J. Koser, M. Markiewicz, R. Dringen and S. Stolte, “Quantification and Biodegradability Assessment of Meso-2,3-Dimercaptosuccinic Acid Adsorbed on Iron Oxide Nanoparticles”, *Nanoscale Advances*, Vol. 1, No. 9, pp. 3670-3679, 2019.

73. Gennari, A., J. Wedgwood, E. Lallana, N. Francini, N. Tirelli, “Thiol-Based Michael-Type Addition. A Systematic Evaluation of Its Controlling Factors”, *Tetrahedron*, Vol. 76, No. 47, 131637, 2020.

74. Y. Sun, H. Liu, L. Cheng, S. Zhu, C. Cai, T. Yang, L. Yang, P. Ding, “Thiol Michael Addition Reaction: A Facile Tool for Introducing Peptides into Polymer-Based Gene Delivery Systems”, *Polymer International*, Vol. 67, No. 1, pp. 25-31, 2018.

75. Aparicio, J. L. and M. Elizalde, “Migration of Photoinitiators in Food Packaging: A Review”, *Packaging Technology and Science*, Vol. 28, No. 3, pp. 181–203, 2015.

76. Scarsella, J. B., N. Zhang and T. G. Hartman, “Identification and Migration Studies of Photolytic Decomposition Products of UV-Photoinitiators in Food Packaging”, *Molecules*, Vol. 24, No. 19, 3592, 2019.

APPENDIX A: COPYRIGHT LICENCES



License Number	5560201457876
License date	Jun 01, 2023

Licensed Content

Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	AIChE Journal
Licensed Content Title	Toward an enhanced understanding and implementation of photopolymerization reactions
Licensed Content Author	Christopher J. Kloxin, Christopher N. Bowman
Licensed Content Date	Oct 6, 2008
Licensed Content Volume	54
Licensed Content Issue	11
Licensed Content Pages	21

Order Details

Type of use	Dissertation/Thesis
Requestor type	University/Academic
Format	Print and electronic
Portion	Figure/table
Number of figures/tables	1
Will you be translating?	No

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

Portions	Figure 1

Requestor Location

	Bogazici University 34342 Bebek/Istanbul Türkiye
Requestor Location	Istanbul, 34342 Turkey Attn: Bogazici University

Tax Details

Publisher Tax ID	EU826007151

Figure A.1. Permission from [12] John Wiley and Sons, Copyright (2008).



ACS Publications
Most Trusted. Most Cited. Most Read.

Termination Mechanism in the Radical Polymerization of Methyl Methacrylate and Styrene Determined by the Reaction of Structurally Well-Defined Polymer End Radicals

Author: Yasuyuki Nakamura, Shigeru Yamago
Publication: Macromolecules
Publisher: American Chemical Society
Date: Sep 1, 2015

Copyright © 2015, American Chemical Society

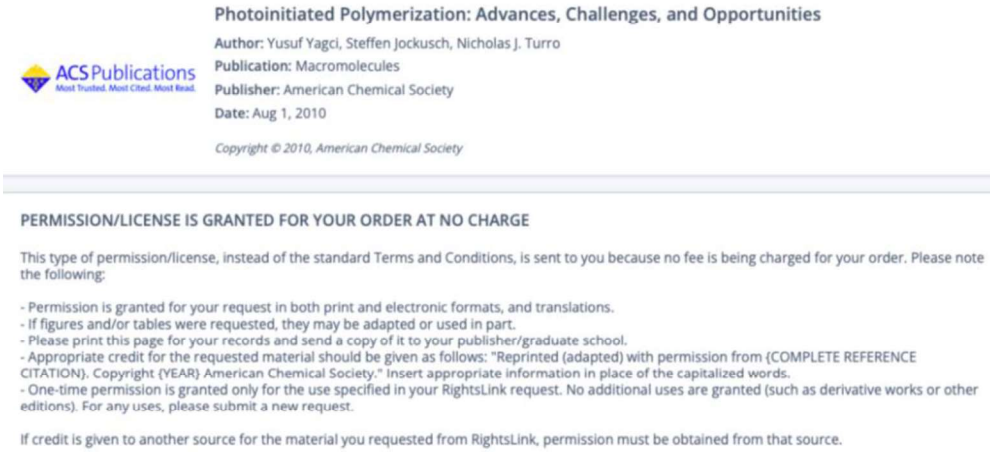
PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

Figure A.2. Permission from [14] American Chemical Society, Copyright (2015).



