

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE**  
**ENGINEERING AND TECHNOLOGY**

**PREVENTION OF OXYGEN INHIBITION IN PHOTOINITIATED FREE  
RADICAL POLYMERIZATION**

**M.Sc. THESIS**

**Faruk OYTUN**

**Department of Chemistry**

**Chemistry Programme**

**JANUARY 2013**



**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE**  
**ENGINEERING AND TECHNOLOGY**

**PREVENTION OF OXYGEN INHIBITION IN PHOTOINITIATED FREE  
RADICAL POLYMERIZATION**

**M.Sc. THESIS**

**Faruk OYTUN**  
**(509101059)**

**Department of Chemistry**

**Chemistry Programme**

**Thesis Advisor: Prof. Dr. Yusuf YAĞCI**

**JANUARY 2013**



**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

**FOTABAŞLATICI SERBEST RADİKAL POLİMERİZASYONDA OKSİJEN  
İNHİBİSYONUNUN ÖNLENMESİ**

**YÜKSEK LİSANS TEZİ**

**Faruk OYTUN  
(509101059)**

**Kimya Anabilim Dalı**

**Kimyagerlik Programı**

**Tez Danışmanı: Prof. Dr. Yusuf YAĞCI**

**OCAK 2013**



**Faruk Oytun**, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID **509101059**, successfully defended the **thesis** entitled “**PREVENTION OF OXYGEN INHIBITION IN PHOTOINITIATED FREE RADICAL POLYMERIZATION**”, which he 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. Gürkan HIZAL**                     .....  
Istanbul Technical University

**Prof. Dr. Tuncer ERCİYES**                     .....  
Istanbul Technical University

**Date of Submission : 17 December 2012**  
**Date of Defense     : 23 January 2013**



*To my family,*



## **FOREWORD**

I would like to thank all the people who support me and made this study possible. It is a pleasant opportunity that I express my gratitude to all of them.

First, I would like to thank my supervisor, Prof. Dr. Yusuf Yađcı, for his encouragement, guidance and support. More importantly, he also educated me how to well carry out a scientific research and he also contributed to develop myself in polymer science.

I would like to express deeply my special gratitude to Muhammet Ü. Kahveci. This thesis would not have been possible without the support and encouragement of his. Everytime, he guided me in many issue and helped me with them kind patience.

I wish to deeply thank to all the members of Yagci Lab for all their help, support and friendship. In particular, Mustafa ifti, Ömer Suat Taşkın, Ali Görkem Yılmaz, Muhammed Aydın, Emre Tun, Umut Uđur Özköse, Cemil Dizman, Kübra Demir, Gökhan Aık, ađatay Altınkök, Semiha Bektaş, Betül Hamamcıođlu, Manolya Kukut, Binnur Aydođan, Burin Gacal, Barıř Kıřkan and Demet Göen olak at with all of you, it has really been a great pleasure.

Finally, during all stages involved in the preparation of this thesis, I'm grateful to my family for their encouragement, understanding, patience and support all through my education.

This work is supported by ITU Graduate School of Science, Engineering and Technology.

December 2012

Faruk OYTUN  
(Chemist)



## TABLE OF CONTENTS

	<u>Page</u>
<b>FOREWORD</b> .....	<b>ix</b>
<b>TABLE OF CONTENTS</b> .....	<b>xi</b>
<b>ABBREVIATIONS</b> .....	<b>xiii</b>
<b>LIST OF TABLES</b> .....	<b>xv</b>
<b>LIST OF FIGURES</b> .....	<b>xvii</b>
<b>SUMMARY</b> .....	<b>xix</b>
<b>ÖZET</b> .....	<b>xxi</b>
<b>1. INTRODUCTION</b> .....	<b>1</b>
<b>2. THEORETICAL PART</b> .....	<b>3</b>
2.1 Photopolymerization .....	3
2.2 Types of Photopolymerization .....	4
2.2.1 Photoinitiated free radical polymerization .....	4
2.2.1.1 Type I photoinitiators (unimolecular photoinitiator system) .....	6
2.2.1.2 Type II photoinitiators (bimolecular photoinitiator system).....	8
2.2.1.3 Monomers .....	11
2.2.2 Photo-initiated anionic polymerization.....	12
2.2.3 Photo-initiated cationic polymerization .....	13
2.3 Oxygen Inhibition .....	14
2.3.1 Importance of O <sub>2</sub> inhibition in industrial applications.....	15
2.3.2 Common methods to overcome O <sub>2</sub> inhibition.....	15
2.4 GOx in Polymer Chemistry .....	17
2.4.1 GOx .....	17
2.4.2 Enzymatic pathway of GOx .....	17
2.4.3 Employment of GOx in polymerizations and polymers .....	18
2.4.4 Potential use of GOx in overcoming O <sub>2</sub> inhibition .....	19
<b>3. EXPERIMENTAL PART</b> .....	<b>21</b>
3.1 Materials.....	21
3.2 Equipments.....	21
3.2.1 Rofin polilight PL400 forensic plus.....	21
3.2.2 Photo-differential scanning calorimetry.....	21
3.3 Preparation of Photo-Curable Formulations .....	22
3.4 Photo-Differential Scanning Calorimetry of Photo-Curable Formulations .....	22
<b>4. RESULTS AND DISCUSSION</b> .....	<b>25</b>
<b>5. REFERENCES</b> .....	<b>31</b>



## ABBREVIATIONS

<b>G</b>	: Glucose
<b>GOx</b>	: Glucose Oxidase
<b>PVA-Py</b>	: Poly(vinyl alcohol)-pyrene
<b>PEGDA</b>	: Poly(ethylene glycol) diacrylate
<b>AAm</b>	: Acrylamide
<b>BAAm</b>	: <i>N,N'</i> -methylenebisacrylamide
<b>DSC</b>	: Differential Scanning Calorimetry
<b>PI</b>	: Photoinitiator
<b>TX-A</b>	: Thioxanthone
<b><math>\Delta G</math></b>	: Gibbs Energy Change
<b>M</b>	: Monomer
<b>FAD</b>	: Flavin Adenine Dinucleotide
<b>DMPA</b>	: 2,2-dimethoxy-2-phenylacetophenone
<b>BP</b>	: Benzophenone
<b>DMA</b>	: <i>N,N'</i> -dimethylaniline



## LIST OF TABLES

	<u>Page</u>
<b>Table 2.1</b> : Structures of typical Type <i>I</i> radical photoinitiators. ....	8
<b>Table 2.2</b> : Structures of typical Type <i>II</i> radical photoinitiators.....	9
<b>Table 4.1</b> : Photo-induced crosslinking polymerization of water soluble monomers the presence or absence of GOx/G under air atmosphere at 20 °C. ....	26



## LIST OF FIGURES

	<u>Page</u>
<b>Figure 2.1</b> : Elementary reactions in free radical photopolymerization.....	5
<b>Figure 2.2</b> : Formation of initiating radicals from decomposition of a Type I photoinitiator .....	7
<b>Figure 2.3</b> : Formation of initiating radicals from photolysis of Type II photoinitiator in the presence of suitable hydrogen donor. ....	10
<b>Figure 2.4</b> : Generation of anionic species from photolysis of 1,1'-dibenzoylferrocene.....	13
<b>Figure 2.5</b> : General scheme of photo-initiated cationic polymerization.....	14
<b>Figure 2.6</b> : Chemical Structure of GOx.....	18
<b>Figure 4.1</b> : Conversion and heat flow profile during the UV curing of PEGDA (52 wt %) initiated by a <i>Type I</i> photoinitiator (DMPA, 1 wt %) in the presence (A) and absence (B) of glucose (1 wt %) and GOx (0.06 wt %) in aqueous solution under air atmosphere. Similar UV curing was performed without GOx and G under nitrogen atmosphere (C). ....	26
<b>Figure 4.2</b> : Photoinitiated free radical polymerization in air in the absence (A) and presence of glucose oxidase and glucose (B). ....	26
<b>Figure 4.3</b> : Conversion and heat flow profile during the UV curing of AAm (49 wt %)/BAAm (2 wt %) initiated by a Type II photoinitiating system in the presence (A) and absence (B) of glucose (1 wt %) and GOx (0.06 wt %) in aqueous solution under air. Benzophenone (1 wt %)/N,N-dimethyl aniline (1 wt %) were used as the Type II initiating system. Similar UV curing was performed without GOx and G under nitrogen atmosphere (C). ....	28



## PREVENTION OF OXYGEN INHIBITION IN PHOTOINITIATED FREE RADICAL POLYMERIZATION

### SUMMARY

Free radical photopolymerization finds role in several applications of various industrial fields due to its features, but suffers from oxygen ( $O_2$ ) inhibition. The use of this polymerization method in industrial applications in air is limited because of the excessive cost of existing methods to prevent  $O_2$  inhibition. Herein, a new route based on an enzymatic pathway in which glucose oxidase acts as catalyst for glucose oxidation using  $O_2$  is described to overcome  $O_2$  inhibition of radical polymerizations.

In a typical application of this redox process, a few examples including a fluorescent probe for G sensing by combination of GOx with poly(vinyl alcohol)-pyrene matrix (PVA-Py) prepared by “Click” chemistry have been previously reported. The PVA-Py matrix appeared to be very attractive, because it possesses both light absorbing chromophoric and oxidizing sites in the structure and does not require additional molecules. Moreover, it provides enhanced stability compared to the systems in which active sites are composed in the independent molecules. Recently, GOx was used in the presence of  $Fe^{2+}$  to produce free radicals for generation of biologically active hydrogels.

Quenching of free radicals by molecular oxygen ( $O_2$ ) is one of the most challenging problems in free radical polymerization techniques. Several attempts including addition of additives quenching with  $O_2$ , use of reactive photoinitiators in the presence of  $O_2$ , performing polymerization under inert atmosphere (Ar,  $N_2$ ,  $CO_2$ , etc.), using wax barrier coats or performing the UV exposure under water have been made in the past to overcome this difficulty. The results obtained from photo-DSC profiles of the polymerizations indicate that addition of GOx and glucose in a typical formulation for photo-induced free radical polymerization resulted in increased conversion and fast polymerization rate. This is an obvious indication of overwhelming molecular oxygen inhibition since GOx uses molecular oxygen in its usual metabolic pathway, in which glucose is oxidized to gluconic acid while molecular oxygen is consumed (Scheme 2).

