İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

THIOXANTHONE DERIVATIVES WITH FLUORENE GROUPS AS VISIBLE LIGHT ABSORBING PHOTOINITIATORS

M. Sc. Thesis by
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Department : Chemistry

Programme : Chemistry

JANUARY 2010

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JANUARY 2010

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

GÖRÜNÜR BÖLGEDE ABSORBSİYONA SAHİP FLOREN-TİYOKSANTON TÜREVLERİ

YÜKSEK LİSANS TEZİ
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January, 2010 Ali Görkem YILMAZ
Chemist

TABLE OF CONTENTS

Page

ABBREVIATIONS

^{1}H-NMR : Hydrogen Nuclear Magnetic Resonance Spectroscopy
FT-IR : Infrared Spectrophotometer
UV-vis : Ultra Violet-Visible
GPC : Gel Permeation Chromatography
DSC : Differential Scanning Calorimetry
CH_2Cl_2 : Dichloromethane
$CDCl_3$: Deuterated Chloroform
THF : Tetrahydrofuran
H_2O : Water
D_2O : Deuterium Monoxide
H_2SO_4 : Sulfuric Acid
NaOH : Sodium Hydroxide
$CaCl_2$: Calciım Chloride
CaH_2 : Calcium Hydride
DMA : Dimetyl aniline
[D_6]-DMSO : Deuterated Dimethl Sulfoxide
$Si(CH_3)_4$: Tetramethyl Silane
DMF : Dimethyl formamide
TMPTA : Trimethylolpropane Triacrylate
MMA : Methyl Methacrylate
PI : Photoinitiator
COI : Coinitiator
FL : Fluorene
TX : Thioxanthone
TX-SH : 2-Mercaptothioxanthone
$TXSCH_2COOH$: 2-Thioxanthone-Thioacetic Acid
FLTXCOOH : Fluorene Carboxylic Acid Thioxanthone
FLTXCOONa : Sodium Fluorene Carboxylate Thioxanthone
CQ : Camphorquinone

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF SYMBOLS

λ : Wavelength
$h\nu$: Radiation
ε : Molar Absorbtivity
$R^{\cdot}$: Radical
R : Alkyl
Ar : Aryl Group
PI : Photoinitiator
M : Monomer
M_n : The number average molecular weight
M_w : The weight average molecular weight
M_w/M_n : The molecular weight distribution
k_q : Rate constant of quenching
δ : Chemical Shift
3D : Three Dimensional
ΔH_0^{theory} : Theoretical heat for complete conversion
ΔH_t : Reaction heat evolved at time t
(C) : Conversion
R_p : Rate of Polymerization

THIOXANTHONE DERIVATIVES WITH FLUORENE GROUPS AS VISIBLE LIGHT ABSORBING PHOTOINITIATORS

SUMMARY

Photoinitiated polymerization is a well-known technique exploited in many technologically important areas. Both free radical and cationic polymerizations have been used, and the mechanisms of initiation have been studied in detail. The free radical mode is in more advanced state due to its applicability to a wide range of formulations based on (meth)- acrylates, unsaturated polyesters, and polyurethanes and the availability of photoinitiators having spectral sensitivity in the near-UV and visible range. Photoinitiators for visible light have found particular interest because of their use in many targeted applications such as dental filling materials, photoresists, printing plates, integrated circuits, laser-induced 3D curing, holographic recordings, and nanoscale micromechanics. Both cleavable and bimolecular hydrogen abstracting type photoinitiating systems, acting in the visible range, are wellknown. Titanocene and camphorquinone in conjunction with an amine are typical examples for the respective systems.

Recently, organic ketones containing germanium were introduced as a new class of cleavable photoinitiators for free radical polymerization under visible light irradiation.

In addition to visible light absorbtion, water solubility of an initiator is also an important parameter for todays green chemistry. İntroduction of hydrophillic groups onto a conventional photoinitiator generally yields water soluble photoinitiator with a little decrease in photoactivity. Still, these salts are shown to display sufficient photoactivity, and scientific studies are intensivly shifting to the water-borne formulations.

In this thesis, synthesis and characterization of two different photoinitiators, namely fluorene carboxylic acid thioxanthone and its sodium salt; the former oil soluble and the latter water soluble, but both with visible range absorbtion characteristics have been reported. Their initiation mechanism have been investigated with Laser Flash Photolysis. The PhotoDSC studies of the photoinitiators in conjuction with the conventional monomer formulations are also included.

GÖRÜNÜR BÖLGEDE ABSORBSİYONA SAHİP FLOREN-TİYOKSANTON TÜREVLERİ

ÖZET

Işıkla başlatılmış polimerizasyon teknolojinin bir çok alanında kullanılan önemli bir tekniktir. Hem radikal hem de katyonik polimerizasyon bu anlamda kullanılmış ve mekanizmaları da detaylı bir şekilde incelenmiştir. Metakrilatlar, doymamış poliesterler, poliüretanlar gibi bir çok formulasyona uygun olan UV ve görünür bölge absorbsansına sahip serbest radikal başlatıcıları çokca mevcut olduğundan serbest radikal polimerizasyonda daha fazla ilerleme kaydedilmiştir. Görünür bölgede absorbansa sahip başlatıcılar çok ilgi çekicidir, zira diş dolgu malzemelerinde, fotorezistlerde, matbaacılıkta, entegre devrelerde, lazer ile uyarılmış 3 boyutlu kaplamalarda, halografik kayıtlarda ve nano boyutlu mikromekaniklerde kullanılmaktadır. Görünür bölgede aktif olan, hem parçalanabilir, hem de bimoleküler hidrojen koparma tipi başlatıcılar iyi bilinmektedir. Titonesen ve kamfokinonun aminle birlikte kullanıldığı sistemler buna örnektir.

Son dönemde görünür bölgede absorbansa sahip germanyum içeren organik ketonların serbest radikal polimerizasyonu için uygun olduğu ortaya konmuştur.

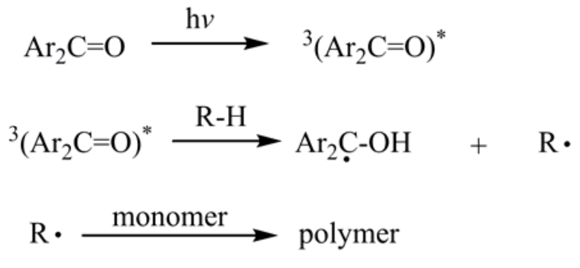
Fotobaşlatıcıların, görünür bölgede absorbansa sahip olmasının yanında suda çözünebiliyor olması da günümüzün çevre dostu kimyası için oldukça önem taşır. Geleneksel fotobaşlatıcılara hidrofilik gruplar bağlandığında suda çözünebilen ancak fotoaktivitesi az da olsa azalmış fotobaşlatıcılar sentezlenebilir. Bununla birlikte, bu başlatıcıların yeterli fotoaktivite gösterdikleri ortaya konmuş ve son zamanlarda önemli miktarda çalışma su bazlı formülasyonlara kaymıştır.

Bu tezde, görünür bölgede absorbansa sahip biri organik çözücülerde diğeri suda çözünebilen floren karboksilik asit tiyoksanton ve onun sodyum tuzunun sentezi sunulmuştur. Her birinin başlatma mekanizmaları Lazer Flash Fotolizi çalışmaları yardımı ile belirlenmiştir. Geleneksel monomer formülasyonları ile yapılmış FotoDSC çalışmaları da tez içerisnde bulunmaktadır.

1. INTRODUCTION

Photoinitiated polymerization is a well-known technique exploited in many technologically important areas [1, 2]. Both free radical and cationic polymerizations have been used, and the mechanisms of initiation have been studied in detail [3-6]. The free radical mode is in more advanced state due to its applicability to a wide range of formulations based on (meth)- acrylates, unsaturated polyesters, and polyurethanes and the availability of photoinitiators having spectral sensitivity in the near-UV and visible range. Photoinitiators for visible light[7] have found particular interest because of their use in many targeted applications such as dental filling materials [8-10], photoresists, printing plates, integrated circuits, laser-induced 3D curing, holographic recordings, and nanoscale micromechanics.

Photoinitiated radical polymerization may be initiated by both cleavage (*Type I*) and H-abstraction type (*Type II*) initiators. Because of their vital role in photopolymerization, photoinitiators are the subject of particularly extensive research. Most of this research has focused on *Type I* photoinitiators, which upon irradiation undergo an α-cleavage process to form two radical species. *Type II* photoinitiators are a second class of photoinitiators and are based on compounds whose triplet excited states are reacted with hydrogen donors, thereby producing an initiating radical (Figure 1.1).



$$Ar_2C{=}O \xrightarrow{h\nu} {}^3(Ar_2C{=}O)^*$$

$$^3(Ar_2C{=}O)^* \xrightarrow{R\text{-}H} Ar_2\dot{C}\text{-}OH + R\bullet$$

$$R\bullet \xrightarrow{monomer} polymer$$

Figure 1.1 : General mechanism for photo-induced polymerization using typical Type II photoinitiator.

