ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

POLY(VINYL ALCOHOL)-THIOXANTHONE AS ONE-COMPONENT *TYPE II* PHOTOINITIATOR FOR FREE RADICAL POLYMERIZATION IN ORGANIC AND AQUEOUS MEDIA

M.Sc. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ORGANİK VE SULU ORTAMLARDA SERBEST RADİKAL POLİMERİZASYONU İÇİN TEK BİLEŞENLİ *TİP II* FOTOBAŞLATICI OLARAK POLİ(VİNİL ALKOL)-TİYOKSANTON

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MAYIS 2015

Senem KÖRK, **a M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID 509131034, successfully defended the **thesis** entitled "**POLY(VINYL ALCOHOL)-THIOXANTHONE AS ONE-COMPONENT *TYPE II* PHOTOINITIATOR FOR FREE RADICAL POLYMERIZATION IN ORGANIC AND AQUEOUS MEDIA**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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

Jury Members : **Prof. Dr. Ümit TUNCA** ....
Istanbul Technical University

Prof. Dr. Nergis ARSU ....
Yıldız Technical University

Date of Submission : 30 April 2015
Date of Defense : 25 May 2015

To my family and Zelish,

FOREWORD

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May 2015 Senem KÖRK

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ABBREVIATIONS

^{1}H NMR : Hydrogen Nuclear Magnetic Resonance Spectroscopy
GPC : Gas Permation Chromatography
UV : Ultra Violet Calorimetry
PVA : Poly(vinyl alcohol)
DMF : N,N-dimethylformamide
DMSO : Dimethyl Sulphoxide
$CDCl_3$: Deuterated Chloroform
THF : Tetrahydrofuran
TX : Thioxanthone
TX-A : Thioxanthone aldehyde
PVA-TX : Poly(vinyl alcohol)-Thioxanthone

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POLY(VINYL ALCOHOL)-THIOXANTHONE AS ONE-COMPONENT *TYPE II* PHOTOINITIATOR FOR FREE RADICAL POLYMERIZATION IN ORGANIC AND AQUEOUS

SUMMARY

In recent years, photoinitiated polymerization has received revitalized interest as it congregates a wide range of economic and ecological anticipations. The most important elements of photoinitiated polymerization are the photoinitiators, which absorps the light to yield the species responsible for the initiation of polymerization. Thus, development of new photoinitiating systems became an important subject for the synthetic researchers in the past few years.

Both free radical and cationic photoinitiators are intensively examined and their initiating mechanisms are examined in detail. Free radical photoinitiators can be divided into *Type I* (α or less common β cleavage) and *Type II* (H-abstraction). Some of the most influential *Type I* initiators are benzoin ether derivaties, benzil katals, hydroxylalkylphenones, a-aminoketones and acylphosphine oxides. Besides that typical *Type II* photoinitiators include aromatic carbonyl ssuch as benzophenone and derivatives thioxanthone (TX), benzil, quinones, and organic dyes, however alcohols, ethers, amines, and thiols are used as hydrogen donors. *Type II* photoinitiators are the most widely used in many technologically important UV curing applications because of their excellent light absorption characteristics.

The radicals formed on the thioxanthone moiety do not actually participate in the initiation process on account of the steric hindrance and delocalization of the single electron on the π-system. Although they exhibit excellent initiation efficiency, the hydrogen donor compounds at high concentrations, have several intrinsic disadvantages such as offensive odor, toxicity, and migration in UV-curing technology. Several strategies have been developed to overcome these problems. The

usual approach is to chemically incorporate the hydrogen-donating sites into TX chromophores.

In this current work, TX moiety was incoperated to the side chains of commercially available poly(vinyl alcohol) (PVA) by a simple acetalization reaction. Initially, the designed thioxanthone structure with aldehyde functionality (TX-A) was facilely synthesized. Afterwards, the obtained TX-A was linked to the PVA counterpart by a simple addition reaction to yield the desired PVA-TX macroinitiator. PVA-TX polymeric photoinitiator exhibits typical TX absorption characteristics and soluble in water and some polar organic solvents such as DMF and DMSO. Moreover, PVA-TX displays one-component nature and initiates the polymerization in both organic and aqueous media without the necessity of additional hydrogen donor donor due to the presence of remaining hydrogen donating hydroxyl groups in the structure.

ORGANİK VE SULU ORTAMLARDA SERBEST RADİKAL POLİMERİZASYONU İÇİN TEK BİLEŞENLİ *TİP II* FOTOBAŞLATICI OLARAK POLİ(VİNİL ALKOL)-TİYOKSANTON

ÖZET

Fotobaşlatılmış polimerizasyon pek çok ekonomik ve ekolojik beklentiyi karşıladığı için son yıllarda hayli ilgi çekmektedir. Fotobaşlatılmış polimerizasyon, sahip olduğu mükemmel avantajları dolayısı ile kaplama, mürekkep, baskı levhaları, optik frekans yönlendiricileri ve mikroelektronik gibi sayısız uygulamaların temelini oluşturmaktadır. Bu avantajlar, oda sıcaklığında yüksek polimerizasyon hızı, düşük enerji tüketimi, çözücüsüz ortamada polimerizasyon, uygulanacak yüzey alanı ve uygulama süresinin kontrol edilebilmesi olarak sıralanabilir.

Fotopolimerizasyon yönteminin en önemli bileşenleri başlatıcılardır. O yüzden birçok araştırmacı yeni yöntemler geliştirmeye çalışmaktadır. Monomer ve başlatıcı arasındaki yapısal uyumluluk, polimerizasyonun ilerleyişi açısından önem kazanmaktadır. Fotobaşlatıcının uygun bir dalga boyundaki ışık absorpsiyonu sonucunda oluşan radikaller tek fonksiyonlu monomerlerin polimerizasyonunu sağlarken çok fonksiyonlu monomerlerde ise çapraz bağlı yapılara dönüştürülmesini sağlar. Polimerik fotobaşlatıcılar çapraz bağlanacak filmin içinde göç edememe ve kolay sentezlenebilme gibi avantajlar taşımaktadır. Buna ilave olarak, fotopolimerizasyon sonucu oluşan ürünlerin küçük moleküllü yapılar olması nedeniyle sağlığa zarar verilmesi engellenmiş olur ve polimer üzerinde çok sayıda fotoaktif grupların bulunması çapraz bağlanma süresince belirgin üstünlükler sağlar. Uygun ışık şiddeti kullanılarak başlatıcı konsantrasyonu ve polimer zincirlerinin boyu ayarlanabilir. Polimerlerin ışığı absorplamasıyla fiziksel ve kimyasal özelliklerinde değişmeler gerçekleşir. Görünür bölgede absorbansa sahip başlatıcılar çok ilgi çekicidir, zira diş dolgu malzemelerinde, fotorezistlerde, matbaacılıkta, entegre devrelerde, lazer ile uyarılmış üç boyutlu kaplamalarda, halografik kayıtlarda ve nano boyutlu mikromekaniklerde kullanılmaktadır.

Fotopolimerizasyon radikal, katyonik ve anyonik olarak başlatılabilse de çok sayıda fotobaşlatıcının ve yüksek reaktivitedeki monomerlerin bulunulabilirliği açısından serbest radikal ve katyonik sistemlere daha fazla ilgi duyulmaktadır. Endüstriyel uygulamalarda serbest radikal fotopolimerizasyon sistemleri kullanılmaktadır.