Photoinitiated Polymerization: Advances, Challenges, and Opportunities

Author: Yusuf Yagci, Steffen Jockusch, Nicholas J. Turro
Publication: Macromolecules
Publisher: American Chemical Society
Date: Aug 1, 2010

Copyright © 2010, American Chemical Society

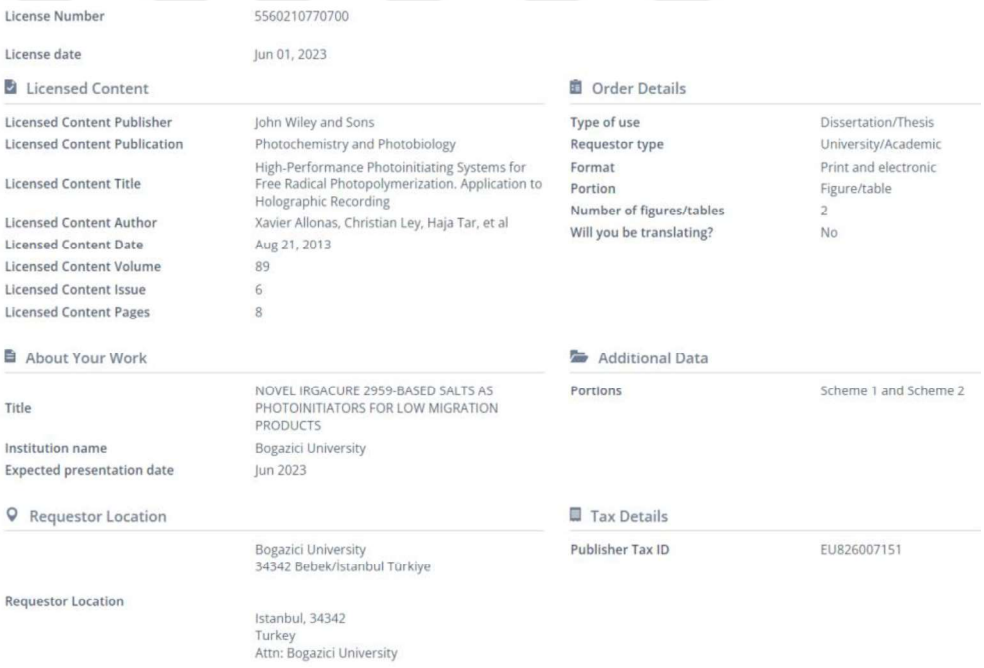
PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

Figure A.3. Permission from [11] American Chemical Society, Copyright (2010).



License Number	5560210770700
License date	Jun 01, 2023

Licensed Content

Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Photochemistry and Photobiology
Licensed Content Title	High-Performance Photoinitiating Systems for Free Radical Photopolymerization. Application to Holographic Recording
Licensed Content Author	Xavier Allonas, Christian Ley, Haja Tar, et al
Licensed Content Date	Aug 21, 2013
Licensed Content Volume	89
Licensed Content Issue	6
Licensed Content Pages	8

Order Details

Type of use	Dissertation/Thesis
Requestor type	University/Academic
Format	Print and electronic
Portion	Figure/table
Number of figures/tables	2
Will you be translating?	No