Here, we take advantage of these features to develop a UV curing system based on free radical polymerization and consumption of  $O_2$  by GOx in its usual enzymatic pathway. Thus, in this approach the polymerization system contains GOx and G in addition to usual components – monomer and initiator. Specifically, UV-curable aqueous formulations containing poly(ethylene glycol) diacrylate (PEG-DA) or acrylamide (AAm)/*N,N'*-methylenebisacrylamide (BAAm) as monomers, and *Type I* or *Type II* photoinitiators in the presence and absence of GOx and G were irradiated and polymerizations were monitored by photo-DSC.



## FOTABAŞLATICI SERBEST RADİKAL POLİMERİZASYONDA OKSİJEN İNHİBİSYONUNUN ÖNLENMESİ

### ÖZET

Işıklı başlatılmış polimerizasyon reaksiyonlarına fotopolimerizasyon denir. Genellikle mor ötesi veya görünür bölge ışık kaynakları kullanılır. Fotobaşlatıcının uygun bir dalga boyundaki ışık absorpsiyonu sonucunda oluşan reaktif türler, tek fonksiyonlu monomerlerin polimerizasyonunu sağlarken, çok fonksiyonlu monomerlerin çapraz bağı yapıllara dönüşmesini sağlar.

Son zamanlarda, fotobaşlatılmış polimerizasyon pek çok ekonomik ve ekolojik beklentiyi biraraya getirdiği için 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. Oda sıcaklığında yüksek polimerizasyon hızı, düşük enerji tüketimi, çözücüsüz ortamada polimerizasyon, uygulanacak yüzey alanı ve uygulama süresinin kontrol edilebilmesi gibi avantajlar sağlamaktadır. Fotopolimerizasyon radikalik, katyonik ve anyonik olarak başlatılabilir de çok sayıda fotobaşlatıcının ve yüksek reaktivitedeki monomerlerin bulunulabilirliği açısından radikalik sistemlere daha fazla ilgi duyulmaktadır.

Fotopolimerizasyon yönteminin kullanıldığı polimerizasyonlar daha düşük sıcaklıklarda gerçekleştirilebilmektedir. Polimerizasyonu düşük sıcaklıklarda gerçekleştirmek bir çok avantaj sağlamaktadır. Öncelikle maksimum çalışma sıcaklığı düşük olan monomerler sadece düşük sıcaklıklarda polimerleştirilebilirler, aksi halde oluşan polimerler depolimerizasyona uğrayarak tekrar monomer halini alırlar. Polimerizasyon sıcaklığının düşürülmesi esterleşme ve çarpaz bağlanma gibi yan reaksiyonların önlenmesini sağlarken, polimerizasyonun daha kontrollü bir şekilde yapılmasını sağlar. Örneğin; tahta, kağıt, metal ve plastik malzemelerin yüzeylerinin kaplanması ve bu kaplamaların fotokimyasal olarak sertleştirilmesi gibi önemli kullanım alanları sağlayan yöntemler geliştirilmiştir. Lazer ile çalışan video disklerinin üretimi ve diğ dolgularının sertleştirilmesi de diğ bir kullanım alanıdır. Bu sistem, çözücüden bağımsız ve ısısal sertleştirmeden sonra yapılan işlemlere gerek duyulmadığından dolayı tehlikesiz olması ve az enerji harcanması açısından, ısısal sertleştirmeye kıyasla daha kullanışlıdır. Bunlara ek olarak enzim ve protein gibi ısıya duyarlı biyoyapıların polimerizasyon işlemiyle polimerlere bağlanması gibi işlemlerde düşük sıcaklıklarda gerçekleştirilmelidir.

Termal polimerizasyonla karşılaştırıldığında fotopolimerizasyon oda sıcaklığında hızlı, zamansal ve mekan kontrollü olmasından dolayı büyük avantajlara sahiptir. Fakat bu avantajların yanında fotopolimerizasyonla elde edilen polimerin moleköl ağırlığı, moleköl ağırlık dağılımı ve fonksiyonallitesi gibi özelliklerin kontrolü mümkün değildir. Bundan dolayı da blok ve aş gibi kopolimerlerin sentezi fotopolimerizasyonla gerçekleşmesi kısıtlıdır. Fotopolimerizasyonda ışığın etkisi

sadece başlama aşamasındadır. Başlama mekanizmasının anlaşılması için başlatıcının fotokimyasını bilmek gerekir. Başlatıcıların morötesi ve görünür bölge aralığındaki ışık tarafından, monomerlerin polimerizasyonunu başlatılabilecek serbest radikal veya iyon gibi reaktif tür üretmeleri ve monomerlerin de bu aralıktaki ışık tarafından bozularak serbest radikal veya iyon vermemeleri gerekir. Monomer sistemlerindeki değişikliklerin pahalı olmasından dolayı, fotobaşlatıcıların etkinliğini artırıcı çalışmalar önem kazanmıştır. Özetle bir fotokimyasal polimerizasyon sisteminde en önemli reaktantlar fotobaşlatıcı ve monomerlerdir.

Fotobaşlatıcılar, radikal oluşturma mekanizmalarına göre (birinci tip fotobaşlatıcılar) ve (ikinci tip fotobaşlatıcılar) fotobaşlatıcılar olmak üzere iki ayrı sınıfa ayrılır.

Birinci tip fotobaşlatıcılar, radikal vermek üzere doğrudan fotoparçalanmaya uğrayan çeşitli fonksiyonel gruplar içeren aromatik karbonil bileşiklerdir. Genellikle fotoparçalanma aromatik karbonil grubun yanındaki bağdan ( $\alpha$  yarılmaması) gerçekleşir. İkinci tip fotobaşlatıcılar, ( $\alpha$  yarılmaması) için gerekli olan yeterli enerjisine sahip olmadıkları için, ancak uygun hidrojen verici moleküllere enerji aktarımı veya bu moleküllerden hidrojen koparma sonucu radikalleri üretirler. En geniş kullanımı olan serbest radikal fotobaşlatıcılar, benzoin, benzil ketalleri, asetofenon türevleri, açilfosfin oksitler (birinci tip fotobaşlatıcılar) ve benzofenon, tiyokzanton, kinon /tersiyer amin kombinasyonlarıdır (ikinci tip fotobaşlatıcılar). UV ışığıyla fotopolimerizasyon için aktive edilen birinci tip fotobaşlatıcı bileşenleri, çok kullanışlı; fakat görünür ışık bölgesindeki kürleşmelerde yetersizlerdir. İkinci tip sistemlerde, polimerizasyonun başlaması hidrojen verici molekül üzerinde oluşan radikaller vasıtasıyla gerçekleşirken etkin olmayan ketil radikalleri birbirleriyle birleşerek ortamdaki kaybolur. İkinci tip fotobaşlatıcılarda hidrojen verici moleküller olarak alkol, amin, eter ve tiyol molekülleri kullanılır. Bu moleküllerin arasında tersiyer aminler en çok tercih edilenlerdir. Ancak tersiyer aminlerin kötü kokulu, zehirli, kolay uçucu olması, göçme gibi olumsuz yönleri vardır.

Serbest radikal fotopolimerizasyon yöntemi malzeme biliminde önemli bir yer kaplar. Özellikle, serbest radikal fotopolimerizasyonu, kaplamalar, dış dolgu malzemeleri, mürekkepler, litografi, yapıştırıcılar, vernikler, destek malzemeleri, kompozitler gibi endüstriyel uygulamalarda önemli bir rol oynar. Bu uygulamalarda oksijen inhibisyonu en önemli problemlerden biridir. Bu önemli teknik, hava ortamında gerçekleştirildiği için, oksijen inhibisyonuna uğrar. Prensipinde başlatıcı radikallerin oluşumu oksijen varlığında engellenir, çünkü, uyarılmış haldeki fotobaşlatıcılar, özellikle Tip II başlatıcılar, oksijen tarafından kuvvetli bir şekilde söndürülürler. Ayrıca, Şema 1 'de gösterildiği gibi, oksijen , fotobaşlatıcının fotoliziyle oluşan serbest radikalleri ve ilerleme esnasında oluşan makro radikalleri, peroksil radikallerine dönüştürür. Yeni oluşan peroksi radikalleri genellikle, polimer ana zincirinden hidrojen kopartarak hidroperoksitleri oluşturur. Bu dezavantajlar, uzun inhibisyon süresinden dolayı, ıslak ve yapışkan yüzeylerin oluşmasına ve polimerizasyonun tamamlanamamasına sebep olur ve polimerizasyon hızı ile dönüşüm oranını azaltır.

Serbest radikal fotopolimerizasyonu için çok önemli bir problem olan oksijen inhibisyonunu engellenmesi için pek çok yöntem geliştirilmiştir. Örneğin; yüksek şiddetli ışık kaynağı kullanılması, ortamın inert hale getirilmesi ve amin ve tiyol gruplarının ilave edilmesi gibi. Bunlara ek olarak fotobaşlatıcı olarak TX-A kullanılması da oksijenin inhibisyon etkisini önler. Polietilen filmleri ile yapılan

kaplamalar gibi bazı fiziksel yöntemler de oksijenin inhibisyonunu engelleyebilir. Fakat bu sistemler pahalı olduğu için fazla tercih edilmezler.