Because the initiation is based on bimolecular reaction, they are generally slower than *Type I* photoinitiators which are based on unimolecular formation of radicals. On the other hand, *Type II* photoinitiators possess better optical absorption properties in the near ultraviolet spectral region. Moreover *Type I* compounds give raise to volatile photodecomposition products due to the cleavage mechanism adding to the migration problem of release of odour. In this respect the *Type II* photoinitiators have a more favorable profile because the ketyl radical either is re-oxidized back to the ketone or gives rise to recombination products with formation of higher molecular weight derivatives with a lower volatility than parent compounds.

Typical *Type II* photoinitiators include benzophenone, thioxanthones, benzil, and quionones while alcohols, ethers, amines and thiols are used as hydrogen donors. Recently, Yagci et al. prepared and studied the initiation mechanisms of different thioxanthone derivates with absorbtions at the visible and/or near UV range. They display photoactivity without an additional H-donor compound. Espacially the case of anthrecene-thioxanthone is really interesting as it initiates free radical polymerization in the presence of air. The initiation mechanism is as follows.

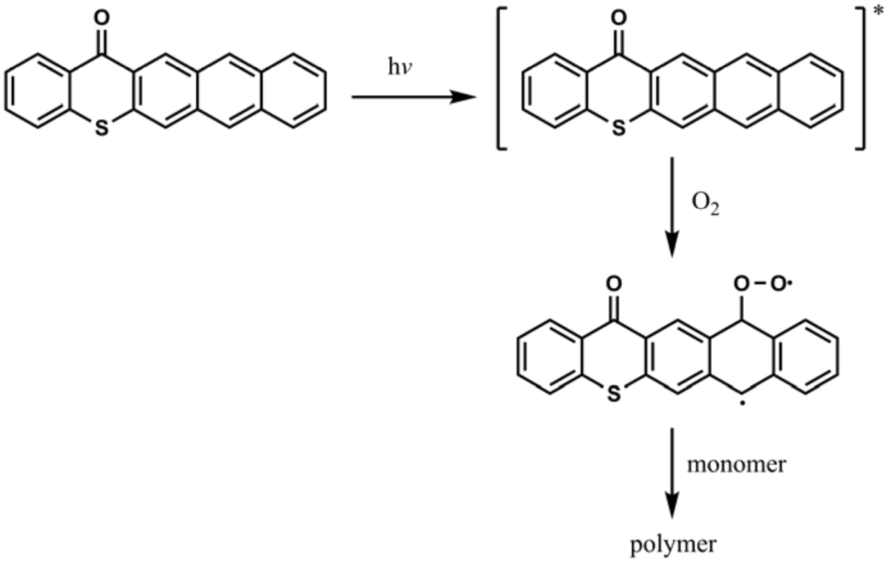


Figure 1.2 : Photoinitiation by anthrecene-thioxanthone photoinitiator.

In addition to visible light absorbtion, water solubility of an initiator is also an important parameter for todays green chemistry. Introduction of hydrophillic groups onto a conventional photoinitiator generally yields water soluble photoinitiator with a little decrease in photoactivity. Still, these salts are shown to display sufficient photoactivity, and scientific studies are intensively shifting to the water-borne formulations.

In this thesis, synthesis and characterization of two different photoinitiators, namely fluorene carboxylic acid thioxanthone and its sodium salt; the former oil soluble and the latter water soluble, but both with visible range absorbtion characteristics have been reported. Notably, the acidic derivate is shown to initiate free radical polymerization without an additional H-donor compound. The initiation mechanism of both of the initiators have been proposed by the help of the Laser Flash Photolysis. The PhotoDSC studies of the photoinitiators in conjuction with the conventional monomer formulations are also included.

2. THEORETICAL PART

2.1 Photoinitiated Polymerization

Photo-initiated polymerization is typically a process that transforms a monomer into polymer by a chain reaction initiated by reactive species (free radicals or ions), which are generated from photo-sensitive compounds, namely photoinitiators and/or photosensitizers, by ultra violet-visible (UV-Vis) light irradiation. In recent decades, it has become a powerful industrial process widely used in various applications including coatings, inks, adhesives, varnishes, electronics, photolithography, and dyes due to its excellent advantages [11-13]. It offers high rate of polymerization at ambient temperatures, lower energy cost, and solvent-free formulation, thus elimination of air and water pollution [12, 13]. It also devotes temporal and spatial control of the polymerization when high initiation rate is reached [14].

Light induced polymerizations are used not only in the formulations containing bi- and multi functional monomers leading to the formation of cross-linked networks, but also synthesis of linear and complex macromolecular structures such as block and graft copolymers, and star polymers [15]. Additionally, the photopolymerization strategy can be of general use in the syntheses of metal and clay/polymer nanocomposites. Both radically and cationically acting systems have successfully been employed, and the mechanisms of initiation have been studied in detail. Compared to the cationic mode, free radical photoinitiation is in more advanced state because of the availability of wide range of monomer formulations and photoinitiators with broad spectral sensitivity in UV and visible range. Many efforts have been paid to develop photoinitiators for both polymerizations acting at different wavelength ranges.

2.1.1 Photoinitiation

Photoinitiated free radical polymerization consists of four distinct steps: [16]

1. Photoinitiation: Absorption of light by a photosensitive compound or transfer of electronic excitation energy from a light absorbing sensitizer to the photosensitive

compound. Homolytic bond rupture leads to the formation of a radical, that reacts with one monomer unit.

2. Propagation: Repeated addition of monomer units to the chain radical produces the polymer backbone.

3. Chain transfer: Termination of growing chains by hydrogen abstraction from various species (e.g., from solvent) and concomitant production of a new radical capable of initiating another chain reaction.

4. Termination: Chain radicals are consumed by disproportionation or recombination reactions. Termination can also occur by recombination or disproportionation with any other radical including primary radicals produced by the photoreaction. These four steps are summarized in Figure 2.1. Notably, the role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating radicals. The reactions of these radicals with monomer, propagation, transfer, and termination are purely thermal processes; they are not affected by light. Because in this chapter the genuine photochemical aspects are to be discussed, propagation, transfer, and termination reactions are not depicted as long as it is not necessary for the understanding of a reaction mechanism. Instead, the photochemically produced initiating species are highlighted by a frame, as illustrated in Figure 2.1.

2.1.2 Absorption of light

The absorption of light excites the electrons of a molecule, what lessens the stability of a bond and can, under favorable circumstances, lead to its dissociation. Functional groups that have high absorbency, like phenyl rings or carbonyl groups, are referred to as chromophoric groups. Naturally, photoinduced bond dissociations do often take place in the proximity of the light absorbing chromophoric groups. In some examples, however, electronic excitation energy may be transferred intramolecularly to fairly distant, but easily cleavable bonds to cause their rupture [16].

If the monomer possesses chromophoric groups and is sensitive toward light (i.e., it undergoes photoinduced chemical reactions with high quantum yields) one can perform photopolymerizations by just irradiating the monomer. In many cases, however, monomers are not efficiently decomposed into radicals upon irradiation. Furthermore, monomers are often transparent to light at $\lambda>320$ nm, where commercial lamps emit. In these cases, photoinitiators are used. These compounds absorb light and bring about the generation of initiating radicals [16].

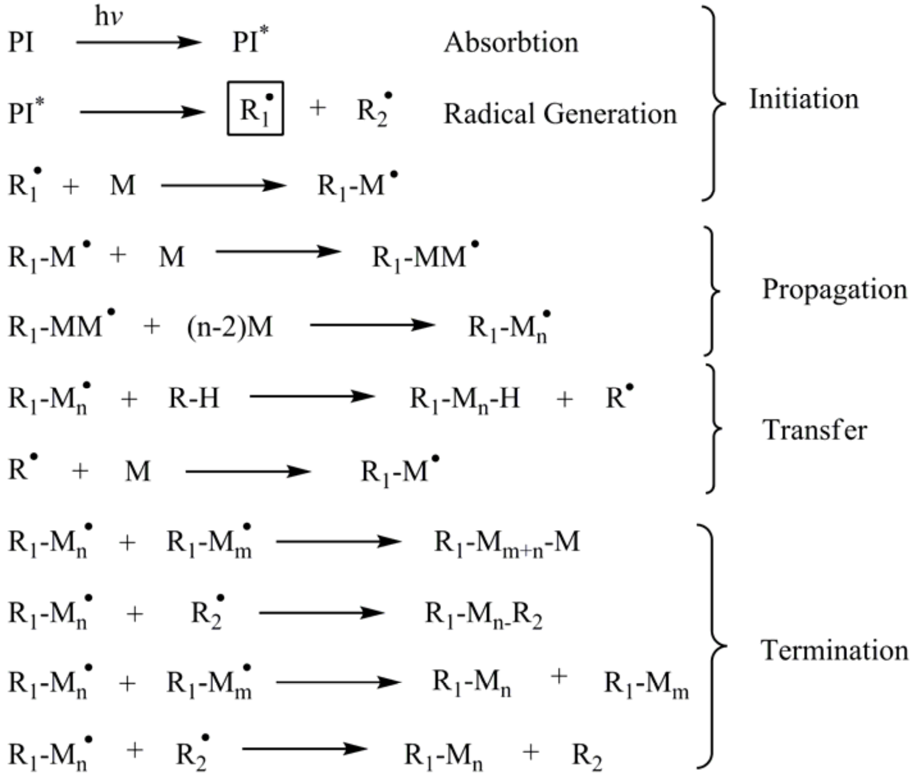


Figure 2.1 : General mechanism for light-induced free radical polymerization.