Fotobaşlatıcılar, radikal oluşturma mekanizmalarına göre *Tip I* ve *Tip II* fotobaşlatıcılar olmak üzere iki ayrı sınıfa ayrılır. *Tip I* fotobaşlatıcılar, radikal vermek üzere doğrudan foto parçalanmaya uğrayan, çeşitli fonksiyonel gruplar içeren aromatik karbonil bileşikleridir. *Tip II* başlatıcılarda, polimerizasyonun başlaması hidrojen verici molekül üzerinde oluşan radikaller vasıtasıyla gerçekleşirken, etkin olmayan ketil radikalleri birbirleriyle kenetlenerek başlatıcı reaktif olarak davranmazlar. Radikal üretimi iki molekülün etkileşimi sonucu olan, *Tip II* fotobaşlatıcılar, tek molekülün parçalanarak radikal oluşturduğu *Tip I*

fotobaşlatıcılara göre daha yavaş çalışmaktadır. Diğer yandan, *Tip II* fotobaşlatıcılar daha iyi optik özelliklere sahip olduklarından, düşük enerjili ışık kaynaklarıyla çalışma imkanı sunmaktadırlar. Ayrıca *Tip I* fotobaşlatıcılar ile elde edilen polimerler, ışığa mağruz kaldıklarında α-bölünme mekanizması sonucu, uçucu yan ürünler meydana getirirler. Oluşan bu ürünler kötü kokuya neden olur . Bu açıdan bakıldığında, *Tip II* fotobaşlatıcılarda ki ketil radikali tekrar ketona yükseltgenebildigi gibi birleşerek yüksek molekül ağırlıklı ve daha az uçucu bileşikler oluşturarak hedef ürünlerden uzaklaşırlar. Bu üstün özelliğinden dolayı, *Tip II* fotobaşlatıcılar daha çok tercih edilir. Etkili bir başlatma olabilmesi için, hidrojen koparma reaksiyonu diğer yan reaksiyonlarla (uyarılmış fotobaşlatıcıların enerjilerini oksijen ya da monomere aktarmasıyla enerjinin boşa harcanması) yarışabilmelidir. Bu sebepten dolayı *Tip II* serbest radikal fotopolimerizasyonu oksijene karşı yüksek seviyede duyarlıdır. Hidrojen verici grupların seçimi bu sistemde büyük önem kazanmıştır. *Tip II* fotobaşlatıcılarda, hidrojen verici moleküller olarak kullanılan amin, eter, alkol ve tiyol molekülleri arasında tersiyer aminler en çok tercih edilenlerdir. Ancak tersiyer aminlerin kötü kokulu, zehirli, kolay uçucu olması, göçme gibi olumsuz yönleri vardır.

Bu sorunların üzerinden gelmek için çeşitli stratejiler geliştirilmiştir. Kimyasal olarak olağan yaklaşım, tiyoksanton kromoformalarının içine hidrojen donörlerin yapıya bağlanmasıdır. Tiyol, amin ve karboksilik asitler hidrojen donörler bulunduran tiyoksanton yapısı sentezlenip ve serbest radikal polimerizasyonu için tek bileşenli fotobaşlatıcı kullanılmıştır. Alternatif olarak, tiyoksanton fonksiyonel gruplarına çeşitli geleneksel polimerler sırasıyla; polistiren, polietilenoksit, mikrogözenekli polimer ağları ve polibenzoksazinler çeşitli organik reaksiyonları ve çıt çıt kimyası yoluyla katılmıştır. Bu yol ile, UV-kürleşme uygulamalarında düşük molar ağırlıklı başlatıcılar ile ilişkili göç sorunlarının üstesinden gelinmiştir. Polinükleer aromatik bileşikler ile tiyoksanton yapılarının birleşimi kullanılarak tiyoksanton fotobaşlatıcılarının absorpsiyon karakterleri daha yüksek dalga boylarına genişletilebilir. Örneğin, tiyoksanton-antrasen sadece hava varlığında ve herhangi bir yardımcı bir başlatıcıya gerek kalmadan akrilik ve stirenik monomerlerinin polimerizasyonunu başlattığından dolayı ilginç bir moleküldür. Oksijen ile üçüncü seviyeye uyarılmış tiyoksantonun söndürmesi yüzünden diğer çeşit tiyoksanton fotobaşlatılar oksijeni engeller ki bu aynı zamanda bir avantaj sağlar.

Tiyoksantonlar, benzofenonlar gibi diğer benzer yapılar üzerinden daha tercih edilebilen bir foto başlatıcı türü olmuştur ve dalga boyu absorpsiyon aralığı ise 380-420 nm arasındadır. Bu durum foto uyarılma için gerekli olan enerjiyi ve elektromanyatik spekturumun görünür bölge aralığındaki radikallerin başlatılmasının sıralı oluşumunu azaltır. Farklı işlevsellerin sübstitüe olması daha yüksek dalga boylarına absorpsiyon bandını kaydırabilir. Bunun yanında farklı ortamlarda çözünürlüğünü kolaylaştırabilir ya da başlatıcının fotoaktifliğini arttırabilir. Başka bir görüşten bakıldığında düşünülmüştür ki kürleşmiş ürünlerin sararması gibi bazı dezavantajlar, tiyoksanton fotobaşlatıcı sistemi kullanılarak büyük ölçüde önüne geçirilebilir. Lazer flaş fotoliz gibi çeşitli spektrokopik tekniklerin gelişimi ile fotobaşlatılmış polimerizasyonun mekanizması tiyoksantonlar kullanılarak kapsamlı bir şekilde araştırılmıştır. İşlem başlatıcı türlerinin oluşumunu gerçekleştirmek için yardımcı bir başlatıcı varlığını gerektirmektedir. Tiyoksanton temelli fotobaşlatıcıların fotoaktivitesi, fotobaşaltıcının sübstitüe motifine, bunun yanında sistemde mevcut durum ve diğer yardımcı bileşiklerin varlığına oldukça bağımlıdır.

Fotobaşlatılmış işlem esnasında fonksiyonellrrin türü ve varlığı maksimum absorpsiyonunu; tiyoksantonun kuantum verimleri ve sönümleme katsayılarını etkileyebilir.

Bu tezde, basit bir asetelizasyon yöntemi kullanılarak ticari olarak bulunan poli(vinil alkol)'ün (PVA) yan zincirlerine tiyoksanton kromoforu birleştirildi. Bu amaçla, aldehit işlevselli tiyoksanton (TX-A) yapısı tasarlandı ve karakterizasyon sentezin başarısını göstermiştir. İstenen PVA-TX makrobaşlatıcı elde etmek için, elde edilen TX-A yapısı PVA ya karşı basit bir katılma reaksiyonu kullanarak bağlandı. Polimerik fotobaşlatıcı PVA-TX suda, dimetilformamit (DMF) ve dimetilsülfoksit (DMSO) gibi bazı organik polar çözücülerde tipik absorpsiyon karakterleri göstermiştir. Ayrıca, yapısında kalan hidrojen donörü hidroksil gruplarının varlığı nedeniyle PVA-TX doğal tek bileşenli fotobaşlatıcı gösterir ve herhangi bir ek hidrojen donörüne gerek olmadan hem organik hem de sulu ortamda polimerizasyonu başlatır. Çalışmamızda PVA-TX polimerik fotobaşlatıcısı, metilmetakrilat (MMA) ve akrilamit (AA) monomerlerinin hem organik hem de sulu ortamda fotopolimerizasyonunu sağlamıştır. PVA-TX yapısında bulunan tiyoksanton kromoformalarının içine hidrojen donörlerin yapıya bağlanması ile yardımcı bir başlatıcıya gerek kalmadan fotopolimerizasyon gerçekleşmiştir.

1. INTRODUCTION

Thioxanthone (TX) and derivatives are the most widely used *Type II* photoinitiators in many technologically important UV curing applications among the huge number of available photoinitiators resulting from their excellent light absorption characteristics [1, 2]. Upon irradiation, triplet excited states of TXs abstract hydrogen from a suitable compound to give initiating radicals (Scheme 1).

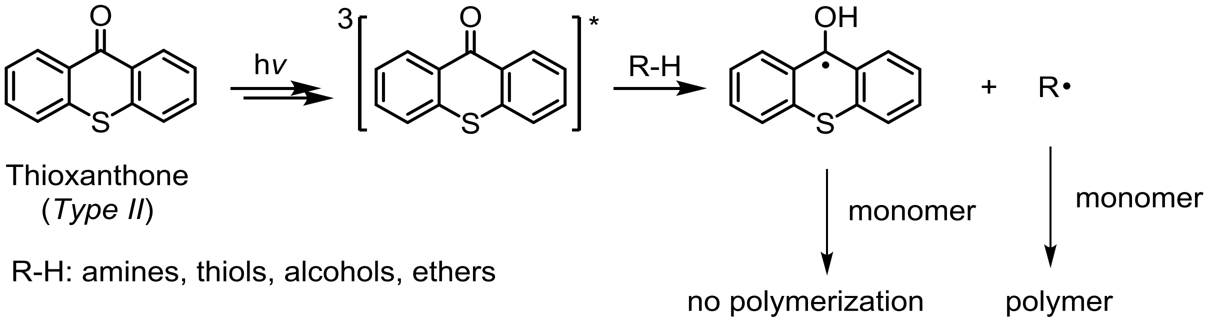


Figure 1.1 : Photoinitiated free radical polymerization by using thioxanthone.