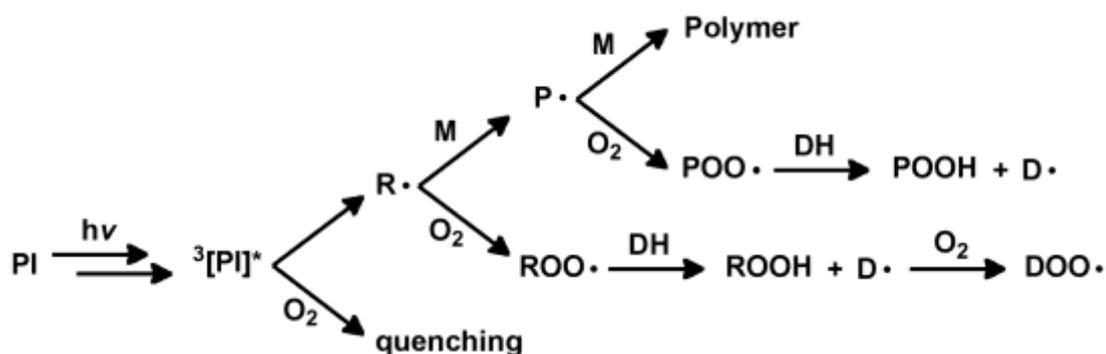
Bu klasik yöntemlerin dışında biz çalışmamızda enzimatik bir yöntem olan GOx/G sistemini geliştirdik. Glikoz oksidaz (GOx;  $\beta$ -D-glucose:oxygen 1-oxido-reductase, E.C. 1.1.3.4) oksijen inhibisyonunun engellenmesi için kullanılan çok değerli bir enzimdir. Glikoz oksidaz genellikle kandaki ve vücut yağlarında, yiyecek ve içeceklerde ve bazı tarım ürünlerindeki glikoz miktarının tayininde kullanılır. Glikoz oksidaz pek çok uygulamada da kullanılır. Örneğin, endüstriyel olarak glikoz oksidaz kullanılarak glukonik asit meydana getirilir. Glukonik asit ise bazı yiyeceklerin bozulmaması için koruyucu madde olarak, serum ve plazmalardaki glikoz miktarının belirlenmesi için kullanılır.

Bu çalışmada, serbest radikal fotopolimerizasyonda önemli bir problem olan oksijen inhibisyonunun önlenmesi için yeni bir teknik geliştirilmiştir. Bu teknik ile, havadaki oksijen radikalleri GOx ve G ile redox tepkimesi vererek, fotoliz sonucunda oluşan reaktif radikallerini inhibe etmeleri önlenmiştir. Enzimatik sistemin, hem Tip 1 hem de Tip 2 fotobaslatıcılarının kullanıldığı serbest radikal fotopolimerizasyonunun etkinliğini artırdığı, foto-DSC sonuçları ile de gösterilmiştir. Bu sistemi sınırlayan tek faktör, polimerizasyonun sadece sulu ortamlarda ki kaplamalarda uygulanabiliyor olmasıdır. Çünkü, redox bileşenleri organik sistemlerde çözünemediği için, yapı modifikasyonu ile çözünmelerini kolaylaştırmak bu çalışmanın uygulanabilirliğinin artmasına neden olacaktır.



## 1. INTRODUCTION

Free radical polymerization methods have played an enormous role in the materials engineering and science. Particularly, photo-initiated mode of radical polymerization has become a key method in countless number of industrial applications such as protective coatings, dental resins, printing inks, lithography, adhesives, varnishes, support materials and composites [1-5]. In these applications, quenching of free radicals by molecular oxygen ( $O_2$ ) is one of the most challenging problems. Since this important technique is generally carried out under air atmosphere, it suffers noticeably from  $O_2$  inhibition [6-8]. Principally, formation of initiating radicals is prevented in the presence of  $O_2$  because excited states of photoinitiators, especially Type II initiators, are strongly quenched by  $O_2$ . Moreover,  $O_2$  scavenges both initiating radicals produced from photolysis of photoinitiators and propagating macro-radicals, and transforms them to stable peroxy radicals that barely participate in further corresponding reactions (Scheme 1) [9]. Newly formed peroxy radicals generally abstract hydrogen atoms from the polymer backbone to generate hydroperoxides. Such drawbacks cause premature polymerization and formation of wet and sticky surfaces as a consequence of long inhibition time, and decrease in both polymerization rate and final conversion ratio [10].



**Scheme 1 :** Main pathways in oxygen inhibition of free radical photopolymerization.

Several attempts including addition of  $O_2$  scavengers [10,11] or producing additional active species, [12-14] use of reactive photoinitiators, [15,16] performing

polymerization under inert atmosphere (Ar, N<sub>2</sub>, CO<sub>2</sub>, etc.), using wax barrier coats or performing the UV exposure under water have been made in the past to overcome this difficulty. In addition, intense illumination or using an excess amount of photoinitiator is an alternative way to overwhelm oxygen inhibition by consuming O<sub>2</sub> dissolved in the resin for preventing, especially for thin films in contact with air [17]. However, all these strategies either require supplementary processes with additional cost or are limited in their available specially designed photoinitiators.

## **2. THEORETICAL PART**

### **2.1 Photopolymerization**

Photopolymerization is one of the most rapidly expanding processes for materials production and is employed over a wide range of applications. Since the technologies are extremely efficient and economical process as well as environmentally favorable process compared to traditional thermal polymerizations, photopolymerization process has continued to expand the growth of plastic market share. The use of light, rather than heat, to drive the reactions leads to a variety of advantages, including solvent-free formulations, very high reaction rates at room temperature, spatial control of the polymerization, low energy input, and chemical versatility since a wide variety of polymers can be polymerized photochemically. These advantages have been exploited in a variety of applications including: traditional films, fabrication of printed circuit boards, coatings for optical fibers, and replication of optical disks. In addition, photopolymerizations demand lower energy requirements because the polymerizations use a fraction of the energy of traditional thermal systems but the process provides high speed and high production rate at low curing temperature. Finally, the process may be used to rapidly form polymers without the use of diluting solvents and leads to lower volatile organic compounds than traditional thermal polymerization.

Photopolymerizations are simply polymerization reactions initiated by light, typically in the ultraviolet or visible region of the light spectrum. Photopolymerizations are initiated by certain types of compounds which are capable of absorbing light of a particular wavelength. 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 produced when the initiator absorbs light and undergoes some type of decomposition, hydrogen abstraction, or electron transfer reaction. If necessary, the effective initiating wavelength may be shifted by adding small amounts of a second

compound, termed a photosensitizer, to the reaction mixture. The photosensitizer absorbs light and populates an excited state which may then react with the photoinitiator to produce an active cation or radical capable of initiating the polymerization. Upon generation of active centers, photopolymerizations propagate and terminate in the same manner as traditional (i.e. thermal) polymerizations. Photopolymerization can be divided into two categories: photoinitiated free radical (e.g. of acrylates) and cationic (e.g. ring opening reaction of epoxides) polymerizations.

Although photoinitiated cationic polymerization has gained importance in recent years, the corresponding free radical polymerization is still the most widely employed route in such applications because of its applicability to a wide 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.

## **2.2 Types of Photopolymerization**

### **2.2.1 Photoinitiated free radical polymerization**

Photoinitiated free radical polymerization is one of the most widely employed route in industrial applications because of its applicability to a wide 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.

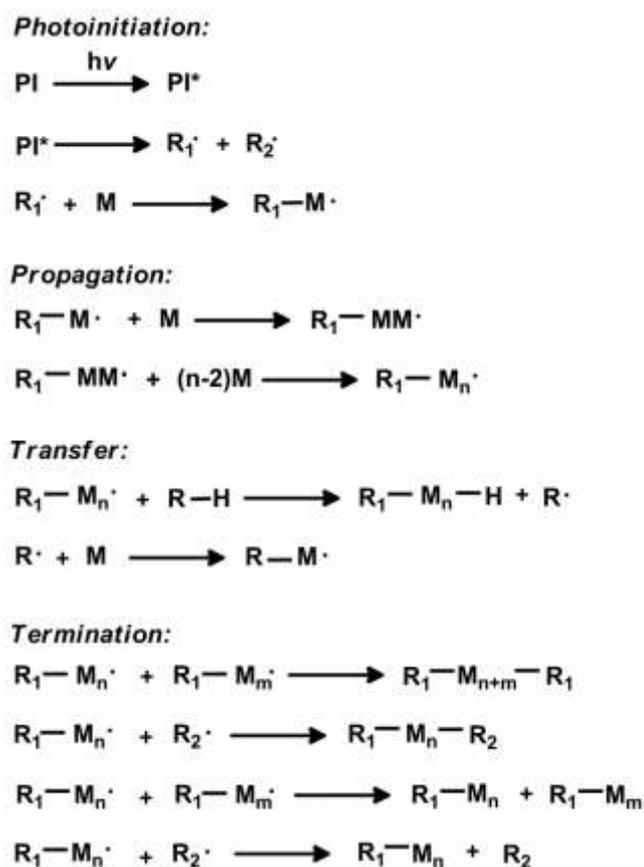
It consists of four distinct steps:

*i) photoinitiation step* involves 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.

*ii) propagation step* involves repeated addition of monomer units to the chain radical produces the polymer backbone.

iii) *chain transfer step* involves termination of growing chains by hydrogen abstraction from various species (e.g., from solvent) and formation of new radicals capable of initiating other chain reactions.

iv) *termination step* involves termination of chain radicals by disproportionation or recombination reactions. Termination can also occur by recombination or disproportionation with any other radical including primary radicals produced by the photoreaction.



**Figure 2.1:** Elementary reactions in free radical photopolymerization.

The role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating radicals. The reaction of these radicals with monomer, propagation, transfer and termination are purely thermal processes; they are not affected by light.

In most cases of photoinduced polymerization, initiators are used to generate radicals. Photoinitiators are generally divided into two classes, Type I and Type II, according to the process by which initiating radicals are formed.