2.1.3 Radical generation

2.1.3.1 Radical generation by monomer irradiation

Some monomers are able to produce radical species upon absorption of light. Studies on various vinyl compounds show that a monomer biradical is formed [16].

$$M \xrightarrow{h\nu} \boxed{\cdot M \cdot}$$

These species are able to react with intact monomer molecules thus leading to growing chains. Readily available monomers, which to some extent undergo polymerization and copolymerization upon UV irradiation, are listed in Table 2.1.

However, regarding technical applications radical generation by irradiation of vinyl monomer does not play a role due to the very low efficiency of radical formation and the usually unsatisfactory absorption characteristics.

Table 2.1 : Photosensitive monomers.

Allyl methacrylate
Barium Acrylate
Cinnamyl Methacrylate
Diallyl Phtalate
Diallyl isophtalate
Diallyl terephtalate
2-Ethylhexyl acrylate
2-Hydoxyethyl methacrylate
2-Hydroxypropyl acrylate
N,N'-Methylenebisacrylamide
Methyl methacrylate
Pentaerithritol tetramethacrylate
Styrene
Tetraethylene glycol dimethacrylate
Tetrafluoroethylene
N-Vinylcarbazole
Vinyl cinnamate
Vinyl 2-fuorate
Vinyl 2-furylacrylate

2.1.3.2 Radical generation by initiators

A photoinitiator is a compound that, under absorption of light, undergoes a photoreaction, producing free radicals. These species are capable of initiating the polymerization of suitable monomers. Photoinitiators are generally divided into two classes according to the process by which initiating radicals are formed.

Compounds which undergo unimolecular bond cleavage upon irradiation as shown in Figure 2.2 are termed as Type I photoinitiators [16].

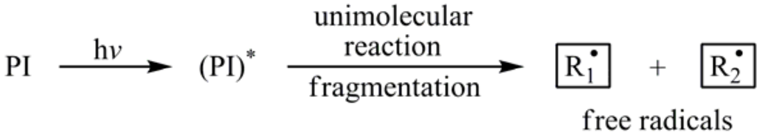


Figure 2.2 : Decomposition of Type I photoinitiators upon irradiation.

If the excited state photoinitiator interacts with a second molecule (a coinitiator) to generate radicals in a bimolecular reaction as shown in Figure 2.3, the initiating system is termed as “Type II Photoinitiator” [16].

Efficient photoinitiators of both classes are known and find everyday usage. *Type I* photoinitiators are highly reactive UV photoinitiators, but are less frequently used in visible light curing systems. *Type II* photoinitiators are versatile initiators for UV curing systems and visible light photoinitiators belong almost exclusively to this class of photoinitiators.

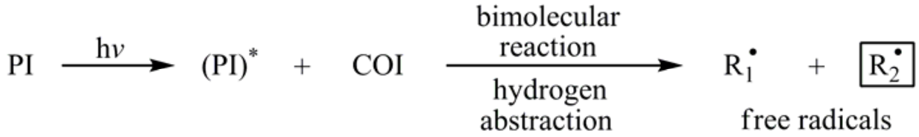


Figure 2.3 : Decomposition of Type II photoinitiators upon irradiation.

The main cleavable photoinitiators include benzil dimethyl ketal, benzoin ethers, alkyl hydroxyphenyl ketones, dialkoxyacetophenones, benzylcyclohexanol, amino alkylketones, acylphosphine oxides and acyl germanes. Except for acylphosphine oxide and acylgermane photoinitiators, the cleavage takes place at carbon–carbon bond. Long wavelength and visible light active acylphosphine oxide and acylgermane photoinititors undergo cleavage at carbon–phosphorous and carbon–germane bonds upon irradiation, respectively (Figure 2.4) [17, 18].

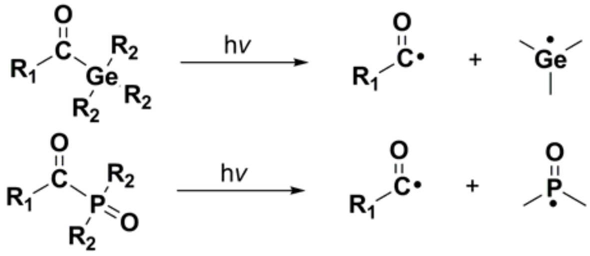


Figure 2.4 : Photolysis of phosphonium and germanium photoinitiators.

Photolysis of aromatic ketones, such as benzophenone, thioxanthones, benzil, and quionones, in the presence of hydrogen donors, such as alcohols, amines, or thiols, leads to the formation of a radical produced from the carbonyl compound (ketyl type radical) and another radical derived from the hydrogen donor.

The photopolymerization of vinyl monomers is usually initiated by the radical produced from the hydrogen donor. The ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electron. The overall mechanism of the photoinitiation is represented in Figure 2.5 on the example of thioxanthone.

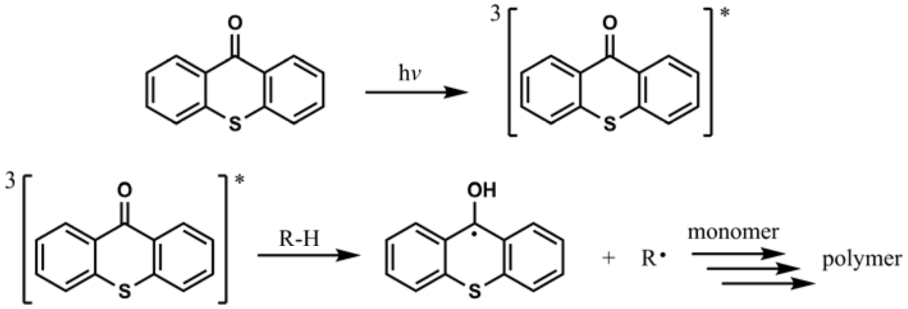
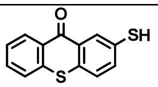
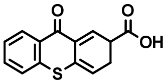
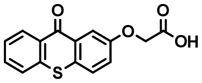
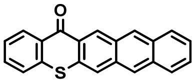


Figure 2.5 : Photo-initiated free radical polymerization using thioxanthone.

One of the disadvantages of Type II systems concerns high usage of high volatile and odorous amines as hydrogen donors [19]. Poly(ethylene oxide) and poly(ethylene imine) based dendrimers of the following structures have been successfully used as polymeric hydrogen donors to replace low molecular weight amines in the formulations.

As part of our efforts to avoid problems associated with the amine hydrogen donors, Yagci and co-workers have recently reported several new thioxanthone derivatives as photoinitiators for free radical polymerization. Interestingly, these photoinitiators do not require an additional coinitiator, that is, a seperate molecular hydrogen donor. The stuctures and the mode of action of such one-component photoinitiators are shown in Table 2.2.

Table 2.2 : Thioxanthone based one-component photoinitiators.

Photoinitiator	**Structure**	**Mode of action**	**Ref.**
2-Mercaptothioxanthone		Hydrogen abstraction	[20, 21]
2-(9-Thioxanthone-2-thio) acetic acid		Hydrogen abstraction	[22, 23]
2-(9-Thioxanthone) acetic acid		Hydrogen a bstraction	[22, 23]
Thioxanthone-anthracene		Endoperoxide formation	[24]

2.2 Thioxanthones

Thioxanthones in conjunction with tertiary amines are efficient photoinitiators [25] with absorption characteristics that compare favorably with benzophenones;

absorption maxima are in the range between 380 to 420 nm (ε = 104 L mol^{-1} cm^{-1}) depending on the substitution pattern. The reaction mechanism has been extensively investigated by spectroscopic and laser flash photolysis techniques.[26-28] It was found that the efficiency of thioxanthones in conjunction with tertiary amines is similar to that of benzophenone/amine systems. The most widely used commercial derivatives are 2-chlorothioxanthone and 2-isopropylthioxanthone. A great advantage is that thioxanthones are virtually colorless and do not cause yellowing in the final products.

More recently, one component bimolecular photoinitiator systems based on the decarboxylation process were reported by Aydin et al [23]. 2-Thioxanthone-thioacetic acid and 2-(carboxymethoxy)thioxanthone were used as photoinitiators for free radical polymerization. These one-component initiators contain light absorbing and electron donating and consequently hydrogen donating sites in one molecule, as opposed to two-component systems in which light absorbing and electron donating acidic sites are composed in independent molecules. The suggested mechanism involves redox reactions. The intermolecular electron-transfer reaction may occur between an excited thioxanthone moiety and the carboxylic acid group of another molecule (Figure 2.6).

