SYNTHESIS AND EVALUATIONS OF CYCLOPOLYMERIZABLE AND CYCLOPOLYMERIC TYPE I PHOTOINITIATORS

by

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Dedicated to my grandfather Baysal Balaban…

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ABSTRACT

SYNTHESIS AND EVALUATIONS OF CYCLOPOLYMERIZABLE AND CYCLOPOLYMERIC TYPE I PHOTOINITIATORS

The aim of this thesis is to synthesize novel cyclopolymerizable and cyclic photoinitiators with high reactivity, water solubility, low migration and high thermal stability. In the first part of this work, two novel cyclopolymerizable Type I photoinitiators (DAA-I2959 and DAA-I184) were synthesized from reaction of diallyl amine (DAA) with tosyl ester of 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959, I2959) in the presence of sodium hydroxide as catalyst or with acrylate ester of 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, I184). A water soluble, linear polymeric photoinitiator (p-DADMAC-*co*-DAA-I2959-QS) was synthesized by thermal copolymerization of DAA-I2959 with diallyldimethylammonium chloride (DADMAC) in the presence of hydrochloric acid. This photoinitiator has five-membered cyclic units on the backbone and its M_n value was in the range of 40,000-60,000 D. DAA-I2959, its copolymer and DAA-I184 have strong absorbances at 272, 266 and 244 nm ($\varepsilon \sim$ 14705, 8000 and 11625), respectively, in methanol. In the second part of this work, reaction of DAA with tosylate ester of Irgacure 2959 was performed in the absence of a catalyst to give a mixture of two quaternary ammonium monomers, DAA-I2959-QS and DAA-Ts (tosylate salt of DAA). This photoinitiator has a strong absorbance at 269 nm ($\varepsilon \sim$ 15731) in methanol. The photoinitiating capabilities of the synthesized photoinitiators for the photopolymerization of poly(ethylene glycol) diacrylate (PEGDA, M_n = 575 D) or 2-hydroxyethyl methacrylate (HEMA) were investigated by differential scanning photo calorimetry (Photo-DSC) and compared with I2959 and I184. DAA-I2959, p-DADMAC-*co*-DAA-I2959-QS and DAA-I2959-QS/DAA-Ts exhibited fairly good migration stabilities (~ 3.5, 6.8 and 15.6 times higher) than that of I2959.

ÖZET

SİKLOPOLİMERLEŞEBİLEN VE SİKLOPOLİMERİK TİP I FOTOBAŞLATICILARIN SENTEZİ VE DEĞERLENDİRİLMESİ

Bu tezin amacı yüksek reaktiflik, suda çözünürlük, düşük sızma ve termal kararlılık özelliklerine sahip siklopolimerleşebilen ve siklik yeni fotobaşlatıcıların sentezidir. Bu çalışmanın ilk bölümünde, iki yeni siklopolimerleşebilen Tip I fotobaşlatıcı (DAA-I2959 ve DAA-I184) diallil amin ile 2-hidroksi-4'-(2-hidroksietoksi)-2-metilpropiofenon (Irgacure 2959, I2959) tosil esterinin sodium hidroksit katalizörlüğünde ya da 1-hidroksisiklohekzil fenil keton (Irgacure 184, I184) akrilat esterinin reaksiyonundan sentezlendi. DAA-I2959'un dialildimetilamonyum klorür (DADMAC) ile hidroklorik asit varlığında kopolimerizasyonundan suda çözünen, lineer bir polimerik fotobaşlatıcı sentezlendi. Bu fotobaşlatıcı ana zincirinde beş üyeli halka içeren birimlere sahip olup M_n değeri 40,000-60,000 D aralığındadır. DAA-I2959, kopolimeri ve DAA-I184 metanolde 272, 266 ve 244 nm'de kuvvetli absorbsiyon (ε ~ 14705, 8000 ve 11625) göstermektedirler. Çalışmanın ikinci bölümünde, DAA'nın I2959'un tosilat esteri ile katalizsiz reaksiyonundan iki kuvaterner amonyum monomerinin, DAA-I2959-QS ve DAA-Ts (DAA-tosilat esteri), karışımı elde edildi. Bu karışım metanolde 269 nm (ε ~15731)'de güçlü abzorbansa sahiptir. Sentezlenen fotobaşlatıcıların poli(etilen glikol) diakrilat (PEGDA, M_n = 575 D) ve 2-hidroksietil metakrilatı (HEMA) fotobaşlatma kapasiteleri diferansiyel taramalı fotokalorimetre (photo-DSC) ile incelendi ve I2959 ve I184 ile kıyaslandı. DAA-I2959, p-DADMAC-*co*-DAA-I2959-QS ve DAA-I2959-QS/DAA-Ts I2959 I2959'dan oldukça yüksek migrasyon kararlılığı (~ 3.5, 6.8 ve 15.6 kat yükek) gösterdi.

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LIST OF SYMBOLS

DAA-I2959	I2959 functionalized diallyl amine
DAA-I184	I184 functionalized diallyl amine
p-DADMAC-*co*-DAA-I2959-QS	Copolymer of DADMAC and I2959 functionalized diallyl amine
DAA-I2959-QS/ DAA-Ts	The mixture of the protonated form of DAA-I2959 (DAA-I2959-QS) and p-toluene sulphonic acid salt of DAA (DAA-Ts).
f	Initiation efficiency
[I]	Initiator concentration
I_0	Light intensity
ISC	Intersystem crossing
I2959-Ts	Ts functionalized I2959
k_p	Propagation rate constant
M_n	Number Average Molar Mass
M	Molar mass of the monomer
[M]	Monomer concentration
$[M_n\bullet]$	Propagating radical concentration
n	Number of double bonds per monomer molecule
PI	Photoinitiator
PPI	Polymeric photoinitiator
Q/s	Heat flow per second
R_i	Rate of initiation step
R_p	Rate of propagation step
R_t	Rate of termination step
R_{pmax}	The maximum rate of polymerization
S_0	Ground state
S_1	An excited state
t_{max}	Time to reach the maximum heat of polymerization
T	Triplet excited state

ΔH_p	Heat evolved in the reaction
ε	Molar absorptivity
λ_{max}	Maximum Absorption Wavelength
Φ	Quantum yield for initiation process

LIST OF ACRONYMS / ABBREVIATIONS

DAA	Diallyl amine
DADMAC	Diallyldimethylammonium chloride
DSC	Differential scanning calorimetry
EDAB	4-dimethylaminobenzoic acid ester
FT-IR	Fourier-transform infrared spectroscopy
GPC	Gel permeation chromatography
HEMA	2-hydroxyethyl methacrylate
I184	1-Hydroxycyclohexyl phenyl ketone
I2959	2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone
Iod	Bis-(4-tert-butylphenyl)-iodonium hexafluorophosphate
NMR	Nuclear magnetic resonance spectroscopy
PEGDA	Poly(ethylene glycol) diacrylate
TGA	Thermal gravimetric analysis
TX	Thioxanthone

1. INTRODUCTION

1.1. Photopolymerization

In photopolymerization, radicals, cations or anions which enable propagation of polymerization, are produced via the absorption of light by dyes, chromophores, or weak complexes generally [1]. Photopolymerization is used in many application areas such as coatings, inks, adhesives, laser imaging, nanotechnology, biomaterials [2], 3D printing [3] and biomedical applications [4]. This wide range of the applications is one of the advantages of photopolymerization. Another one is that it is fast. In addition, it is energy-saving. It can be performed in solvent-free conditions and it allows spatial and temporal control [2], [4-6]. It is also usable in application areas where heating is not possible; unlike thermal polymerization [2]. Therefore, photopolymerization is considered as one of the ways to obtain friendly, cheap, reliable and flexible functional polymers [1].

1.1.1. Free Radical Photopolymerization

There are four basic steps of free radical photopolymerization which are initiation, propagation, chain transfer and termination (Figure 1.1) [7].

The step in which the free radical active centers are formed is the initiation. The initiation of the propagating chain was performed by these free radical centers [7]. The monomer units are added to the growing chain during propagation [7]. The growing chain is ended by the chain transfer or termination [7].

The rate of initiation step is determined by the following equation [8]

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

where Φ represents quantum yield for initiation process. I_0 represents light intensity whereas [I] represents the concentration of initiator. ε represents molar absorptivity whereas f represents efficiency [8].

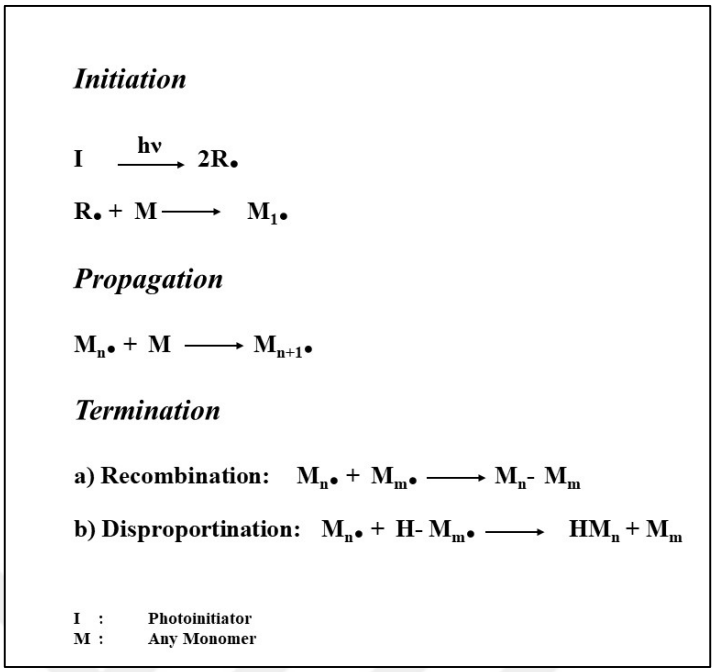


Figure 1.1. The steps of a free radical photopolymerization reaction [7,8]. Permission from [8] American Institute of Chemical Engineers (AIChE), Copyright (2008). No permission is required from [7].

The rate for propagation step is expressed as

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

In this equation, k_p indicates the propagation rate constant. The double bond concentration was shown by [M] whereas the total propagating radical concentration was shown by $[M_n\bullet]$. This is assumed that two radicals are involved for a bimolecular reaction in termination reaction [8].

The rate of the termination reaction is determined as

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

In this equation, k_t represents the rate constant of termination. According to steady state assumption the rate of initiation is equal to the rate of termination,

$$R_i = R_t. \quad (1.4)$$

From there, the rate for entire polymerization is determined as

$$R_p = k_p [M](R_i/2k_t)^{1/2}. \quad (1.5)$$

1.1.2. Free Radical Photoinitiators and Their Classification

A photoinitiator (PI) is one of the main components of a photopolymerization reaction, the other two being light and a monomer. The choice of the photoinitiating system is important, since there are outcomes which can be impacted by the choice of the photoinitiating system such as performance, the speed of curing and the final properties of the polymer [4]. In photopolymerization, light is absorbed by the PI and this absorption causes the conversion of the light energy into the chemical energy by the production of the reactive intermediates [9]. In the case of free radical photoinitiators, these reactive intermediates are free radicals. The mechanism of the formation of these reactive intermediates can be explained by Jablonski Diagram which shows the different electronic states of a molecule [10, 11]. A schematic Jablonski Diagram is shown in Figure 1.2 [12].

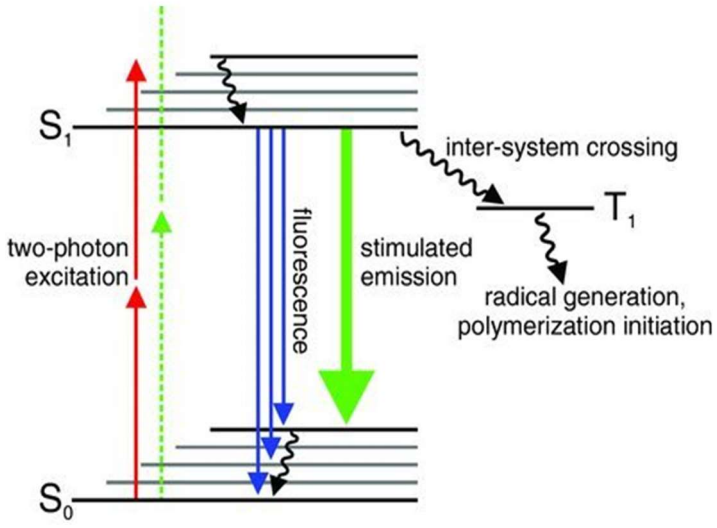


Figure 1.2. Jablonski diagram for radical generation. Permission from [12] John Willey and Sons, Copyright (2010).

The excitation of an electron from a ground state (S_0) to an excited state (S_1) is caused by the absorption of a photon [11]. There are some different pathways which can be followed after this excitation. One of these pathways is the deactivation to S_0 by emitting light (fluorescence, $S_1 \rightarrow S_0$) [11],[13]. It may also lose energy by heat (internal conversion (S→S).

Another pathway is intersystem crossing (ISC) which causes an electron spin inversion. Electron spin inversion causes transition to excited triplet state (S→T) from which the photochemical processes can occur. 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)) [13]. Monomer quenching and oxygen quenching are other processes which can deactivate free radicals [13].

In radicalic photopolymerization, PIs are classified into two categories as Type I and Type II according to the mechanism of formation of free radicals [14]. From the triplet states, initiating species can be created from one of two reactions: the intramolecular scission of an α-bond or the intermolecular H abstraction [13]. Type I photoinitiators are known as one component photoinitiators whereas Type II photoinitiators are known as two component systems [15].

1.1.2.1. Type I PIs. In Type I systems the chemical bond is cleaved via absorption of light [1]. These PIs are known as α or β cleavable [15]. Benzoin derivatives, acylphosphine oxides, zirconocenes, silyl gloxylates or acylgermanes are some examples of the PIs which behave as Type I [1]. In Figure 1.3, the structures of some commercial Type I PIs are shown.

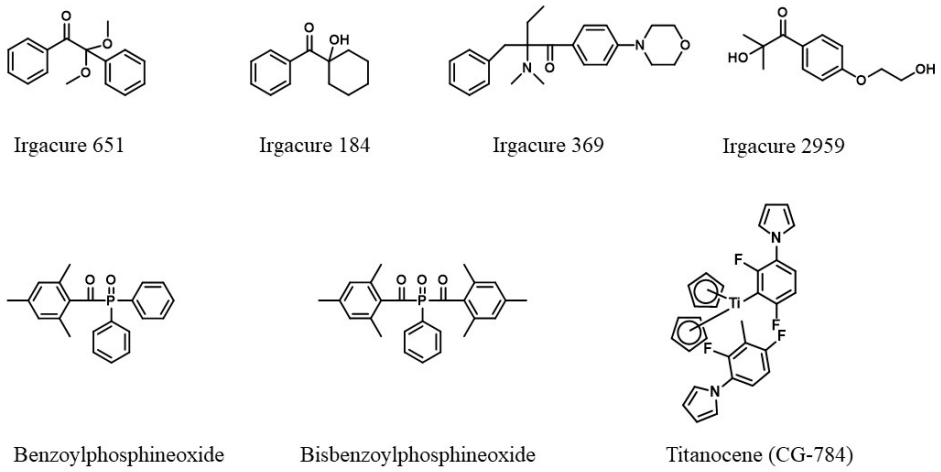


Figure 1.3. Structures of some Type I PIs [4], [16]. Permission from [16] The American Society of Photobiology, Copyright (2013). No Permission is required from [4].

One group of Type I PIs are α-hydroxy ketones which are among commonly used PIs in free radical polymerization [17]. The commercial PIs used in this thesis, I2959 and I184 are the α-hydroxy ketones and $^{1}\pi\pi^{*} \rightarrow {}^{1}n\pi^{*} \rightarrow {}^{3}\pi\pi^{*} \rightarrow {}^{3}n\pi^{*}$ transitions are involved in their photodissociation mechanism. The transition which is essential for the cleavage to the benzoyl and ketyl radicals is the last transition [18,19].

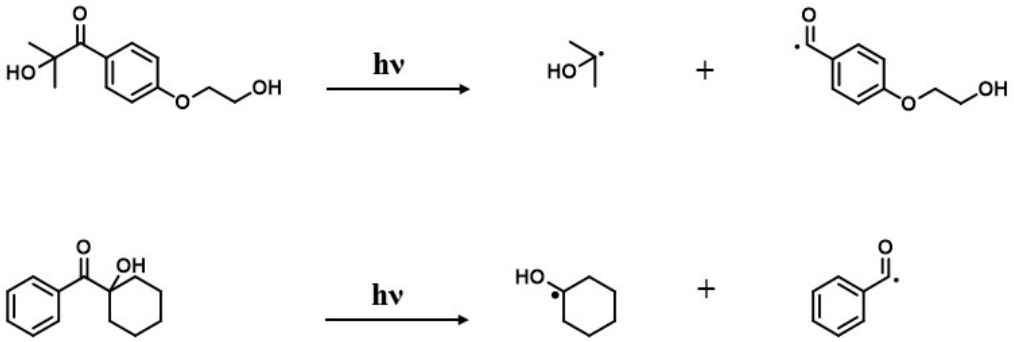


Figure 1.4. The cleavage of I2959 and I184 under UV light.

1.1.2.2. Type II PIs. In contrast to Type I PIs, non-cleavable dyes or carbonyl compounds are called Type II systems [1]. In Type II systems, the initiation of polymerization takes place by hydrogen abstraction or electron/proton transfer from the coinitiator to photoinitiator (Figure 1.5) [20,21]. Therefore, the presence of a coinitiator is required for Type II photoinitiators [20]. The schematic representation of electron and hydrogen atom abstraction processes between benzophenone and an amine is shown in Figure 1.5 as an example of a Type II system [21].

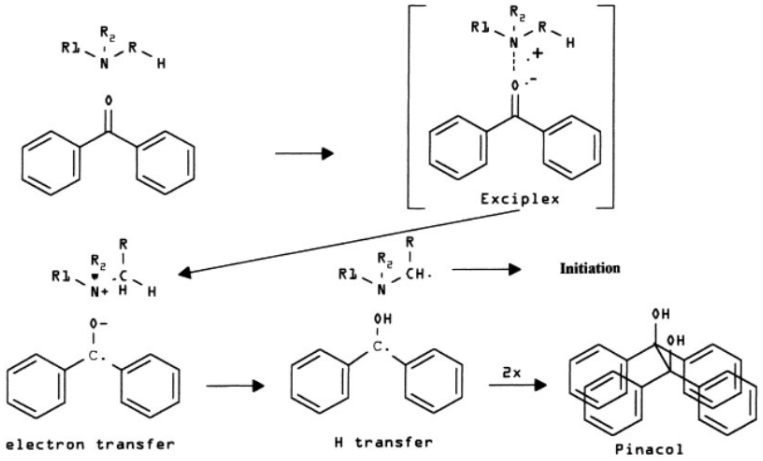


Figure 1.5. The schematic representation of electron and hydrogen atom abstraction processes between benzophenone and an amine. Permission from [21] Copyright 1999 Elsevier Science S.A.

Some examples for Type II systems are thioxanthone/amine or camphorquinone/amine systems [1], [22, 23]. In Figure 1.6, structures of some commercial photoinitiators which are used in Type II systems are shown.

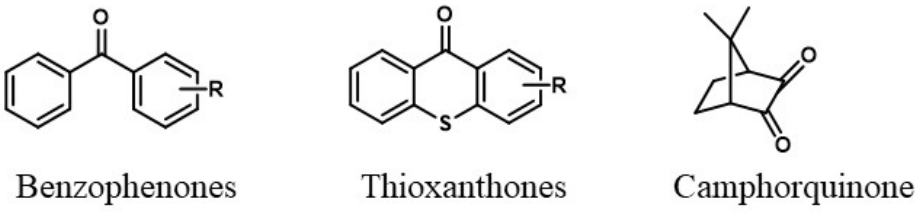


Figure 1.6. Structures of some Type II PIs [16]. Permission from [16] The American Society of Photobiology, Copyright (2013).

It is also possible to synthesize one component Type II PIs which have both PI and coinitiator functionality in the same molecule. There are some examples for such systems in the literature [24-26]. The structures of two one-component visible light PIs synthesized by Wu et al. are shown in Figure 1.7. The synthesized PIs have thioxanthone based acrylated structures (Figure 1.7) [24]. A one component copolymeric PI containing pendant

thioxanthone and amine moieties was also synthesized by Eren et al. [26]. Higher reactivity and polymerization efficiency were observed for the synthesized copolymeric PIs as compared to the TX itself [26].