### 2.2.1.1 Type I photoinitiators (unimolecular photoinitiator system)

Photoinitiators termed unimolecular are so designated because the initiation system involves only one molecular species interacting with the light and producing free-radical active centers. These substances undergo a homolytic bond cleavage upon absorption of light (eq. 2.1). The fragmentation that leads to the formation of radicals is, from the point of view of chemical kinetics, a unimolecular reaction (eq. 2.2).



$$\frac{d[R_1]}{dt} = \frac{d[R_2]}{dt} = k[PI^*] \quad (2.2)$$

The number of initiating radicals formed upon absorption of one photon is termed as quantum yield of radical formation ( $\phi_{R\cdot}$ ) (eq. 2.3).

$$\phi_{R\cdot} = \frac{\text{Number of initiating radicals formed}}{\text{Number of photons absorbed by the photoinitiator}} \quad (2.3)$$

Hypothetically, cleavage type photoinitiators should have a  $\phi_{R\cdot}$  value of two since two radicals are formed by the photochemical reaction. The values observed, however, are much lower because of various deactivation routes of the photoexcited initiator other than radical generation. These routes include physical deactivation such as fluorescence or non-radiative decay and energy transfer from the excited state to other, ground state molecules, a process referred to as quenching. The reactivity of photogenerated radicals with polymerizable monomers is also to be taken into consideration. In most initiating systems, only one in two radicals formed adds to monomer thus initiating polymerization. The other radical usually undergoes either combination or disproportionation. The initiation efficiency of photogenerated radicals ( $f_p$ ) can be calculated by the following formula:

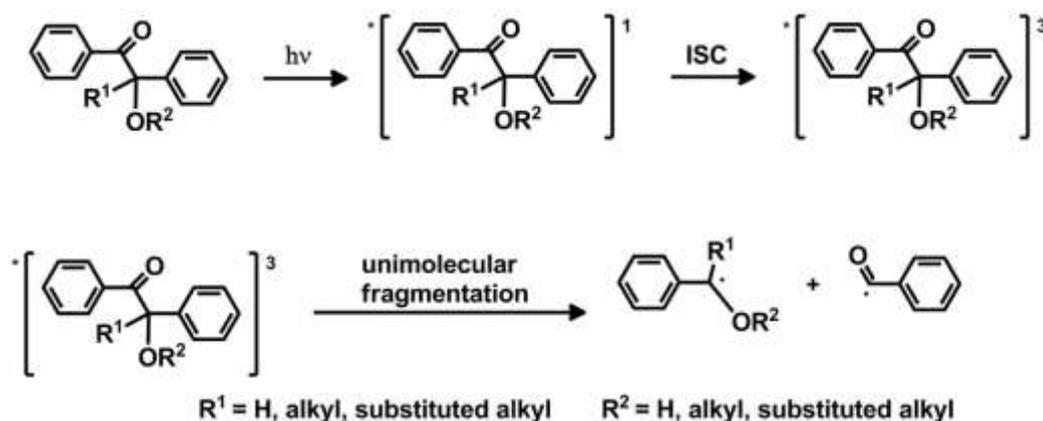
$$f_p = \frac{\text{Number of chain radicals formed}}{\text{Number of primary radicals formed}} \quad (2.4)$$

The overall photoinitiation efficiency is expressed by the quantum yield of photoinitiation ( $\phi_P$ ) according to the following equation:

$$\Phi_p = \Phi_R \cdot x \cdot f_p \quad (2.5)$$

Regarding the energy necessity, it has to be said that the excitation energy of the photoinitiator has to be higher than the dissociation energy of the bond to be ruptured. The bond dissociation energy, on the other hand, has to be high enough in order to ensure long term storage stability.

Initiating radicals, formed by direct photofragmentation process ( $\alpha$  or less common  $\beta$  cleavage) of Type I photoinitiators upon absorption of light, are capable of triggering polymerization. As illustrated in Figure 2.2, the photoinitiator forms an excited singlet state, which then undergoes rapid intersystem crossing to form a triplet state. In the triplet state, two radicals (benzoyl and benzyl radicals) are generated by  $\alpha$ -cleavage fragmentation. The benzoyl radical is the major initiating species, while, in some cases, the benzyl radical may also contribute to the initiation.



**Figure 2.2** : Formation of initiating radicals from decomposition of a Type I photoinitiator.

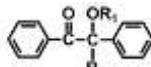
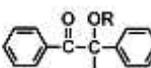
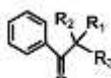
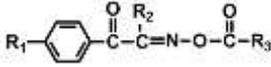
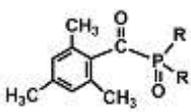
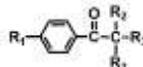
Most of the Type I photoinitiators are aromatic carbonyl compounds with appropriate substituents. Benzoin ether derivatives, benzil ketals, hydroxylalkylphenones,  $\alpha$ -aminoketones and acylphosphine oxides are the most efficient ones (Table 2.1) [18-21].

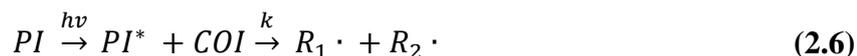
### 2.2.1.2 Type II photoinitiators (bimolecular photoinitiator system)

The excited states of certain compounds do not undergo Type I reactions because 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, however, react with another component of the polymerization mixture (co-initiator (COI)) to produce initiating radicals (eq. 2.6). In this case, radical generation follows second-order kinetics (eq. 2.7).

Classic Type II photoinitiators include aromatic carbonyls such as benzophenone and derivatives [22-25], thioxanthone and derivatives [26-31], benzyl [23], quinines [23], and organic dyes [31-36], whereas alcohols, ethers, amines, and thiols are used as hydrogen donors. Recently, thiol and carboxylic acid derivatives of thioxanthenes have been reported to initiate photopolymerization without co-initiators as they contain functional groups with H-donating nature [37-39].

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

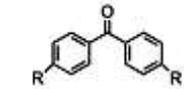
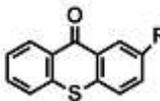
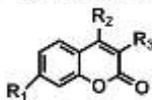
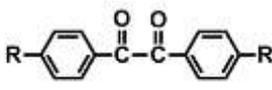
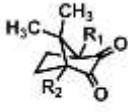
Photoinitiators	Structure	$\lambda_{\max}$ (nm)
Benzoin ethers	 $R_1 = \text{H, alkyl}$ $R_2 = \text{H, substituted alkyl}$	323
Benzil ketals	 $R = \text{CH}_3, \text{C}_6\text{H}_7, \text{CH}_2$	365
Acetophenones	 $R_1 = \text{OCH}_3, \text{OC}_2\text{H}_5$ $R_2 = \text{OCH}_3, \text{H}$ $R_3 = \text{C}_6\text{H}_5, \text{OH}$	340
Benzyl oximes	 $R_1 = \text{H, SC}_6\text{H}_5$ $R_2 = \text{CH}_3, \text{C}_6\text{H}_{13}$ $R_3 = \text{C}_6\text{H}_5, \text{OC}_2\text{H}_5$	335
Acylophosphine Oxides	 $R = \text{C}_6\text{H}_5, \text{OCH}_3$	380
Aminoalkyl phenones	 $R_1 = \text{SCH}_2, \text{morpholine}$ $R_2 = \text{CH}_2, \text{CH}_2\text{Ph}, \text{C}_2\text{H}_5$ $R_3 = \text{N}(\text{CH}_2)_2, \text{morpholine}$	320



$$\frac{d[R_1 \cdot]}{dt} = \frac{d[R_2 \cdot]}{dt} = k[PI^*][COI] \quad (2.7)$$

Alternative approach concerns the attachment of both chromophoric and hydrogen donating groups into polymer chains. This way, the odor and toxicity problems observed with the conventional photoinitiators and amine hydrogen donors were overcome.

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

Photoinitiator	Structure	$\lambda_{max}$ (nm)
Benzophenones	 $R = H, OH, N(C_2H_5)_2, C_6H_5$	335
Thioxanthenes	 $R = H, Cl, isopropyl$	390
Coumarins	 $R_1 = N(C_2H_5)_2, N(CH_3)_2$ $R_2 = CH_3, cyclopentane$ $R_3 = benzothiazole, H$	370
Benzils	 $R = H, CH_3$	340
Camphorquinones	 $R_1 = CH_3, H$ $R_2 = H, CH_3$	470

A novel thioxanthone based photoinitiator have also been developed possessing anthracene group that does not require an additional hydrogen donor for radical formation and initiates the polymerization of both acrylate and styrene monomers in the presence of air [40]. In addition, TX-A possesses excellent optical absorption properties in the near-UV spectral region, ensuring efficient light absorption. Quite recently, thioxanthone-fluorene carboxylic acid (TX-FLCOOH) and its sodium salt (TX-FLCOO<sup>-</sup> Na<sup>+</sup>) were synthesized as efficient photoinitiators in visible light [41].

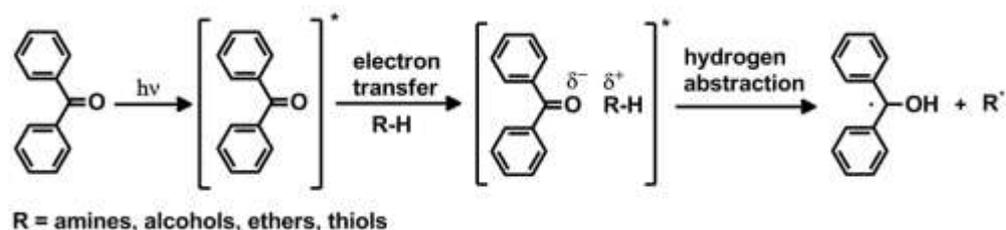
In fact, photoinitiators with higher wavelength absorption characteristics are desired as they cost lower energy and are defined to be “green”.

Typical photoinitiators for Type II system are listed in Table 2.2.

Radical generation by Type II initiating systems has two distinct pathways:

*Hydrogen abstraction from a suitable hydrogen donor*

Bimolecular hydrogen abstraction is limited to diaryl ketones [42]. The free radical generation process is the H-abstraction reaction of triplet photoinitiator from hydrogen donors (R-H) such as amines and alcohols. The radical derived from the donor can initiate the polymerization, whereas ketyl radicals stemming from aromatic carbonyl compound are usually not reactive toward vinyl monomers because of bulkiness, the delocalization of the unpaired electrons, or both. The overall process is depicted in the example of benzophenone in Figure 2.3.

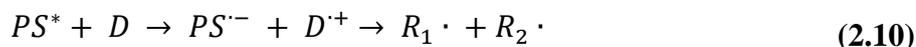
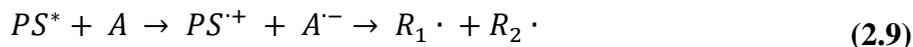


**Figure 2.3 :** Formation of initiating radicals from photolysis of Type II photoinitiator in the presence of suitable hydrogen donor.

*Photoinduced electron transfer reactions and subsequent fragmentation*

Photoinduced electron transfer is a more general process, which is not limited to a certain class of compounds and is more important as an initiation reaction comprising the majority of bimolecular photoinitiating systems. The photoexcited compounds (sensitizer) can act as either an electron donor with the coinitiator as an electron acceptor or vice-versa. The radical ions obtained after the photoinduced electron transfer can generally undergo fragmentation to yield initiating radicals (eq. 2.8-2.10).