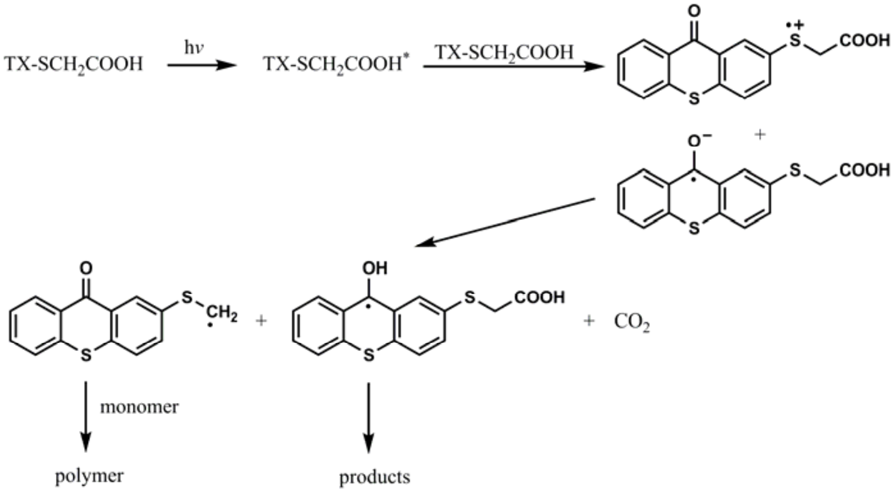


Figure 2.6 : Photo-induced polymerization using thioxanthone-thioacetic acid derivatives.

The intramolecular electron transfer should also be considered. Although a favorable interaction of the excited carbonyl group with carboxylic acid hydrogen is facilitated with flexible S-CH_2 or O-CH_2 spacer groups, the actual initiation involves electron transfer from a sulfur or oxygen atom. It appears that the interaction of excited carbonyl with the sulfur or oxygen atoms of the same molecule separated with a rigid aromatic ring, is unlikely to occur [23].

Photoinitiators with higher wavelength absorbtion characteristics are desired as they cost lower energy and are defined to be "green". Photoinitiators for visible light [7, 29] have found particular interest because of their use in many targeted applications such as dental filling materials [8-10], photoresists, printing plates, highly pigmented coatings, integrated circuits, laser-induced 3D curing, holographic recordings, and nanoscale micromechanics. The very well known examples are the titanocene [8] and camphorquinone [30] in conjunction with an amine for the respective systems. More recently, organic ketones containing germanium were introduced as a new class of cleavable photoinitiators [31, 32]. Yagci et. al. have recently demonstarted that these type of photoinitiators can promote cationic polymerization under visible light [33].

Another important issue in the practical application of photoinitiators is related to their water solubility. There is a clear shift from organic solvents towards water-borne formulations particularly in the paints and coatings industry. Water as a green solvent has several attractive properties such as non-toxicity, cheap cost, and readily availability for coatings technology. The water solubility is usually achieved by incorporation of water solubilising groups such as quartinized ammonium or sulfate, to the main body of the photoinitiators. Direct substitution of such groups on the photoinitiator affects the nature of the chromophore and consequently its photoactivity. Generally, water soluble photoinitiator have reduced photoactivity to that of its parent oil soluble initiator. Example of the typical structure of water-soluble photoinitiators are derivatives of benzophenones [34], thioxanthones [35], benzyl [36], hydroxy alkyl ketones [37] and phenyl trimethyl benzoyl phosphinates [38]. Recently, Yagci et. al. also synthesized phenacyl pyridinium oxalate as a water soluble photoinitiator and investigated its initiating behaviour with water soluble monomers [39]. The initiation mechanism of this initiator is postulated to be as follows:

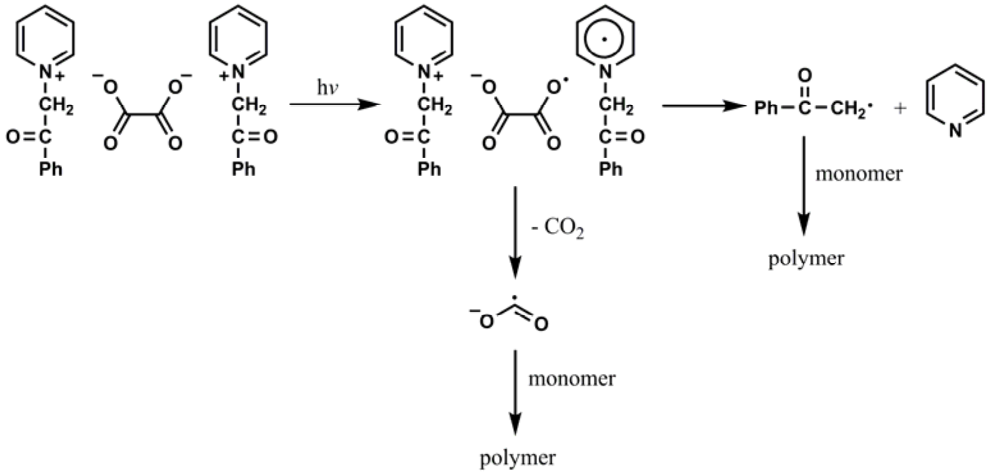


Figure 2.7 : Photopolymerization mechanism using phenacyl pyridinium oxalate.

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3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Methyl methacrylate (MMA, 99%, Aldrich) : Methyl methacrylate were washed with 5% aqueous NaOH solution, dried over CaCl2, and distilled over CaH2 under vacuum just before use.

Trimethylolpropane triacrylate (TMPTA, 99%, Sigma-Aldrich) : Trimethylolpropane triacrylate was used as recieved.

2-(2-phosphono-ethoxymethyl)-acrylic acid ethyl ester (EAEPA, IVOCLAR VIVADENT AG (FL-9494 Schaan)) : 2-(2-phosphono-ethoxymethyl)-acrylic acid ethyl ester (EAEPA) was used as recieved.

N,N-diethyl-1,3-bis(acrylamido)propane (DEBAAP, IVOCLAR VIVADENT AG (FL-9494 Schaan)) : N,N-diethyl-1,3-bis(acrylamido)propane (DEBAAP) was used as recieved.

3.1.2 Solvents

Methanol (Technical) : Methanol was used for the precipitation of polymers without further purification.

Tetrahydrofuran (THF) (99.8%, J.T.Baker) : Predried over magnesium sulfate followed by sodium wire and then distilled from sodium wire and benzophenone immediately before use.

Diethylether (Sigma-Aldrich) : Diethylether was used as recieved.

Hexane (Sigma) : Hexane was used without further purification.

Acetonitrille (99 %, Across) : Acetonitrille was used as recieved.

3.1.3 Other chemicals and reagents

Thiosalysilic acid (97%, Sigma-Aldrich) : Thiosalysilic acid was used as recieved.

Fluorene 4-carboxylic acid (96%, Alfa Aesar) : Fluorene 4-carboxylic acid was used as recieved.

Ethyl 4-dimethylaminobenzoate (99% Alfa Aesar) : Ethyl 4-dimethylaminobenzoate was used as recieved.

Dimethyl aniline (DMA, 99%, Aldrich) : Dimethyl aniline (DMA) is distilled over CaH_2 under reduced pressure just before use.

p-Dioxane (99,9%, JT Baker) : p-Dioxane was used as recieved.

Sulfuric acid (H_2SO_4, 95-97%, Fluka) : Sulfuric acid was used as recieved.

Sodium hydroxide (NaOH, Carlos Erba) : Sodium hydroxide were used as recieved.

3.2 Equipments

3.2.1 ^{1}H Nuclear magnetic resonance spectroscopy (^{1}H-NMR)

^{1}H-NMR spectra of 5–10 % (w/w) solutions in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer.

3.2.2 Infrared spectrophotometer (IR)

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer.

3.2.3 Photoreactor

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

3.2.4. UV-visible spectrophotometer

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

3.2.5. Differential scanning calorimeter (DSC)

Differential scanning calorimeter (DSC) was performed on a Perkin Elmer Diamond DSC with a heating rate of 10 ^{o}C min^{-1} under nitrogen flow.

3.2.4 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL GPC columns ($G2000H_{HR}$, $G3000H_{HR}$ and $G4000H_{HR}$), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were 456–42,800, 1050–107,000, and 10,200–2,890,000, respectively. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 30°C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Molecular weights were calculated with the aid of polystyrene standards.

3.3 Preparation Methods

3.3.1 Synthesis of fluorene carboxylic acid thioxanthone (FLTXCOOH)

Thiosalysilic acid (0.2 g, 1.3 mmol) was slowly added to concentrated sulfuric acid (10 mL), and the mixture was stirred for 5 min to ensure through mixing. Fluorene-4-carboxylic acid (0.85 g, 3.9 mmol) was added slowly to the stirred mixture over a period of 30 min. After the addition, the reaction mixture was stirred at 75°C for 2 hours and later it was left to stand at room temparature overnight. Afterwards, the resulting mixture was poured carefully with stirring into a 10-fold excess of boiling water, and it was then boiled further for 5 min. The solution was cooled and filtered. The residue was recrystallized from dioxane/water mixture to give the pure bright yellow solid. Yield: 52%, ^{1}H-NMR ([D6]DMSO, 250 MHz): δ = 9.01–7.51 (m, 9H, aromatic), 4.03 (s, 2H, CH2), 13.5 (s, 1H, COOH); FT-IR (ATR): 3420, 2883, 1703, 1584, 1438, 1395, 1256, 1175, 1082, 873, 762 cm^{-1}.