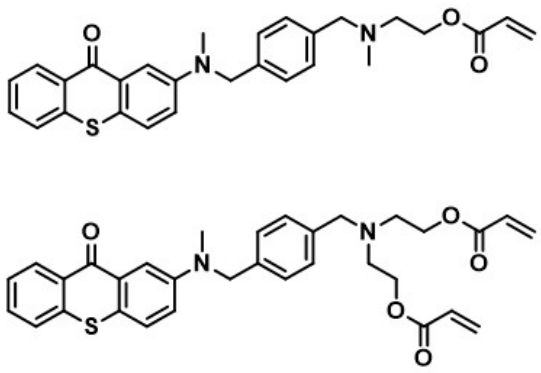


Figure 1.7. Structures of one component visible light PIs [24]. Permission from [24] WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Copyright (2017).

1.1.3. Tertiary Amines and Charge Transfer Complexes

Polymerization reactions which can be induced by visible light are preferred in many application areas such as biomedical applications [4]. On the other hand, the PIs which are applicable in visible light are mostly Type II PIs [24]. One group of species initiated by visible light are charge transfer complexes (CTCs) [27]. Another name for CTCs is electron donor acceptor (EDA) complexes [27]. The ground state association of an electron donor and an acceptor, results in the formation of a CTCs [27]. One of the important characteristics of the CTCs is that for some of them visible light absorption can be observed even though free donor and acceptor do not have visible light absorption property [27]. There are some examples for charge transfer complexes used in free radical photopolymerization [28-30]. It is known that amines can be used as the donor for the formation of CTCs [31-33], for example with iodonium salts [31] [34]. In such CTCs amines are used as reducing agents which are electron donors whereas iodonium salts are used as electron acceptors which are oxidizing agents [27]. Wang et al. also studied the relationship between the structure of the amine and the initiation performance of the CTSs [31]. One important reason for the choice

of CTC is to change absorption to visible wavelengths [27]. Due to this ability, they are applicable in some areas such as 3D printing [27].

1.1.4. Photopolymerization in Biomedical Applications and Water Soluble PIs

There are many biomedical application areas such as 3D bioprinting, drug delivery systems, dentistry, and cell encapsulation for which photopolymerization is preferred [4] [35]. A biodegradable, photopolymerizable, thermosensitive hydrogel was investigated to be used in tissue engineering by Censi et al. They concluded that the investigated biomaterial has potential to be used as synthetic extracellular matrix for engineering cartilage [35]. One of the advantageous of photopolymerization is that it can be performed at ambient temperatures without need of a solvent in a fast manner [4]. Since organic solvents are not required during photopolymerization, the associated toxicity is avoided [36]. The requirements for photoinitiating systems to be used in the biomedical applications are non-cytotoxicity to cells, compatibility with visible low-power light sources and water solubility [4]. There are some studies in which these properties were investigated for the photoinitiating systems. The cytotoxicity of the three PIs, namely 2-hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959), 1-hydroxycyclohexyl-1-phenyl ketone (Irgacure 184), and 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651) were investigated by Williams et al. [37]. Among these PIs minimum toxicity was found for I2959 [37]. Another essential factor for the biomedical applications is the water solubility, reasonable when the aqueous environment of most tissues are considered [36]. There are many literature examples in which the synthesis of water soluble PIs or the enhancement of water solubility for the PIs was aimed [38-53]. One way to obtain water soluble PIs or to enhance water solubility of PIs is the covalent attachment of ionic groups. Some of these groups are quaternary ammonium salts [38], [43], carboxylic acid salts [39] and sulfonates [47], [51]. Aubry et. al. synthesized two novel Type I PIs which were water soluble from Irgacure 1173 [38]. To obtain one of the PIs, a trimethylammonium salt was introduced to Irgacure 1173 whereas the methyl analogue of the synthesized PI was prepared to obtain the other PI [38] (Figure 1.8).

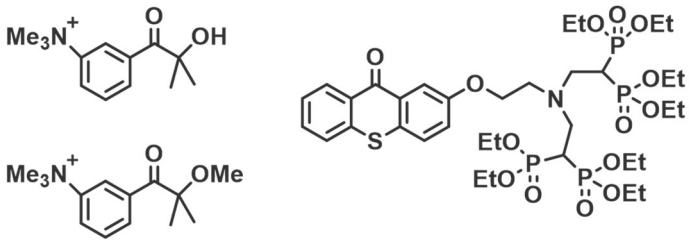


Figure 1.8. Some water soluble PIs in the literature [38], [53]. Permission from [53] Elsevier Ltd. Copyright (2020). No permission is required from [38].

Eren et al. synthesized a water soluble PI by functionalization of thioxanthone with bisphosphonate (TXBP2) (Figure 1.8) [53]. Quaternization or protonation is considered as one of the ways to obtain water soluble PIs. Le et al. synthesized a novel Type I diphenylphosphine oxide photoinitiator and they provide the water solubility by the protonation or quaternization reaction of a tertiary amino group in the para position of the benzoyl group [42]. In addition to the introduction of ionic groups, another way which is used for the syntheses of water soluble PIs or for the enhancement of the water solubility of PIs is the functionalization with polymers or macromers which are water soluble [47-49]. To illustrate, the combination of carbohydrates which are water soluble with some Type II PIs which are based on benzophenone and thioxanthone was performed by Liska [48]. The functionalization of carbohydrates with I2959 was also performed by Liska et. al. and Knaus et al. [47] [52].

1.1.5. Monomeric and Polymeric PIs

One of the disadvantages of photopolymerization is “migration”. If the formed radicals are unstable, further rearrangement, combination, oxidation, decomposition reactions can be possible for Type I and Type II PIs. In this case, the formed low molecular weight products can migrate [14]. Some of the problems which can be caused due to migration are yellowing, odor, blooming, contamination, and toxicity [14] [54]. As these outcomes are considered, this can be said that the migration can be a serious problem in some application areas such as food packaging and biomedical applications [14] [54-56]. One way to prevent the migration problem is to have monomeric (polymerizable) and polymeric PIs [14]. The use of monomeric PIs can lessen the migration since they can bind to the product. The use of

polymeric PIs is another way since their migration is difficult due to their large size [57]. There are some examples in the literature for the syntheses of polymerizable PIs [20], [58-69] and polymeric PIs [26], [36], [58], [70-83]. As mentioned in section 1.3, one-component visible light PIs which have thioxanthone based acrylated structures were synthesized by Wu et al. [24] (Figure 1.7). The migration stability for these PIs was also investigated by measuring the amount of the extracted PI from HDDA films via UV-visible spectroscopy. High migration stability of these PIs indicated that they can be good candidates for use in food packaging or biomedical fields [24]. In some cases, it is possible to observe higher photoinitiation efficiency for the synthesized monomeric or polymeric PIs as compared to the commercial PIs from which the monomeric or polymeric PIs were synthesized. Benzophenone and I2959 based monomeric and polymeric PIs were synthesized by Cesur et al. [58] (Figure 1.9). Higher photoinitiation efficiency was observed as compared to benzophenone itself [58].

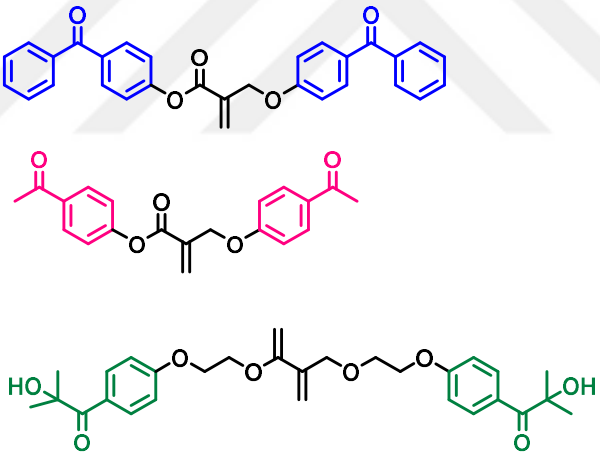


Figure 1.9. Structures of monomeric PIs synthesized by Cesur et al. [58]. Permission from [58] Elsevier B.V. Copyright (2015).

1.2. Cyclopolymerization

When multifunctional monomers are polymerized, usually crosslinked and insoluble polymers are obtained [84]. On the other hand, linear, soluble polymers can be obtained by the polymerization of some multifunctional monomers such as 1,6-heptadienes [85]. The

cyclic structures are contained in the main chain of such polymers [84] and they are called as cyclopolymers.

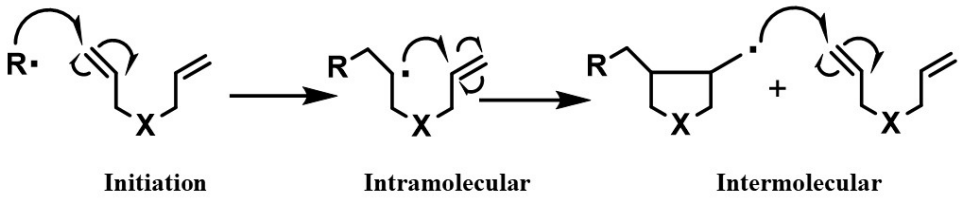


Figure 1.10. Mechanism of cyclopolymerization [86]. Permission from [86]. Wiley Periodicals LLC. Copyright (2021).

The mechanism of cyclopolymerization can be explained by intramolecular and intermolecular polymerization [86]. Firstly, intramolecular radical cyclization takes place then intermolecular propagation takes place during the propagation step of polymerization [86] (Figure 1.10). There are many advantages of cyclopolymers. Some of these advantages are the enhanced mechanical properties and low shrinkage behavior [86]. Due to these advantages, there are many application areas of cyclopolymers such as dental industry [87] and 3D printing [86].

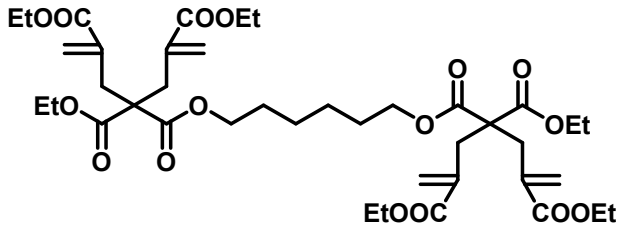


Figure 1.11. Cyclopolymerizable monomer based cross-linker synthesized by Peer et al. [88]. Permission from [88] American Chemical Society Copyright (2020).

A novel cyclopolymerizable monomer based cross-linker was synthesized by Peer et al. [88] (Figure 1.11). Lower volumetric shrinkage was observed for the synthesized cyclopolymerizable monomer based cross-linker as compared to its methacrylic counterpart. Therefore, the synthesized cross-linker was considered as a good candidate for additive

manufacturing or dental resins [88]. There are many factors which affect cyclopolymerization efficiency. One of these factors which increases the efficiency is to perform the polymerization in dilute solutions [84]. The presence of bulky side groups is generally considered as beneficial for the cyclopolymerization [84]. Another feature of bulky side groups is the hinderance of crystallization [89]. It is possible to increase the reactivity of vinyl or allyl based molecules via the presence of electron withdrawing groups which are adjacent to the radically reactive double bond [89]. Poly-diallyldimethylammonium salt (poly-DADMAC), one of the best known cyclopolymers, was reported by Butler in 1951 [90,91].

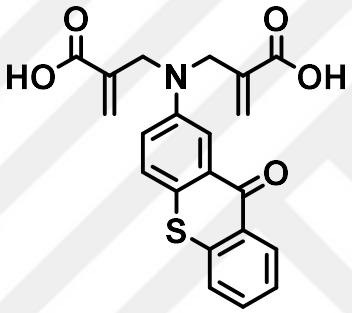


Figure 1.12. Structure of thioxanthone-functionalized 1,6-heptadiene monomeric PI [59].
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In the literature the first PI which has 1,6-heptadiene structure was reported by Eren et al [59] (Figure 1.12). The synthesized thioxanthone functionalized 1,6-heptadiene monomeric PI was also a one component PI due to its hydrogen donating tertiary amine functionality. In addition to this, the synthesized monomeric PI showed a better migration stability as compared to thioxanthone.

2. OBJECTIVES

The aim of this study is to synthesize novel cyclopolymerizable and cyclopolymeric (first PI with a cyclic backbone in the literature) photoinitiators, combining the high reactivity of two commercial water soluble photoinitiators from the Irgacure family with advantageous properties of cyclopolymerizable and/or cyclic structures. These properties include high reactivity, water solubility, migration stability, less shrinkage during polymerization and excellent thermal stabilities. Three novel monomeric PIs were synthesized by the attachment of diallyl amine group to commercial PIs I2959 and I184. Two of the synthesized monomeric PIs were in the neutral form and one was a quaternary ammonium salt. One polymeric PI was synthesized by the copolymerization of one of the synthesized monomeric PIs with DADMAC. These PIs are characterized and evaluated using NMR, FTIR, GPC, TGA, photo-DSC and UV-vis spectroscopy.

3. CYCLOPOLYMERIZABLE AND CYCLOPOLYMERIC PHOTOINITIATORS FROM DIALLYL AMINE AND α-HYDROXY KETONES

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3.1. Introduction

In this chapter, synthesis and characterization of three novel (two cyclopolymerizable and one cyclopolymeric) photoinitiators are described. Cyclopolymerizable photoinitiators (DAA-I2959 and DAA-I184) were synthesized by attachment of DAA to I2959 or I184. The water soluble cyclocopolymeric PI, p-DADMAC-*co*-DAA-I2959-QS (first PI with a cyclic backbone in the literature) was synthesized by radical copolymerization of DAA-I2959 with DADMAC. The photoinitiation efficiencies of these PIs for the photopolymerization of PEGDA (M_n = 575 D) or HEMA were investigated. The ability of DAA-I2959 to be used as a hydrogen donor for a Type II photoinitiating system was also determined. The solubility, UV absorbance, photolysis, migration and thermal stabilities of the synthesized PIs were investigated.

3.2. Experimental

3.2.1. Materials and Characterization

3.2.1.1. Materials. 1-Hydroxycyclohexyl phenyl ketone (Irgacure 184), 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959), acryloyl chloride, diallylamine, diallyldimethylammonium chloride (DADMAC, 65 wt% aqueous solution), 2-hydroxyethyl methacrylate (HEMA), poly(ethylene glycol) diacrylate (PEGDA, M_n = 575 D), 2,2′-azobis(2-methylpropionamidine)dihydrochloride (V50), ethyl 4-(dimethylamino)benzoate

(EDB), thioxanthone (TX) and the other reagents and solvents were obtained from Aldrich Chemical Co. (St Louis, MO) and used without purification. Bis-(4-tert-butylphenyl)-iodonium hexafluorophosphate (Iod or Speedcure 938) was obtained from Lambson Ltd. 2-(4-(2-Hydroxy-2-methylpropanoyl)phenoxy) ethyl 4-methylbenzenesulfonate (I2959-Ts) and 1-benzoylcyclohexyl acrylate was synthesized according to the literature procedures [92,93].

3.2.1.2. Characterization. NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer with deuterated methanol (MeOD) or chloroform ($CDCl_3$) as solvent. 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.

3.2.2. Synthesis of PIs

3.2.2.1. Synthesis of DAA-I2959. I2959-Ts (0.1811 g, 0.48 mmol) and diallylamine (0.4045 g, 4.16 mmol) in an ethanol (0.6 mL)/water (0.12 mL) mixture were stirred at 80 °C for 3 h. Then, the temperature was decreased to 40 °C and 1.4 mL NaOH (30 wt%) was added. After stirring at 40 °C for 3 h, the organic phase was separated and the aqueous phase was extracted with dichloromethane (DCM) (3 × 5 mL). The organic phases were combined and extracted with water (3 × 5 mL), dried over anhydrous sodium sulfate, filtered and the solvent was removed under reduced pressure. The pure product was obtained as a light yellow oil in 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.61 (s, 6H, CH_3), 2.89 (t, 2H, CH_2-N), 3.20 (d, 4H, N-CH_2-CH=), 4.07 (t, 2H, O-CH_2), 5.17 (m, 4H, CH=CH_2), 5.86 (m, 2H, CH=CH_2), 6.92 (d, 2H, Ar-CH), 8.03 (d, 2H, Ar-CH) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, δ): 28.83 (CH_3), 51.79 (CH_2-N), 57.79 (N-CH_2), 66.72 (O-CH_2), 75.98 (*C*-C=O), 114.14 (CH=*C*H_2), 118.21 (O=C-*C*-Ar), 126.02 (*C*H-Ar), 132.20 (*C*H-Ar-O), 135.52 (*C*H=CH_2), 162.82 (Ar-*C*-O), 202.69 (C=O) ppm.

FTIR (ATR): 3434 (O-H), 1666 (C=O), 1599 and 1571 (C=C) cm^{-1}.

Q-Tof-MS (m/z): calcd for $C_{18}O_3NH_{25}$, 303.18. Found: 304.19 $[M + H]^+$.

3.2.2.2. Synthesis of DAA-I184. 1-Benzoylcyclohexyl acrylate (107.6 mg, 0.4164 mmol) and diallylamine (309.5 mg, 3.1855 mmol) were stirred at room temperature for 48 h. Excess diallylamine was removed by washing with water. The crude product was purified by column chromatography (silica gel, hexane–ethyl acetate: 90/10) and the pure product was obtained as a transparent oil in 35% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.30 (m, 1H, CH_2-C*H*$_2$), 1.62 (m, 4H, CH_2-C*H*$_2$ and m, 1H, CH_2-C*H*$_2$), 1.89 (t, 2H, C-CH_2), 2.34 (m, 2H, C-CH_2), 2.46 (m, 2H, O=C-CH_2), 2.67 (t, 2H, CH_2-C*H*$_2$-N), 3.04 (d, 4H, N-C*H*$_2$-CH), 5.14 (d, 2H, =CH_2), 5.78 (m, 4H, C*H*=CH_2), 7.38 (m, 2H, Ar-CH), 7.46 (m, 1H, Ar-CH), 7.97 (d, 2H, Ar-CH-C) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.57, 25.10 (*C*H_2-CH_2), 32.69 (C-*C*H_2), 32.90 (*C*H_2-C=O), 48.48 (N-*C*H_2), 56.83 (CH-*C*H_2-N), 86.27 (O-*C*), 117.84 (*C*H_2=CH), 128.44 (Ar-*C*), 128.65 (O=C-Ar-*C*), 132.41 (Ar-*C*), 135.28 (CH_2=*C*H-CH_2), 135.47 (O=C-*C*-Ar), 171.58 (O=*C*-O), 199.95 (O=*C*-Ar) ppm.

FTIR (ATR): 3458 (O-H), 3075, 2929 (C-H), 1731, 1682 (C=O) cm^{-1}.

3.2.2.3. Synthesis of Polymeric PI. DAA-I2959 (32.4 mg, 0.1068 mmol) and DADMAC (0.4272 mmol, 106.2 mg of 65 wt% aq. DADMAC solution) were added to a test tube. The total monomer concentration was adjusted to 10.5 M by adding water. Then the pH of the solution was adjusted to 1 with 6 M HCl solution and V50 (1.11 mg, 0.0041 mmol) was added. The tube was subjected to three freeze–evacuate–thaw cycles and placed in a 70 °C

oil bath. After 2–4 h, the copolymer was precipitated into hot acetone and dried under reduced pressure to give the product as a pinkish white solid in 21–25% yield.

3.2.3. UV-vis Spectroscopy Experiments

UV-vis measurements of the PIs in methanol and chloroform were carried out on a Carry 3 UV/vis spectrophotometer from Varian. For the photolysis experiment, methanol solution of DAA-I2959 was irradiated with a 320–500 nm light source (Omnicure 1000). Samples were taken at pre-determined time intervals, and the UV-vis spectra were recorded.

3.2.4. Photopolymerization Experiments

A TA Instruments DSC 250 differential photocalorimeter with an Omnicure 2000 mercury lamp light source (320–500 nm or 400–500 nm filter) was used for photopolymerization experiments. The HEMA or PEGDA (M_n = 575 D) monomer (3–4 mg) containing 0.1, 1 or 5 wt% of PIs or the references were exposed to irradiation at 25–40 °C under nitrogen. The heat flow was monitored as a function of time, and the polymerization rate was calculated using the equation [94]

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

where Q/s is the heat flow per second, M is the molar mass of the monomer, n is the number of double bonds per monomer molecule, ΔH_p is the heat evolved in the reaction and m is the mass of the monomer in the sample. The theoretical heat for the total conversion of methacrylate and acrylate double bonds are 55 and 86.5 kJ mol^{-1}.