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

Portions	Scheme 1 and Scheme 2

Requestor Location

Bogazici University
34342 Bebek/Istanbul Türkiye

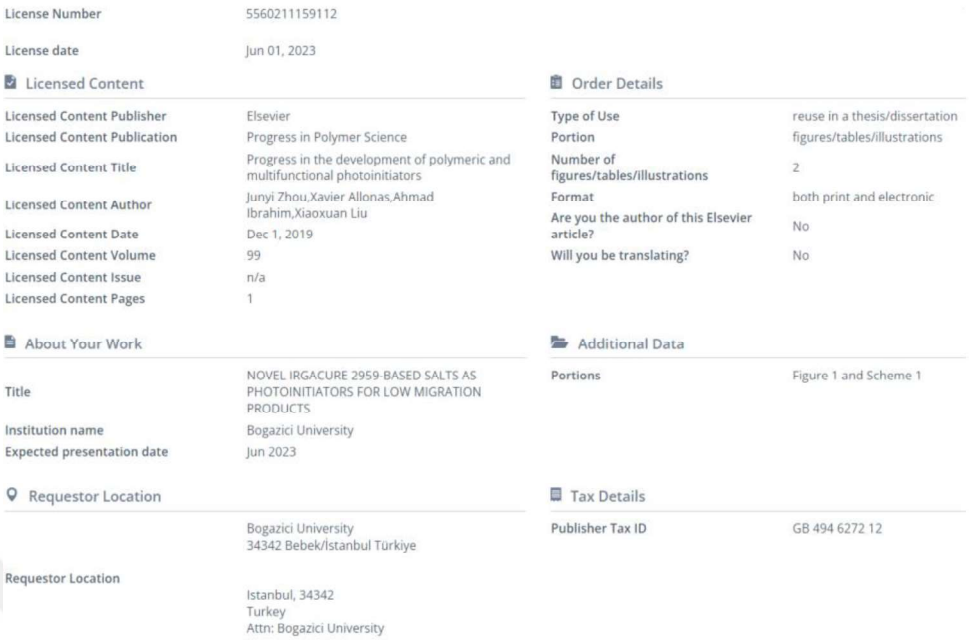
Requestor Location

Istanbul, 34342
Turkey
Attn: Bogazici University

Tax Details

Publisher Tax ID	EU826007151

Figure A.4. Permission from [13] John Wiley and Sons, Copyright (2013).



License Number	5560211159112
License date	Jun 01, 2023

Licensed Content

Licensed Content Publisher	Elsevier
Licensed Content Publication	Progress in Polymer Science
Licensed Content Title	Progress in the development of polymeric and multifunctional photoinitiators
Licensed Content Author	Junyi Zhou,Xavier Allonas,Ahmad Ibrahim,Xiaoxuan Liu
Licensed Content Date	Dec 1, 2019
Licensed Content Volume	99
Licensed Content Issue	n/a
Licensed Content Pages	1

Order Details

Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	2
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