3.3.2 Synthesis of sodium fluorene carboxylate thioxanthone (FLTXCOONa)

Fluorene carboxylic acid thioxantone (0,2 g, 0.58 mmol) was added into 50 ml NaOH solution (2.9 x 10^{-5} mol L^{-1}). The suspension was refluxed at 100°C overnight. The mixture was filtered, and the resulting orange-brown solid was dried at vacum owen for two days. Yield: 98%. ^{1}H-NMR ([D2]D_2O, 250 MHz): δ = 8.42–6.85 (m, 9H, aromatic), 3.15 (s, 2H, CH2); FT-IR (ATR): 2888, 1772, 1713, 1588, 1424, 993, 878, 737 cm^{-1}.

3.3.3 General procedure for photopolymerization

Appropriate solutions of the monomers, photoinitiators and the coinitiators were irradiated with a Polilight PL400 Universal Forensic Light Source at 415 nm in nitrogen atmosphere. Polymers were obtained after precipitation in methanol and drying under vacuum. Conversions were calculated for all samples gravimetrically.

3.3.4 Photocalorimetry (Photo-DSC)

The photo-differential scanning calorimetry (Photo-DSC) measurements were carried out by means of a modified Perkin-Elmer Diamond DSC equipped with a high pressure mercury arc lamp (320–500 nm). A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 53 mW cm^{-2} by a UV radiometer capable of broad UV range coverage. The mass of the sample was 8 mg, and the measurements were carried out in an isothermal mode at 30°C under a nitrogen flow of 20 mL min^{-1}. The reaction heat liberated in the polymerization was directly proportional to the number of acrylate groups reacted in the system. By integrating the area under the exothermic peak, the conversion of the acrylate groups (C) or the extent of the reaction was determined according to eq 3.1:

$$C = \Delta H_t / \Delta H_0^{\mathrm{theory}} \qquad \textbf{(3.1)}$$

where ΔH_t is the reaction heat evolved at time t and $\Delta H_0^{\mathrm{theory}}$ is the theoretical heat for complete conversion. $\Delta H_0^{\mathrm{theory}}$ = 86 kJ mol^{-1} for an acrylic double bond.[42] The rate of polymerization (R_p) is directly related to the heat flow ($\mathrm{d}H/\mathrm{d}t$) by eq 3.2:

$$R_\mathrm{p} = \mathrm{d}C / \mathrm{d}t = (\mathrm{d}H / \mathrm{d}t) / \Delta H_0^{\mathrm{theory}} \qquad \textbf{(3.2)}$$

4. RESULTS AND DISCUSSION

4.1 Synthesis and Characterization of the Photoinitiators

Fluorene carboxylic acid thioxanthone (FLTXCOOH), 13-oxo-7, 13-dihydroindeno[1,2-*b*]thioxanthene-11-carboylic acid, was synthesized by a modified literature [20] procedure described for the synthesis of 2-hydroxythioxanthone according to Figure 4.1. Sodium fluorene carboxylate thioxanthone, (FLTXCOONa), sodium 13-oxo-7, 13-dihydroindeno[1,2-*b*]thioxanthene-11-carboxylate, was simply synthesized by the treatment of suspension of aqueous FLTXCOOH with sodium hydroxide (Figure 4.1).

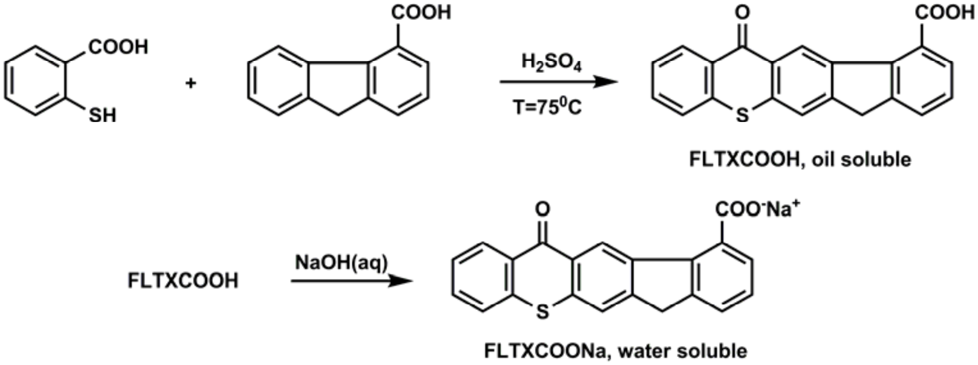

Figure 4.1 : Synthesis of fluorene carboxylic acid thioxanthone (FLTXCOOH) and sodium fluorene carboxylate thioxanthone (FLTXCOONa).

The structures of the photoinitiators were confirmed by spectroscopic analysis (see experimental section). As can be seen from Figure 4.2 both compounds exhibit characteristic protons leading to the formation of thioxanthone structure. The disappearance of the carboxylic acid proton around 13.5 ppm prooves the complete neutralization of the carboxylic acid function with the sodium hydroxide (Figure 4.2b).

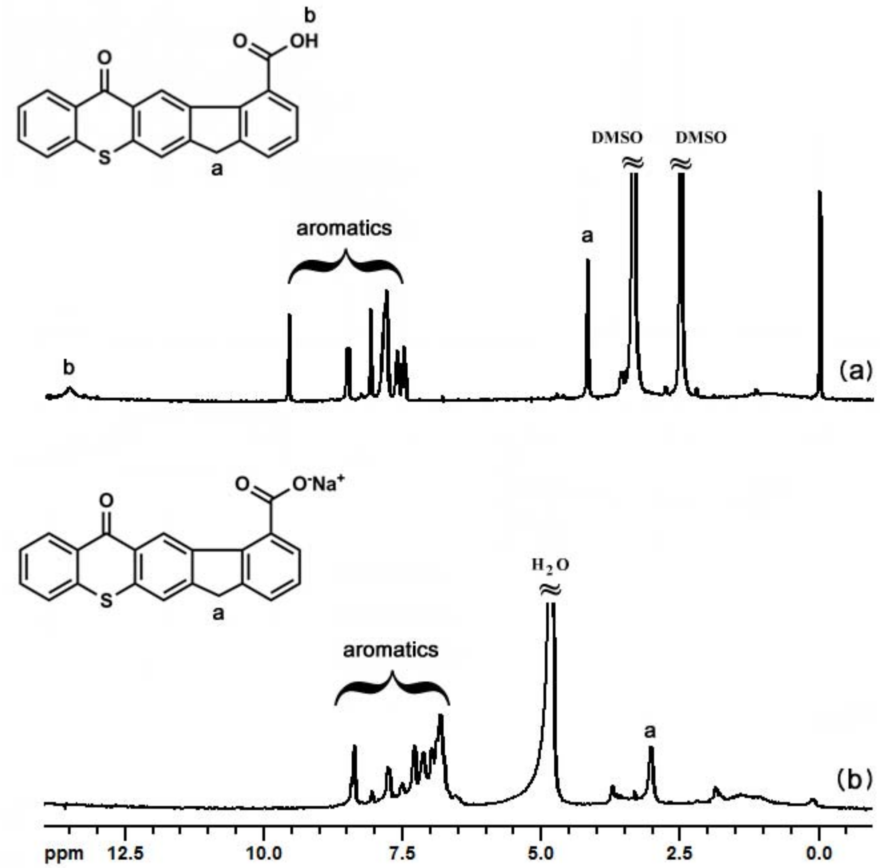

Figure 4.2 : The comparison of the ^{1}H-NMR spectra of (a) fluorene carboxylic acid thioxanthone (FLTXCOOH) in [*D*$_6$]-DMSO and (b) sodium fluorene carboxylate thioxanthone (FLTXCOONa) in D_2O.

Figure 4.3 demonstrates the comparison of UV spectra of FLTXCOOH and FLTXCOONa, with the parent thioxanthone and fluorene. As can be seen, FLTXCOOH and FLTXCOONa both possess an absorption characteristic similar to the thioxanthone with a maximum at 393 nm (ε= 3512 L mol^{-1} cm^{-1}) and 375 nm (ε= 2015 L mol^{-1} cm^{-1}) (Figure 4.3). The high molar absorptivity makes these thioxanthone derivatives attractive as photoinitiators because of their efficient light absorption.

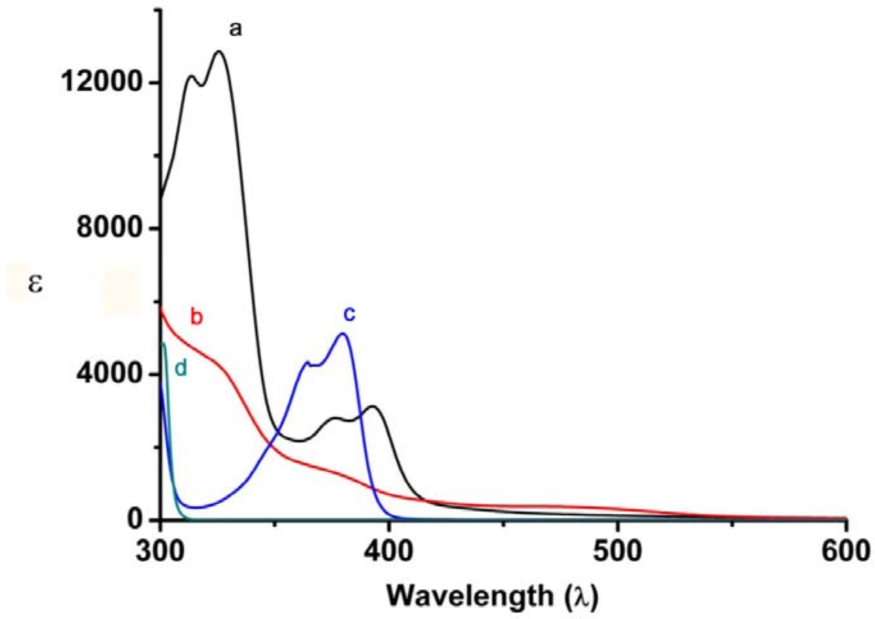

Figure 4.3 : The comparison of UV spectra of (a) fluorene carboxylic acid thioxanthone (FLTXCOOH), (b) sodium fluorene carboxylate thioxanthone (FLTXCOONa), (c) thioxanthone (TX) and (d) fluorene (FL).