3.2.5. Migration Stability

PEGDA (M_n = 575 D) was photopolymerized in the presence of I2959 (1 wt%) and DAA-I2959 (1 wt%) via UV irradiation for 1 h in glass vials under air. Because p-DADMAC-co-DAA-I2959- QS is not soluble in PEGDA, a formulation containing water (95 : 5 : 300 PEGDA : PPI: water, wt : wt : wt) was used. The crosslinked polymers were immersed in 25 or 50 mL methanol for 3 days. The percentages of the extracted PIs were determined by UV–vis spectroscopy [95].

3.3. Results and Discussion

3.3.1. Synthesis of DAA-I2959, DAA-I184 and p-DADMAC-*co*-DAA-I2959-QS

Two novel polymerizable photoinitiators, DAA-I2959 and DAA-I184, were prepared by attaching diallyl groups to I2959 and I184 (Figure 3.1). DAA-I2959 was synthesized in two steps: formation of I2959-Ts from the reaction of I2959 and tosyl chloride [92] followed by the nucleophilic substitution reaction of diallyl amine with I2959-Ts in the presence of sodium hydroxide. This PI was obtained in a yield of 88% as an oil. The second PI, DAA-I184, was also synthesized in two steps: preparation of acrylate ester derivative I184 [93] followed by its Michael addition reaction with diallyl amine without the catalyst. DAA-I184 was obtained as a transparent oil in 35% yield.

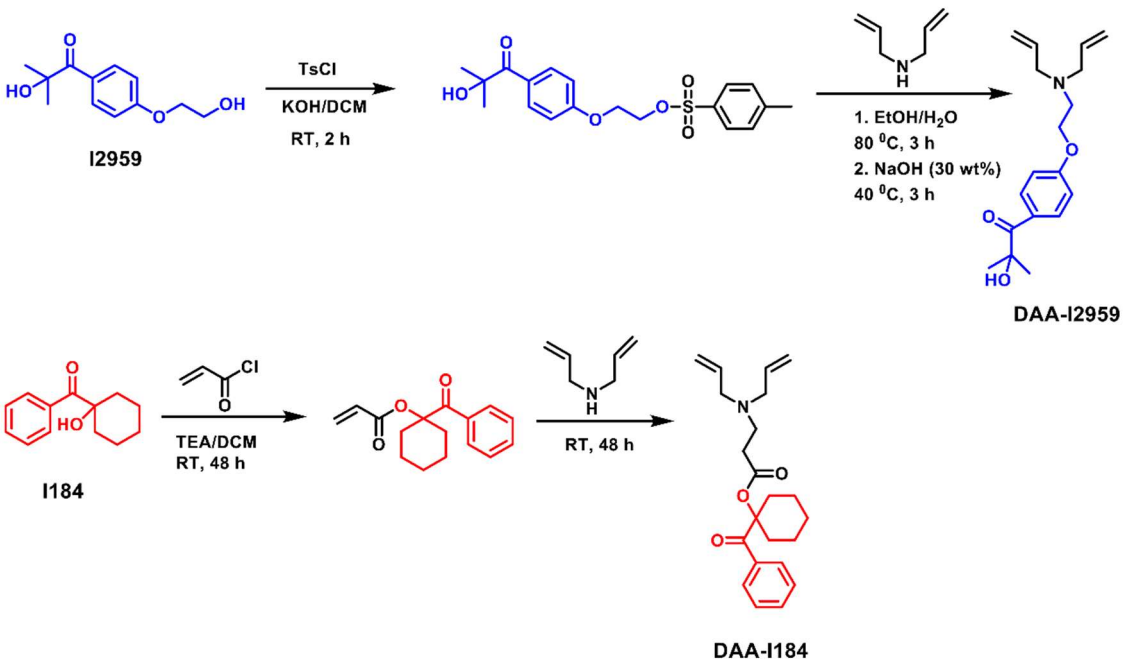


Figure 3.1. Synthesis of cyclopolymerizable PIs.

The ^{1}H NMR spectra of DAA-I2959 and DAA-I184 together with the intermediates, I2959-Ts and acrylate ester derivative of I184, indicate I2959 or I184 substitution on DAA (Figure 3.2, Figure 3.3 and Figure 3.4). The ^{13}C NMR spectra of the PIs are consistent with

their structures (Figure 3.5 and Figure 3.6). The FTIR spectrum of DAA-I2959 shows a ketone C=O peak at 1666 cm^{-1}, similar to I2959 (Figure 3.7). In the FTIR spectrum of DAA-I184, the ketone and ester C=O absorb at 1682 and 1731 cm^{-1}, compared to only one ketone C=O of I184 absorbing at 1669 cm^{-1}. Also, the characteristic OH stretching peak of I184 disappears (Figure 3.8).

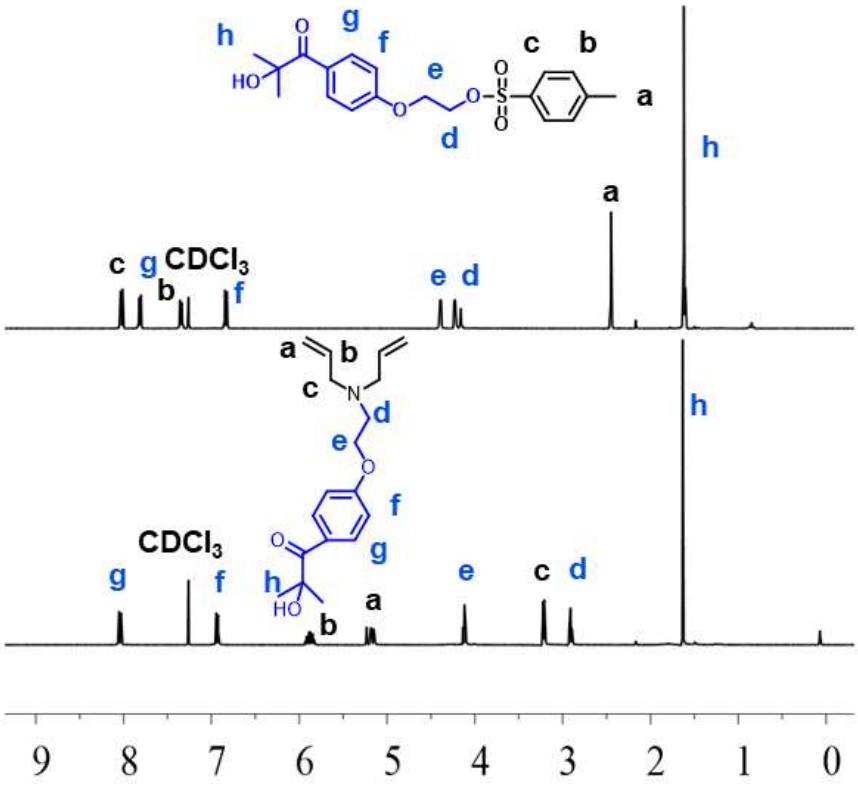


Figure 3.2. ^{1}H NMR spectra of I2959-Ts and DAA-I2959.

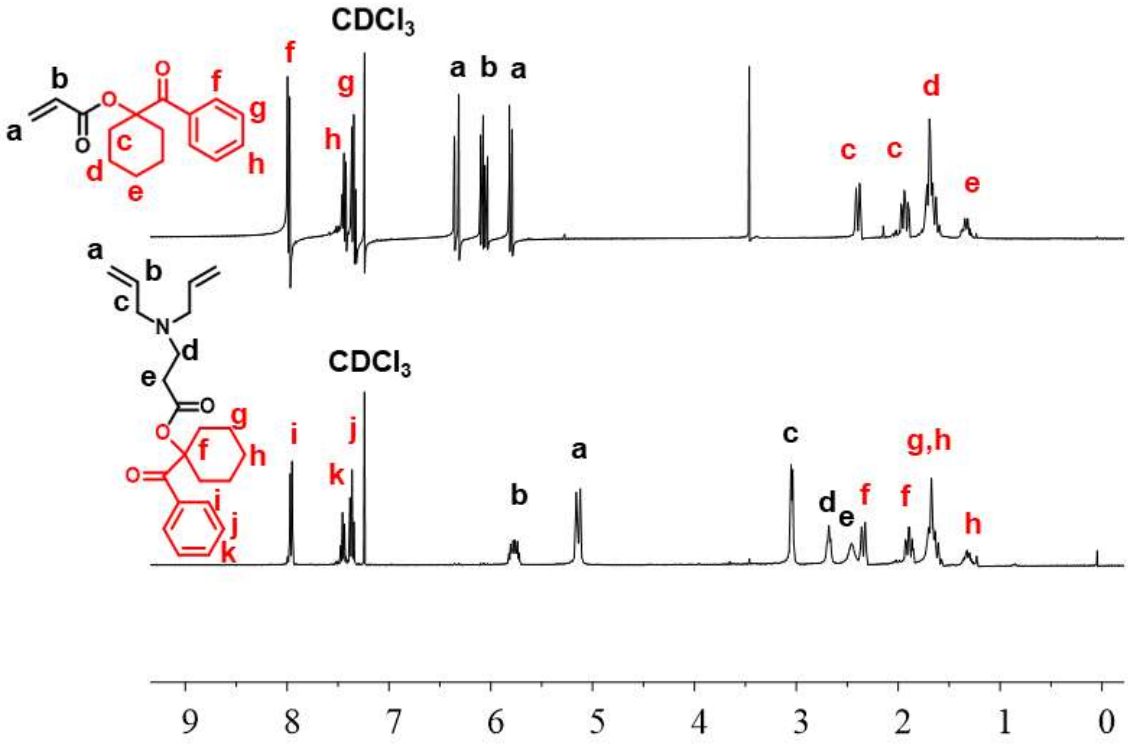


Figure 3.3. ^{1}H NMR spectra of acrylate ester of I184 and DAA-I184.

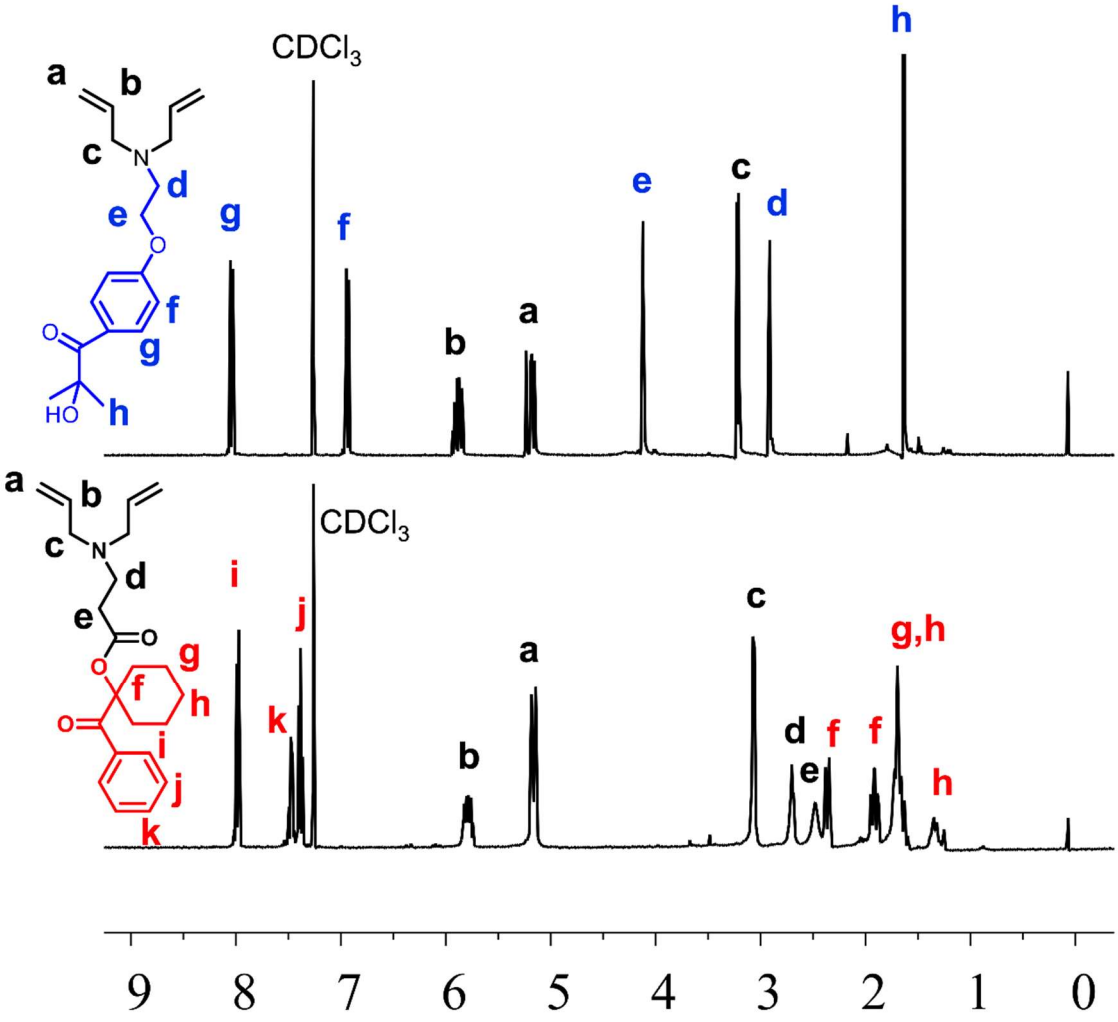


Figure 3.4. ^{1}H NMR spectra of DAA-I2959 and DAA-I184.

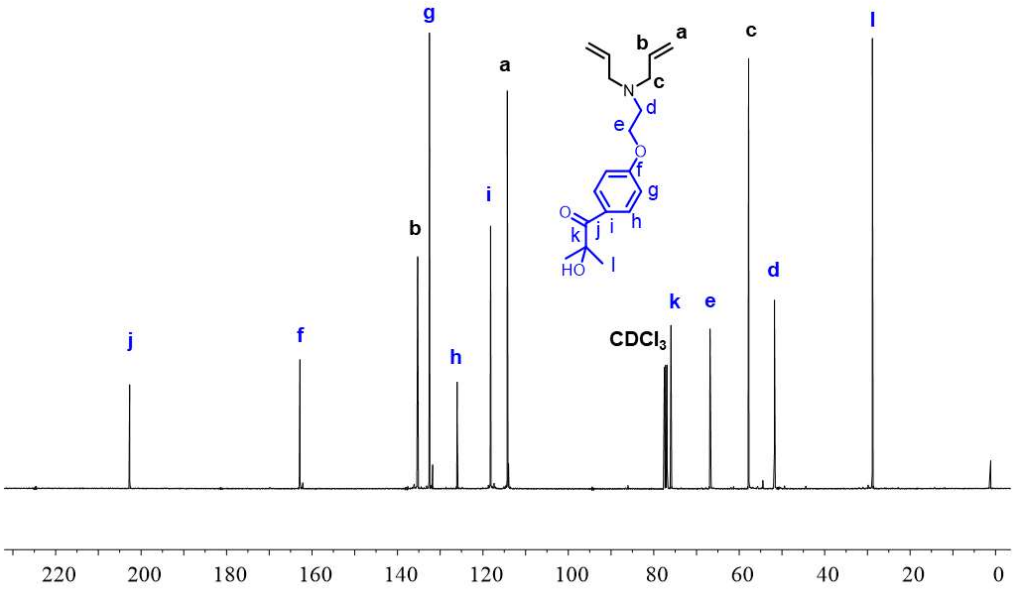


Figure 3.5. ^{13}C NMR spectrum of DAA-I2959.

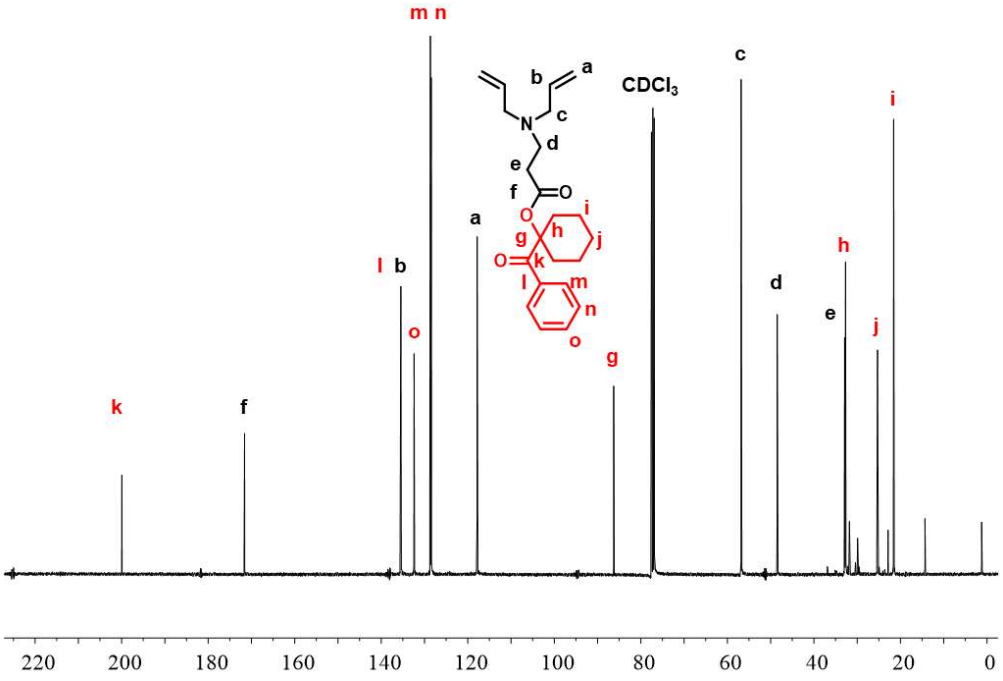


Figure 3.6. ^{13}C NMR spectrum of DAA-I184.

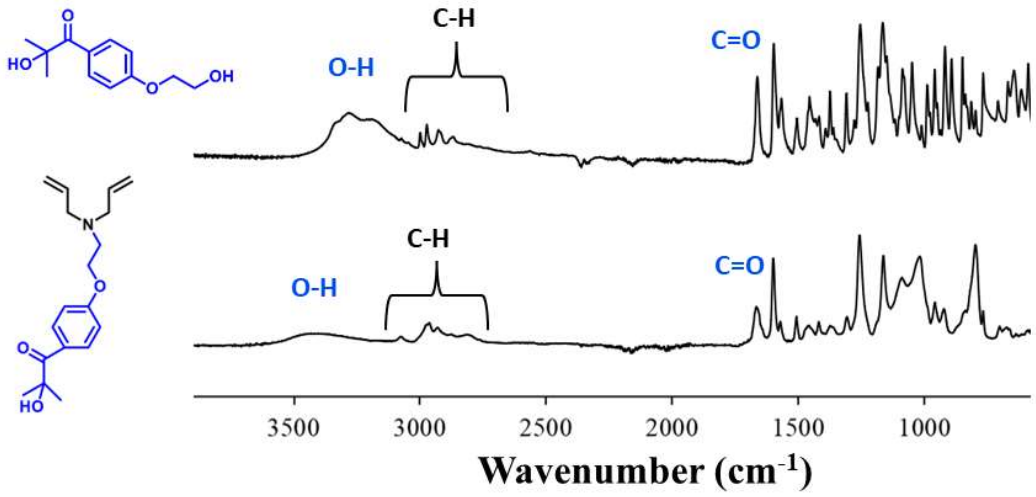


Figure 3.7. FTIR spectra of DAA-I2959 and I2959.