Portions	Figure 1 and Scheme 1

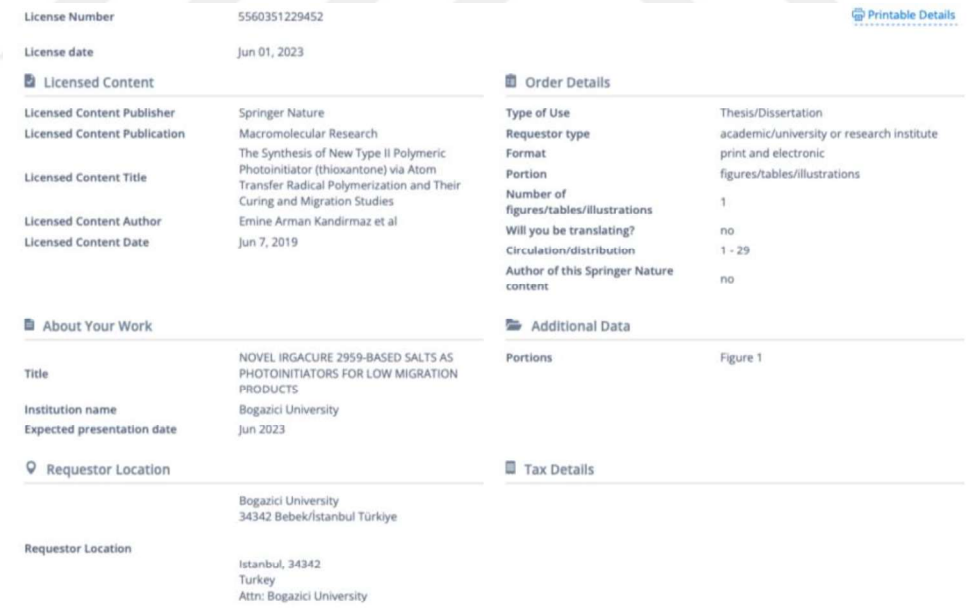
Requestor Location

	Bogazici University 34342 Bebek/Istanbul Türkiye
Requestor Location	Istanbul, 34342 Turkey Attn: Bogazici University

Tax Details

Publisher Tax ID	GB 494 6272 12

Figure A.5. Permission from [21] Elsevier, Copyright (2019).



Printable Details

License Number	5560351229452
License date	Jun 01, 2023

Licensed Content

Licensed Content Publisher	Springer Nature
Licensed Content Publication	Macromolecular Research
Licensed Content Title	The Synthesis of New Type II Polymeric Photoinitiator (thioxantone) via Atom Transfer Radical Polymerization and Their Curing and Migration Studies
Licensed Content Author	Emine Arman Kandirmaz et al
Licensed Content Date	Jun 7, 2019

Order Details

Type of Use	Thesis/Dissertation
Requestor type	academic/university or research institute
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Will you be translating?	no
Circulation/distribution	1 - 29
Author of this Springer Nature content	no

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

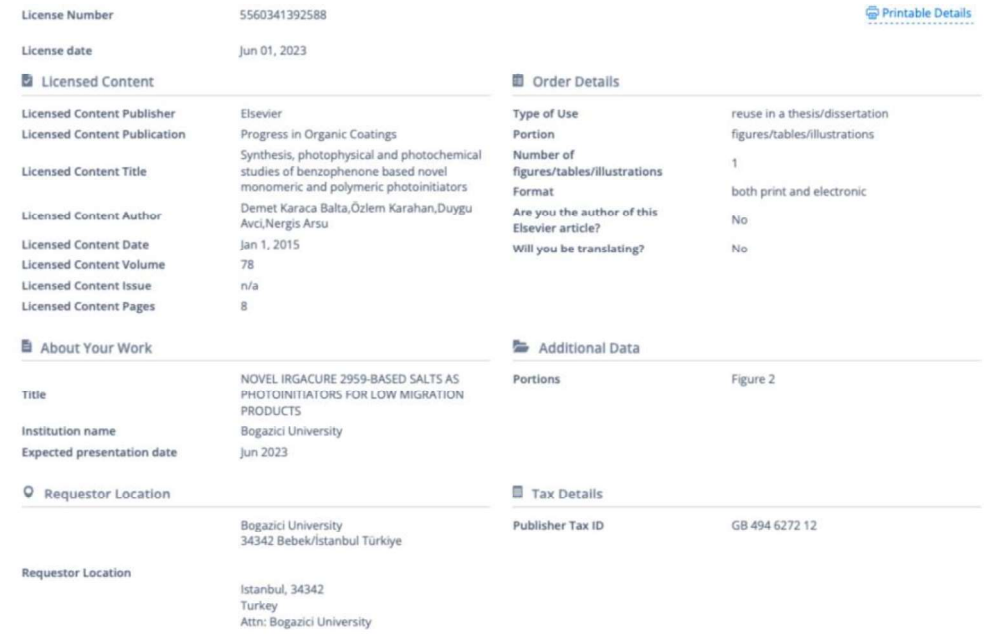
Portions	Figure 1

Requestor Location

	Bogazici University 34342 Bebek/Istanbul Türkiye
Requestor Location	Istanbul, 34342 Turkey Attn: Bogazici University

Tax Details

Figure A.6. Permission from [39] Springer Nature, Copyright (2019).