The electron transfer is thermodynamically allowed, if Gibbs Energy Change ( $\Delta G$ ) calculated by the Rehm-Weller equation (eq. 2.11) is negative [43].



$$\Delta G = F[E_{1/2ox}(D/D^+) - E_{1/2red}(A/A^-)] - E_s + \Delta E_c \quad (2.11)$$

where

F = Faraday constant

$E_{1/2ox}(D/D^+) - E_{1/2red}(A/A^-)$  = Redox potentials of the donor and acceptor.

$E_s$  = Excitation state of the reactive state of the sensitizer;  $E_s = h\nu$

$\Delta G$  = Coulombic stabilization energy

Electron transfer is often observed for aromatic ketone/amine pairs and always with dye/coinitiator systems. Dyes comprise a large fraction of visible light photoinitiators because their excited electronic states are more easily attained. Coinitiators, such as tertiary amines, iodonium salts, triazines, or hexaarylbisimidazoles, are required since dye photochemistry entails either a photo-reduction or photo-oxidation mechanism. Numerous dye families are available for selection of an appropriate visible initiation wavelength; examples of a thiazine dye (with an absorption peak around 675 nm), acridine dyes (with absorption peaks around 475nm), xanthene dyes (500–550 nm), fluorone dyes (450–550 nm), coumarin dyes (350–450 nm), cyanine dyes (400–750 nm), and carbazole dyes (400 nm). The oxidation or reduction of the dye is dependent on the co-initiator; for example, methylene blue can be photo-reduced by accepting an electron from an amine or photo-oxidized by transferring an electron to benzyltrimethyl stannane [44]. Either mechanism will result in the formation of a free-radical active center capable of initiating a growing polymer chain.

### 2.2.1.3 Monomers

Unsaturated monomers, which contain a carbon–carbon double bond (C=C), are used extensively in free radical photopolymerizations. The free-radical active center reacts with the monomer by opening the C=C bond and adding the molecule to the growing

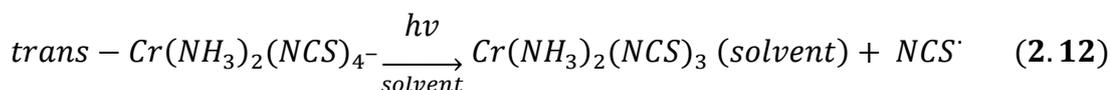
polymer chain. Most unsaturated monomers are able to undergo radical polymerization because free-radical species are neutral and do not require electron-donating or electron-withdrawing substituents to delocalize the charge on the propagating center, as is the case with ionic polymerizations. Commercial consideration in formulation development is therefore given to the final properties of the polymer system, as well as the reactivity of the monomer. Acrylate and methacrylate monomers are by far most widely used in free-radical photopolymerization processes. These monomers have very high reaction rates, with acrylates having an even faster reaction rate than their methacrylate counterparts [45]. This makes them especially amenable for high speed processing needed in the films and coatings industry.

Multiacrylates increase the mechanical strength and solvent resistance of the ultimate polymer by forming cross-linked networks rather than linear polymer chains, whereas monoacrylates reduce the viscosity of the prepolymer mixture for ease of processing [45, 46]. One of the drawbacks of acrylate and methacrylate systems is their relatively large polymerization shrinkage. Shrinkage is caused by the formation of covalent bonds between monomer molecules. When a covalent bond is formed between two monomer molecules, the distance between them is approximately half as much as that between two molecules experiencing van der Waal's forces in solution. This shrinkage causes stresses in the polymer parts, which can affect their ultimate performance, especially in applications such as stereo lithography, dentistry, and coatings. One way to overcome this disadvantage is to develop oligomeric acrylates. These oligomers contain 1 to 12 repeat units formed through step-growth polymerization; the ends are then capped with two or more (meth) acrylate functional groups. Diallyldiglycolcarbonate has been used for many years in optical components such as lenses [47]. Acrylamide is used in stereo lithography and to prepare holographic materials [48-50]. N-vinylpyrrolidinone is copolymerized with acrylates and methacrylates for cosmetic and biomedical applications [51]. Norbornene is copolymerized with thiols for optical fiber coatings [52].

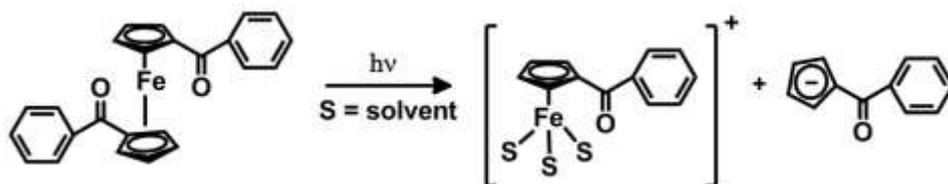
### **2.2.2 Photo-initiated anionic polymerization**

Anionic photopolymerization had received less attention compared to cationic and free radical counterparts [53]. However, anionic photopolymerization receive further

attention after introduction of a new initiating system depending on  $\text{trans-Cr(NH}_3)_2(\text{NCS})_4^-$  (Reineckate anion). In fact, irradiation of ligand field absorption bands of transition metal complexes results in ligand substitution reactions. This process can be employed for the controlled photogeneration of anions from a stable precursor.  $\text{trans-Cr(NH}_3)_2(\text{NCS})_4^-$  is considered as an ideal anion source since  $\text{K}^+[\text{trans-Cr(NH}_3)_2(\text{NCS})_4^-]$  is readily soluble in a variety of organic solvents, resistant to thermal substitution in nonhydroxylic media, and its quantum efficiency is quite high ( $> 10\%$ ) for releasing of  $\text{NCS}^-$  (eq. 2.12) upon ligand field excitation with near-UV/Vis light [54-56]. In the presence of a monomer containing electron-withdrawing substituents to stabilize the negative charge, such as ethyl  $\alpha$ -cyanoacrylate, anionic polymerization is initiated.



In another report, acyl-substituted ferrocenes, namely benzoylferrocene and 1,1'-dibenzoylferrocene, were utilized as photoinitiator for the anionic polymerization of ethyl  $\alpha$ -cyanoacrylate [57]. Generation of anionic initiating species is schematized in Figure 2.4.  $\text{Pt}(\text{acac})_2$  or a cyclopentadienyl complex of Fe or Ru have been also utilized as anionic photoinitiators [58].



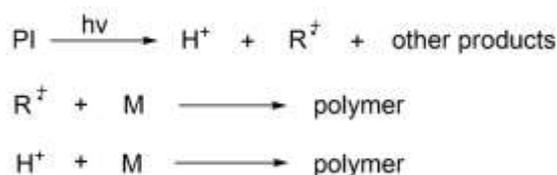
**Figure 2.4 :** Generation of anionic species from photolysis of 1,1'-dibenzoylferrocene.

### 2.2.3 Photo-initiated cationic polymerization

Much effort has been devoted to free radical photopolymerizations [59,60] mainly due to the availability of a wide range of photoinitiators and the great reactivity of acrylate-based monomers. Although the most popular industrial applications are based on the photo-initiated free radical polymerization there are some drawbacks associated with this type of polymerization. For instance, free radical species are

inhibited by molecular oxygen and inhibits almost polymerization based on free radicals. Moreover, post-cure limitations, which may affect the properties of the final product and toxicity of the monomers are another drawbacks. Several advantages of the photo-initiated cationic polymerization over the photo-initiated free radical polymerization have also been reported [61, 62, 63]. Cationic photopolymerization overcomes volatile emissions, limitations due to molecular oxygen inhibition, toxicity, and problems associated to high viscosity. Furthermore, once initiated, cationically polymerizable monomers such as vinyl ethers and epoxides undergo dark-polymerization in which they slowly polymerize without radiation.

General scheme for photo-induced cationic polymerization is depicted in Figure 2.4. A photo-sensitive compound, namely photoinitiator (PI), absorbs incident light and undergoes decomposition leading to production of initiating species. Active species, namely a radical cation ( $R^+$ ) in turn, react with cationic polymerizable monomers (M), and yield polymer (Figure 2.5).



**Figure 2.5 :** General scheme of photo-initiated cationic polymerization.

### 2.3 Oxygen Inhibition

One of the major drawbacks of photoinitiated free radical polymerization is related to the well-known oxygen inhibition. Various reactive species playing a role in the polymerization, such as excited states as well as initiating and propagating radicals are quenched by  $O_2$  (Scheme 1). While quenching of the excited states results in inefficiency of the primary photochemical reaction, the diffusion-controlled reaction of oxygen with initiating and propagating radicals yield highly stable peroxy radicals which cannot participate in any further polymerization initiation reactions. Therefore, the polymerization only proceeds efficiently after oxygen is consumed.

In free-radical polymerization, the rate constants for quenching of an initiating and propagating radical species by oxygen are extremely fast,  $\sim 5 \times 10^8$  and  $10^9$  L/mol/s, respectively, due to the triplet state biradical nature of oxygen [64]. The equilibrium concentration of molecular oxygen dissolved in monomers, i.e. acrylates, is about  $10^{-3}$

<sup>3</sup> M, [65,66] and there is continuous diffusion of oxygen into polymerization media. Generally, inhibition of free-radical polymerization by oxygen continues until the oxygen concentration in the sample is significantly lowered. Propagation can occur and compete with oxygen consumption reaction only when the oxygen consumption rate is much faster than oxygen diffusion into the sample. It was reported by Decker et al. [65] that the steady state oxygen concentration which allows polymerization is about  $4.2 \times 10^{-6}$  mol/L. Considering that for (meth)acrylates, the oxygen concentration is approximately  $10^{-3}$  mol/L [65,66], the initial oxygen concentration must be reduced by more than 100 fold before polymerization occurs. Therefore, the extent of oxygen inhibition strongly depends on how fast oxygen is consumed. Successful reduction in the sensitivity of photocuring systems to oxygen would provide a significant advantage in curing of thin films for electronic applications and pigmented coatings.