Figures 4.4a and 4.4b demonstrates the comparison of UV spectra of both of the photoinitiators and CQ. Both FLTXCOOH and FLTXCOONa have greater molar absorbtivities compared to that of camphorquinone.

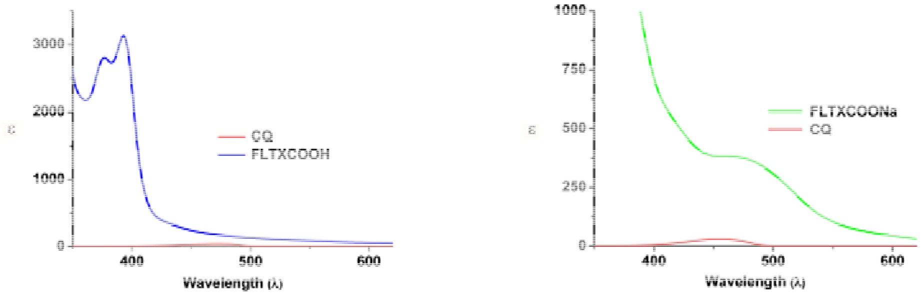

Figure 4.4 : The comparison of the UV spectra of a) FLTXCOOH and CQ in CH_2Cl_2 and b) FLTXCOONa and CQ in water.

Figure 4.5 and 4.6 show that a nearly mirror-image-like relation exists between absorption and emission of both FLTXCOOH and FLTXCOONa. The fluorescence spectra of these photoinitiators represents the characteristics of TX indicating their successful synthesis.

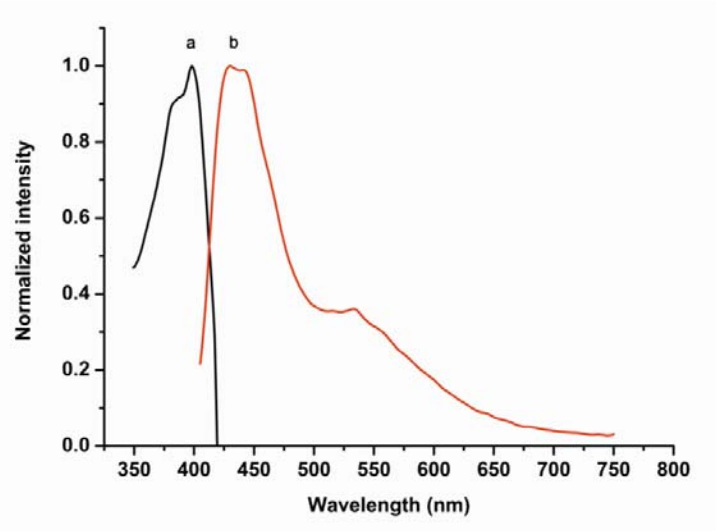

Figure 4.5 : Normalized excitation (a) and emission (b) fluorescence spectra of fluorene carboxylic acid thioxanthone (FLTXCOOH) in THF at room temperature.

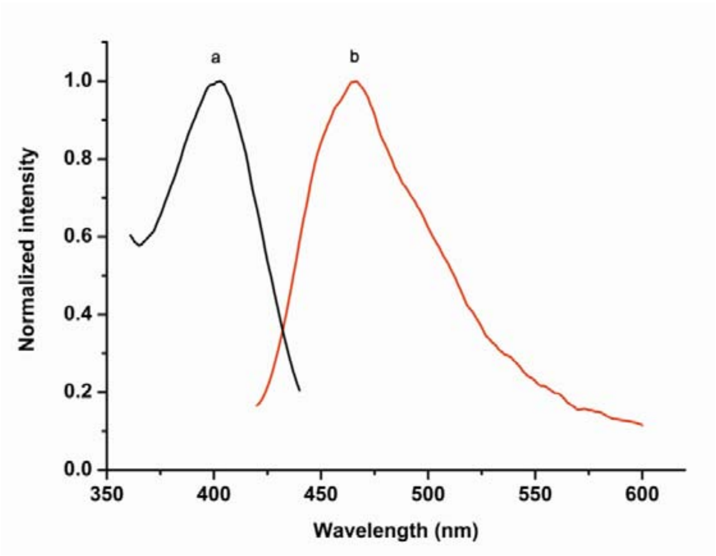

Figure 4.6 : Normalized excitation (a) and emission (b) fluorescence spectra of sodium fluorene carboxylate thioxanthone (FLTXCOONa) in H_2O at room temperature.

4.2 Photopolymerization Using Fluorene Carboxylic Acid Thioxanthone

FLTXCOOH was used as photoinitiator for the polymerization of methyl methacrylate at 415 nm in nitrogen atmosphere. The results obtained from polymerization of MMA with either TX or FLTXCOOH in the presence or absence of a hydrogen donor are compiled in Table 4.1. For comparison, photopolymerization by using TX itself in combination with the same hydrogen donor is also included. As can be seen TX is not efficient at the irradiation wavelength. It should be pointed out that FLTXCOOH is also efficient in the absence of the hydrogen donor.

Table 4. 1 : Photoinitiated polymerization of methyl methacrylate (MMA) by FLTXCOOH at 415 nm in DMF.

Run[a]	**[FLTXCOOH] (mol L^{-1})**	**[DMA] (mol L^{-1})**	**[TX] (mol L^{-1})**	**Conv. (%)**	**M_n**[b] **(× 10^{-3} g mol^{-1})**	**M_w/M_n**
1	1.0×10^{-3}	3.0×10^{-3}	-	11.1	33.7	1.24
2	5.0×10^{-3}	1.5×10^{-2}	-	29.6	13.6	1.38
3	1.0×10^{-2}	3.0×10^{-2}	-	8.1	11.8	1.35
4	5.0×10^{-3}	-	-	8.2	26.5	1.98
5	-	1.5×10^{-2}	5.0×10^{-3}	0	-	-

Irradiation time = 15 min
[a] [MMA] = 4.68 mol L^{-1}; FLTXCOOH= Fluorene carboxylic acid thioxanthone; TX= Thioxanthone, DMA= *N*,*N*-dimethylaniline
[b] Determined by GPC using polystyrene standards

For the possibility of using the described photoinitiator in practical applications, the efficiency of FLTXCOOH in the presence or absence of *N*,*N*-dimethylaniline (DMA) in the photocuring of formulations containing multifunctional monomers such as trimethylolpropane triacrylate (TMPTA) was also studied. PhotoDSC profiles of these experiments and their comparison with TX/DMA are shown in Figure 4.7. Figure 4.8 displays the plots of the conversion versus irradiation time derived from Figure 4.7.

The results verify that FLTXCOOH can efficiently be used in multifunctional UV curable systems.

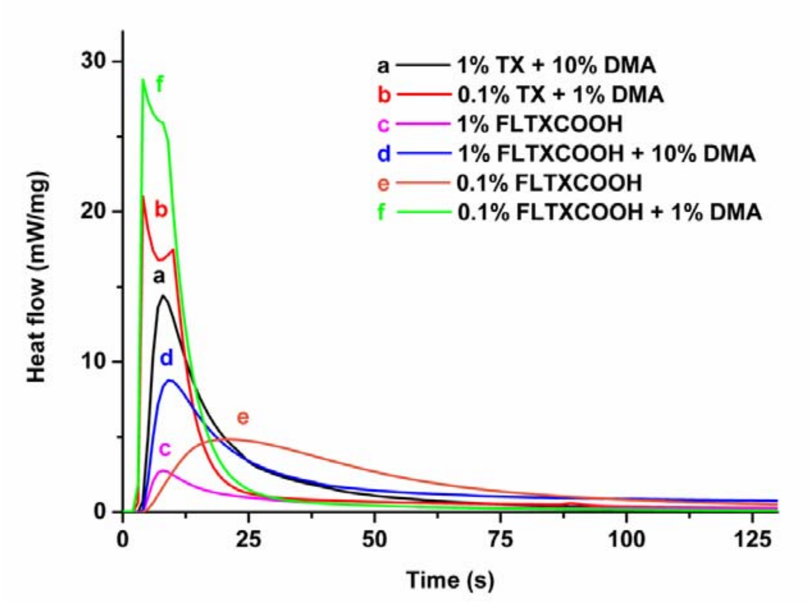

Figure 4.7 : PhotoDSC profiles for photopolymerization of TMPTA irradiated at 30 ^{o}C by UV light with an intensity of 58 mW cm^{-2}.