License Number	5560341392588
License date	Jun 01, 2023

Printable Details

Licensed Content

Licensed Content Publisher	Elsevier
Licensed Content Publication	Progress in Organic Coatings
Licensed Content Title	Synthesis, photophysical and photochemical studies of benzophenone based novel monomeric and polymeric photoinitiators
Licensed Content Author	Demet Karaca Balta,Özlem Karahan,Duygu Avci,Nergis Arsu
Licensed Content Date	Jan 1, 2015
Licensed Content Volume	78
Licensed Content Issue	n/a
Licensed Content Pages	8

Order Details

Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

Portions	Figure 2

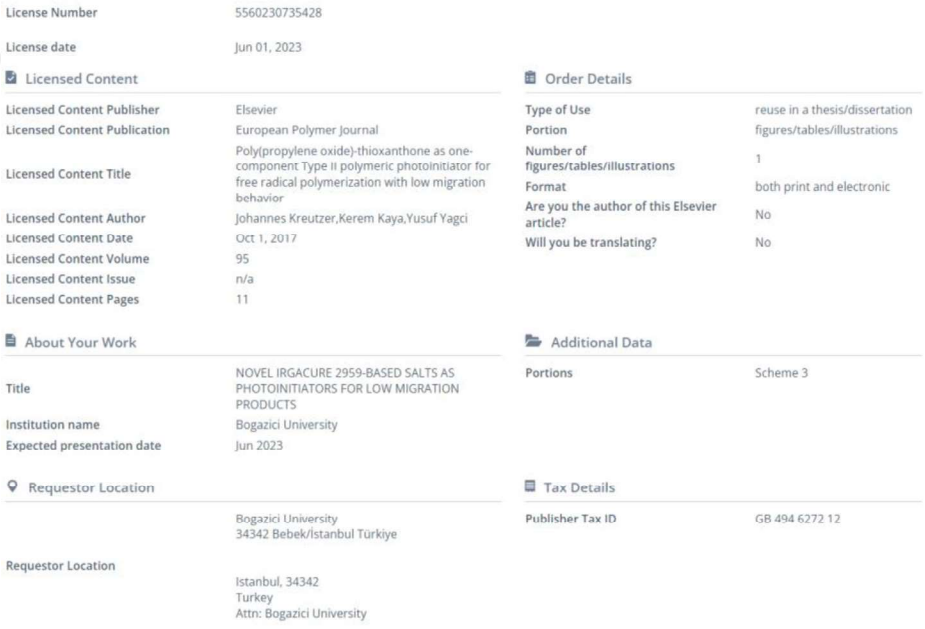
Requestor Location

	Bogazici University 34342 Bebek/Istanbul Türkiye
Requestor Location	Istanbul, 34342 Turkey Attn: Bogazici University

Tax Details

Publisher Tax ID	GB 494 6272 12

Figure A.7. Permission from [28] Elsevier, Copyright (2015).



License Number	5560230735428
License date	Jun 01, 2023

Licensed Content

Licensed Content Publisher	Elsevier
Licensed Content Publication	European Polymer Journal
Licensed Content Title	Poly(propylene oxide)-thioxanthone as one-component Type II polymeric photoinitiator for free radical polymerization with low migration behavior
Licensed Content Author	Johannes Kreutzer,Kerem Kaya,Yusuf Yagci
Licensed Content Date	Oct 1, 2017
Licensed Content Volume	95
Licensed Content Issue	n/a
Licensed Content Pages	11

Order Details

Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

Portions	Scheme 3

Requestor Location

	Bogazici University 34342 Bebek/Istanbul Türkiye
Requestor Location	Istanbul, 34342 Turkey Attn: Bogazici University

Tax Details

Publisher Tax ID	GB 494 6272 12

Figure A.8. Permission from [40] Elsevier, Copyright (2017).