In the process, the polymerization is initiatiated only by the radicals formed from the hydrogen donor compounds such as amines, thiols, alcohols and ethers [3-5]. The radicals formed on the thioxanthone moiety do not actually participate in the initiation process due to the steric hindrance and delocalization of the single electron on the π-system. Although they exhibit excellent initiation efficiency, the hydrogen donor compounds, particularly amines and thiols at high concentrations, have several intrinsic disadvantages such as offensive odor, toxicity[6], and migration in UV-curing technology and cause a decrease in the pendulum hardness of the cured films [7]. Several strategies have been developed to overcome these problems. The usual approach is to chemically incorporate the hydrogen-donating sites into TX chromophores. TX compounds with thiol, amine and carboxylic acid hydrogen donating sites were successfully synthesized and used as one-component photoinitiators for free radical polymerization [8-17]. Alternatively, TX moieties were profitably incorporated into several traditional polymers, namely polystyrene, poly(ethylene oxide), microporous conjugated polymer networks and polybenzoxazines through various organic reactions and click chemistry[18-30]. This approach overcomes migration problems associated with low molar mass photoinitiators in UV curing applications. The absorption characteristics of TX photoinitiators can be extended to higher wavelengths by combining TX structures with polynuclear aromatic compounds [16, 17, 31] facilitating their use in UV curing applications of pigmented formulations. Among several examples, thioxanthone anthracene is an interesting molecule as it initiates polymerization of acrylic and styrenic monomers without a co-initiator only in the presence of air [18, 32, 33]. This is an additional advantage since for other TX type photoinitiators oxygen inhibits polymerization because of quenching of excited triplet TX with oxygen. Detailed mechanistic studies revealed that the initiation mechanism involves the formation of singlet oxygen by energy transfer from triplet thioxanthone-anthracene and addition to the anthracene moiety to form endo-peroxide. Photoexcitation of this intermediate leads to alkoxy or peroxy radicals, which are able to initiate free radical polymerization.

In this current work, TX moiety was incorporated to the side chains of commercially available poly(vinyl alcohol) (PVA) by a straighforward acetalization reaction. For this purpose, a thioxanthone structure with aldehyde functionality (TX-A) was designed and facilely synthesized. Afterwards, the obtained TX-A was linked to the PVA counterpart by a direct addition reaction to yield the desired PVA-TX macroinitiator. PVA-TX polymeric photoinitiator exhibits typical TX absorption characteristics and soluble in water and some polar organic solvents such as DMF and DMSO. Moreover, due to the presence of remaining hydrogen donating hydroxyl groups in the structure, PVA-TX displays one-component nature and initiates the polymerization in both organic and aqueous media without the necessity of additional hydrogen donor.

2. THEORETICAL PART

2.1 Photoinitiated polymerization

In recent years, photopolymerization is one of the most swiftly widening procedures for materials production and also is employed over a broad range of applications. Photopolymerization process has continued to expand the growth of plastic market share since the technologies are extremely efficient, environmentally favorable and economical process in proportion to conventional thermal polymerizations. The use of light to handle the reactions leads to a variety of advantages, as well as solvent-free formulations, very high reaction rates at room temperature, spatial control of the polymerization, low energy input, and chemical versatility since a wide diversity of polymers can be polymerized photochemically. Photopolymerization method is powerful industrial process broad used in several applications including in coatings, adhesives, inks, printing plates, optical waveguides and microelectronics. Additionally, this method uses lower energy requietments in view of the fact that the polymerizations use a fraction of the energy of traditional thermal systems on the other hand process ensures high speed and production rate at low curing temperature. Eventually, the process may be used to rapidly form polymers without the use of diluting solvents and leads to lower evaporating organic compounds than conventional thermal polymerization.

Photopolymerization is a typicall method which transforms a monomer into polymer via a chain reaction initiated via reactive species (free radicals or ions) that are produced from photosensitive compounds by ultra violet-visible (UV-Vis) light irradiation [34]. Certain types of compounds which are capable of absorbing light of a particular wavelength initiate photopolymerizations. The wavelength or range of wavelengths of the initiating source is determined by the reactive system including the monomer(s), the initiator(s), and any photosensitizers, pigments or dyes which may be present. An active center is generated when the iniator absorbs light, comes over some of decomposition, hydrogen abstraction or electron transfer reaction.

Even though photopolymerization can be initiated radically, cationically and ionically, the corresponding free radical polymerization with photoinitiated cationic polymerization is still the most widely employed route in such applications. Thus, its applicability to a large range of formulations based on acrylates, unsaturated polyesters, and polyurethanes and the availability of photoinitiators having spectral sensitivity in the near-UV or visible range.

2.1.1 Photoinitiated free radical polymerization

Photoinitiated free radical polymerization consists of photoinitiation, propagation, chain transfer and termination as shown in Figure 2.1

$$\left.\begin{array}{ll} PI \xrightarrow{h\nu} PI^{\bullet} & \text{Absorption} \\ PI^{\bullet} \longrightarrow R_1^{\bullet} + R_2^{\bullet} & \text{Radical Generation} \\ R_1^{\bullet} + M \longrightarrow R_1{-}M^{\bullet} & \end{array}\right\}\text{Photoinitiator}$$

$$\left.\begin{array}{l} R_1{-}M^{\bullet} + M \longrightarrow R_1{-}MM^{\bullet} \\ R_1{-}MM^{\bullet} + (n\text{-}2)M \longrightarrow R_1{-}M_n^{\bullet} \end{array}\right\}\text{Propagation}$$

$$\left.\begin{array}{l} R_1{-}M_n^{\bullet} + R{-}H \longrightarrow R_1{-}M_n{-}H + R^{\bullet} \\ R^{\bullet} + M \longrightarrow R{-}M^{\bullet} \end{array}\right\}\text{Transfer}$$

$$\left.\begin{array}{l} R_1{-}M_n^{\bullet} + R_1{-}M_m^{\bullet} \longrightarrow R_1 - M_{n+m} - R_1 \\ R_1{-}M_n^{\bullet} + R_2^{\bullet} \longrightarrow R_1 - M_n - R_1 \\ R_1{-}M_n^{\bullet} + R_1{-}M_m^{\bullet} \longrightarrow R_1{-}M_n + R_1{-}M_m \\ R_1{-}M_n^{\bullet} + R_2^{\bullet} \longrightarrow R_1{-}M_n + R_2 \end{array}\right\}\text{Termination}$$

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

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

In most instances photoinitiated polymerization, a initiator undergoes a photoreaction, generating free radicals. These species can initiate the polymerization of suitable monomers. Generally, photoinitiators are divided into two classes; *Type I* and *Type II* according to the process by which initiating radicals are formed.

2.1.1.1 *Type I* photoinitiators (Unimolecular photoinitiator systems)

Photoinitiators termed unimolecular are so appointed owing of the fact that the initiation system includes only one molecular species interacting with the light and producing free radical active centers. These substances sustain a homolytic bond cleavage upon absorption of light as shown in Figure 2.2. *Type I* photoinitiators sustain a straight photofragmentation procedure (α or less common β cleavage) upon absorption of light and configuration of initiating radicals capable of inducing polymerization.

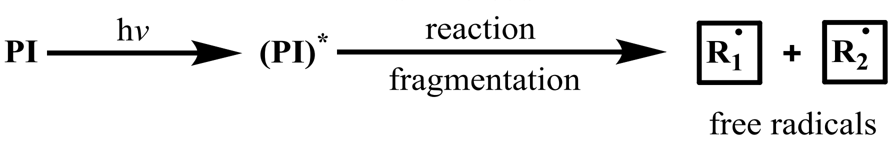


Figure 2.2 : Decomposition of *Type I* photoinitiators upon irradiation.