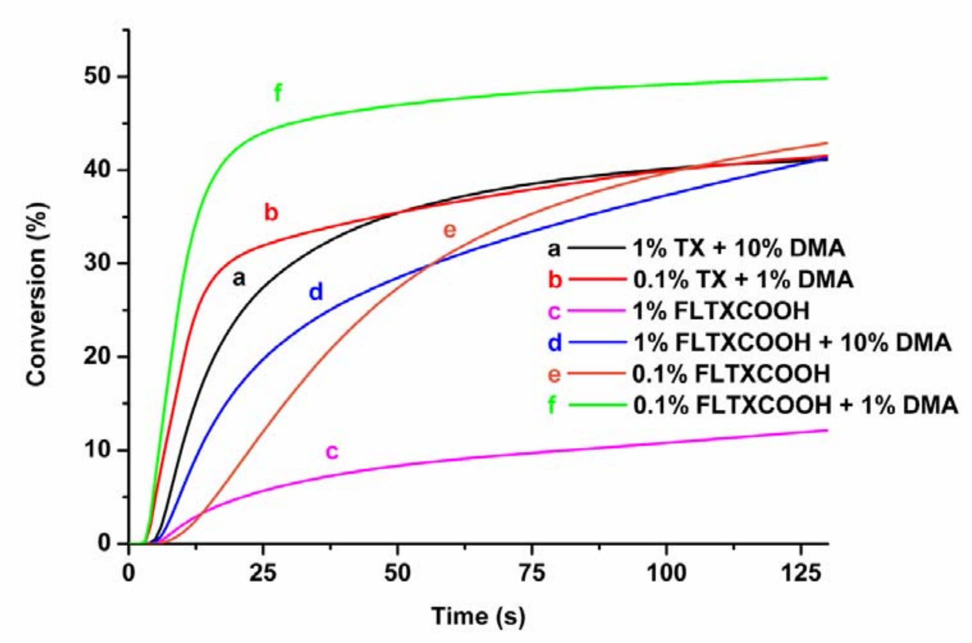

Figure 4.8 : Conversion vs time curves for photopolymerization of TMPTA irradiated at 30 ^{o}C by UV light with an intensity of 58 mW cm^{-2}.

The possibility of using FLTXCOONa as a water soluble photoinitiator has also been seperately investigated. In a stationary experiment, FLTXCOONa and CQ has been used used in conjuction with the dental formulation which contains the specific multifunctional monomers and the H-donor, ethyl 4-dimethylaminobenzoate. The nitrogen saturated solutions have been irradiated by a light with λ= 415 nm. The gelation time and the gel content comparison has been done for FLTXCOONa and the commercially used CQ. The results have been collected in Table 4.2.

Table 4.2 : The gelation time and gel content comparison of dental formulations with the photoinitiators, FLTXCOONa and CQ.

Photoinitiators	Gelation Time	Gel Content
FLTXCOONa	20’	98
CQ	1’	98

Dental Formulation : 40% EAEPA [molecular weight of EAEPA = 238 g mol$_{-1}$, theoretical enthalpy of EAEPA (DH$_{0E}$) = 62,900 J mol$_{-1}$], 20% DEBAAP [molecular weight of DEBAAP = 238 mol g$_{-1}$, theoretical enthalpy of DEBAAP (DH$_{0D}$) = 120,600 J mol$_{-1}$], and 40% water was used as a standard resin.
λ=415 nm

This stationary experiment demostrated that the FLTXCOONa can initiate photopolymerization in water under appropriate conditions. However, the gelation time for camphorquinone is found to be much shorter, which means that CQ is more convenient for dental applications, where shorter gelation times are desired.

4.3 Laser Flash Photolysis Experiments

Laser flash photolysis was performed to investigate the triplet states of photoinitiators FLTXCOOH and FLTXCOONa. Figure 4.9a and 4.9b show the transient absorption spectra of deoxygenated acetonitrile solution containing FLTXCOOH recorded at 280 and 680 ns after irradiation with laser pulses of 355 nm and deoxygenated aqueous solution containing FLTXCOONa recorded at 11 and 27 μs after irradiation with laser pulses of 355 nm, respectively. Both spectra show two peaks; for FLTXCOOH at 680 and 320 nm, and for FLTXCOONa at 630 and 350 nm. The peaks at 680 and 630 nm were assigned to the triplet-triplet absorption of FLTXCOOH and FLTXCOONa based on similarities with triplet-triplet spectra of TX[27], TX-SH[21] and $TXSCH_2COOH$[22]. Figure 4.10a and 4.10b show the decay kinetic of the transient absorptions of FLTXCOOH and FLTXCOONa at 680 and 630 nm, respectively. The triplet-triplet absorption at 680 nm decayed in a first-order kinetic corresponding to a lifetime of 632 ns. Distinctively, the triplet-triplet absorption at 630 nm decayed in a first-order kinetic corresponding to a lifetime of 26 μs.

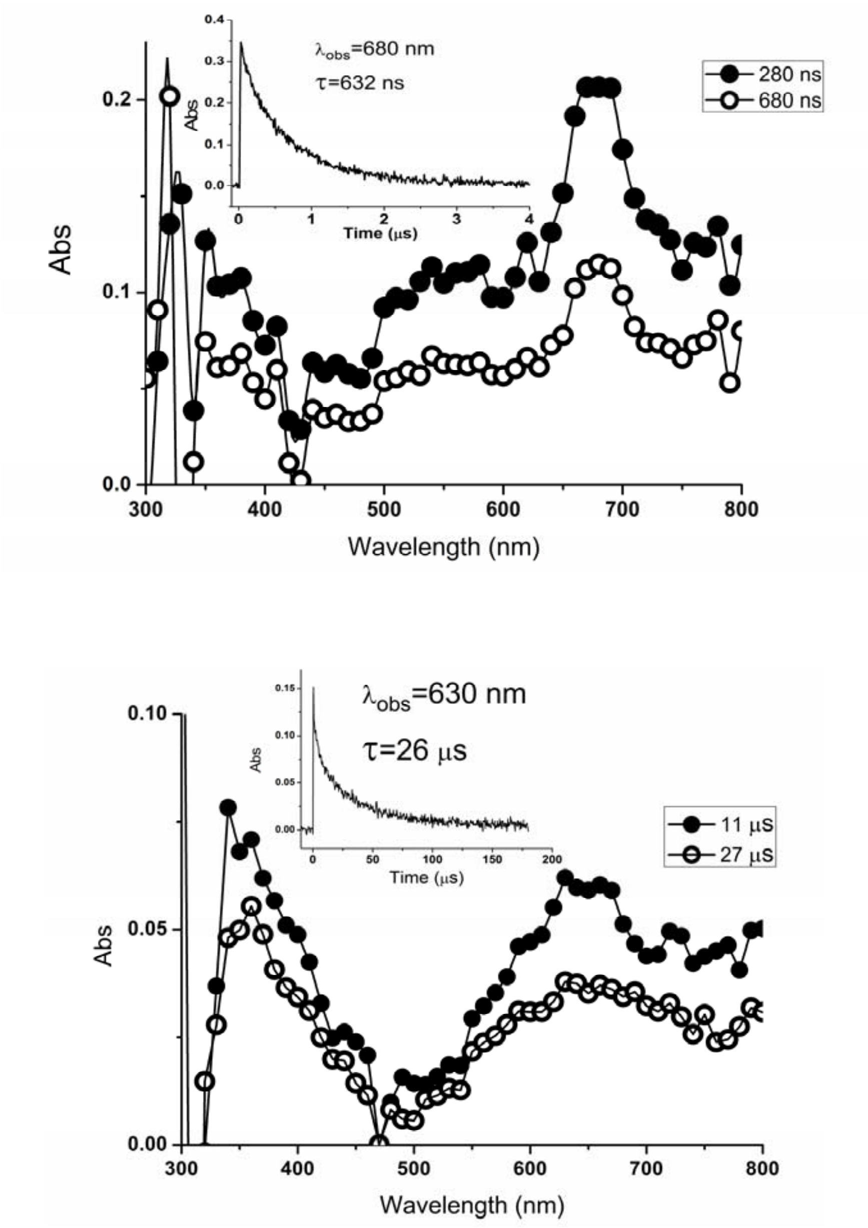

Figure 4.9 : Transient optical absorption spectra recorded a) at 280 and 680 ns following laser excitation (355 nm, 5 ns) of FLTXCOOH in argon saturated acetonitrile solution and b) at 11 and 27 μs following laser excitation (355 nm, 5 ns) of FLTXCOONa in argon saturated water solution.

Typically, triplet states of TX derivatives, such as TX or TX-SH possess triplet lifetimes longer than 10 μs (TX-SH: τ_T= 21 μs).[21] In contrast, FLTXCOOH showed a triplet lifetime of only 632 ns (observed at 680 nm), which indicates the involvement of a fast intramolecular quenching process.