License Number	5560250916022
License date	Jun 01, 2023

Licensed Content

Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Macromolecular Chemistry and Physics
Licensed Content Title	Water-Soluble Photoinitiators from Dimethylamino-Substituted Monoacylphosphine Oxide for Hydrogel and Latex Preparation
Licensed Content Author	Abraham Chemtob, Héloïse Thérien-Aubin, Lorena Infante, et al
Licensed Content Date	Aug 13, 2021
Licensed Content Volume	222
Licensed Content Issue	19
Licensed Content Pages	10

Order Details

Type of use	Dissertation/Thesis
Requestor type	University/Academic
Format	Print and electronic
Portion	Figure/table
Number of figures/tables	1
Will you be translating?	No

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

Portions	Figure 1

Requestor Location

Requestor Location	Bogazici University 34342 Bebek/Istanbul Türkiye Istanbul, 34342 Turkey Attn: Bogazici University

Tax Details

Publisher Tax ID	EU826007151

Figure A.9. Permission from [42] John Wiley and Sons, Copyright (2021).



License Number	5560250453810
License date	Jun 01, 2023

Licensed Content

Licensed Content Publisher	Elsevier
Licensed Content Publication	Biomaterials
Licensed Content Title	Photoinitiated polymerization of PEG-diacrylate with lithium phenyl-2,4,6-trimethylbenzoylphosphinate: polymerization rate and cytocompatibility
Licensed Content Author	Benjamin D. Fairbanks,Michael P. Schwartz,Christopher N. Bowman,Kristi S. Anseth
Licensed Content Date	Dec 1, 2009
Licensed Content Volume	30
Licensed Content Issue	35
Licensed Content Pages	6

Order Details

Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

Portions	Figure 1

Requestor Location

Requestor Location	Bogazici University 34342 Bebek/Istanbul Türkiye Istanbul, 34342 Turkey Attn: Bogazici University

Tax Details

Publisher Tax ID	GB 494 6272 12

Figure A.10. Permission from [43] Elsevier, Copyright (2009).

License Number	5560251137978
License date	Jun 01, 2023

Licensed Content

Licensed Content Publisher	Elsevier
Licensed Content Publication	International Journal of Biological Macromolecules
Licensed Content Title	Influence of photoinitiator concentration and irradiation time on the crosslinking performance of visible-light activated pullulan-HEMA hydrogels
Licensed Content Author	Elbadawy A. Kamoun,Alaa El-Betany,Henning Menzel,Xin Chen
Licensed Content Date	Dec 1, 2018
Licensed Content Volume	120
Licensed Content Issue	n/a
Licensed Content Pages	9

Order Details

Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

Portions	Figure 1

Requestor Location

	Bogazici University 34342 Bebek/İstanbul Türkiye
Requestor Location	Istanbul, 34342 Turkey Attn: Bogazici University

Tax Details

Publisher Tax ID	GB 494 6272 12

Figure A.11. Permission from [44] Elsevier, Copyright (2018).

License Number	5560251384024
License date	Jun 01, 2023

Licensed Content

Licensed Content Publisher	Elsevier
Licensed Content Publication	Journal of Photochemistry and Photobiology A: Chemistry
Licensed Content Title	One-pot synthesis of water-soluble polymeric photoinitiator via thioxanthonation and sulfonation process
Licensed Content Author	Gokhan Temel,Nergis Arsu
Licensed Content Date	Feb 5, 2009
Licensed Content Volume	202
Licensed Content Issue	1
Licensed Content Pages	4

Order Details

Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

Portions	Scheme 2

Requestor Location

	Bogazici University 34342 Bebek/İstanbul Türkiye
Requestor Location	Istanbul, 34342 Turkey Attn: Bogazici University

Tax Details

Publisher Tax ID	GB 494 6272 12

Figure A.12. Permission from [46] Elsevier, Copyright (2009).