### **2.3.1 Importance of O<sub>2</sub> inhibition in industrial applications**

Over the past several decades, the effect of oxygen on free-radical photopolymerization has been a subject of much interest [67–70] since free-radical polymerizations are severely inhibited by oxygen, and most free-radical photocuring processes proceed in air. Oxygen inhibition causes numerous insalubrious effects on free-radically cured products including slow polymerization rates, long induction periods, low conversion, short polymer kinetic chain length and tacky surface properties [67–70].

### **2.3.2 Common methods to overcome O<sub>2</sub> inhibition**

Overcoming oxygen inhibition is achieved industrially by using large amounts of photoinitiators and/or high light intensities to consume oxygen dissolved in polymerization media with large concentrations of initiator radicals generated. Physical methods such as blanketing coatings with nitrogen or polyethylene film can be another alternative to suppress oxygen inhibition, but these methods are expensive [67–70].

Many strategies have been developed to combat O<sub>2</sub> inhibition including use of high-intensity lamps/high cure dosage, inert atmospheres, and additives such as amines and thiols. A number of cyclic and acyclic N-vinylamides and N-alkylamides were

also shown to have significant effect for the reduction of oxygen inhibition, resulting in rapid rates of polymerization in air even at low light intensities [71]. The use of TX-A (vide supra) as photoinitiator is one way to prevent oxygen inhibition since the presence of O<sub>2</sub> is essential for the polymerization to proceed.

The addition of amines, which undergo readily a chain peroxidation reaction and thus consume the dissolved O<sub>2</sub> [72]. Unfortunately, the presence of amines in the coating has some deleterious effects, such as yellowing of the film, odor, plasticizing effect, softening of the coating resulting from chain transfer reactions. Moreover, the hydroperoxides thus formed will have a detrimental effect on the weathering resistance of the UV-cured polymer.

A conversion of the dissolved oxygen into its excited singlet state by means of a red light irradiation in the presence of a dye sensitizer. The resulting O<sub>2</sub> will be rapidly scavenged by a 1,3-diphenylisobenzofuran molecule to generate a compound (1,2-dibenzoylbenzene) which can work as photoinitiator [73,74]. However, as the coating is slightly colored, in spite of the photobleaching of the dye, this method cannot be used for a wide range of applications.

An increase of the formulation reactivity to shorten the UV exposure during which atmospheric oxygen diffuses into the film. This can be achieved by increasing the photoinitiator concentration and by operating at high light intensities [75]. Oxygen inhibition can further be reduced by using high intensity flashes which generate large concentrations of initiator radicals reacting with O<sub>2</sub>, but here again hydroperoxides are being formed.

Wax barrier coats [76] or performing the UV exposure under water [77], to slow down the diffusion of atmospheric oxygen into the UV-curable coating. But this will affect the surface properties of the V-cured polymer.

Performing the radical photopolymerization under inert conditions [78,79], which is obviously the most efficient way to overcome oxygen inhibition. Nitrogen is typically used to flush continuously the sample during the UV exposure. On an industrial UV-curing line, which cannot be made completely airtight, nitrogen losses can yet be important, thus making the process expensive, and even more so if argon is used to achieve an O<sub>2</sub>-free environment.

Several techniques have been utilized to combat the effects of oxygen inhibition. The use of high-intensity irradiation sources increases the initiation rate by increasing the production of primary radicals such that it becomes much greater than their consumption by oxygen. Another alternative is to polymerize the samples in an inert environment, whereby the oxygen is eliminated from the polymerization. There are also several methods that include the addition of molecules to reduce the inhibitory effect of oxygen. Decker developed a method whereby the dissolved oxygen in a monomer system was consumed prior to and during polymerization using a dualinitiation method with the addition of an oxygen singlet generator and acceptor molecule. Furthermore, the addition of thiols and amines to monomer systems is known to decrease the deleterious effects of oxygen.

## **2.4 GOx in Polymer Chemistry**

### **2.4.1 GOx**

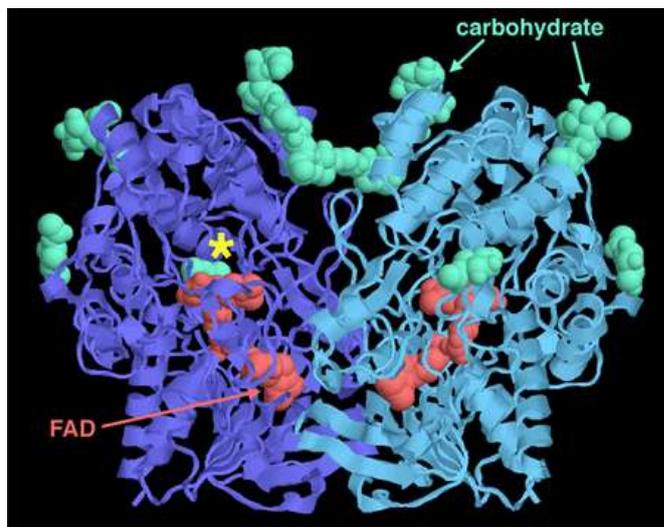
Glucose oxidase (GOx;  $\beta$ -D-glucose:oxygen 1-oxido-reductase, E.C. 1.1.3.4), which is extremely valuable enzyme from not only metabolic but also industrial point of view, is a good candidate for prevention of oxygen inhibition. It is widely employed in the determination of free glucose amount in blood and body fluids, foods, drinks and agricultural products. It catalyzes specifically the oxidation of  $\beta$ -D-glucose to D-glucono- $\delta$ -lactone and hydrogen peroxide in the presence of molecular oxygen and water (Scheme 2). Here, we take advantage of these features to develop a UV curing system based on free radical polymerization and consumption of O<sub>2</sub> by GOx which utilizes O<sub>2</sub> in its usual enzymatic pathway.

Glucose oxidase has been used in many applications. Industrially it has been used to produce gluconic acid. It is also used as a food preservative and for the measurement of glucose in foodstuffs, beverages and in diagnostics such as determination of glucose in blood, serum, or plasma.

### **2.4.2 Enzymatic pathway of GOx**

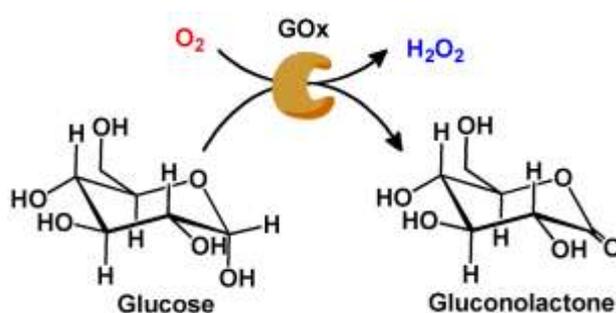
The oxidation reaction is performed by the FAD cofactors bound deep inside the enzyme, shown in red. The active site where glucose binds is just above the FAD, in

a deep pocket shown with a star. Notice that the enzyme, like many proteins that act outside of cells, is covered with carbohydrate chains, shown in green.



**Figure 2.6 :** Chemical Structure of GOx.

GOx act by oxidising its substrates, accepting electrons in the process and thereby changing to an inactivated reduced state. This enzyme is normally returned to their active oxidised state by transferring these electrons to molecular oxygen, resulting in the production of hydrogen peroxide ( $H_2O_2$ ):

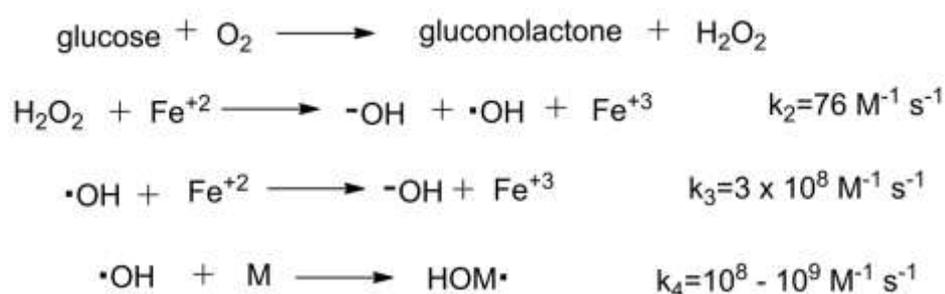


**Scheme 2 :** Oxidation of  $\beta$ -D-glucose to D-glucono- $\delta$ -lactone in the presence of molecular oxygen.

### 2.4.3 Employment of GOx in polymerizations and polymers

Enzyme-mediated initiation systems involving oxidase enzymes that produce  $H_2O_2$ , including the glucose oxidase (GOx) enzyme, offer a beneficial approach for rapidly polymerizing hydrogels. In the GOx initiation system, the enzyme binds to the glucose substrate generating gluconolactone and subsequently regenerates the flavin

adenine dinucleotide (FAD) cofactor by binding oxygen and producing H<sub>2</sub>O<sub>2</sub>. By coupling ferrous ions to this enzymatic process, hydroxyl radical species are produced. Notably, a unique aspect of this system involves the utilization and elimination of oxygen, a powerful inhibitor of radical chain polymerization, by the GOx enzyme during the initiation process. This feature offers unique advantages, including the ability to reduce initiator quantities and eliminate the requirement of performing reactions under inert atmospheric conditions which precludes the ability to encapsulate cells. For example, the GOx initiation system was actually completely suppressed under a nitrogen atmosphere until the introduction of oxygen whereupon polymerization quickly commenced. This compatibility with oxygen further prompted the use of this GOx system for the polymerization of detachable balloon catheters used in endovascular surgery where oxygen flow to blood and tissue is critical. The tolerance of the GOx system to oxygen and the elimination of an extraneous energy source for initiation, such as light or heat, prompted our investigations to understand further the polymerization kinetics and employ this system for cellular encapsulation. The GOx enzyme catalyzes the oxidation of glucose to gluconolactone and subsequently regenerates the FAD cofactor by reducing O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. By combining the enzymatically produced H<sub>2</sub>O<sub>2</sub> with ferrous ions, a hydroxyl radical initiator is generated, which may further react with vinyl monomer [M] to produce a chain initiating species or react with additional ferrous ion to inhibit polymerization.