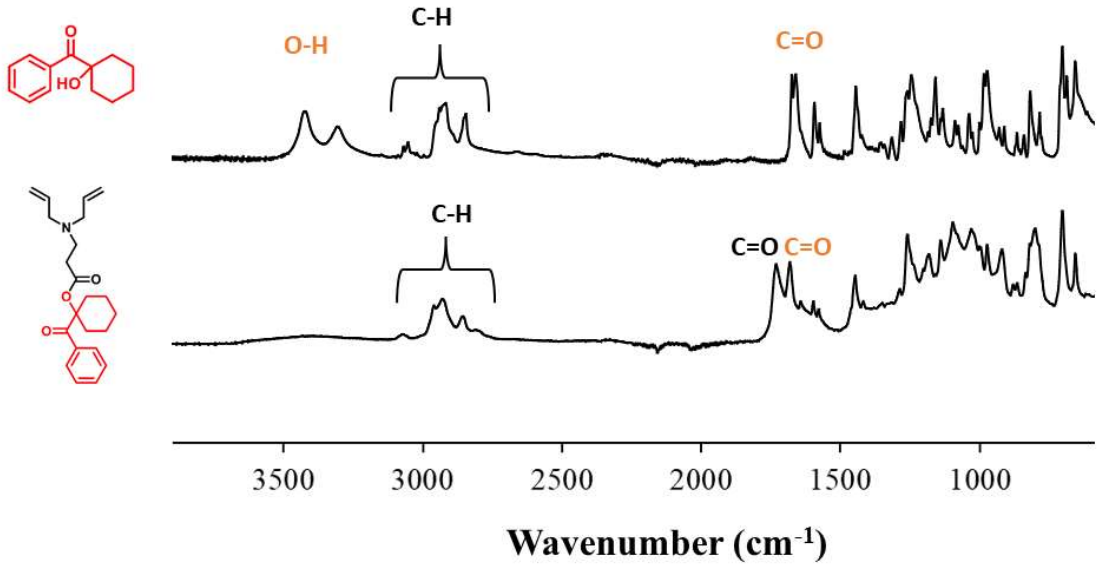


Figure 3.8. FTIR spectra of DAA-I184 and I184.

In general, N,N-diallylamine monomers give low molecular weight polymers due to the degradative chain transfer reaction which occurs by abstraction of an α-hydrogen atom of the allyl group of the monomer with radicals to generate a stable allyl radical [96,97]. The polymerization rate and molecular weight of these polymers can be increased by the protonation of amines to give quaternary ammonium salts. This can be achieved by

conducting the polymerization in an acidic medium. The protonation of monomers increases the α-C–H bond strength and hence decreases the chain transfer. Therefore, in order to obtain high molecular weight and a water soluble PPI, thermal copolymerization of DAA-I2959 with DADMAC in 20: 80 mol% ratio was investigated in aqueous solution in the presence of acid (HCl) using V50 as the initiator (Figure 3.9). The polymer (p-DADMAC-co-DAA-I2959-QS) was purified by precipitation into hot acetone, and obtained in a moderate yield of 21–25% in 2–4 h. The M_n value of this polymer ranged from 40 000 to 60 000 D. We assume that the polymer has five-member ring units due to DADMAC and DAA-I2959 units [90,91].

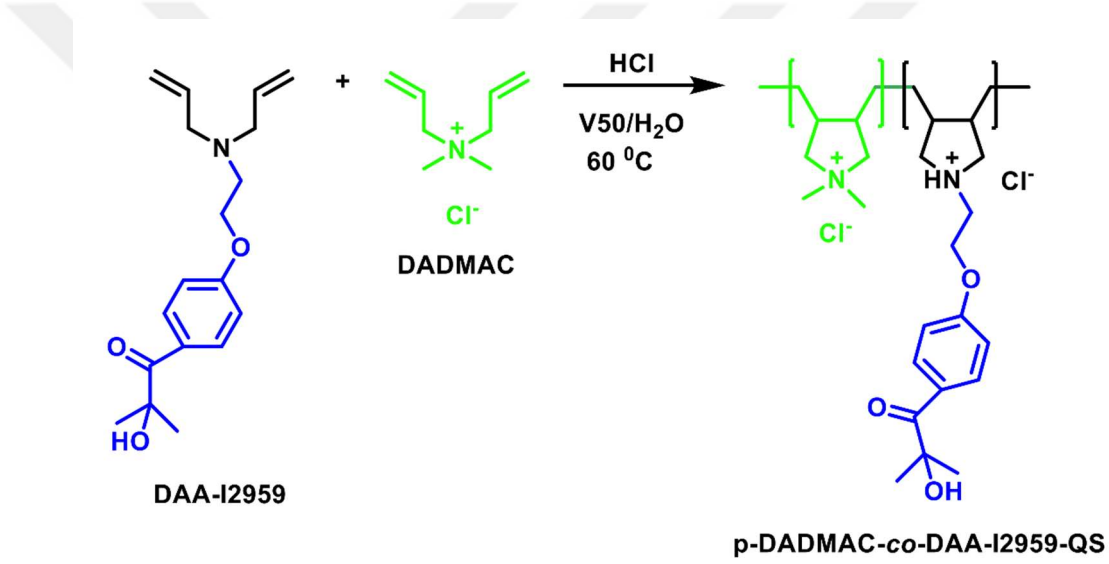


Figure 3.9. Synthesis of PPI.

^{1}H NMR of p-DADMAC-co-DAA-I2959-QS (Figure 3.10) shows peaks at around 1.5 ppm for backbone methylene protons in the cis and trans configurations of DADMAC. The peaks at 3.25 and 3.83 ppm are due to methyl and methylene protons attached to nitrogen. The aromatic protons show two peaks at 7.07 and 8.18 ppm. Since we did not detect the allyl pendant groups, the degree of cyclization is very high. Both double bonds are used up during the cyclization process and are not available for crosslinking. Also, chain termination via the abstraction of allylic protons of DAA-I2959 does not occur. The copolymer compositions were calculated from the ratio of peak areas of aromatic CH groups of DAA-I2959-QS units to methylene groups attached to the nitrogen of DADMAC (3.83 ppm) and found to be in

mol ratio of 25.4:74.6. Thus, the molar fractions of DAA-I2959-QS units in the copolymer were greater than those in the feed composition, indicating that DAA-I2959-QS is clearly much more reactive than DADMAC. The FTIR spectrum of the copolymer exhibited a broad absorption at 3360 cm^{-1} due to the presence of OH and NH groups and one intense peak at 1660 cm^{-1} due to stretching of the ketone carbonyl group (Figure 3.11).

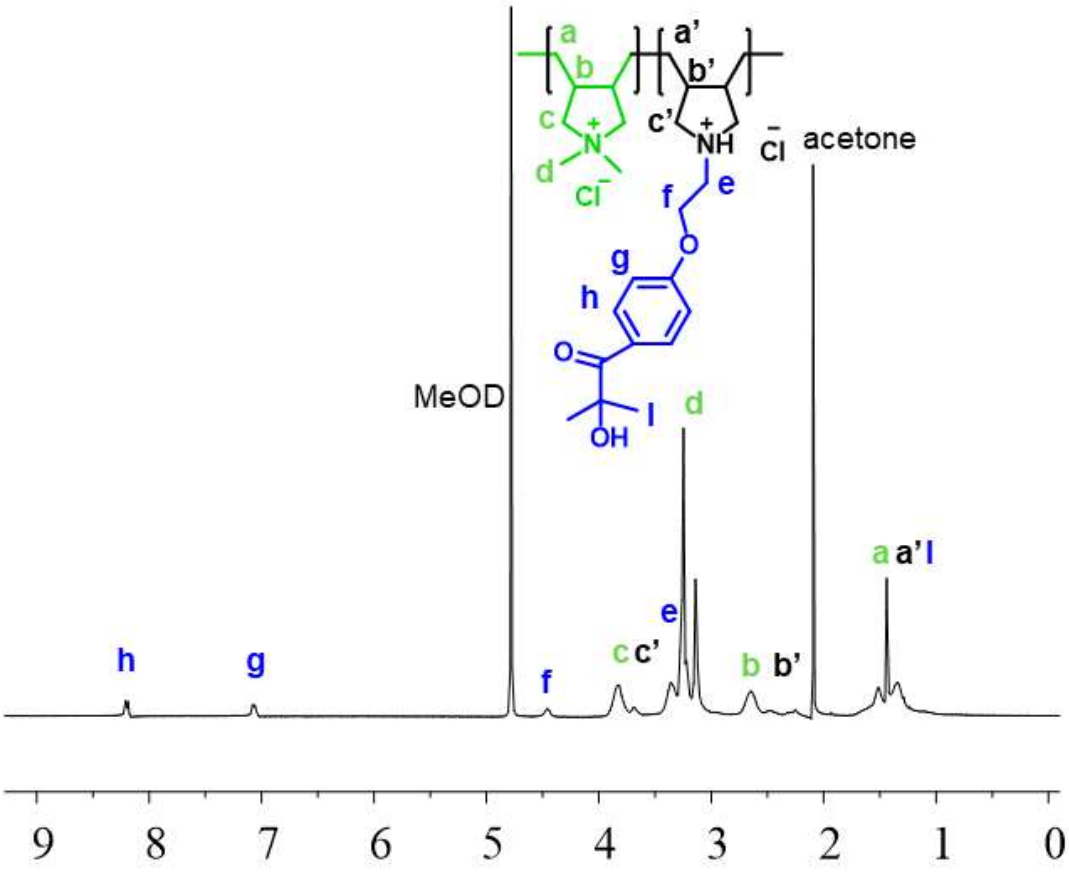


Figure 3.10. ^{1}H NMR spectrum of p-DADMAC-*co*-DAA-I2959-QS.

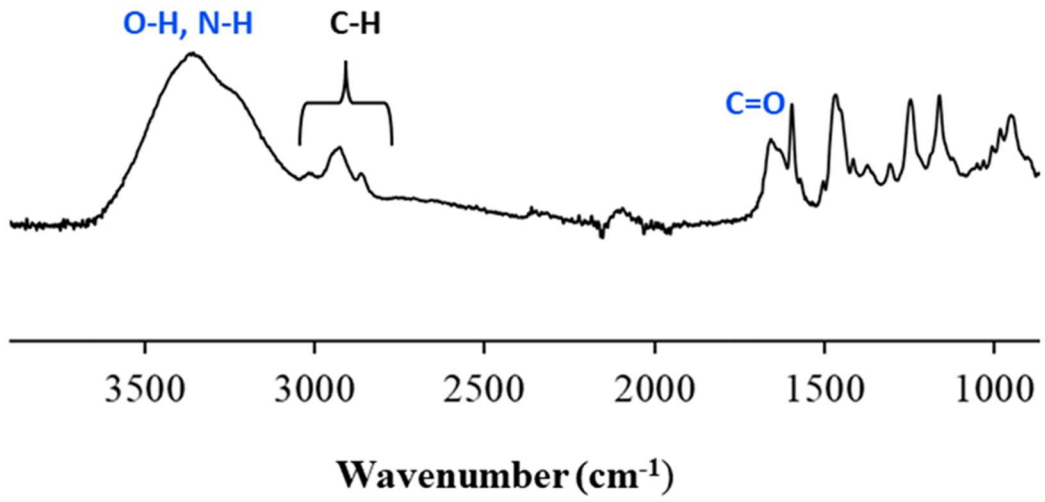


Figure 3.11. FTIR spectrum of p-DADMAC-*co*-DAA-I2959-QS.

Table 3.1 summarizes the solubility of the synthesized PIs and the commercial references. The synthesized polymerizable PIs are not soluble in water but the copolymer of one of them with DADMAC is highly soluble in water, making it suitable for water based formulations. DAA-I2959 and DAA-I184 are soluble in other polar and low polarity solvents such as diethyl ether, DCM and THF, whereas the copolymeric PIs are only soluble in water and methanol. Moreover, the novel neutral polymerizable PIs have good compatibility with HEMA and PEGDA.

Table 3.1. Solubilities of the synthesized and commercial PIs.

PI	H_2O	Methanol	Diethyl ether	CH_2Cl_2	THF	DMF
I2959	+	+	+	+	+	+
DAA-I2959	-	+	+	+	+	+
p-DADMAC-*co*-DAA-I2959-QS	+	+	-	-	-	-
I184	+/-	+	+	+	+	+
DAA-I184	-	+	+	+	+	+

Thermogravimetric analysis of DAA-I2959 shows a single step weight loss starting at around 200 °C while PPI showed a multistep weight loss due to the loss of moisture from the sample (9 wt% loss at 100 °C) and two step degradation (~35 wt% loss at 250–385 °C and 53 wt% loss at 385–485 °C), which involves dissociation of quaternary ammonium salts to form tertiary amines and methyl chloride, similar to the homopolymer of poly-DADMAC (Figure 3.12) [98].

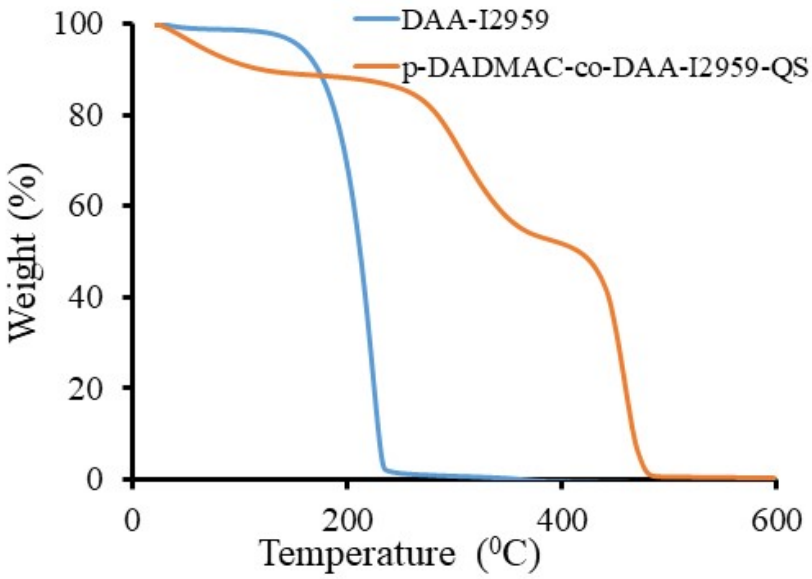


Figure 3.12. TGA spectrum of DAA-I2959 and p-DADMAC-*co*-DAA-I2959-QS.

3.3.2. Light Absorption

Absorption characteristics of both monomeric and polymeric PIs were examined by UV-vis spectroscopy (Figure 3.13, Figure 3.14, Table 3.2). DAA-I2959 shows a maximum absorption wavelength in the UV region at 272 nm in methanol and 280 nm in chloroform corresponding to the π–π* transition with an extinction coefficient of 14 705 and 16 333. These values were similar to the reference PI (Table 3.2, Figure 3.13), I2959 (λ_{max} = 272 nm and ε = 13 359 in methanol), indicating that substitution of the DAA group causes almost no change in absorption properties. The polymeric PI showed a slight shift to lower wavelength absorption (λ_{max} = 266 nm) compared to DAA-I2959 and I2959 which can be attributed to

the replacement of electron donating N (in DAA-I2959) and O (in I2959) atoms by electron withdrawing quaternary ammonium N. This PI also has an effective extinction coefficient (ε =8000) which is roughly consistent with the order of magnitude estimated from the concentration of DAA-I2959 units in the polymer. The high water solubility and reasonably high extinction coefficient make this PI a good candidate for photopolymerizations in aqueous solutions. The maximum absorption wavelength and extinction coefficient of DAA-I184 were also similar to those of I184 (Figure 3.15). It is known that the photodissociation mechanism of I2959 involves $^{1}\pi\pi^{*} \rightarrow {}^{1}n\pi^{*} \rightarrow {}^{3}\pi\pi^{*} \rightarrow {}^{3}n\pi^{*}$ transitions and the last one is important for cleavage to the benzoyl and ketyl radicals [19]. A shoulder peak is observed for DAA-I184 at around 280 nm corresponding to the n–π* transition (Figure 3.14). However, no n–π* transition peak was observed for DAA-I2959 which may be due to the overlap with the intense π–π* transition peak.

Table 3.2. Absorption characteristics of DAA-I2959 and DAA-I184.

	Solvents	λ_{max} (nm)	ε (M^{-1} cm^{-1})
DAA-I2959	MeOH	272	14705
DAA-I2959	$CHCl_3$	280	16333
I2959	MeOH	272	13359
DAA-I184	MeOH	244	11625
I184	MeOH	244	11300[1]

[1]In acetone [99].

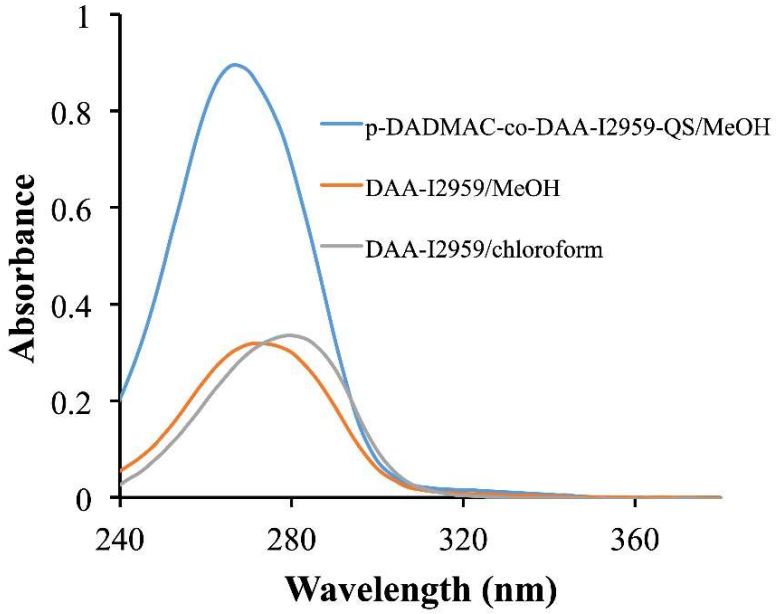


Figure 3.13. UV–vis absorption spectra of DAA-I2959 ($2x10^{-5}$ M) in MeOH and $CHCl_3$ and p-DADMAC-*co*-DAA-I2959-QS ($0.2x10^{-6}$ M) in methanol.

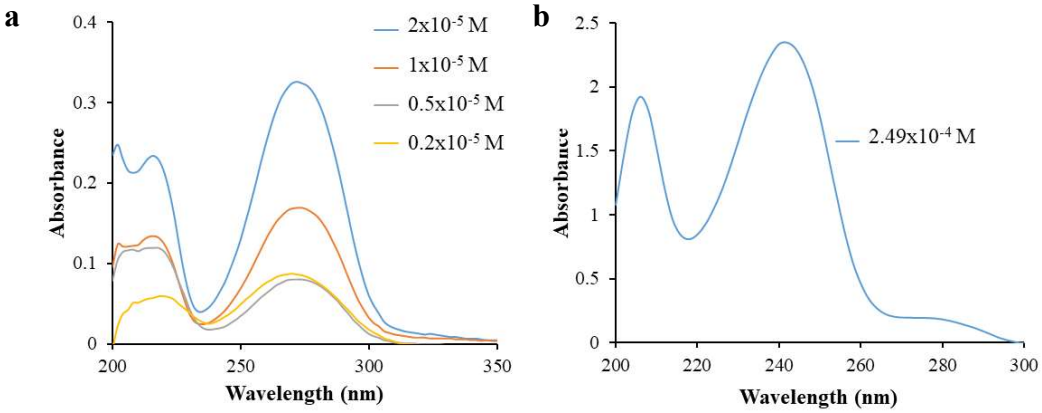


Figure 3.14. UV–vis absorption spectra of (a) I2959 and (b) DAA-I184 in methanol.

When DAA-I2959 was irradiated using a 320–500 nm light source, the intensity of the peak at 272 nm decreased and we also observed a new peak at about 251 nm, reaching a maximum absorbance in 246 s (Figure 3.15). Huo et al. indicated a similar peak during the

photolysis of a PEG based alpha-hydroxyalkylphenone photoinitiator and assigned to acetone generated by the cleavage of hydroxyketone [100].

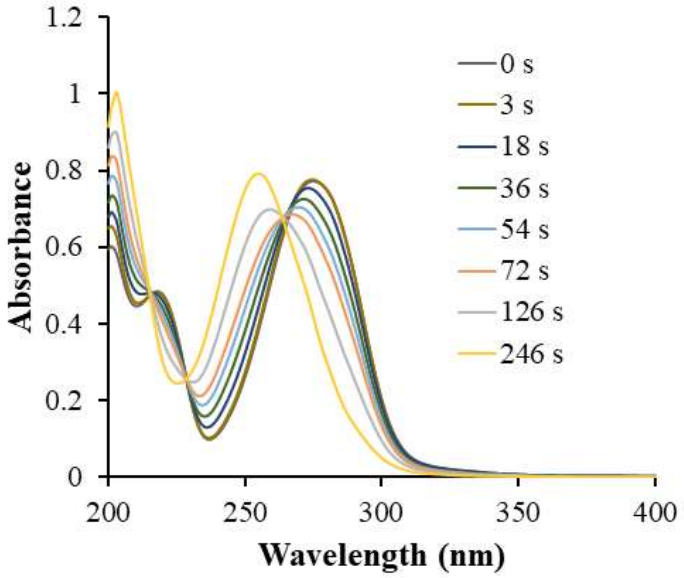


Figure 3.15. Photolysis of DAA-I2959 (4.12 x 10^{-5} M) in methanol using a 320-500 nm light source.