License Number	5560260162790
License date	Jun 01, 2023

Licensed Content

Licensed Content Publisher	Elsevier
Licensed Content Publication	Journal of Photochemistry and Photobiology A: Chemistry
Licensed Content Title	A facile method to prepare a polyethylene glycol modified polysilane as a waterborne photoinitiator
Licensed Content Author	Qiuhong Liang,Liping Zhang,Ying Xiong,Qingqing Wu,Hongding Tang
Licensed Content Date	Feb 15, 2015
Licensed Content Volume	299
Licensed Content Issue	n/a
Licensed Content Pages	9

Order Details

Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

Portions	Scheme 1

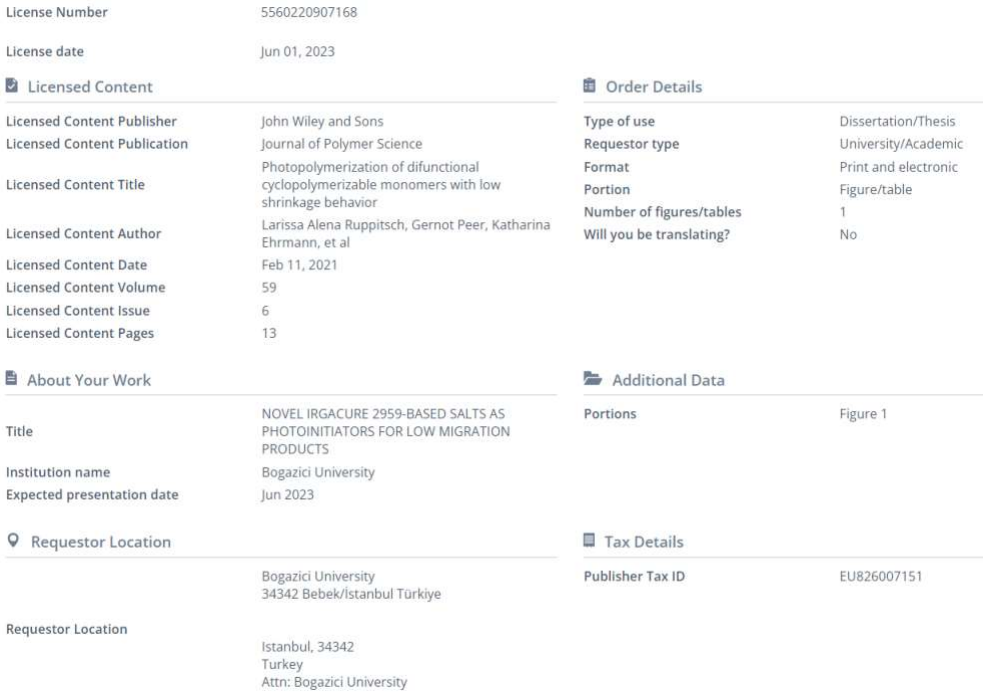
Requestor Location

	Bogazici University 34342 Bebek/Istanbul Türkiye
Requestor Location	Istanbul, 34342 Turkey Attn: Bogazici University

Tax Details

Publisher Tax ID	GB 494 6272 12

Figure A.13. Permission from [47] Elsevier, Copyright (2015).



License Number	5560220907168
License date	Jun 01, 2023

Licensed Content

Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Journal of Polymer Science
Licensed Content Title	Photopolymerization of difunctional cyclopolymerizable monomers with low shrinkage behavior
Licensed Content Author	Larissa Alena Ruppitsch, Gernot Peer, Katharina Ehrmann, et al
Licensed Content Date	Feb 11, 2021
Licensed Content Volume	59
Licensed Content Issue	6
Licensed Content Pages	13

Order Details

Type of use	Dissertation/Thesis
Requestor type	University/Academic
Format	Print and electronic
Portion	Figure/table
Number of figures/tables	1
Will you be translating?	No

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

Portions	Figure 1

Requestor Location

	Bogazici University 34342 Bebek/Istanbul Türkiye
Requestor Location	Istanbul, 34342 Turkey Attn: Bogazici University

Tax Details

Publisher Tax ID	EU826007151

Figure A.14. Permission from [52] John Wiley and Sons, Copyright (2021).