As illustrated in Figure 2.2, absorption of ultroviolet light and rapid intersystem crossing to the triplet state induced the photoinitiator. The bond to the carbonyl group, producing an active benzoyl radical fragment and other fragment in the triplet state.

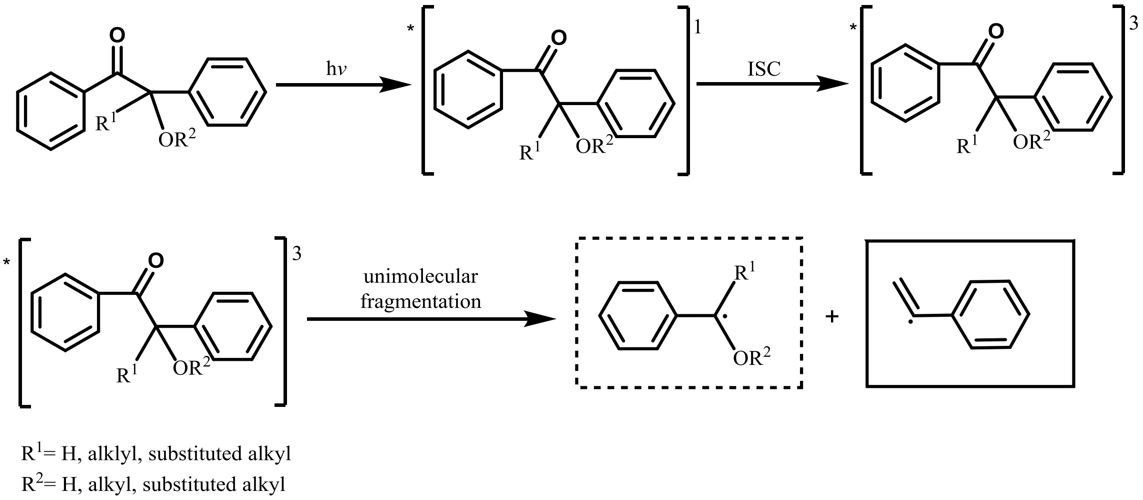
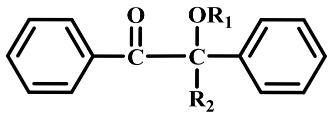
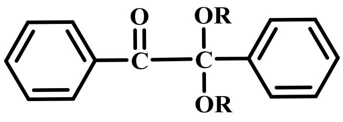
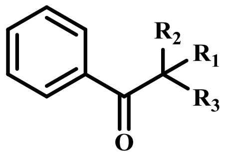
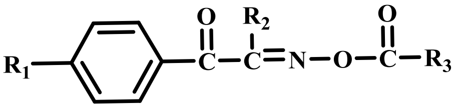
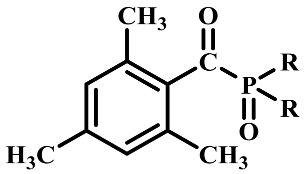
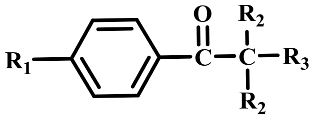


Figure 2.3 : Absorption of ultraviolet light of photoinitiator.

The benzoyl radical is the one of the most crucial iniating species, as in some instances, the other fragment may also subscribe to the initiation. Some of the most influential *Type I* initiators are benzoin ether derivaties, benzil katals, hydroxylalkylphenones, a-aminoketones and acylphosphine oxides as can be seen in Table 2.1 [35]

Table 2.1 : Structures of typical *Type I* radical photoinitiators.

Photoinitiators	Structure	λ_{max}(nm)
Benzoin ethers	 R_1 = H, alkyl R_2 = H, substituted alkyl	323
Benzil ketals	 R = CH_3, C_3H_7, CH_2	365
Acetophenones	 R_1 = OCH_3, OC_2H_5 R_2 = OCH_3, H R_3 = C_6H_5, OH	340
Benzyl oximes	 R_1 = H, SC_6H_5 R_2 = CH_3, C_6H_5 R_3 = C_6H_5, OC_2H_5	335
Acylphosphine Oxides	 R = C_6H_5, OCH_3	380
Aminoalkyl phenones	 R_1 = SCH_3, morpholine R_2 = CH_3, CH_2Ph, C_2H_5 R_3 = $N(CH_3)_3$, morholine	320

2.1.1.2 *Type II* photoinitiators (Bimolecular photoinitiator systems)

Type II photoinitiators, biomolecular photoinitiator systems, are two molecular species that are requires to compose the propagating radical as shown in Figure 2.4.

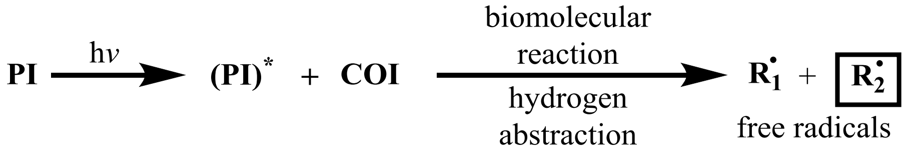
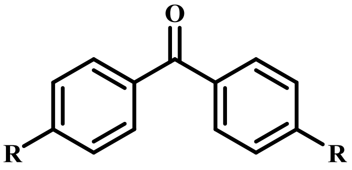
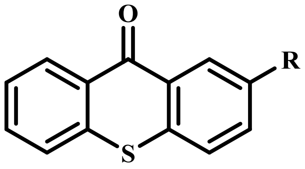
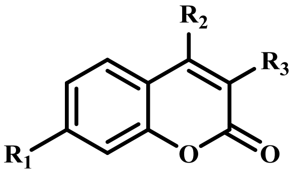
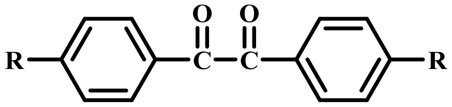
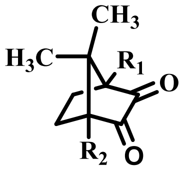


Figure 2.4 : Decomposition of *Type II* photoinitiators upon irraditation.

A photoiniator absorbs the light and the co-initiator serves as a hydrogen or electron donor. These photoinitiators do not undergo *Type I* reactions because of that their excitation energy is not high enough for fragmentation, i.e., their excitation energy is lower than the bond dissociation energy. The excited molecule can react with co-initiator to produce initiating radicals. Photons are absorbed in the near UV and visible wavelengths in these systems.

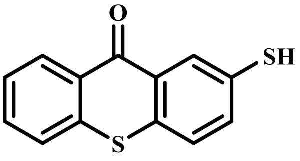
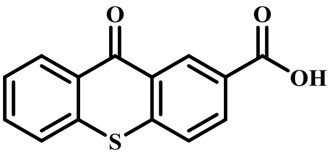
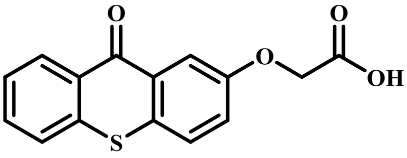
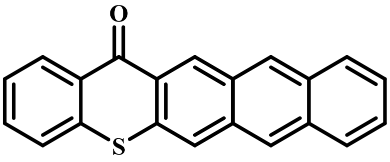
Typical *Type II* photoinitiators include aromatic carbonyls such as benzophenone and derivatives [36-38], thioxanthone and derivatives [11, 39-42], benzyl [36] quinines [36], and organic dyes [43-48], however alcohols, ethers, amines, and thiols are used as hydrogen donors. Recently, thiol and carboxylic acid derivatives of thioxanthones have been reported to initiate photopolymerization without co-initiators as they contain functional groups with H-donating nature [13-15]. List of *Type II* photoinitiators are shown in Table 2.2.

Table 2.2 : Structures of typical *Type II* photoinitiators.

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

As polymeric hydrogen donors to replace low molecular weight amines successfully use poly(ethylene oxide) and poly(ethylene imine) based dendrimers of the following structures in the formulations. As part of our efforts to avoid problems linked to the amine hydrogen donors, Yagci and co-workers have recently reported several new thioxanthone derivatives as photoinitiators for free radical polymerization. Curiously, these photoinitiators do not need an additional coinitiator, that is, a seperate molecular hydrogen donor. The structures and the mode of action of such one-component photoinitiators are shown in Table 2.3.