3.3.3. Photopolymerization

α-Hydroxy ketones undergo classical Type I cleavage upon irradiation to produce benzoyl and ketyl radicals which add to monomers to initiate free radical polymerization. The rate and efficiency of the cleavage process as well as the addition rate constant of the radicals to monomers are important factors for determining the photoinitiation efficiency of photoinitiators. Jockusch et al. investigated the effects of the substituent attached to benzoyl on α-cleavage, using derivatives of 2-hydroxy-2-methyl-1-phenyl propanone [18]. They also found that benzoyl radicals are less efficient at initiation compared to the counterradicals [17]. DAA-I2959 will give a monomer-bound benzoyl and free ketyl radicals upon irradiation (Figure 3.16). Based on this, [18] it is expected that ketyl radicals are more active as initiating moieties than benzoyl radicals which may give termination reactions. Therefore, this monomeric PI may have photoinitiating reactivity similar to I2959. The corresponding

polymeric PI, p-DADMAC-*co*-DAA-I2959-QS, with free ketyl radicals and polymer-bound benzoyl radicals having low termination capabilities due to the steric effect, is expected to give rise to high reactivity. However, DAA-I184 will represent a reverse situation in which the benzoyl radical is free and the counterradical is linked to the monomer. These monomer-linked ketyl radicals are expected to be less reactive compared to those obtained from DAA-I2959 due to the steric effect. Therefore DAA-I184 is expected to have lower photoinitiating reactivity compared to I184.

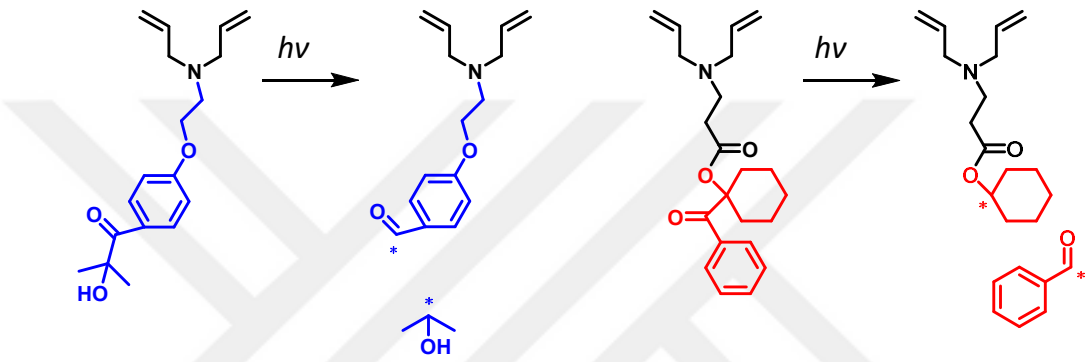


Figure 3.16. Type I cleavage of DAA-I2959 and DAA-I184 to generate benzoyl-ketyl radical pairs.

Also, it is reported that the replacement of the hydroxyl function of α-hydroxyketones with the ester functionality (e.g. acetate) either does not lead to α-cleavage [101] or does so very slowly [18]. On the other hand Eichler et al. state that methyl and acetyl substituted ones are capable of photoreduction in the presence of suitable hydrogen donors such as amines (N-methyldiethanol amine) to form ketyl and amine radicals [101]. Therefore, we expect that DAA-I184 generates radicals by α-cleavage to a minor extent, and/or the hydrogen transfer mechanism.

To determine the photoinitiation efficiency of the synthesized PIs, photo-DSC measurements were carried out under UV-vis (320–500 nm) and visible (400–500 nm) irradiation at 25 or 40 °C and the results were compared with those of I2959 and I184. DAA-I2959 alone, HEMA and/or PEGDA formulations containing 1 or 0.1 wt% PI were used. Figure 3.17 reports the rate of polymerization and the conversion of HEMA using DAA-I2959 as a function of time. As expected, increasing the DAA-I2959 concentration from 0.1

to 1 wt% resulted in a shorter induction time of photopolymerization without changing R_{pmax} and conversion values significantly. At the same PI concentrations, DAA-I2959 showed similar results (R_{pmax} = 0.0177 s^{-1}, t_{max} = 1.49 min, conversion = 98%) to I2959 (R_{pmax} = 0.0168 s^{-1}, t_{max} = 1.4 min, conversion = 98%).

The photoreactivity of DAA-I184 was also investigated in the polymerization of HEMA and PEGDA under UV light and compared with I184. As can be seen in Figure 3.18, DAA-I184 shows much slower kinetics compared to I184; DAA-I184 (R_{pmax} = 0.0303 s^{-1}, t_{max} = 0.33 min, conversion = 92% for PEGDA) and I184 (R_{pmax} = 0.182 s^{-1}, t_{max} = 0.03 min, conversion = 95% for PEGDA), which may stem from inefficient α-cleavage and/or the higher steric hindrance of the initiating alkyl radicals.

It is known that tertiary amines as donors and iodonium salts as acceptors form charge transfer complexes (CTC) which can generate radicals under near-UV or visible light irradiation to initiate free radical polymerization [33]. DAA-I2959 and DAA-I184 containing a tertiary amine functionality are expected to form CTC with Iod. Therefore, the photoinitiation efficiency of DAA-I2959 was also tested in the presence of Iod under UV and visible light irradiation. A decrease in induction time with no change in R_{pmax} and conversion under UV light irradiation was observed (Figure 3.17). However, when the polymerization was conducted under visible light a significant increase was observed in both R_{pmax} and conversion with a decrease in t_{max}, DAA-2959/Iod (R_{pmax} = 0.0027 s^{-1}, t_{max} = 10 min, conversion = 84%) compared to DAA-2959 (R_{pmax} = 0.0021 s^{-1}, t_{max} = 15.14 min, conversion = 69%) (Figure 3.19). This result indicates that in addition to the alkyl and benzoyl radicals generated through homolysis of I2959, aryl radicals generated by photolysis of CTC are contributing to the polymerization of HEMA.

In the literature, it was shown that acylphosphine oxide compounds containing a diallyl amino group were effective coinitiators in Type II photoinitiating systems due to their tertiary amine functionality [60]. The photoinitiation efficiency of 4-diallylaminoacyl phosphonic oxide derivatives/2,4-diethyl9H-thioxanthen-9-one (DETX) was found to be higher than that of the 4-dimethylaminobenzoic acid ester (EDAB)/DETX under LED@420 nm. This improvement in the photoinitiation efficiency was explained by the more stable

secondary free radical formation compared to the primary free radical formation on EDAB. Therefore, we expect our PIs to work as Type I only in UV light and also part of Type II initiating systems under UV or visible light depending on the absorbance of the Type II photoinitiator. We tested the efficiency of DAA-I2959 as a hydrogen donor in Type II photoinitiation systems using TX, and compared it with a common hydrogen donor, EDB (Figure 3.19). The photopolymerization of HEMA was investigated in the presence of TX/DAA-I2959 and compared with that of TX/ EDB and DAA-I2959 alone under visible light. The TX/ DAA-2959 (R_{pmax} = 0.0033 s^{-1}, t_{max} = 6.71 min, conversion = 72%) system is significantly more reactive than DAA-I2959 alone (R_{pmax} = 0.0021 s^{-1}, t_{max} = 15.14 min, conversion = 69%) system, indicating contribution of DAA-I2959 to TX as a hydrogen donor. Although TX/DAA-2959 and TX/EDB systems have similar R_{pmax} values, TX/EDB system has much lower t_{max} and higher conversion values. The lower reactivity of the TX/ DAA-I2959 system can be attributed to the steric hindrance of DAA-I2959.

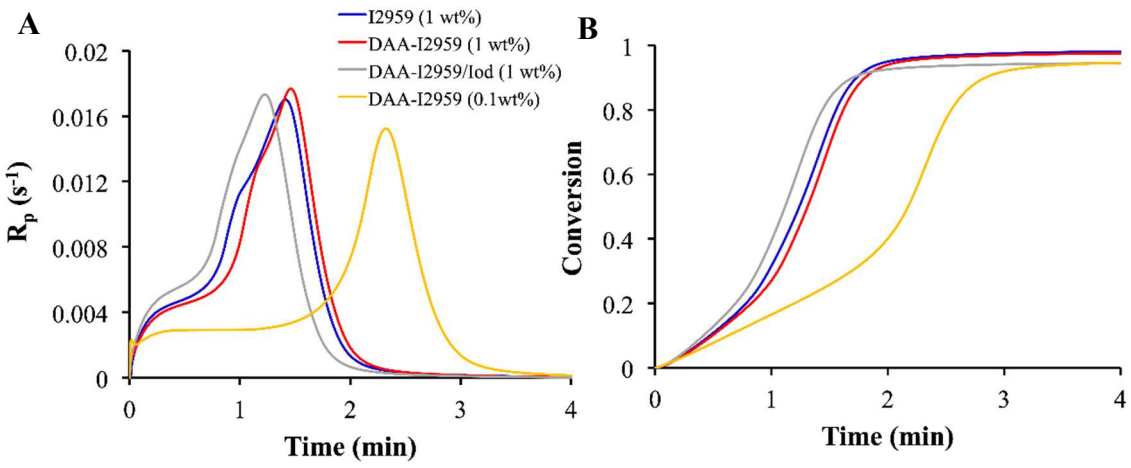


Figure 3.17. (a) Rate–time and (b) conversion–time plots for HEMA containing DAA-I2959 (0.1 wt%), DAA-I2959 (1 wt%), DAA-I2959 (1 wt%)/Iod (1 wt%), and I2959 (1 wt%) at 25 °C under nitrogen and 320–500 nm irradiation.

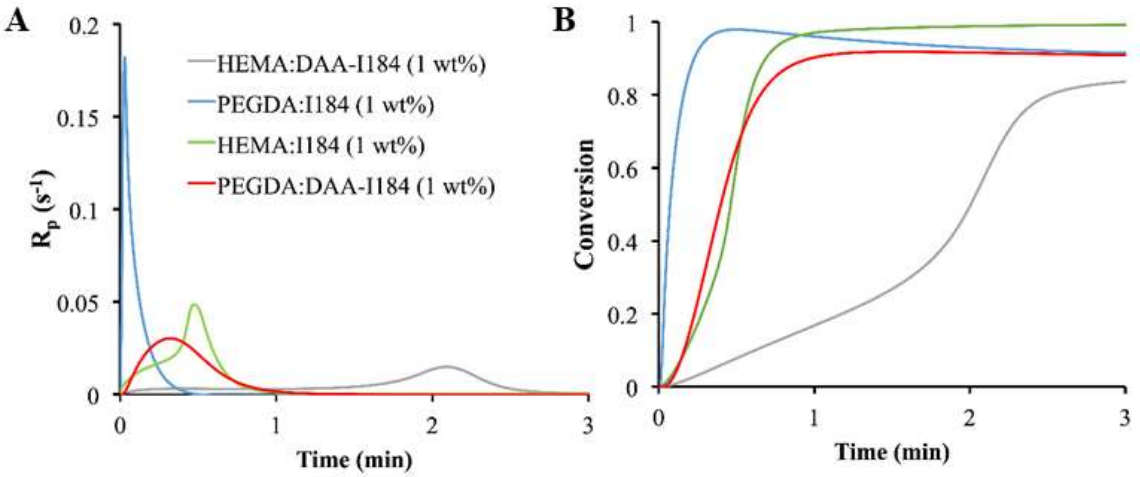


Figure 3.18. (a) Rate–time and (b) conversion–time plots for HEMA and PEGDA containing DAA-I184 (1 wt%) and I184 (1 wt%) at 25 °C under nitrogen and 320–500 nm irradiation.

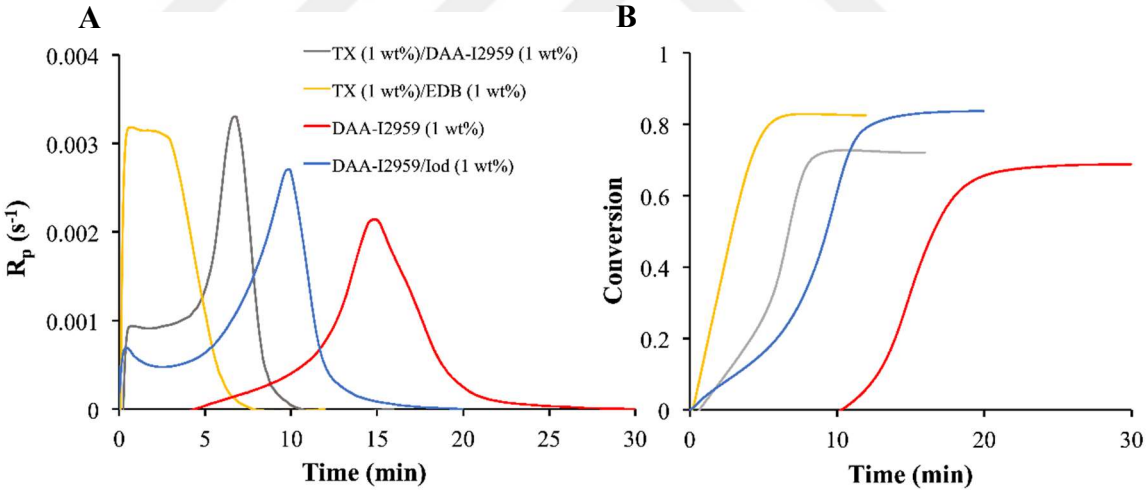


Figure 3.19. (a) Rate–time and (b) conversion–time plots for HEMA containing DAA-I2959 (1 wt%), DAA-2959/Iod (1/1 wt%), TX/DAA-I2959 (1/1 wt%) and TX/EDB (1/1 wt%) at 25 °C under nitrogen and 400–500 nm irradiation.

The reactivity of DAA-I2959 as a monomer was also investigated with photo-DSC under UV-vis (320–500 nm) irradiation. Figure 3.20 shows the exotherm recorded during the photopolymerization, indicating that DAA-I2959 shows polymerization upon irradiation,

although it is slow. This is attributed to the degradative chain transfer reaction observed for N,N-diallylamine monomers.

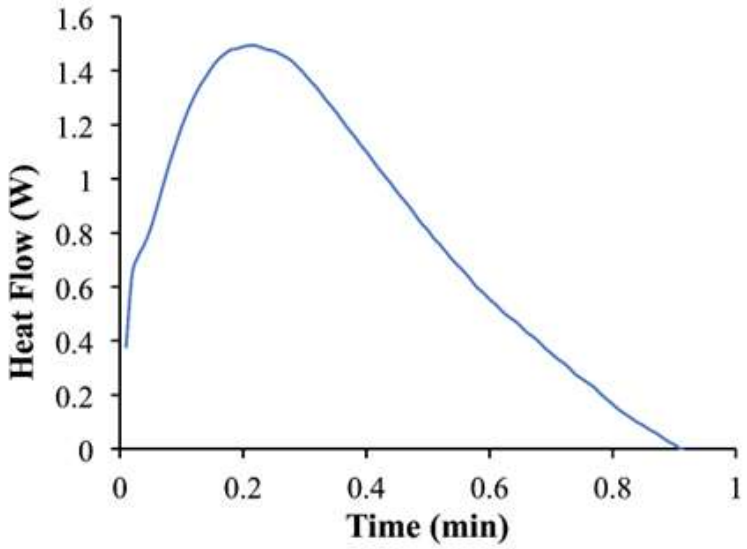


Figure 3.20. Heat flow-time plot for DAA-I2959 at 30 °C under nitrogen irradiated by 320-500 nm.

The photopolymerization performance of p-DADMAC-*co*-DAA-I2959-QS using UV-visible radiation (320–500 nm) under nitrogen was also examined in the polymerization of PEGDA using photo-DSC (Figure 3.21). A formulation containing 1.4 I2959- equivalent wt% of PI (5 wt% PI approximately contains 27 wt% I2959, calculated by NMR) was used. Since this amount of PI was not completely soluble in PEGDA, a small amount of water (2 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. This can be attributed to the higher viscosity of the PPI solution compared to that of the reference. At high viscosity, the initiation, propagation and termination reactions are diffusion limited; thus decreasing both the rate of polymerization and conversion [102]. However, when temperature is increased propagation and termination rate constants will increase, delaying auto-deceleration due to diffusion-limited propagation [103]. In order to see the effect of

temperature on rate and conversion, we performed polymerizations also at 40 °C. Both rate and conversion of the formulation containing PPI and I2959 slightly increased.

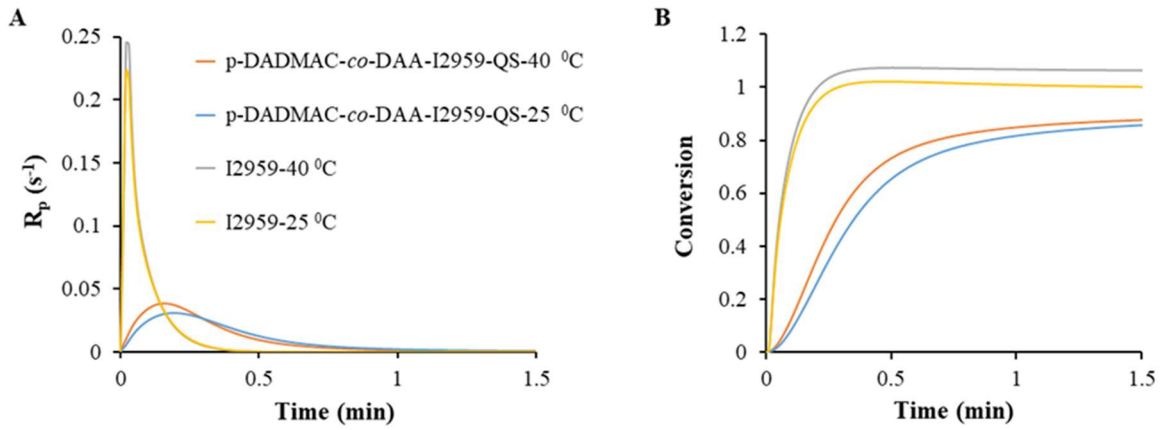


Figure 3.21. (a) Rate–time and (b) conversion–time plots for PEGDA containing p-DADMAC-*co*-DAA-I2959-QS (1.4 I2959-equivalent wt% of PI) and I2959 (1 wt%) at 25 and 40 °C under nitrogen and 320–500 nm.

In order to investigate charge transfer complex (CTC) formation between DAA-I2959 and Iod, UV-vis absorbances of HEMA containing DAA-I2959 (0.1 wt%) and DAA-I2959 (0.1 wt%)/Iod (0.5 wt%) were measured (Figure 3.22). A small bathochromic shift in the wavelength with the addition of Iod may be the indication of the CTC, supporting our DSC experiments (Figure 3.17 and Figure 3.19).

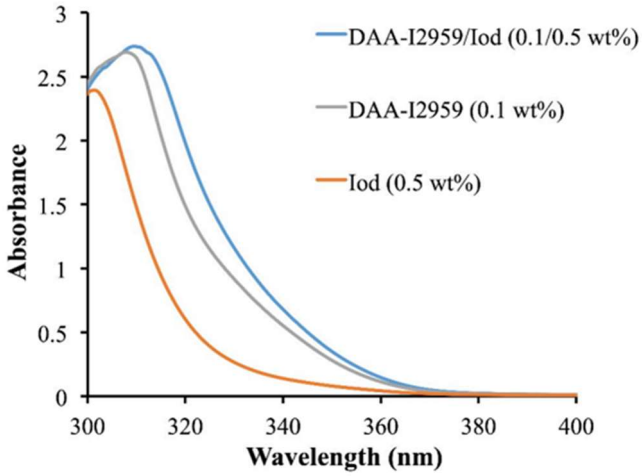


Figure 3.22. Absorption spectra of DAA-I2959/Iod (0.1/0.5 wt%), DAA-I2959 (0.1 wt%) and Iod (0.5 wt%) in HEMA.

3.3.4. Migration Stability

The migration stability of DAA-I2959 and p-DADMAC-*co*-DAA-I2959-QS was analyzed together with I2959. The residual PI in the cured PEGDA samples was extracted into methanol and determined by UV–vis absorption spectroscopy. It was found that the migration of DAA-I2959 is about 3.5 times lower than that of I2959 (Figure 3.23). The much higher migration stability of DAA-I2959 compared to I2959 is due to its incorporation into the network by polymerization, although this monomer has a low rate of polymerization alone due to the chain transfer reaction. Therefore, we can say that increasing polymerizability of DAA-I2959 and DAA-I184 by quaternization via acids will further increase the migration stability. Because p-DADMAC-*co*-DAA-I2959-QS was not soluble in PEGDA, photopolymerization was conducted in water, resulting in a hydrogel. The migration stability of p-DADMAC-*co*-DAA-I2959-QS was found to be very high (6.8 times lower than that of I2959) probably due to its macromolecular nature and incorporation into the PEGDA network (Figure 3.23).