License Number	5560221500295
License date	Jun 01, 2023

Licensed Content

Licensed Content Publisher	Elsevier
Licensed Content Publication	Progress in Organic Coatings
Licensed Content Title	Thioxanthone-functionalized 1,6-heptadiene as monomeric photoinitiator
Licensed Content Author	Tugce Nur Eren,Bernadette Graff,Jacques Lalevee,Duygu Avci
Licensed Content Date	Mar 1, 2019
Licensed Content Volume	128
Licensed Content Issue	n/a
Licensed Content Pages	9

Order Details

Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

Portions	Figure 1

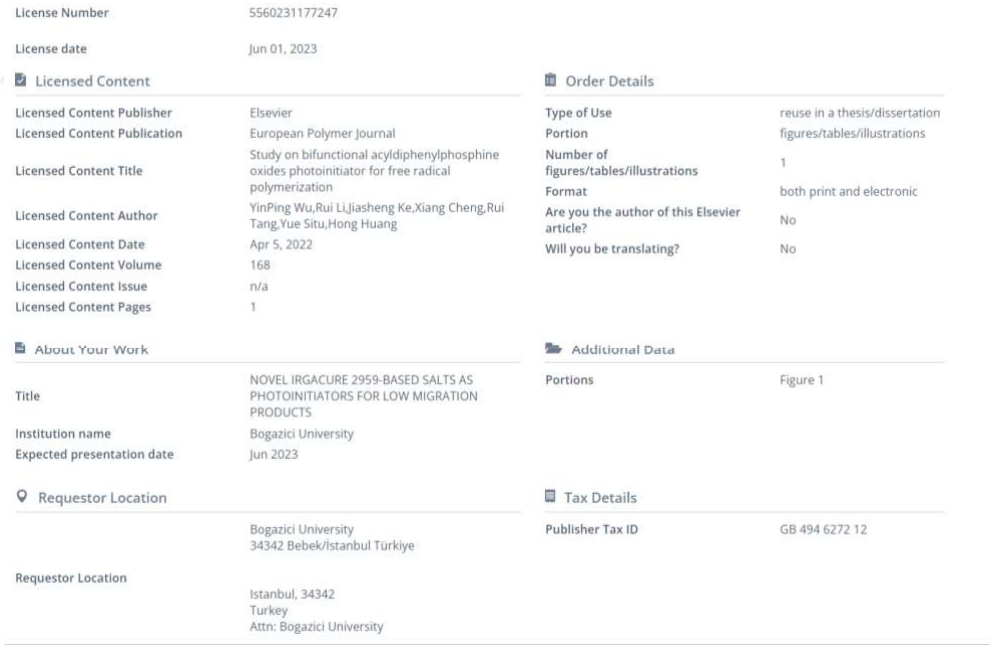
Requestor Location

	Bogazici University 34342 Bebek/Istanbul Türkiye
Requestor Location	Istanbul, 34342 Turkey Attn: Bogazici University

Tax Details

Publisher Tax ID	GB 494 6272 12

Figure A.15. Permission from [17] Elsevier, Copyright (2019).



License Number	5560231177247
License date	Jun 01, 2023

Licensed Content

Licensed Content Publisher	Elsevier
Licensed Content Publication	European Polymer Journal
Licensed Content Title	Study on bifunctional acyldiphenylphosphine oxides photoinitiator for free radical polymerization
Licensed Content Author	YinPing Wu,Rui Li,Jiasheng Ke,Xiang Cheng,Rui Tang,Yue Situ,Hong Huang
Licensed Content Date	Apr 5, 2022
Licensed Content Volume	168
Licensed Content Issue	n/a
Licensed Content Pages	1

Order Details

Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

About Your Work

Title	NOVEL IRGACURE 2959-BASED SALTS AS PHOTOINITIATORS FOR LOW MIGRATION PRODUCTS
Institution name	Bogazici University
Expected presentation date	Jun 2023

Additional Data

Portions	Figure 1

Requestor Location

	Bogazici University 34342 Bebek/Istanbul Türkiye
Requestor Location	Istanbul, 34342 Turkey Attn: Bogazici University

Tax Details

Publisher Tax ID	GB 494 6272 12

Figure A.16. Permission from [53] Elsevier, Copyright (2022).