Table 2.3 : Thioxanthone based one-component photoinitiators.

Photoinitiator	Structure	Mode of action	Ref.
2-Mercaptothioxanthane		Hydrogen abstraction	[14, 49]
2-(9-Thioxanthone-2-thio) acetic acid		Hydrogen abstraction	[13, 15]
2-(9-Thioxanthone) acetic acid		Hydrogen abstraction	[13, 15]
Thioxanthone-Anthrace		Endoperoxide formation	[18]

2.1.1.3 *Polymeric* Photoinitiators

Polymeric photoinitiators can be described as macromolecular systems that contain pendant or in-chain chromophores which through a light absorption process. They can generate active species able to initiate the polymerisation and crosslinking of mono- and multi-functional monomers and oligomers [50]. They have higher cost by the various advantages compared to their corresponding low molecular weight analogues from an industrial viewpoint. The presence of the polymer chain enhances the convenience in the formulation and decreases the migration onto the film surface [50, 51]. Thence, they contribute to manufacture low-odouring and non-toxic coatings [51].

Moreover, as result of energy migration along the polymer chain, or intramolecular reactions responsible for the formation of more reactive species improve the photoinitiation activity [52]. The macromolecular chain can maintain the active species, like a cage effect. Inclusion of the chromophore as a pendant or in terminal position in a polymer, or copolymerising the chromophore may accomplish so that it is present in the macromolecular backbone [53]. The copolymerisation of photosensitive monomers with traditional co-monomers present the probability of macromolecular design, nature of the co-monomer and in this connection of nature and distance from the backbone of the pendant photosensitive moieties. The synthesis of copolymers carrying dissimilar photosensitive groups may supply prospective synergistic effects of activity and giving dissimilar features to the polymeric photoinitiator.

A wide variety of macromolecules contain the two main types of free radical photoinitiators: photofragmenting (*Type I* photoinitiators) and hydrogen-abstracting chromophores (*Type II* photoinitiators), that are described in the literature. Generally, *Type II* photoinitiators initiate more slower than *Type I* photoinitiators. That’s why these systems are more sensitive to the quenching of the excited triplet states and also are the reactive precursors of light induced chemical changes for carbonyl compounds.

Recently, several thioxanthone derivatives have introduced as a new class of *Type II* photoinitiators for free radical polymerization of olefinic compounds [39]. The noticeable initiating capacity of these compounds is based on the fact that both light absorbing and hydrogen donating sites are composed in one molecule. In compliance with the mode of formation of free radicals, they are described as one-component *Type II* photoinitiators. The thioxanthone structure was choosen for two justifications. The first one is applications quite frequently problems arise with respect to the selection of appropriate intiators in photoinitiated free radical polymerization and also the light absorption of the additives should not screen [54]. In this regard thioxanthone derivatives are considerable in view of the fact that they are capable of overcoming these difficulties to a certain extend, via having absorption bands in the near UV wavelength range. The second one is by a simple coupling reaction can easily incorporate desired substituents into thioxanthone structure.

2.1.2 Thioxanthones

Thioxanthone and derivatives are the most widely used *Type II* photoinitiators on account of their excellent light absorption characteristics despite that there exist huge number of photoinitiators available.

Thioxanthones associated with tertiary amines are more efficient photoinitiators [39] with absorption characteristics that compare favorably with benzophenones; absorption maxima are in the range between 380 to 420 nm ($\varepsilon = 104$ L mol^{-1} cm^{-1}) depending on the substitution pattern. Spectroscopic and laser flash photolysis techniques extensively investigate the reaction mechanism [52, 55, 56]. It was realized the fact that the efficiency of thioxanthones in conjunction with tertiary amines is similar to benzophenone/amine systems. 2-chlorothioxanthone and 2-isopropylthioxanthone are used as the most widely commercial derivatives. Thioxanthones are virtually colorless and do not cause yellowing in the final products so that this is a great advantage.

More lately, Aydin et al report one component bimolecular photoinitiator systems based on the decarboxylation process [13]. As photoinitiators for free radical polymerization, 2-thioxanthonethioacetic acid and 2-(carboxymethoxy)thioxanthone were used. 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 independent molecules compose light absorbing and electron donating acidic sites and also the suggested mechanism involves redox reactions. The intermolecular electron-transfer reaction may happen between an excited thioxanthone moiety and the carboxylic acid group of another molecule as shown in Figure 2.5 and besides that the intramolecular electron transfer should also be considered.

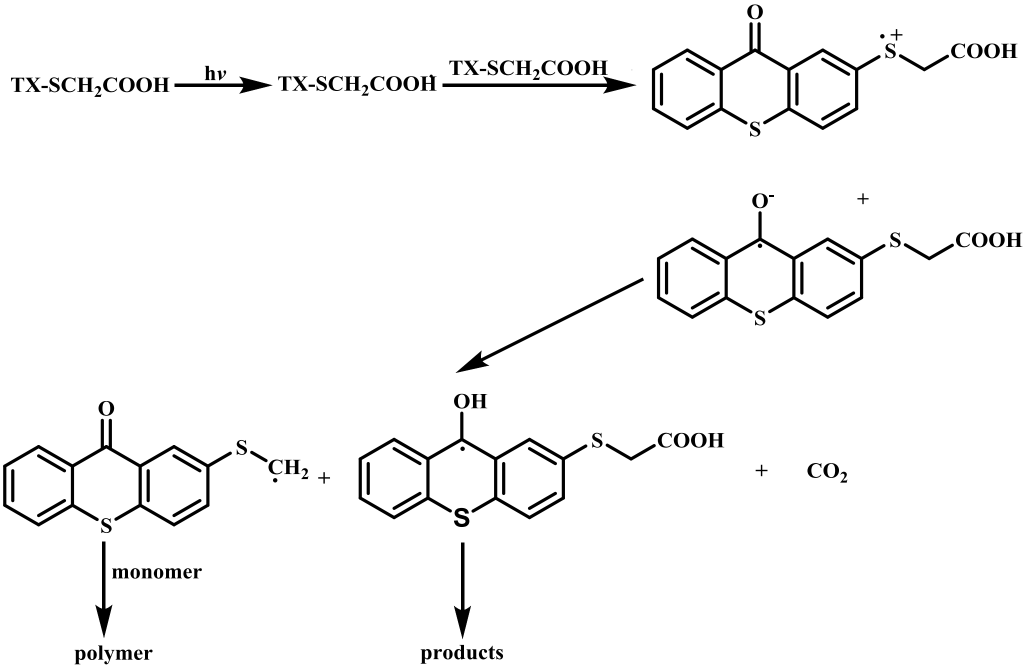


Figure 2.5 : Photo-induced polymerization using thioxanthone-thioacetic acid derivatives.

The actual initiation involves electron transfer from a sulfur or oxygen atom despite that a convenient interaction of the excited carbonyl group with carboxylic acid hydrogen is facilitated with flexible S-CH_2 or O-CH_2 spacer groups. The interaction of excited carbonyl with the sulfur or oxygen atoms of the same molecule separated with a rigid aromatic ring, is improbable to occur [13].

Photoinitiators cost lower energy and are defined to be “green” with higher wavelength absorbtion characteristics. Photoinitiators for visible light [18, 39, 52, 55-58] have found particular interest because of their use in many technologically applications such as dental filling materials [59-61], photoresists, printing plates, highly pigmented coatings, integrated circuits, laser-induced 3D curing, holographic recordings, and nanoscale micromechanics. The titanocene [59] and camphorquinone [62] in conjunction with an amine are well known examples for the respective systems. More recently, as a new class of cleavable photoinitiators introduce organic ketones containing germanium [63, 64]. Yagci et. al. have recently showed that these type of photoinitiators can promote cationic polymerization under visible light [65].