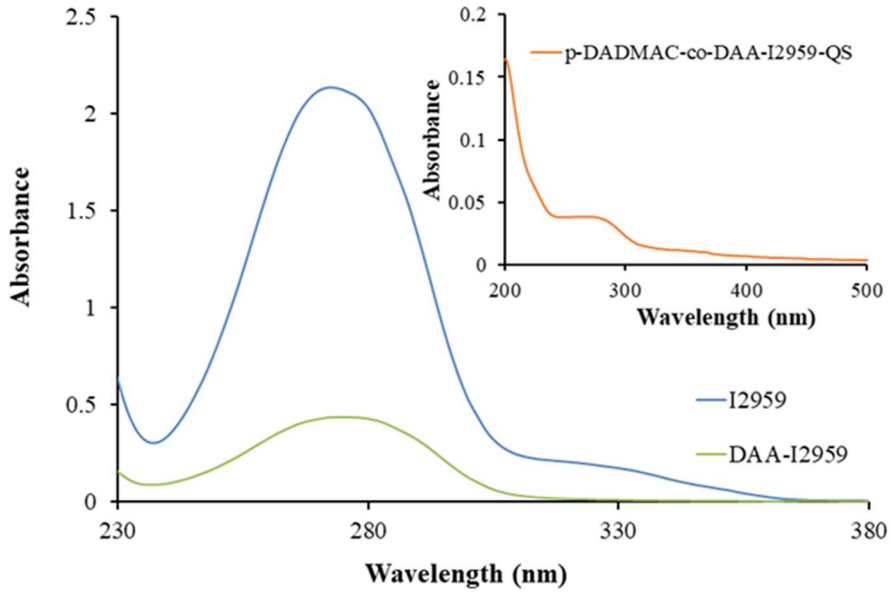


Figure 3.23. UV-vis absorption spectra of DAA-I2959 (1 wt%), I2959 (1 wt%) and p-DADMAC-co-DAA-I2959-QS (2.2 equivalent wt% of DAA-I2959) extracted with methanol from PEGDA gels.

4. AN IRGACURE 2959-BASED WATER SOLUBLE DIALLYLAMMONIUM SALT PHOTOINITIATOR SYSTEM

4.1. Introduction

In the previous chapter, one of the monomeric PIs (DAA-I2959) was synthesized by attachment of diallyl amine to I2959 in the presence of a catalyst (sodium hydroxide). In this part, we report a novel water-borne, low migration monomeric photoinitiator system by attachment of DAA to I2959 without a catalyst. The catalyst was used in the previous work to eliminate the byproduct; however it can also polymerize to integrate into the final product without disturbing the desired properties. In this chapter, a water soluble, cyclopolymerizable photoinitiator system which is a mixture of Irgacure 2959-based diallylammonium salt and diallylammonium tosylate was obtained by attachment of diallyl amine to I2959 without using a base catalyst. It is also expected that this PI system can be used not only initiate polymerization but also impart antibacterial properties to the coatings. The photoinitiating reactivity of the novel monomeric PI system was studied under UV-visible light irradiation in the photopolymerization of HEMA and PEGDA by differential scanning photocalorimetry. The solubility, UV-visible absorption, photolysis and migration properties were investigated.

4.2. Experimental

4.2.1. Materials and Characterization

4.2.1.1. Materials. 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959, I2959), diallylamine (DAA), 2-hydroxyethyl methacrylate (HEMA), poly(ethylene glycol) diacrylate (PEGDA, M_n = 575 D) and the other reagents and solvents were obtained from Aldrich Chemical Co. (St. Louis, MO) and used without purification. 2-(4-(2-hydroxy-2-methylpropanoyl)phenoxy) ethyl 4-methylbenzenesulfonate (I2959-Ts) was synthesized according to a literature procedure [92].

4.2.1.2. Characterization. NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer with deuterated chloroform ($CDCl_3$) as solvent. IR spectra were obtained by using a Nicolet 6700 FT-IR spectrophotometer. UV-vis spectra were recorded on a Varian®Cary 3 spectrometer. A 320–500 nm light source (Omnicure 1000) was used to irradiate the methanol solutions of DAA-I2959-QS/DAA-Ts for the photolysis experiments.

4.2.2. Synthesis of DAA-I2959-QS/DAA-Ts

I2959-Ts (0.1086 g, 0.29 mmol) and diallylamine (0.224 g, 2.31 mmol) in dry DMF (1 mL) was stirred at 100 °C for 6 h. The crude product was washed with petroleum ether. The product was obtained as a light brown oil.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.58 (s, 6H, CH_3), 2.33 (s, 3H, CH_3-Ar), 2.85 (NH), 3.56 (dd, 2H, CH_2-N, 4H, CH=CH_2), 3.83 (m, 4H, N-CH_2-CH=), 4.54 (s, 2H, O-CH_2), 5.35 (dd, 4H, CH=CH_2), 5.54 (dd, 4H, CH=CH_2), 5.91 (ddt, 2H, CH=CH_2), 6.05 (m, 2H, CH=CH_2), 6.90 (d, 2H, Ar-CH), 7.14 (d, 2H, CH_3-Ar-CH), 7.70 (d, 2H, CH-Ar-SO_3), 8.02 (d, 2H, Ar-CH) ppm.

^{13}C NMR (100 MHz, $CDCl_3$, δ):21.45 (CH_3), 28.70 (CH_3-Ar), 48.55 (CH_2-CH), 51.28 (CH_2-N+H), 55.88 (HN+-CH_2), 63.45 (O-CH_2), 76.31 (HO-C), 114.31 (O=C-C), 123.99 (C-Ar), 125.95 (CH-CH_2), 127.95 (CH-CH_2), 129.03 (Ar-CH-C), 132.59 (CH=CH_2), 140.49 (CH_3-C-Ar), 142.07 (C-SO_3), 161.13 (Ar-C-O), 202.77 (C=O) ppm.

FTIR (ATR): 3390 (O-H), 2984, 2809 (C-H), 1667 (C=O), 1119 (SO_2) cm^{-1}.

4.2.3. UV-vis Spectroscopy

Carry 3 UV/vis spectrophotometer was used for UV-vis measurements of DAA-I2959-QS/DAA-Ts in methanol. 320–500 nm light source (Omnicure 1000) was used to irradiate methanol solution of DAA-I2959-QS/DAA-Ts for the photolysis experiment.

4.2.4. Photopolymerization Experiments

During the photopolymerization experiments, HEMA (3-4 mg) containing 1 or 0.5 wt% of DAA-I2959-QS/DAA-Ts or I2959 was exposed to irradiation at 25 °C under nitrogen. For the calculation of the rate of the polymerization the following formula was used [94]

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

where Q/s represents heat flow per second, M represents the molar mass of the monomer, n represents the number of double bonds per monomer molecule, ΔH_p represents the heat evolved in the reaction and m represents the mass of monomer in the sample. The theoretical heat for the total conversion of a methacrylate double bond is 55 kJ mol^{-1}.

4.2.5. Migration Studies

The photopolymerization of PEGDA was performed in the presence I2959 (0.2 wt%) and DAA-I2959-QS/DAA-Ts (0.2 I2959-equivalent wt%) under air for 1 h in glass vials via 365 nm irradiation. The cross-linked polymers were soaked in 25 mL methanol for 3 days. UV-vis spectroscopy was used for the determination of the extracted PIs [95].

4.2.6. Preparation of Hydrogels

The formulations containing DAA-I2959-QS/DAA-Ts:PEGDA 5.0:95.0 (I2959 equivalent wt%:wt%) and I2959:PEGDA 5.0:95.0 (wt%:wt%) were prepared. Then water, 3 times the total weight of DAA-I2959-QS or I2959 and PEGDA, was added. The solutions were photopolymerized under air for an hour via 365 nm light source. The gels were washed with ethanol and water to remove residual monomers and photoinitiator and freeze-dried.

4.3. Results and Discussion

4.3.1. Synthesis and Characterization of DAA-I2959-QS/DAA-Ts

A monomeric PI (DAA-I2959-QS) was synthesized in two steps: i) preparation of I2959-Ts from the reaction between I2959 and tosyl chloride, ii) nucleophilic substitution of diallyl amine with I2959-Ts (Figure 4.1). This reaction gives a mixture of two monomers with quaternary ammonium functionality. One of them (DAA-I2959-QS) is protonated DAA-I2959 and the other one (DAA-Ts) is just p-toluene sulphonic acid salt of DAA, both of them with Ts counterion. The first one is the PI we wanted as desired, the presence of the second one (which does not contain I2959) does not prevent or hurt the working of the first one. Therefore, we did not attempt to separate the two products.

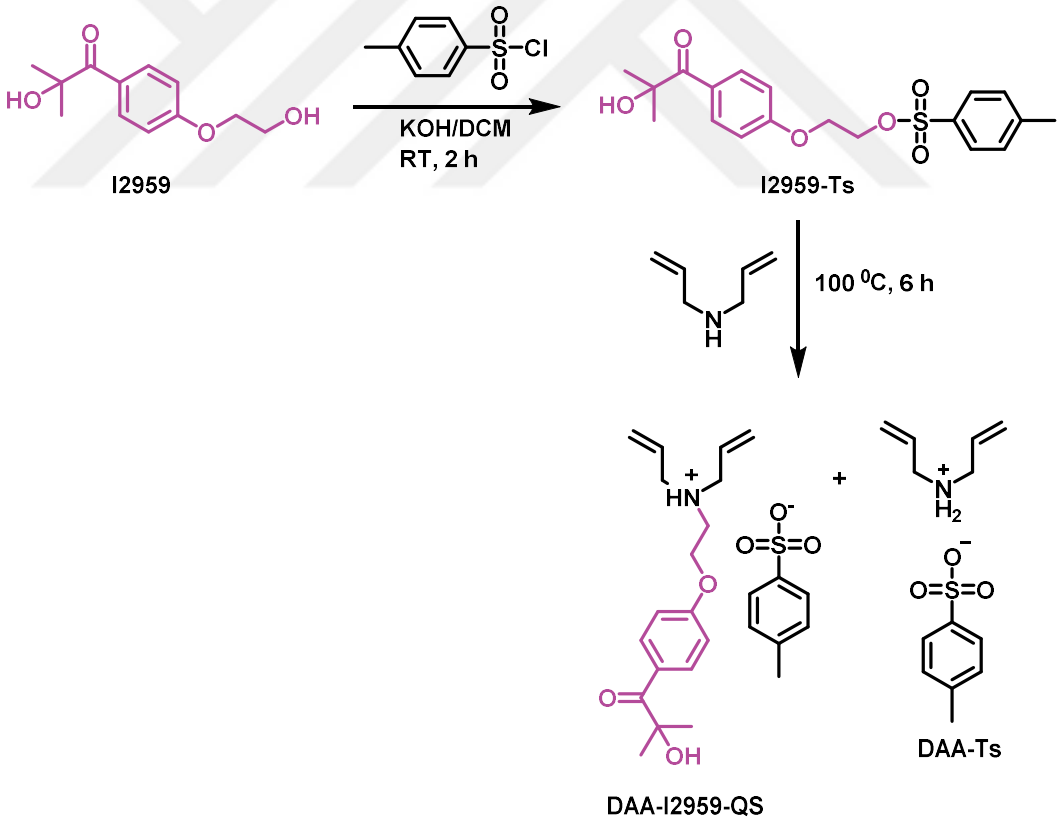


Figure 4.1. Synthesis of DAA-I2959-QS/DAA-Ts.

^{1}H NMR, ^{13}C NMR and FTIR were used to characterize DAA-I2959-QS/DAA-Ts product mixture (Figure 4.2, Figure 4.4, Figure 4.5). In order to identify the peaks of DAA-Ts in the product mixture ^{1}H NMR of DAA-Ts was also taken (Figure 4.3). ^{1}H NMR spectrum of the product mixture shown in Figure 4.2 indicated the presence of DAA-Ts as a component in the synthesized product mixture. The presence of aromatic protons of I2959 at 6.90 and 8.02 ppm and double bond protons at 5.35 ppm and 5.91 ppm indicate substitution of DAA with I2959. The peaks at 7.14 and 7.70 ppm correspond to aromatic protons of Ts counter ion. The integrals of the double bond protons of DAA-I2959-QS and DAA-Ts were used in order to calculate the ratio of the two components in the product mixture. The mole ratio of DAA-Ts to DAA-I2959-QS was found to be 1.7:1. The weight % of DAA-I2959-QS was also calculated as 50.3% in the mixture. The FTIR spectrum of DAA-I2959-QS/DAA-Ts was shown in Figure 4.4. NH and OH-stretching were observed at nearly 3400 cm^{-1} whereas carbonyl stretching was observed at 1667 cm^{-1} for the product mixture. Symmetric and antisymmetric S=O stretching were observed at 1119 and 1160 cm^{-1}. ^{13}C NMR spectra obtained for the product mixture was also consistent with the structure (Figure 4.5).

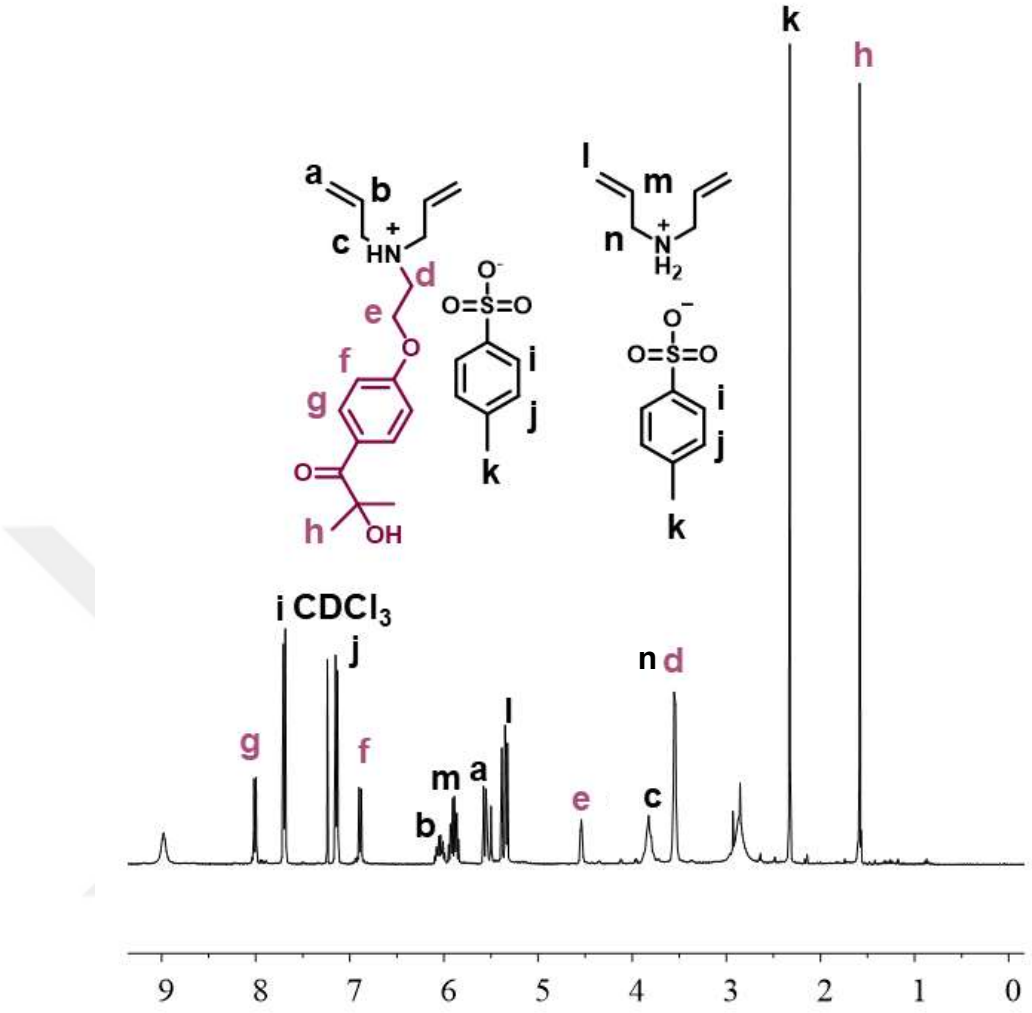


Figure 4.2. ^{1}H NMR spectrum of DAA-I2959-QS/DAA-Ts.

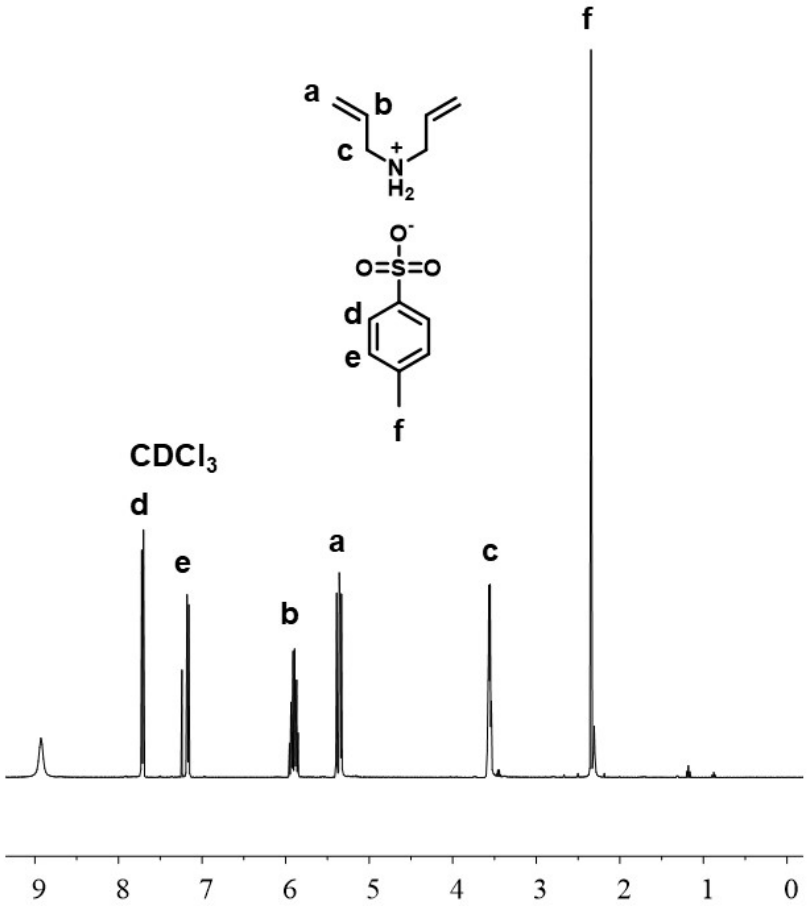


Figure 4.3. ^{1}H NMR spectrum of p-toluene sulphonic acid salt of DAA.

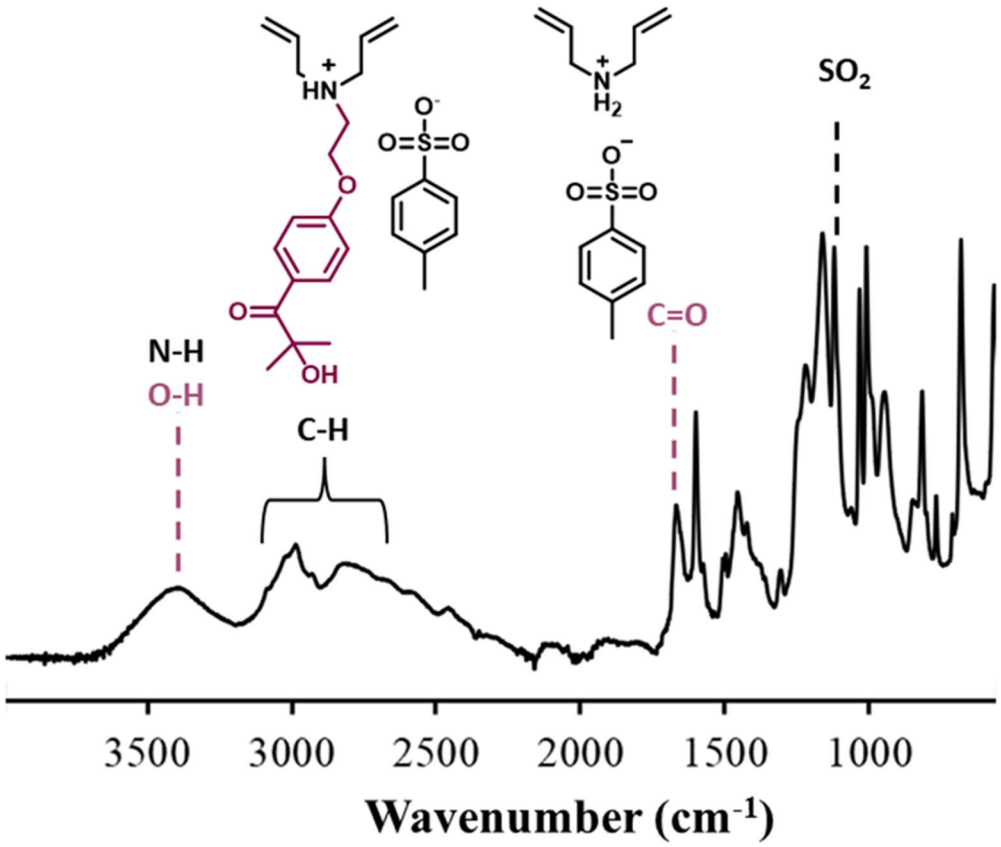


Figure 4.4. FTIR spectrum of DAA-I2959-QS/DAA-Ts.