#### 2.4.4 Potential use of GOx in overcoming O<sub>2</sub> inhibition

Inspired by nature, (polymer) chemists have begun to take advantage of the properties of biomolecules toward diverse applications. For instance, the integration of biomolecules with synthetic materials or processes is a rapidly progressing interdisciplinary research field for preparation of functional and smart materials widely employed in medicine[80], drug delivery systems, biochemistry, bio-sensing

platforms[81,82] and many other research activities and industrial applications. Certainly, one can recruit any biomolecule in production of a material for a specific purpose by providing suitable conditions. Unearthing the secret of how nature is able to use sugar (i.e. glucose) in order to generate power (energy) gives alternative way to eliminate oxygen from a medium. Particularly, glucose oxidase (GOx;  $\beta$ -D-glucose:oxygen 1-oxido-reductase, E.C. 1.1.3.4), extremely valuable enzyme from not only metabolic but also industrial point of view, is a potential candidate for the prevention of oxygen inhibition. It is widely employed in the determination of free glucose amount in blood and body fluids, foods, drinks and agricultural products. It catalyzes specifically the oxidation of  $\beta$ -D-glucose (G) to D-glucono- $\delta$ -lactone in the presence of O<sub>2</sub> and water (Scheme 2).

### **3. EXPERIMENTAL PART**

#### **3.1 Materials**

The monomers, poly(ethyleneglycol) diacrylate (PEGDA) (Aldrich, Mn ~ 575 g/mol) and acrylamide (AAm) (Fluka); the cross-linker, N,N'-methylenebisacrylamide (BAAm) (Merck); the initiators, 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propane-1-one (Irgacure 2959) (Ciba), 2,2-dimethoxy-2-phenylacetophenone (DMPA) (Ciba), benzophenone (BP) (Acros, 99%); and the hydrogen donor, N,N'-dimethylaniline (DMA) (Fluka, 99,5%), were used as received. Glucose oxidase (GOx, 2,5 mg/mL) and D-glucose (G) were purchased from Sigma-Aldrich. Solvents were purified by conventional drying and distillation procedures.

#### **3.2 Equipments**

##### **3.2.1 Rofin polilight PL400 forensic plus**

A Rofin Polilight light source emitting light at 350, 415, 430, 450, LP530, 490, 505, 515, 530, 550, 560, LP560, 570, 590, 620, 650 (with a bandwidth of ca.  $\pm 20$  nm), white, half white and blank was used for photopolymerizations.

##### **3.2.2 Photo-differential scanning calorimetry**

Kinetics of some photocuring experiments was performed on a photo-DSC. The polymerizations were carried out under a N<sub>2</sub> and without N<sub>2</sub> atmosphere in a modified Perkin Elmer DSC-7 to allow for irradiation of the sample and reference pans by use of a bifurcated fiber optic guide leading to minimization of the thermal heating effect of the light source. The Rofin Polilight PL400 was employed as an UV light source in the photo-DSC studies using wavelengths of 350 $\pm$ 20nm. The irradiation time was controlled by a shutter between the radiation source and the light guide.

### 3.3 Preparation of Photo-Curable Formulations

Photo-induced crosslinking of PEGDA or AAm/BAAm was carried out using 1 wt % of both *Type I* and *Type II* photoinitiating system (DMPA or BP/DMA) in presence or absence of GOx/G (0.06 wt % / 1 wt %). All formulations are listed in Table 4.1. All components except GOx solution were put in an Eppendorf tube and dissolved. Then GOx solution was added into this mixture and immediately used in photopolymerizations. A typical photopolymerization performed on photo-differential scanning calorimetry (Photo-DSC) is as follows: 4.5 mg of *Type I* photoinitiator (DMPA, 1 wt %), 4.5 mg of G (1 wt %) was dissolved in PEGDA (0.2 mL, 52 wt %) and 0.1 mL of water. Just before irradiation, 0.1 mL of GOx solution (containing 0.25 mg of the enzyme) was added into the reaction solution (total volume: 0.4 mL). Then 6-10 mg of the reaction solution was transferred to a DSC pan for liquid sample.

### 3.4 Photo-Differential Scanning Calorimetry of Photo-Curable Formulations

The photocuring of PEGDA and AAm/BAAm was studied by Photo-DSC at 20°C under air or nitrogen atmosphere. The formulations prepared according to Table 4.1 were dropped (6-10 mg) onto an aluminum pan and the film samples were placed into the sample holder of photo-DSC instrument. The polymerizations were carried on a Perkin-Elmer Diamond DSC equipped with a UV-Vis light source (Omniscure Series 2000 emitting light in the range of 320-500 nm). A uniform UV light intensity is delivered across the DSC cell to the sample and the reference pans. The measurements were carried out in an isothermal condition at 20 °C under air atmosphere. The DSC run was begun, but for the first 60 s, a shutter prevented irradiation of the sample to stabilize the light source and to establish the heat flow baseline. When the light was switched on, an exotherm was observed. Irradiation was continued after the exotherm peak until no change was observed in the heat flow. To remove the slight imbalance of the thermal heating effect on the sample and reference pans, the cured sample was again irradiated with the same conditions to produce a background which was subtracted from the data of the first run.

The reaction heat liberated from the polymerization was directly proportional to the number of acrylate or acrylamide groups reacted in the system. By integrating the

area under the exothermic peak, the conversion of the vinyl groups (C) or the extent of the reaction was determined as follows:

$$C (\%) = (\Delta H_t / \Delta H_0^{\text{theory}}) \times 100$$

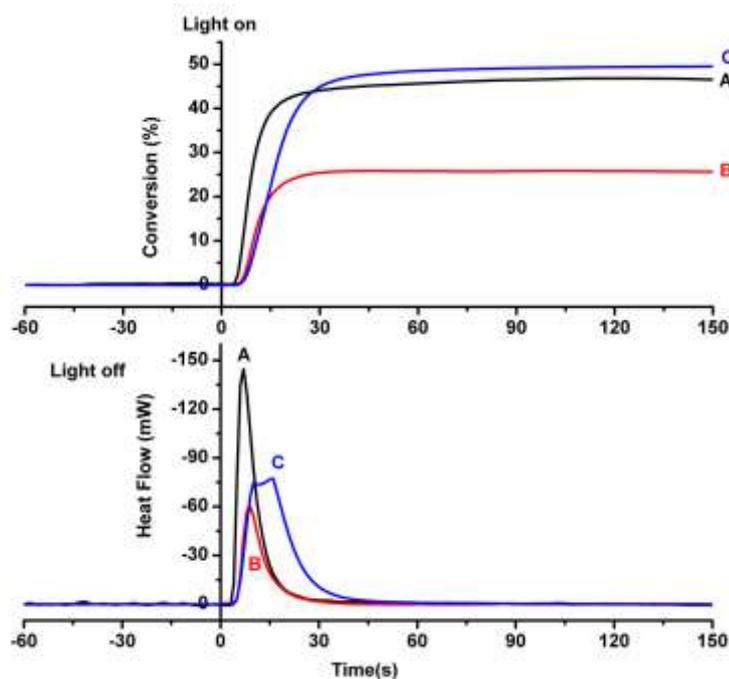
where  $\Delta H_t$  is the reaction heat evolved at time t and  $\Delta H_0^{\text{theory}}$  is the theoretical heat for complete conversion.  $\Delta H_0^{\text{theory}}$  equals to  $80 \text{ kJ}\cdot\text{mol}^{-1}$  and  $78 \text{ kJ}\cdot\text{mol}^{-1}$  for an acrylic double bond and acrylamide, respectively.



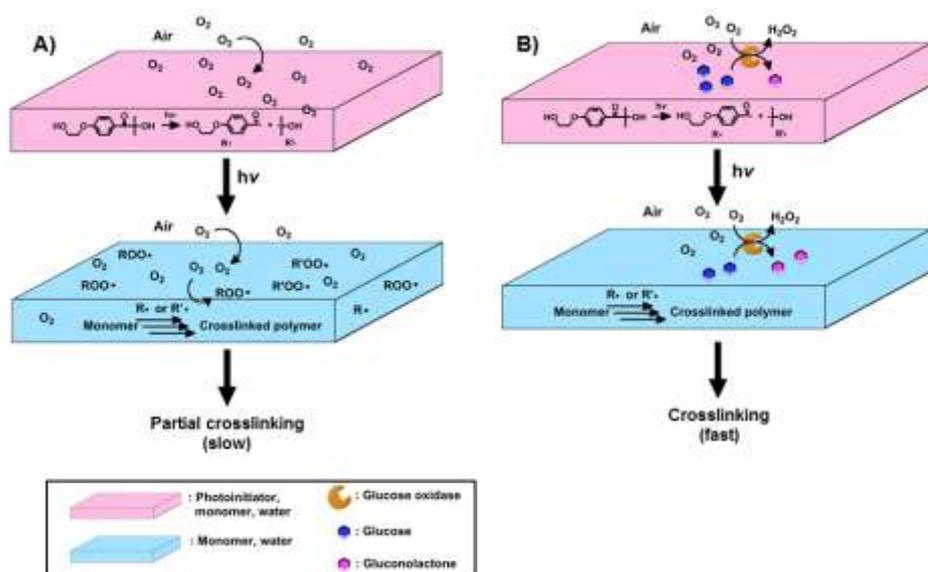
#### 4. RESULTS AND DISCUSSION

In the current study, we aim to develop a UV curing system based on free radical polymerization and consumption of O<sub>2</sub> by GOx in its usual enzymatic pathway. Thus, in this approach the polymerization system contains GOx and G in addition to usual components – monomer and initiator. Specifically, UV-curable aqueous formulations containing poly(ethylene glycol) diacrylate (PEG-DA) or acrylamide (AAm)/*N,N'*-methylenebisacrylamide (BAAm) as monomers, and *Type I* or *Type II* photoinitiators in the presence and absence of GOx and G were irradiated and polymerizations were monitored by photo-DSC.