Another essential issue in the practical application of photoinitiators is concerned with their water solubility. There is a certain shift from organic solvents towards waterborne formulations especially in the paints and coatings industry. Water as a green solvent has various attractive features for instance non-toxicity, cheap cost, and easily availability for coatings technology. Incorporation of water solubilising groups such as quartinized ammonium or sulfate to the main body of the photoinitiators usually accomplish the water solubility. 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. Benzophenones [66], thioxanthones [67], benzyl [68], hydroxy alkyl ketones [69] and phenyl trimethyl benzoyl phosphinates [70] are derivatives of some example of the typical structure of watersoluble photoinitiators. Lately, Yagci et. al. also synthesized phenacyl pyridinium oxalate as a water soluble photoinitiator and investigated its initiating behaviour with water soluble monomers [71]. The initiation mechanism of this initiator is postulated to be as follows in Figure 2.6.

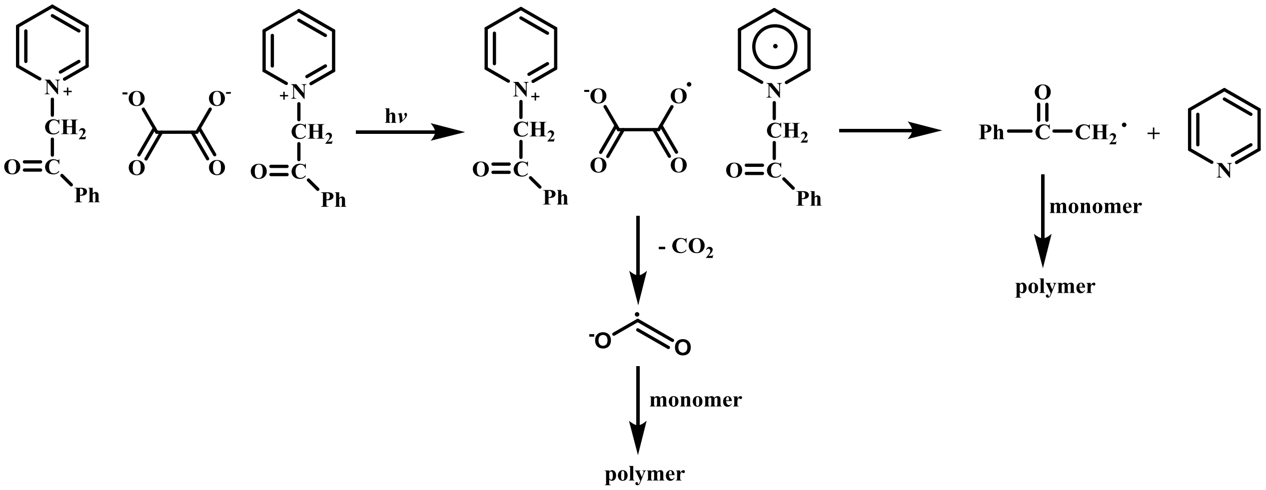


Figure 2.6 : Photopolymerization mechanism using phenacyl pyridinium oxalate.

3. EXPERIMENTAL PART

3.1 Materials and Chemicals

3.1.1 Monomers

Methyl methacrylate (MMA, ≥99%, Aldrich) was passed through basic alumina column before use to remove the inhibitor.

Acrylamide (AA, ≥99%, Aldrich) : It was used as received.

3.1.2 Solvents

p-Dioxane (J.T. Baker, 99.9 %) : It was used as received.

Dimethylformamide (DMF, Aldrich, 99 %) : It was used as received.

Toluene (Aldrich, 99.8%): It was used as received.

Diethyl ether (Sigma-Aldrich, ≥ 99.0%) : It was used as received.

Acetone (Sigma-Aldrich, ≥ 99.0 %) : It was used to precipitate.

Methanol (J.T. Baker, 99.8 %) : It was used to precipitate.

3.1.3 Chemicals

Thiosalicylic acid (Sigma-Aldrich, 97%) : It was used as received.

Benzaldehyde (Aldrich, ≥ 98%) : It was used as received.

Poly(vinyl alcohol) (Aldrich, M_w: 89,000-98,000, 99%) : It was used as received.

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

p-toluene sulfonic acid (Aldrich, ≥ 98.5%) : It was used to catalize the reaction.

Triethylamine (TEA, Aldrich, ≥99.5%) : It was used as received.

3.2 Characterization

3.2.1 Nuclear magnetic resonance spectroscopy (NMR)

^{1} H-NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument.

3.2.2 UV- Visible spectrophotometer

UV spectra were recorded on a Shimadzu UV-1601 spectrometer.

3.2.3 Gel permeation chromatography (GPC)

Molecular weights of the polymers soluble in organic solvents were determined by a gel permeation chromatography (GPC) instrument, Viscotek GPCmax Autosampler system, consisting of a pump, three ViscoGEL GPC columns ($G2000H_{HR}$, $G3000H_{HR}$, and $G4000H_{HR}$), and a Viscotek differential refractive index (RI) detector with a THF flow rate of 1.0 mL min^{-1} at 30 °C. The RI detector was calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. GPC measurements with the water-soluble polymers were performed at room temperature with a setup consisting of a pump (HP 1050), a refractive index detector (HP 1047A), and three high-resolution Waters columns (AQ3.0, AQ4.0, and AQ5.0). The effective molecular weight ranges were 1000−60 000, 10 000−400 000, and 50 000−4 000 000, respectively. Water was used as eluent at a flow rate of 0.5 mL/min at room temperature. Data analyses were performed with HP Chemstation Software. Calibration with linear poly(ethylene oxide) standards (Polymer Laboratories) was used to estimate the molecular weights.

3.3 Synthesis

3.3.1 Synthesis of Thioxanthone-Aldehyde (TX-A)

Thiosalicylic 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. Benzaldehyde (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 h, and later it was left to stand at room temperature 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 a yellow solid. Yield: 80%. ^{1}H-NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 10.01$ (s, CHO), 8.01−7.30 (m, 7H, aromatic).

3.3.2 Synthesis of Poly(vinyl alcohol)-Thioxanthone (PVA-TX)

Commercially available PVA was purified using Dean-Stark technique by refluxing PVA in toluene and reprecipitation in acetone**.** After drying, PVA (300 mg), TX-A (500 mg) and *p*-toluenesulfonic acid (39,5 mg) were dissolved in toluene (100 mL) and the reaction mixture was heated at 60-70 °C for 24 h. The reaction mixture was poured into a large excess of acetone to yield a yellowish-white precipitate. ^{1}H-NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = 7.50$-7.10 (m, aromatic), 5.32 (s, O-CH-O), 2.18 (s, CH_3-C=O), 1.85-1.26 (m, aliphatic backbone).

3.3.3 General procedure for photopolymerizations

A typical photopolymerization procedure is as follows. A Pyrex tube was heated in vacuo with a heat gun and flushed with dry nitrogen. Then PVA-TX, DMF and MMA were introduced to the tube. The resulting mixture was further bubbled with dry nitrogen and the tube was properly sealed. The stirring solution was irradiated with a light source emitting light at $\lambda \sim 350$ nm for 2h and precipitated into methanol. Similar procedure was applied for the polymerization of AA, except water was used as solvent and the corresponding polymer was precipitated in ethanol. The obtained polymers were dried under reduced pressure. Conversions for all samples were determined gravimetrically.

3.3.4 Photocalorimetry (Photo-DSC)

The photodifferential 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 3 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 methacrylate groups_reacted in the system. By integrating the area under the exothermic peak, the conversion of the methacrylate groups (C) or the extent of the reaction was determined according to the following equation 3.1.

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

where ΔH_t is the reaction heat evolved at time t and ΔH_0 theory is the theoretical heat for complete conversion. ΔH_0^{theory} = 86 kJ mol^{-1} for an acrylic double bond.

4. RESULTS AND DISCUSSIONS

In this study, PVA bearing TX moiety was readily prepared owing to ease of preparation via simple acetalization reaction between neighbouring hydroxyl groups and aldehydes.

For this purpose, aldehyde functional thioxanthone (TX-A) was synthesized according to a modified reported procedure and linked to the side chain of PVA as pendant groups to afford the desired macroinitiator. The overall process is demonstrated in Figure 4.1.