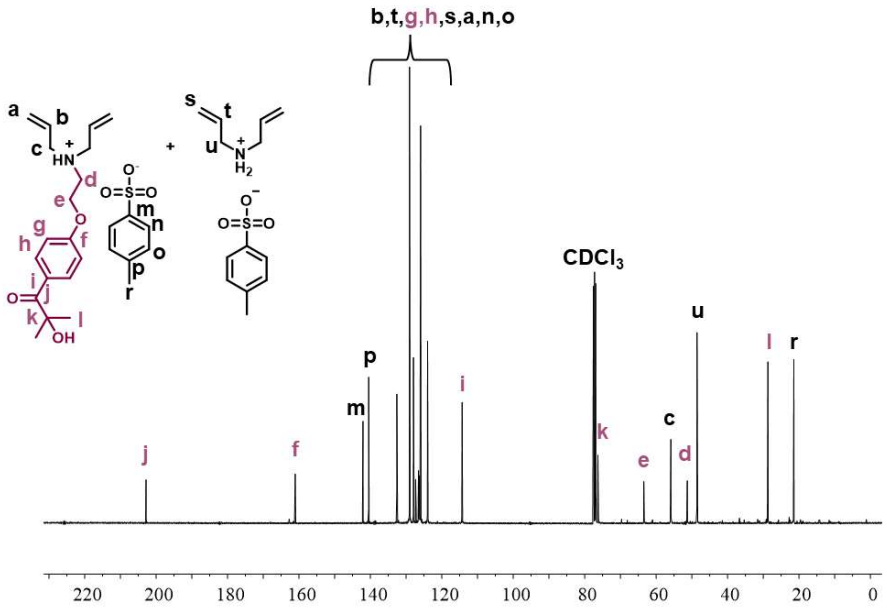


Figure 4.5. ^{13}C NMR spectrum of DAA-I2959-QS/DAA-Ts.

Table 4.1. Solubilities of DAA-I2959-QS/DAA-Ts in the selected solvents

PI	H_2O	Methanol	Diethyl ether	CH_2Cl_2	THF	DMF
DAA-I2959-QS/DAA-Ts	+	+	-	+	+	+

Table 4.1. summarizes the solubility characteristics of DAA-I2959-QS/DAA-Ts in the selected solvents. DAA-I2959-QS/DAA-Ts was soluble in polar protic solvents such as water and methanol. The product mixture was also soluble in methylene chloride, tetrahydrofuran and dimethylformamide whereas it is insoluble in diethyl ether.

4.3.2. Light Absorption

UV-vis spectroscopy was used for the investigation of the light absorption characteristics of DAA-I2959-QS/DAA-Ts product mixture (Table 4.2, Figure 4.6). For DAA-I2959-QS/DAA-Ts product mixture effective extinction coefficient, based on concentration of DAA-I2959-QS, was calculated as 15731. Since the extinction coefficient and λ_{max} values were similar to I2959, it can be concluded that the substitution of the DAA

group causes almost no change in absorption property of I2959. As in the case of DAA-I2959, n-π* transition was not observed for DAA-I2959-QS/DAA-Ts product mixture. The reason can be the overlap with the intense π-π* transition peak.

Table 4.2. Absorption characteristics of DAA-I2959-QS/DAA-Ts

PI	Solvents	λ_{max} (nm)	ε (M^{-1} cm^{-1})
DAA-I2959-QS/DAA-Ts	MeOH	269	15731

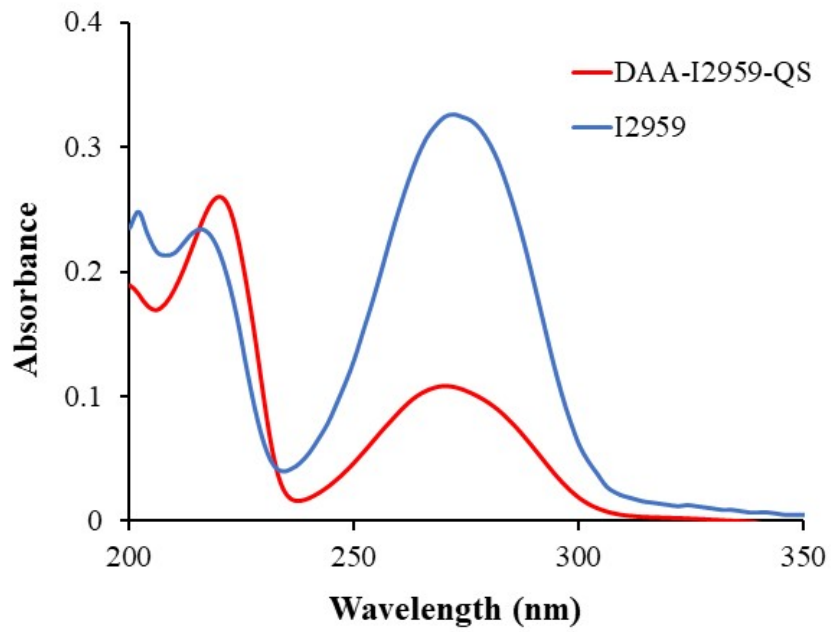


Figure 4.6. UV-vis absorption spectra of DAA-I2959-QS/DAA-Ts (0.78 x10^{-5} M DAA-I2959-QS) and I2959 (2.00x10^{-5} M) in methanol.

Figure 4.7 shows the photolysis of DAA-I2959-QS/DAA-Ts in methanol which was performed by the irradiation with a 320–500 nm light source (Omnicure 1000). During the photolysis the intensity of the peak which was nearly at 269 nm was decreased whereas a new peak at 254 nm was formed (Figure 4.7). A similar peak was also observed by Huo et al. during the photolysis of a PEG based alphahydroxyalkylphenone PI. The observed peak

was assigned to acetone which was generated by the cleavage of hydroxyketone [100]. A similar peak was also observed for the photolysis of DAA-I2959.

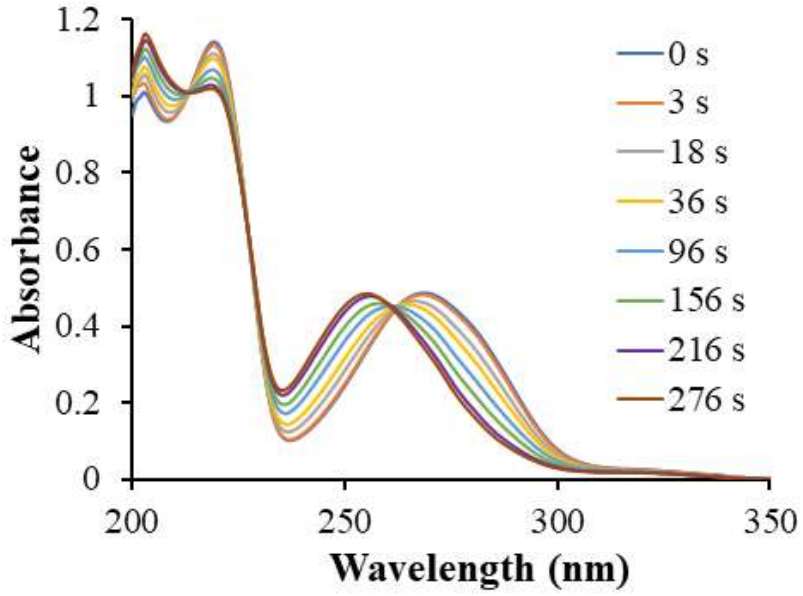


Figure 4.7. Photolysis of DAA-I2959-QS/DAA-Ts (3.15 x10^{-5} M DAA-I2959-QS) in methanol using a 320-500 nm light source.

4.3.3. Photoinitiating Activity

The photopolymerization efficiency of DAA-I2959-QS/DAA-Ts was investigated under UV-vis (320–500 nm) irradiation at 25 °C by photo-DSC. HEMA containing 1 wt% DAA-I2959-QS/DAA-Ts (1 wt% PI approximately contains 0.5 wt% I2959, calculated by NMR) and HEMA containing 0.5 wt% I2959 were polymerized. Figure 4.8 illustrates the rate-time and conversion-time plots. DAA-I2959/DAA-Ts mixture (R_{pmax} = 0.0188 s^{-1}, t_{max}= 1.2 min, conversion = 93%) showed similar reactivity to I2959 (R_{pmax} = 0.0219 s^{-1}, t_{max} = 1.2 min, conversion = 87%). In order to see the effect of water on photopolymerization behaviour 1.4 wt% water was added to HEMA containing 1 wt% of DAA-I2959-QS/DAA-Ts. No significant change was observed both in rate and conversion (R_{pmax} = 0.0201 s^{-1}, t_{max}= 1.19 min, conversion = 95%).

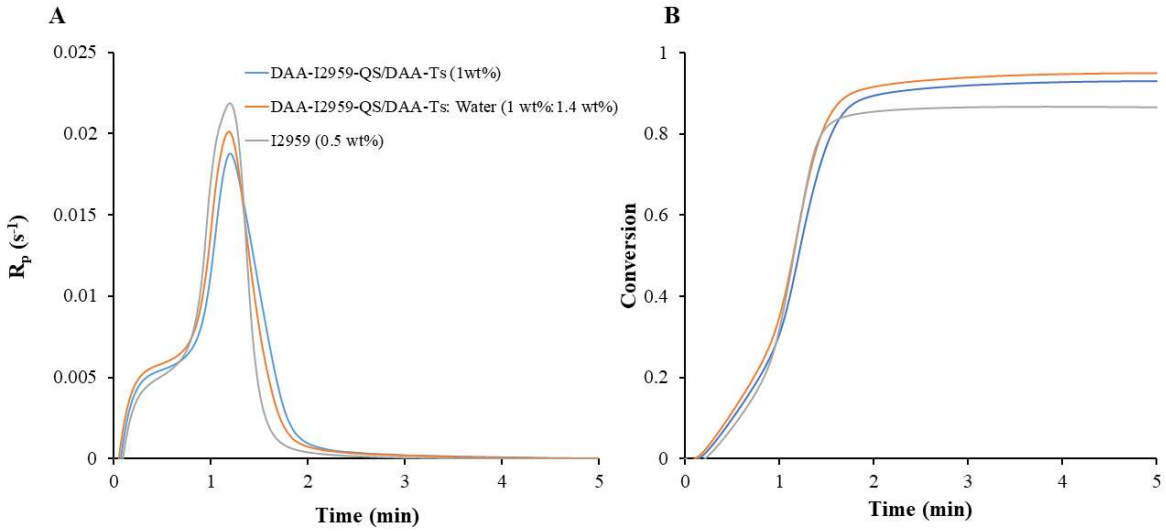


Figure 4.8. (a) Rate-time and (b) conversion-time plots for HEMA containing DAA-I2959-QS/DAA-Ts (1 wt% PI approximately contains 0.5 wt% I2959) and I2959 (0.5 wt%) at 25 °C under nitrogen and 320-500 nm irradiation.

4.3.4. Migration Stability

Migration stability of DAA-I2959-QS/DAA-Ts was investigated and compared with I2959. Hydrogels of PEGDA (M_n=575 D) were prepared using I2959 (0.2 wt%) and DAA-I2959-QS/DAA-Ts (0.2 I2959-equivalent wt% I2959) and were immersed into the methanol. After three days the amounts of the extracted PIs were determined as 3.5 % and 54.8 % for DAA-I2959-QS/DAA-Ts and I2959 using UV-vis spectroscopy (Figure 4.9). The effective extinction coefficient of DAA-I2959-QS/DAA-Ts was used in the calculations. The migration of DAA-I2959-QS was nearly 15.6 times lower than that of I2959, which indicates the ability of DAA-I2959-QS/DAA-Ts to incorporate into the network.

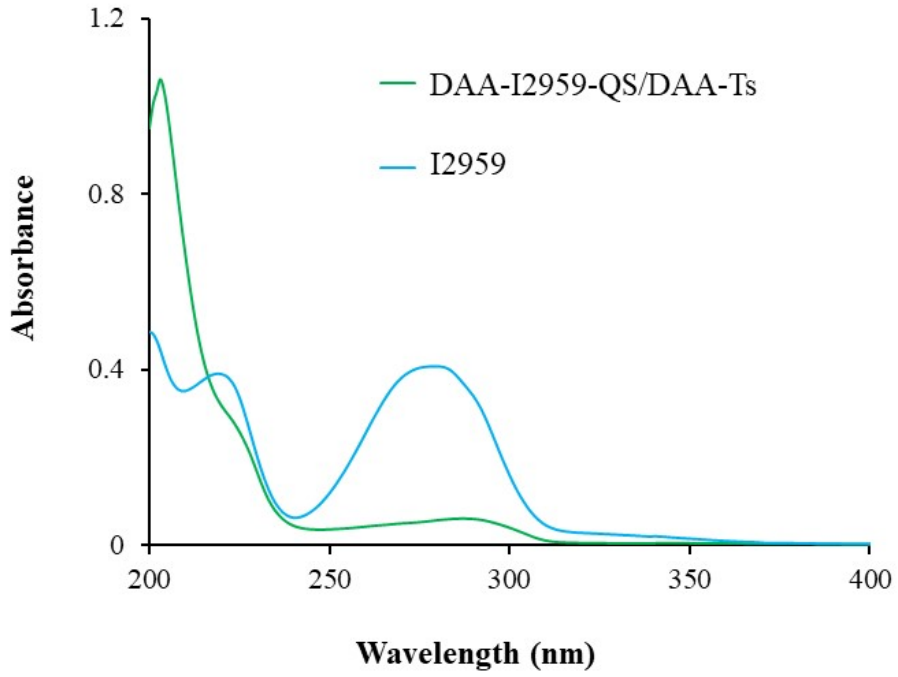


Figure 4.9. UV-vis absorption spectra of DAA-I2959-QS/DAA-Ts and I2959 extracted into methanol from PEGDA samples.

4.3.5. Synthesis of Hydrogels

In order to see the effect of the synthesized water soluble PI on hydrogel properties, two hydrogel samples, PEGDA: DAA-I2959-QS/DAA-Ts 95:5 (I2959 equivalent wt%:wt%) and PEGDA: I2959 95:5 (wt%:wt%), were prepared. SEM images were taken to analyse the morphology of the hydrogels (Figure 4.10). The hydrogels prepared from the synthesized PI were found to have larger pores (15.44 μm) compared to those of commercial PI (6.32 μm). These large pores may be due to the more hydrophilic nature of the PI, resulting from quaternary ammonium structure of both DAA-I2959-QS and DAA-Ts. Pore size is an important property of hydrogels used in biomedical applications such as tissue engineering. Since tissue formation and function depends on the porosity of scaffolds, the ability to control porosity using photoinitiator may be a new useful technique.

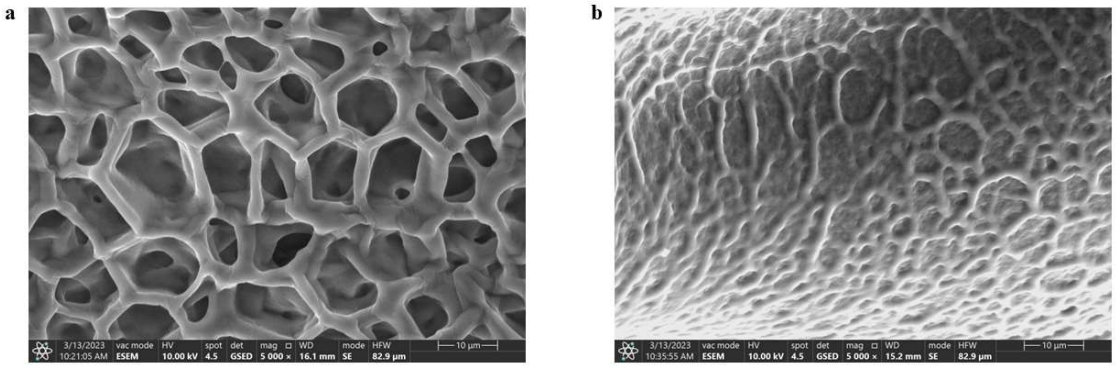


Figure 4.10. SEM images of the hydrogels (a) PEGDA:DAA-I2959-QS/DAA-Ts 95:5 (I2959 equivalent wt%:wt%) and (b) PEGDA:I2959 95:5 (wt%:wt%).

5. CONCLUSION

In this thesis, three novel cyclopolymerizable (DAA-I2959, DAA-I184 and DAA-I2959-QS) and one cyclic (p-DADMAC-*co*-DAA-I2959) PI were synthesized by attachment of DAA to commercial PIs, I2959 and I184. It was shown that neutral (tertiary amine) or charged (quaternary ammonium) monomeric PIs can be obtained depending on the reaction conditions, the neutral one under basic conditions and the charged without base. A novel water soluble, high molecular weight polymer with a high degree of cyclization was synthesized by radical copolymerization of DAA-I2959 with DADMAC under acidic conditions. This polymer is the first cylic PI in the literature. The structures of PIs were confirmed by ^{1}H-NMR, ^{13}C-NMR, FT-IR and mass spectroscopies. The PIs have similar absorption behaviour to the PIs they are synthesized from. Their photolysis indicated formation of benzoyl and ketyl radicals.

DAA-I2959 and DAA-I2959-QS/DAA-Ts showed similar photoinitiating reactivity towards (meth)acrylic double bonds compared to I2959, investigated during polymerizations of PEGDA (M_n = 575 D) and HEMA. The I184-functionalized PI shows much slower kinetics compared to I184. Neutral PIs can also be used as coinitiators for Type II photoinitiators due to their hydrogen donating capabilities. All of the PIs showed fairly good migration stability compared to I2959 due to their incorporation into network structures.