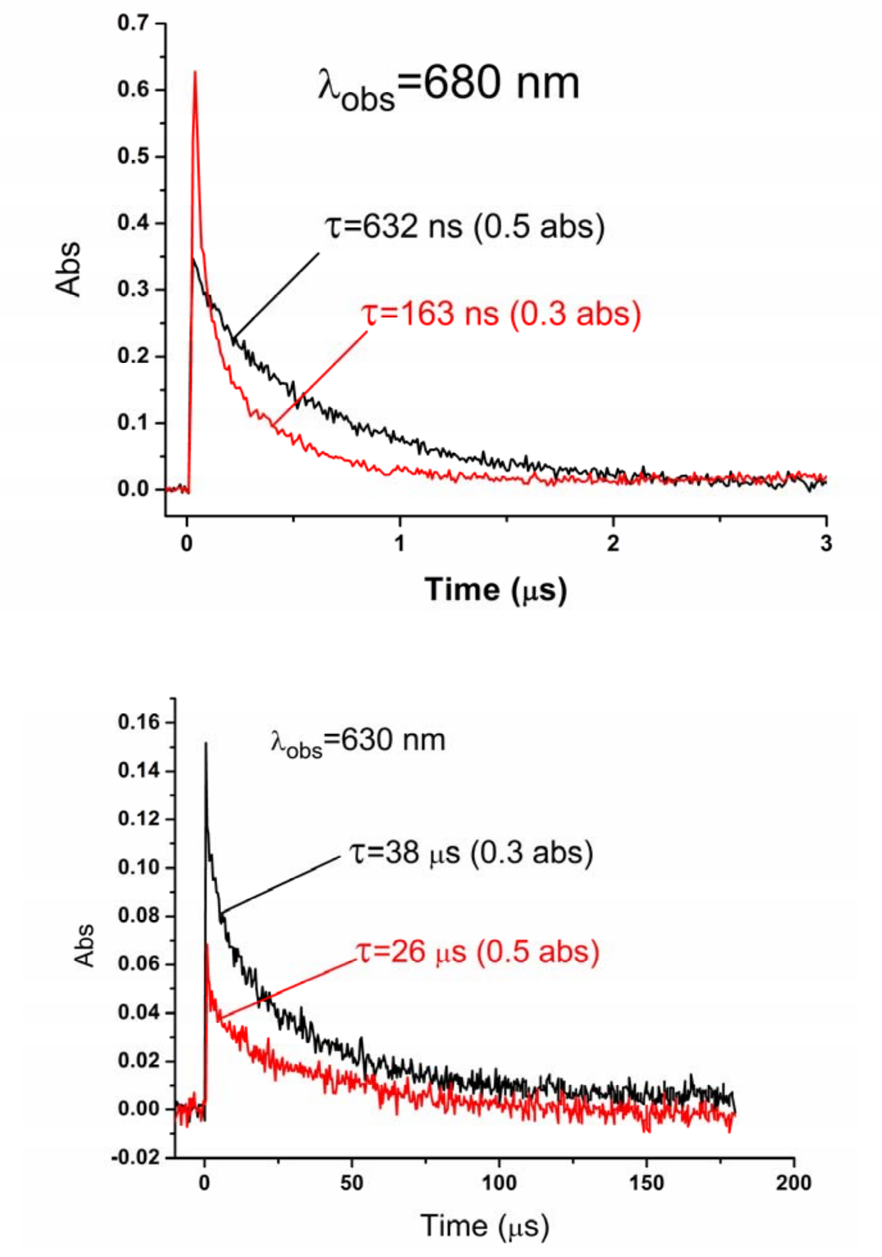

Figure 4.10 : Transient absorption kinetics observed a) at 680 nm following laser excitation (355 nm, 5 ns) of FLTXCOOH in argon saturated acetonitrile solution and b) at 630 nm following laser excitation (355 nm, 5 ns) of FLTXCOONa in argon saturated water solution.

We propose that the fast intramolecular quenching proces is a fragmentation reaction leading to carbon centered radicals, which than can initiate the polymerization. As it was shown above, FLTXCOOH is a good photoinitiator to initiate free radical polymerization of acrylates, indicating that it generates radicals efficiently. To test if triplet quenching occurs in an intramolecular process or intermolecular process, laser flash photolysis experiments were performed at two different concentrations of FLTXCOOH, 1.01 x 10 $^{-4}$ and 6.09 x 10^{-5}.

To investigate if bimolecular quenching can occur at higher concentrations, FLCOOH was used as quencher of triplet states of FLTXCOOH (Figure 4.11). Laser flash photolysis experiments were performed with deoxygenated acetonitrile solutions of FLTXCOOH (1.01 x 10^{-4} M) and different concentrations of FLCOOH (0-6 × 10^{-5} M). Pseudo-first-order treatment of the decay kinetics of the FLTXCOOH triplet states observed at 680 nm gave a quenching rate constant of 7.46 × 10^{9} M^{-1} s^{-1}. This shows that a bimolecular quenching process, where the triplet of FLTXCOOH gets quenched by FLCOOH in the ground state, can only compete with the intramolecular quenching at concentrations in the order of several millimolar.

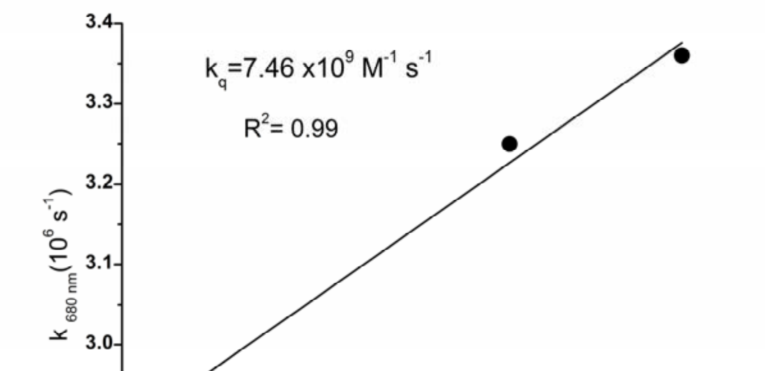

Figure 4.11 : Quenching of FLTXCOOH triplets by FLCOOH in acetonitrile, dependence of the pseudo-first-order rate constant of the decay at 680 nm on the concentration of FLCOOH.

Both the Laser Flash Photolysis experiments and the PhotoDSC experiments done with the FLTXCOOH photoinitiator showed that, FLTXCOOH can initiate polymerization both in the presence and in the absence of an additional co-initiator, where the dominant initiation mechanism can be intamolecular or intermolecular H-abstraction depending on the initiator concentration (Figure 4.12).

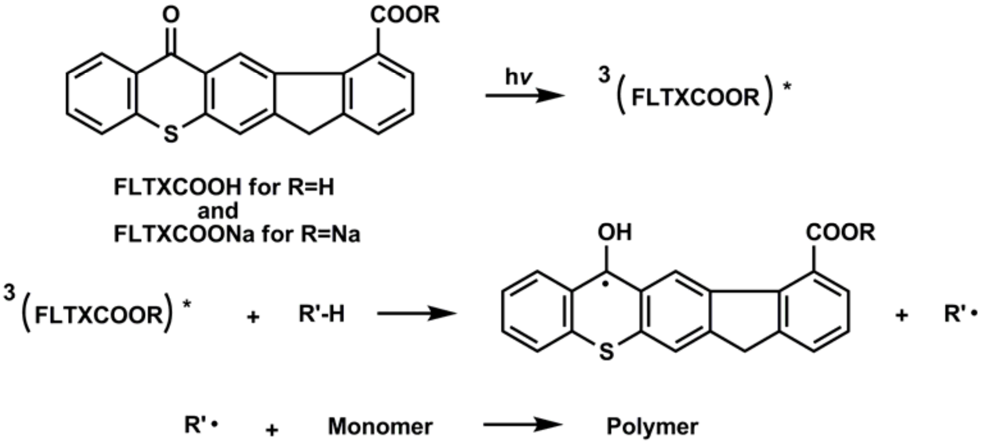

Figure 4.12 : Photoinduced free radical polymerizations using FLTXCOOH and FLTXCOONa.

An intramolecular H-abstraction is dominant in the lower concentrations of FLTXCOOH, whereas at relatively higher concentrations, an intermolecular H-abstraction is favorable (Figure 4.13).

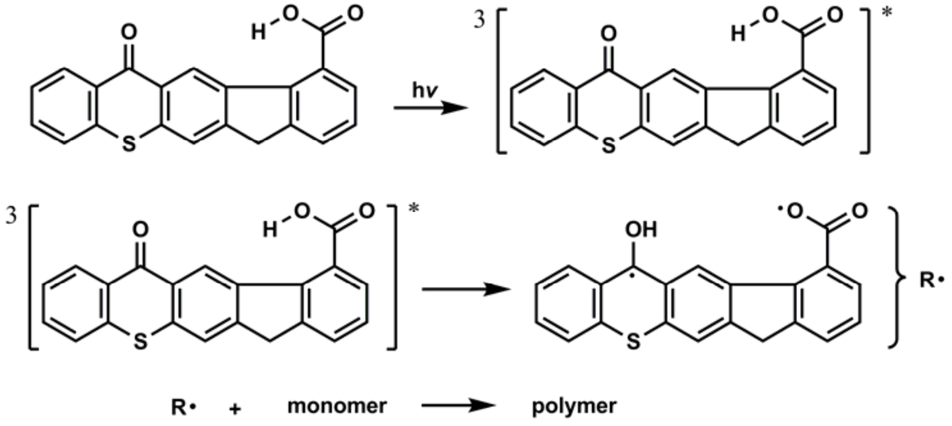

Figure 4.13 : Photopolymerization induced by FLTXCOOH in absence of hydrogen donor.

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