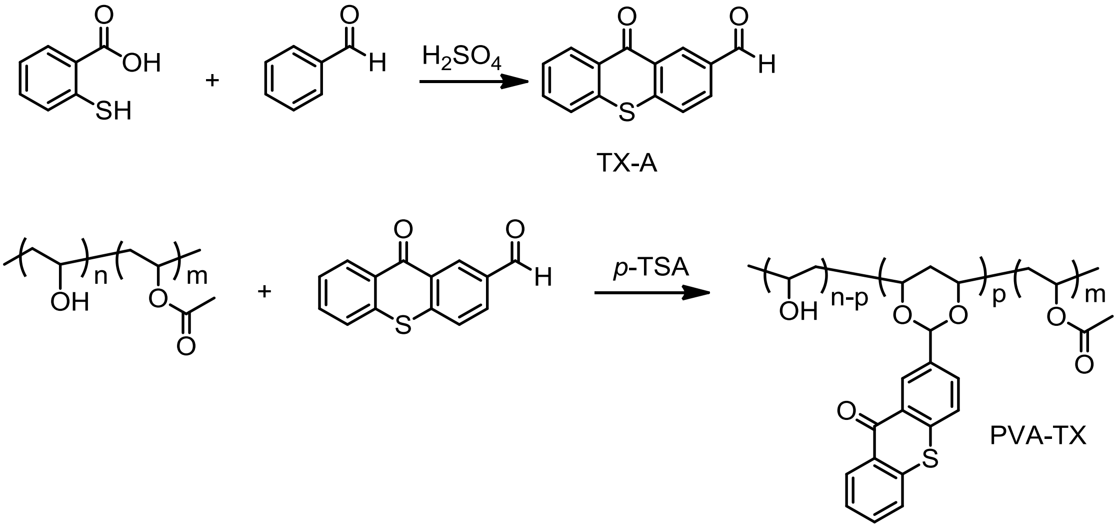


Figure 4.1 : Synthesis of poly(vinyl alcohol)-thioxanthone macro-photoinitiator.

The structure of the PVA-TX was confirmed by ^{1}H-NMR analysis. The presence of the aromatic and acetal protons at around 7.5-7.1 ppm and 5.2 ppm, respectively indicates successful ligation of TX moieties onto PVA structure. Moreover, the absence of the aldehyde protons at 10.0 ppm suggests quantitative incorporation of TX-A and the resulting polymer does not contain free low molar mass chromophoric compound (Figure 4.2).

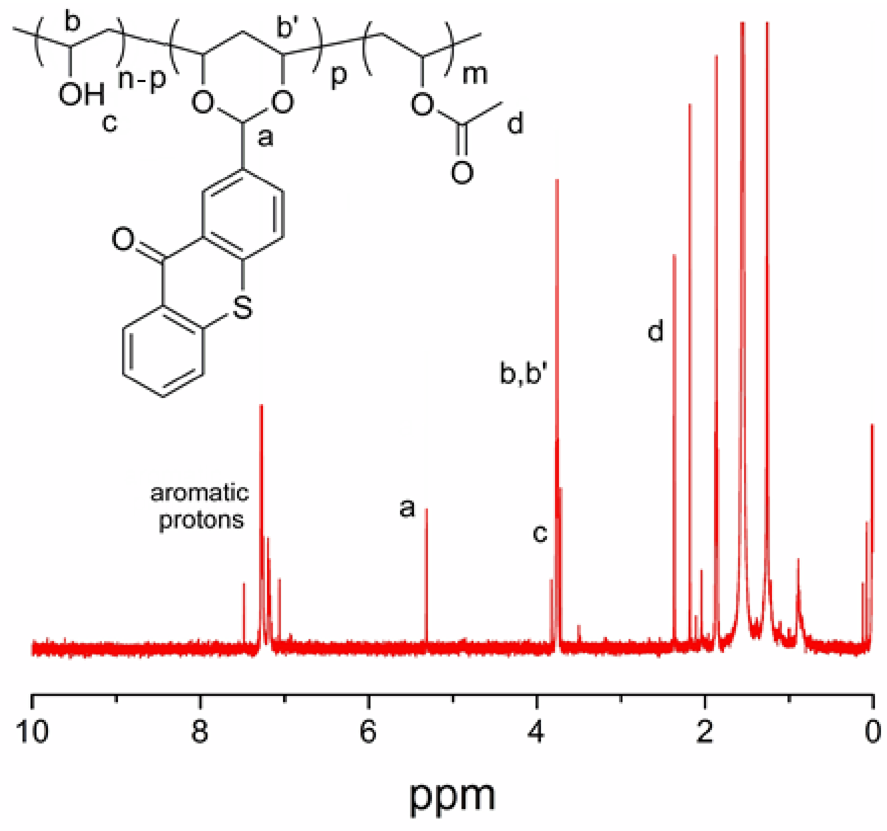


Figure 4.2 : ^{1}H-NMR spectrum of PVA-TX.

The absorption characteristics of the polymeric photoinitiator and precursors were examined by UV spectroscopy. As can be seen from Figure 4.3a, compare to the parent unmodified TX, TX-A has blue shifted absorption due to the electron withdrawing carbonyl group. However, the absorption is shifted to longer wavelengths after the acetalization process. Notably, PVA-TX undergoes an irreversible photolysis leading to the structural changes of TX moiety. This was further confirmed by the spectral changes on UV irradiation. Representative result for the photobleaching of PVA-TX is shown in Figure 4.3b. UV spectra were recorded after the DMF solution had been exposed to the light at λ~350 nm for subsequent intervals of 30 min each.

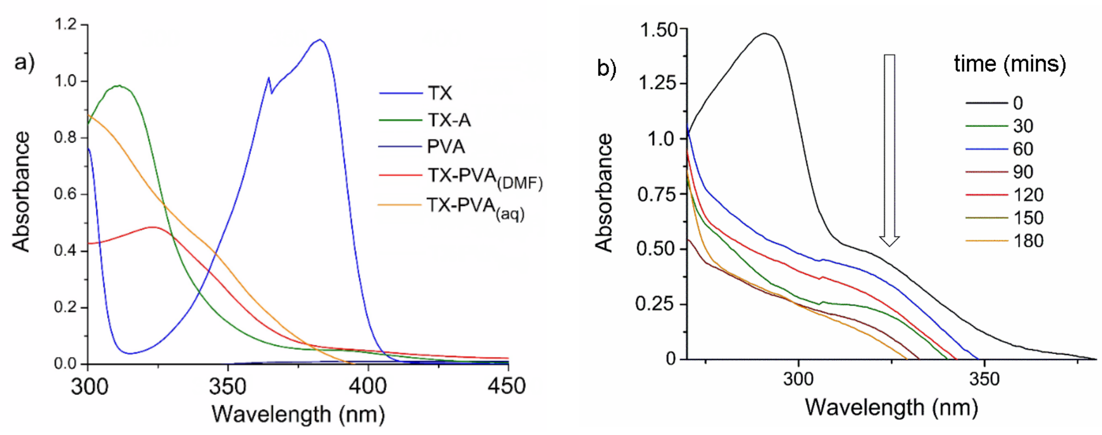


Figure 4.3 : a) UV spectra of PVA, TX-A and PVA-TX and b) Bleaching of PVA-TX upon UV irradiation at λ~350 nm.

Since PVA-TX is soluble in some polar organic solvents and water, it was used as photoinitiator for the polymerization of industrially important monomers, namely methyl methacrylate (MMA) and acrylamide (AA), in organic and aqueous media, respectively. The results are compiled in Table 4.1.

Table 4.1 : Photoinitiated Polymerization Experiments[a] Using PVA-TX as Initiator.

Run	Initiating System	Concentration (mg/L)	Monomer/ Solvent	Conv.[b] (%)	M_n[c] (g/mol)	M_w/M_n[c]
1	PVA-TX	10	MMA/DMF	19.2	103000	1.83
2	PVA-TX	20	MMA/DMF	21.3	80000	1.63
3[d]	PVA-TX	10	MMA/DMF	30	24100	2.21
4[e]	PVA + TX	10	MMA/DMF	4.6	26700	1.54
5[e]	PVA + TX	20	MMA/DMF	6.2	37600	4.77
6	PVA-TX	10	AA/Water	~100	410000	1.70
7	PVA-TX	20	AA/Water	~100	312000	1.67

[a] [Monomer]: 4.7 M, $V_{solvent}$: 2 mL, λ~350 nm, irradiation time: 2 h.