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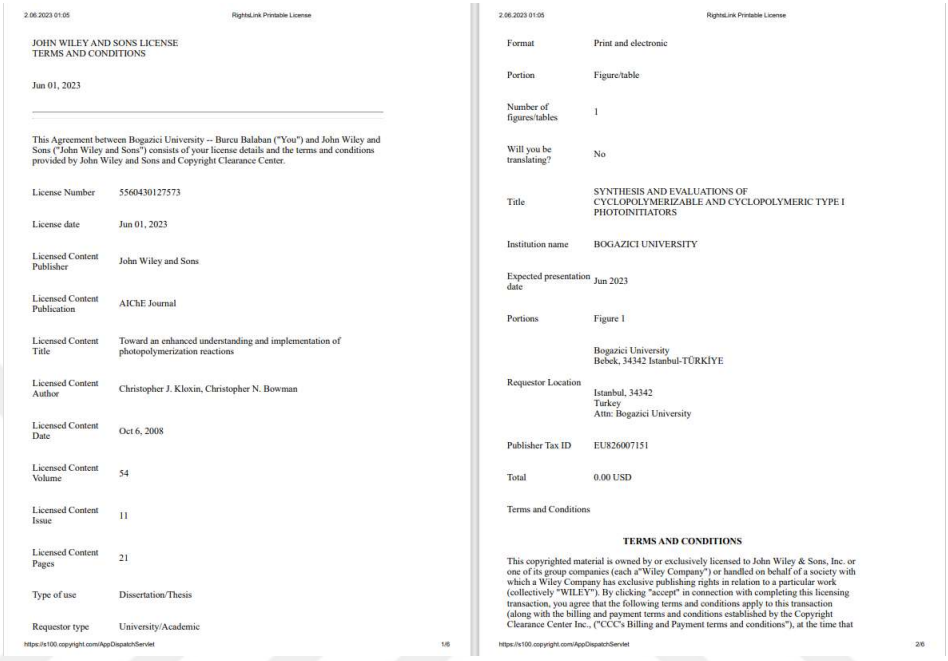
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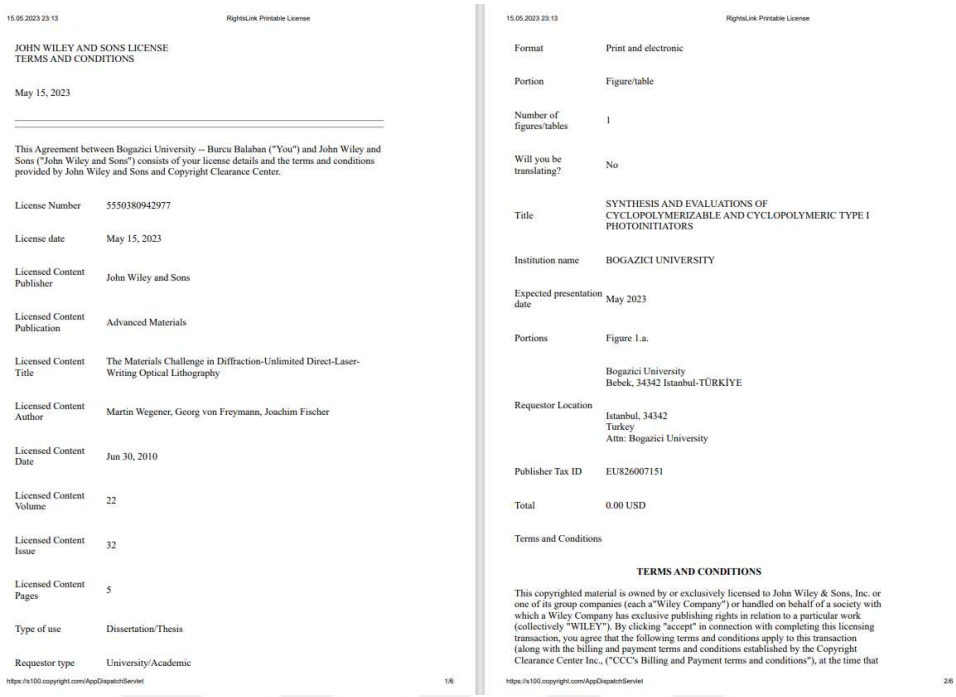
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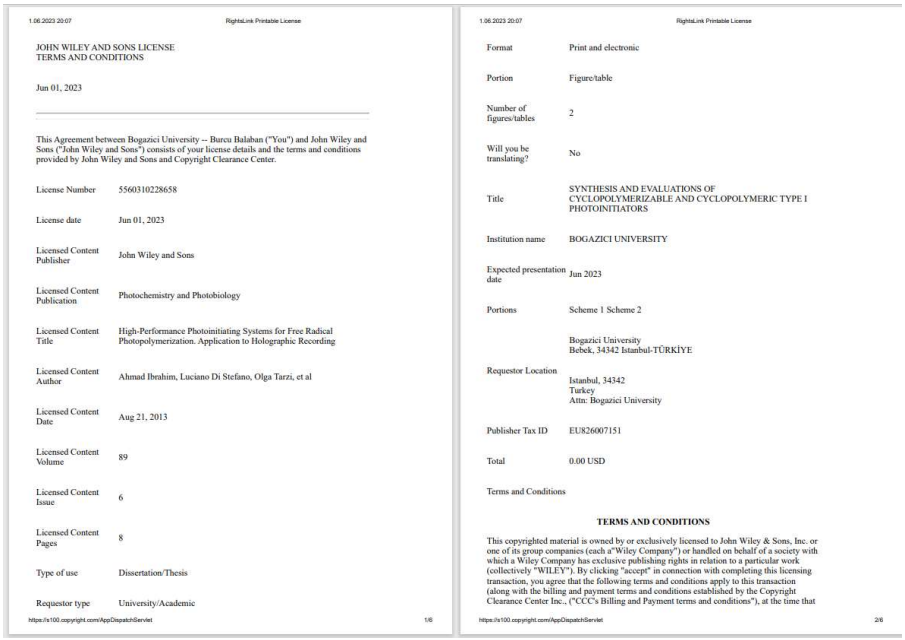
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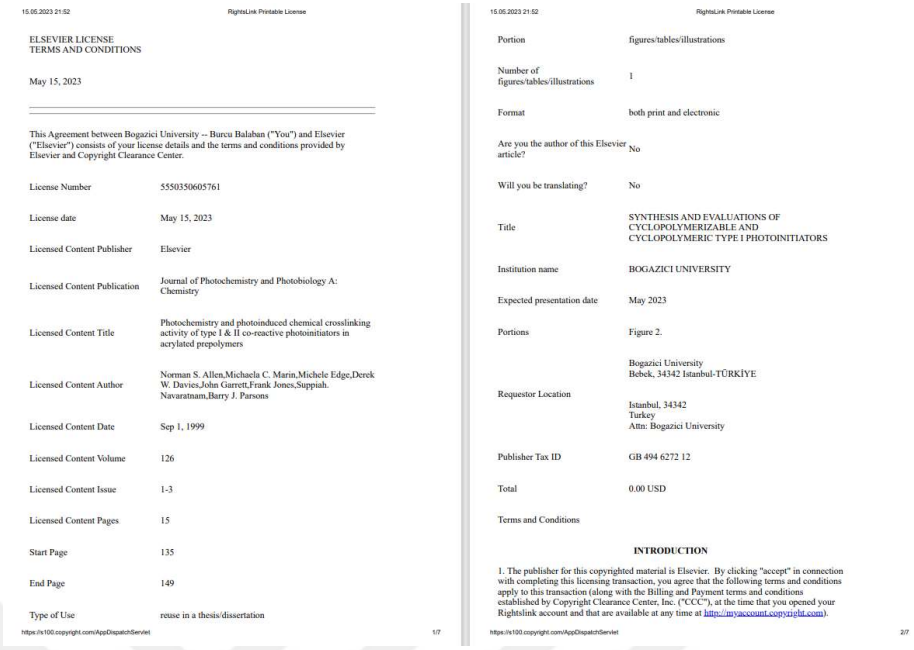
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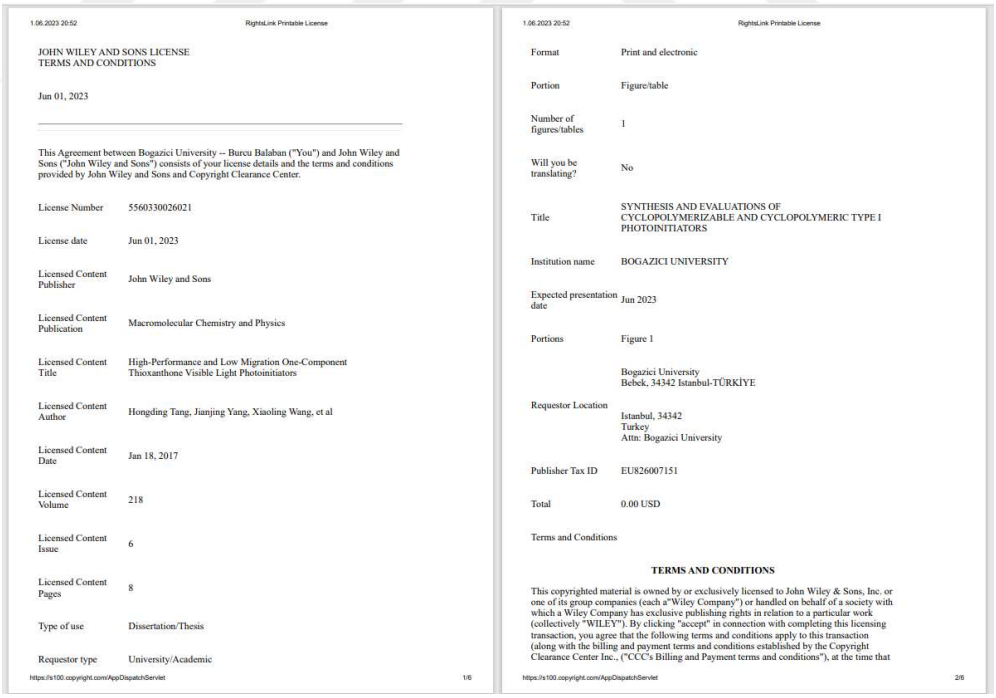
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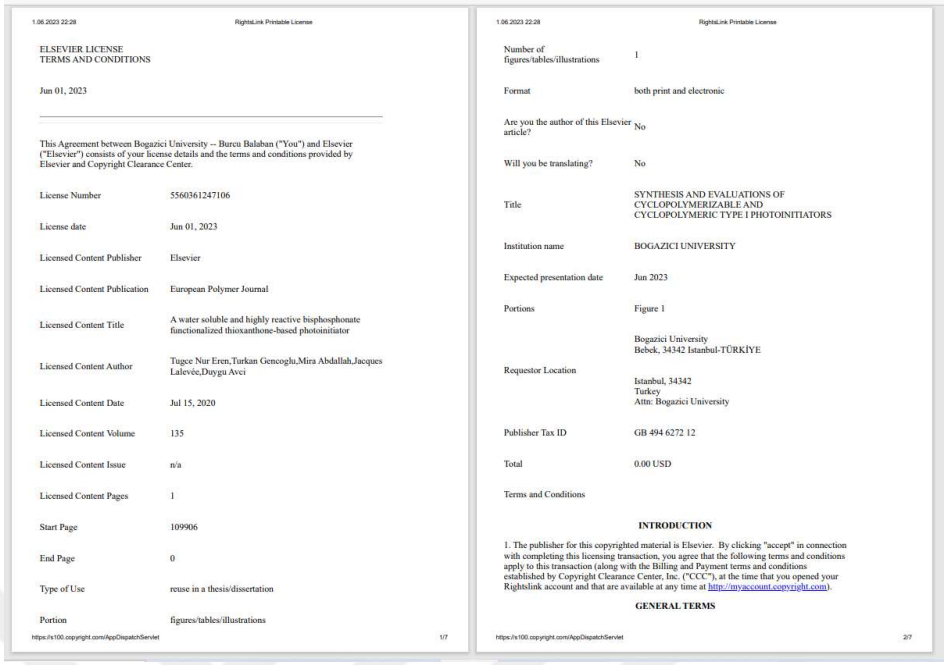
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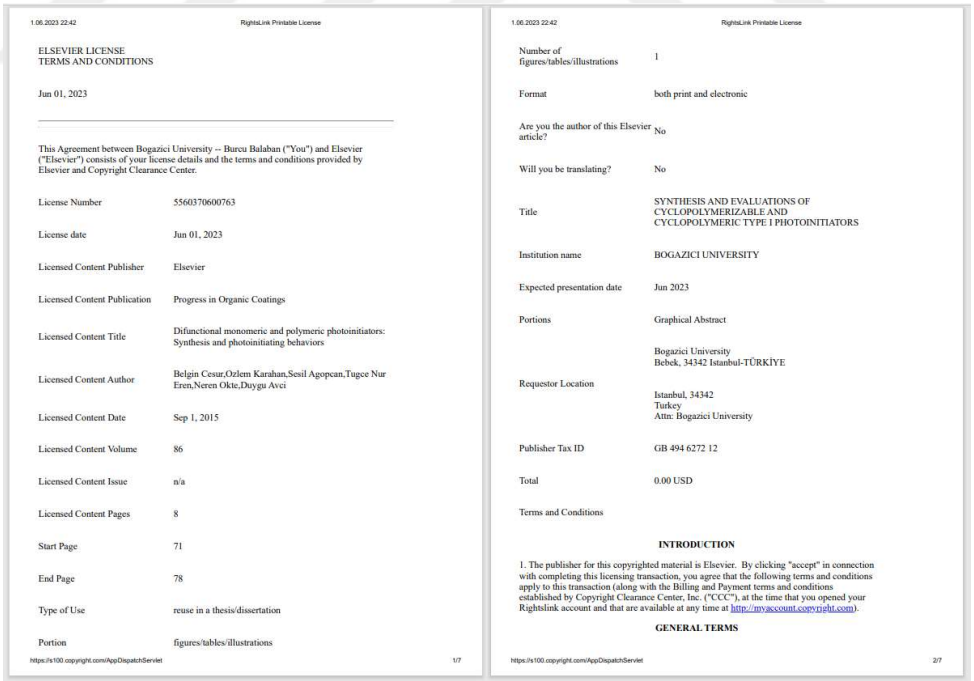
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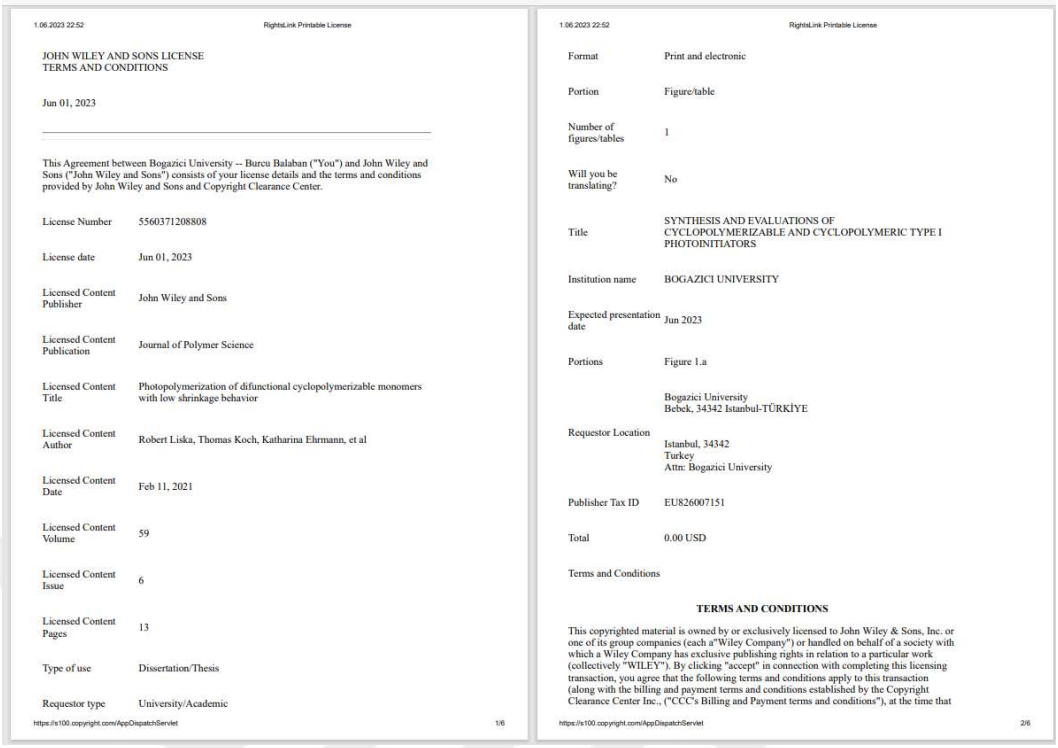
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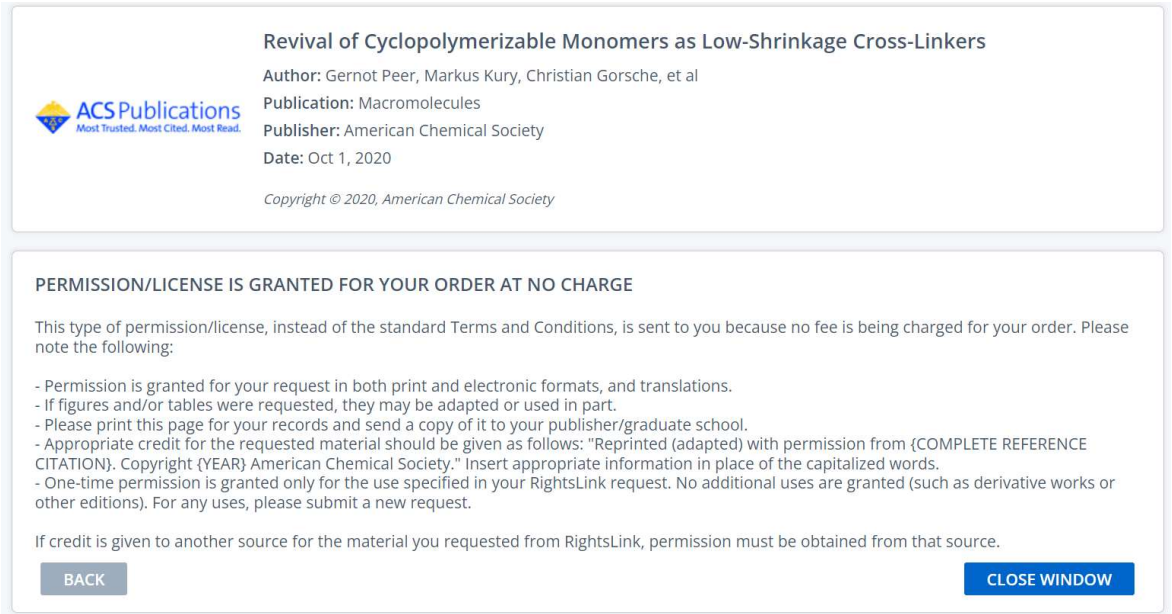
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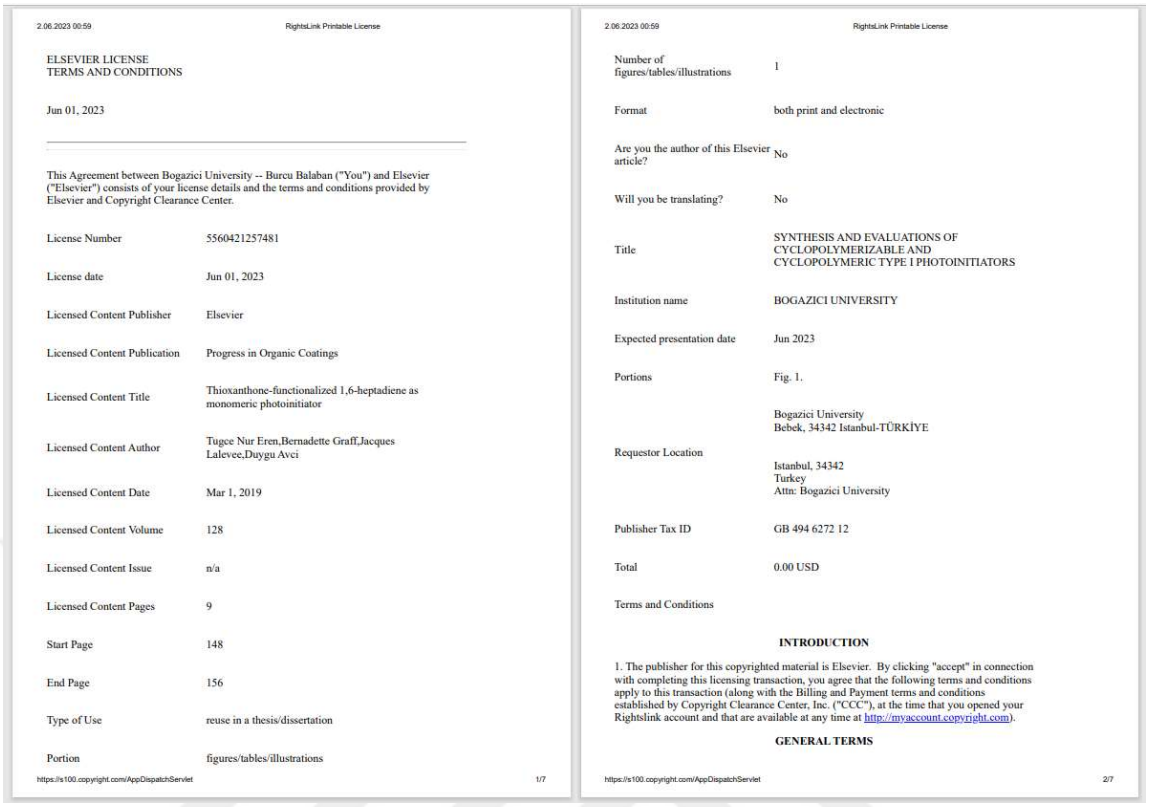
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