[b] Determined gravimetrically.

[c] For runs 1,2 and 3, determined by gel permeation chromatography (GPC) using polystyrene standards using THF as eluent. For runs 4 and 5, determined by (GPC) using poly(ethylene glycol) standards where using water as eluent.

[d] Triethylamine is used as an added hydrogen donor.

[e] Unmodified PVA and bare TX are used as the initiating system (W_{PVA}/W_{TX}: 10/6).

As can be seen, although higher conversions were attained with triethylamine (TEA), PVA-TX can initiate the polymerization even in the absence of an added co-initiator. In the presence of TEA, polymers with lower molecular weights but higher dispersities were obtained due to the formation of both low molar mass and polymeric radicalic species capable of initiating polymerization. For comparison, typical polymerization experiments were also performed using unmodified PVA and bare TX as the initiating sytem (Runs 4 and 5). Expectedly, much lower conversions were attained with the two component initiating system due to the bimolecular initiation nature. Notably, almost quantitative conversions were reached with AA monomer. This behavior can be attributed to the much higher propagation rate constant of AA (k_p = 18000 L mol^{-1} s^{-1}) compare to that of MMA (k_p = 143 L mol^{-1} s^{-1}) [72].

Figure 4.4 demonstrates the postulated polymerization mechanism of MMA, using PVA-TX as the initiator. The first steps concern the excitation and intersystem crossing of TX moiety, which in turn abstract hydrogen from the main chain possessing hydroxylic and etheric sites to yield radicals. The radicals formed on the polymer segment are responsible for the initiation. For steric and electronic reasons discussed in the introduction part, ketyl radicals are inefficient to add monomers (*vide ante*).

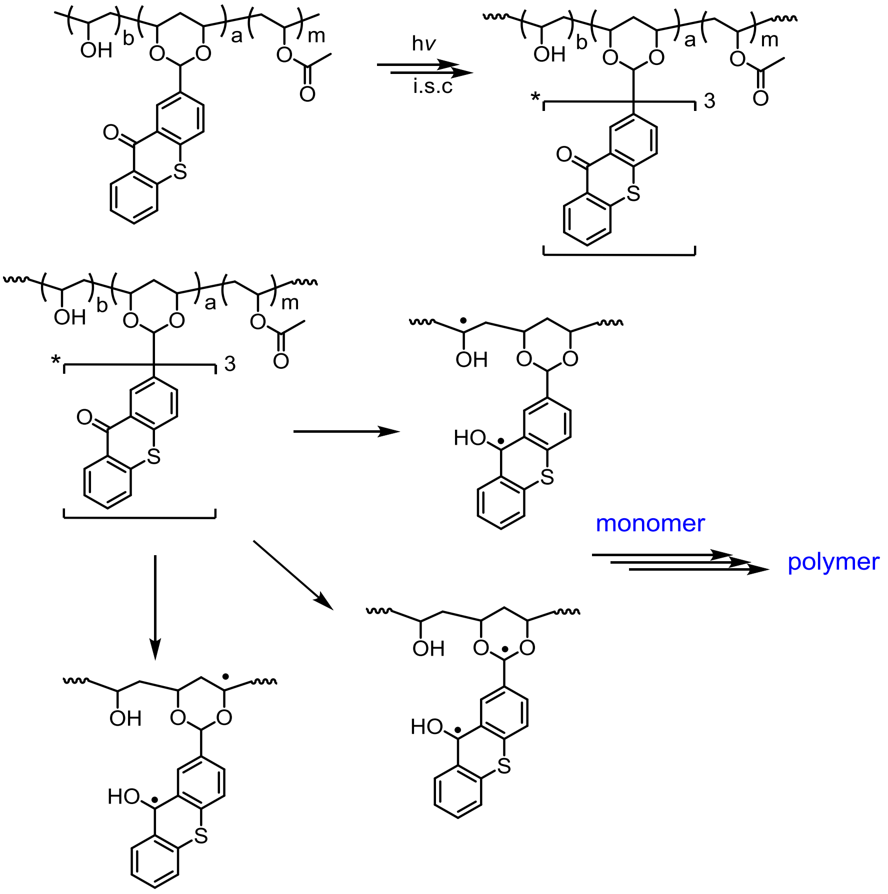


Figure 4.4 : Photopolymerization mechanism using poly(vinyl alcohol)-thioxanthone as initiator.

In order to investigate kinetic behavior of the polymerization, photoDSC studies were also performed. Photo-DSC technique is based on measuring the exposed heat during the photopolymerization process, which is directly proportional to the number of methacrylic bonds reacted in the photopolymerization process. Thus, the rate of polymerization (the number of monomers being consumed over total number of monomers per time), R_P (1/s), can be determined according to the following equation 4.1.

$$R_P = (Q_t) \times 1000/[n \times (E_{db})] \qquad \textbf{(4.1)}$$

where Q_t (J mol^{-1} s^{-1}) is the amount of released heat at time t, n is the number of methacrylic bonds, and E_{db} (kJ mol^{-1}) is the energy of enthalpy of polymerization (~55 kJ mol^{-1}). By integrating the area under the R_p-t graph, the conversion of the MMA monomer is obtained. Figure 4.5 shows the kinetics of the photo-polymerization of MMA in DMF using PVA-TX as the initiator.

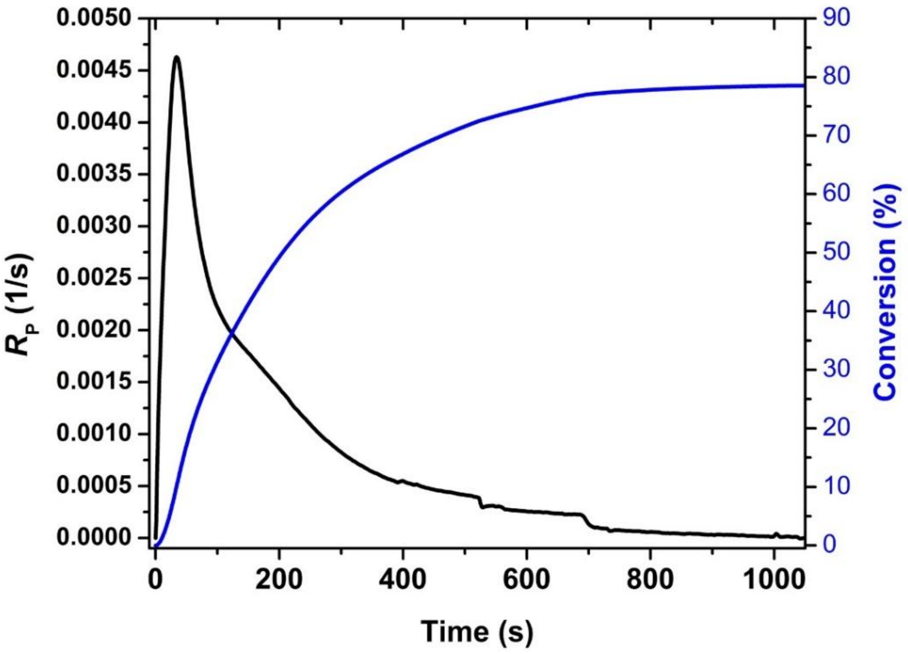


Figure 4.5 : Kinetics of the photopolymerization of MMA using PVA-TX in DMF obtained by photo-DSC. Black line: rate of polymerization, R_P (1/s), Blue line: conversion (%).

5. CONCLUSIONS

In conclusion, a new one-component TX macrophotoinitiator was synthesized via simple acetalization reaction between PVA and TX-A. The obtained polymer exhibits spectral sensitivity in the near UV region and readily initiates free radical polymerizations of vinyl monomers in both organic and aqueous media even in the absence of a co-inititiator. Facile synthesis from commercially available polymer, solubility behavior, photocatalytic activity without additional hydrogen donor and polymeric nature excluding likely drawbacks connected with low molar mass photoinitiators suggest that PVA-TX may find widespread applications in oil and water based UV curing formulations.

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