In a model application, free radical photopolymerization of PEGDA using a *Type I* photoinitiator, 2, 2-dimethoxy-2-phenyl acetophenone (DMPA), is enhanced by the presence of the redox components, GOx and G. The biological activity of GOx obviously leads to increase in the rate of the polymerization and monomer conversion (see curves A and B in Figure 4.1). The action of the additives must be related to the consumption of O<sub>2</sub> during oxidation of G, thus the initiating and propagating radicals readily react with monomers without forming inefficient peroxy radicals. As a consequence of this effect, shorter induction periods are observed in such formulations. Full mechanisms for the polymerizations in air in the absence and presence of GOx and G are proposed in Figure 4.2. The proposed mechanism of the photopolymerization depends on prevention of photochemically formed radicals from molecular oxygen presenting in the close proximity. Complimentary polymerizations under nitrogen were also performed (curve C in Figure 4.1). It is noted that the addition of GOx and G gave higher rates but similar conversion values to those obtained with the polymerizations conducted with nitrogen saturation. Efficiency of a *Type II* initiating system consisting of benzophenone (BP) and *N,N*-dimethyl aniline (DMA) was also investigated in photo-crosslinking of PEGDA. The effect of the GOx/G was the same for also this system (Run 4 and 5, Table 1).



**Figure 4.1 :** Conversion and heat flow profile during the UV curing of PEGDA (52 wt %) initiated by a *Type I* photoinitiator (DMPA, 1 wt %) in the presence (A) and absence (B) of glucose (1 wt %) and GOx (0.06 wt %) in aqueous solution under air atmosphere. Similar UV curing was performed without GOx and G under nitrogen atmosphere (C).



**Figure 4.7:** Photoinitiated free radical polymerization in air in the absence (A) and presence of glucose oxidase and glucose (B).

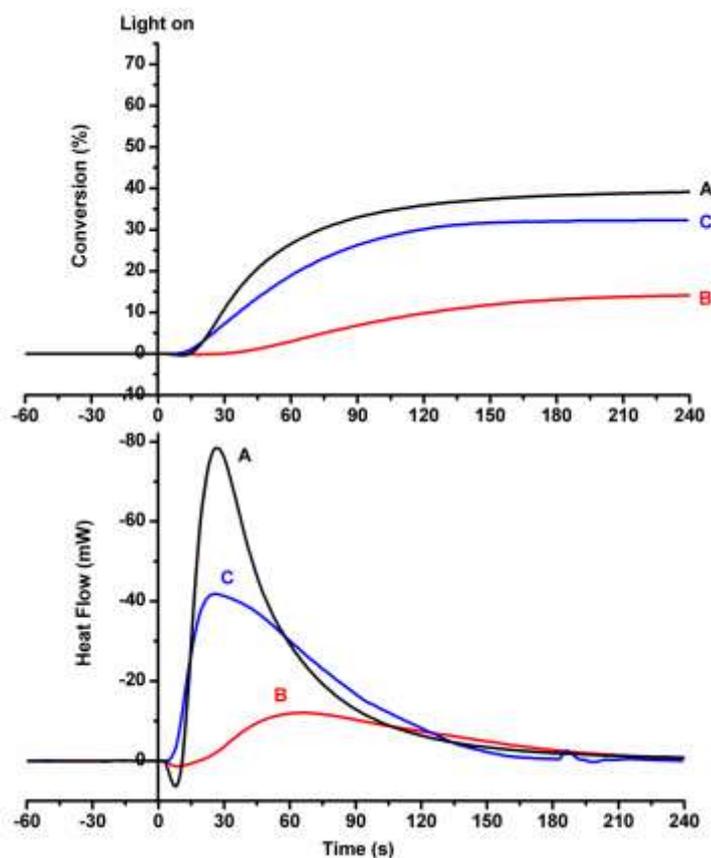
**Table 4.1** : Photo-induced crosslinking polymerization of water soluble monomers the presence or absence of GOx/G under air atmosphere at 20 °C.

Run	Monomer <sup>a</sup>	PI <sup>b</sup>	[G] (wt%)	[GOx] (wt%)	t <sub>max</sub> (s) <sup>c</sup>	Conv. (%) <sup>d</sup>
1	PEGDA	DMPA	1	0.06	7	47
2	PEGDA	DMPA	-	-	9	26
3	PEGDA	DMPA	-	-	10	49
4	PEGDA	BP/DMA	1	0.06	12	45
5	PEGDA	BP/DMA	-	-	14	32
6	AAm/BBAm	BP/DMA	1	0.06	27	39
7	AAm/BBAm	BP/DMA	-	-	66	14
8	AAm/BBAm	BP/DMA	-	-	28	32
9	AAm/BBAm	DMPA	1	0.06	8	24
10	AAm/BBAm	DMPA	-	-	10	22

<sup>a</sup> PEGDA: poly(ethylene glycol) diacrylate (52 wt %); AAm: acrylamide (49 wt %); BAAM: *N,N'*-methylenebisacrylamide (2 wt %). <sup>b</sup> DMPA: 2, 2-dimethoxy-2-phenyl acetophenone (1 wt %); BP: benzophenone (1 wt %); DMA: *N,N'*-dimethylaniline (1 wt %). <sup>c</sup> t<sub>max</sub> = The time required to reach maximum rate. <sup>d</sup> Conversions (%) of double bonds were calculated from integral areas of heat flow values using heat of polymerization ( $\Delta H_0$ ) values for acrylate as 80 kJ·mol<sup>-1</sup> and 78 kJ·mol<sup>-1</sup>, respectively. See supporting information for details. <sup>e</sup> Polymerizations were performed under nitrogen atmosphere.

Efficiency of this new system was also evaluated for acrylamide-based formulations. UV curing behavior of AAm/BAAM monomer pair initiated by BP/DMA is very similar, although the conversion changes as function of time for both systems vary somewhat.

Because the polymerization is slower in the acrylamide system, oxygen affects the process more significantly (Figure 4.3, Curve B). Interestingly, the enzymatic route exhibits ability to prevent oxygen inhibition even better than deaeration with nitrogen. Analogous with results from *Type II* photoinitiator, comparable improvement in the rate and final conversion was attained by employing GOx/G in the formulations containing *Type I* photoinitiator (DMPA) (Run 9 and 10, Table 1).



**Figure 8.3 :** Conversion and heat flow profile during the UV curing of AAm (49 wt %)/BAAm (2 wt %) initiated by a *Type II* photoinitiating system in the presence (A) and absence (B) of glucose (1 wt %) and GOx (0.06 wt %) in aqueous solution under air. Benzophenone (1 wt %)/*N,N*-dimethyl aniline (1 wt %) were used as the *Type II* initiating system. Similar UV curing was performed without GOx and G under nitrogen atmosphere (C).

To describe all these effects quantitatively, we performed polymerizations using different combinations of monomers and initiating systems (Table 4.1). In all cases, substantial increase in the rate and conversion of polymerization were achieved upon addition of redox components. Moreover, the time required to reach maximum rate ( $t_{\max}$ ) was much shorter in the presence of the GOx and G.

In summary, we developed a new method to overwhelm  $O_2$  inhibition in photoinitiated free radical polymerization which is of considerable technical and commercial importance. The use of GOx and G for consuming oxygen in photoinitiated free radical polymerization offers a very simple approach that is controlled by the redox process. Detailed photo-DSC investigations reveals that the enzymatic system enhances the efficiency of the free radical photopolymerization

initiated with both *Type I* and *Type II* photoinitiators. The current limiting factor of the system is that it can only be applied to water-born coatings involving aqueous photo polymerizations. Because the redox components are insoluble in organic systems, facilitating their dissolution through structural modifications should lead to a much wider practical applications.



## 5. REFERENCES

- [1] Kloosterboer, J.G. (1988), *Adv. Polym. Sci.*, 84, 1-61.
- [2] Drury, J.L., Mooney, D.J. (2003), *Biomaterials*, 24, 4337-4351.
- [3] Decker, C. (1996), *Prog. Polym. Sci.*, 21, 593-650.
- [4] Scott, T. F. Kowalski, B.A., Sullivan, A.C., Bowman, C.N., McLeod, R.R. (2009), *Science*, 324, 913-917.
- [5] Kahveci, M.U., Beyazkilic, Z., Yagci, Y. (2010), *J. Polym. Sci., Part A: Polym. Chem.*, 48, 4989-4994.
- [6] Fouassier, J.P. (1995), Photoinitiation, Photopolymerization and Photocuring: Fundamentals and Applications; *Hanser Publishers*: Munich.
- [7] Davidson, R.S. (1998), Exploring the science, technology and applications of U.V and E.B. curing; *SITA Technology Ltd.*: London.
- [8] Pappas, S.P. (1985) UV curing: Science and Technology.; *Technology Marketing Corporation*: Stamford.
- [9] Studer, K., Decker, C., Beck, E., Schwalm, R. (2003), *Prog. Org. Coat.*, 48, 92-100.
- [10] Belon, C., Allonas, X., Croutxe-Barghorn, C., Lalevee, J. (2010), *J. Polym. Sci. Pol. Chem.*, 48, 2462-2469.
- [11] Shenoy, R., Bowman, C. N. (2010), *Macromolecules*, 43, 7964-7970.
- [12] Lalevee, J., Telitel, S., Tehfe, M.A., Fouassier, J.P., Curran, D.P., Lacote, E. (2012), *Angew. Chem. Int. Ed.*, 51, 5958-5961.
- [13] El-Roz, M., Lalevee, J., Allonas, X., Fouassier, J.P. (2009), *Macromolecules*, 42, 8725-8732.
- [14] Lalevee, J., Dirani, A., El-Roz, M., Allonas, X., Fouassier, J.P. (2008), *Macromolecules*, 41, 2003-2010.
- [15] Balta, D.K., Arsu, N., Yagci, Y., Jockusch, S., Turro, N.J. (2007), *Macromolecules*, 40, 4138-4141.
- [16] Balta, D. K.; Arsu, N., Yagci, Y., Sundaresan, A.K., Jockusch, S., Turro, N. J. (2011), *Macromolecules*, 44, 2531-2535.
- [17] Yagci, Y., Jockusch, S., Turro, N. J. (2010), *Macromolecules*, 43, 6245-6260.
- [18] Davidson, R.S. (1993), The Chemistry of Photoinitiators - Some Recent Developments, *Journal of Photochemistry and Photobiology a-Chemistry*, 73, 81-96.
- [19] Gruber, H.F. (1992), Photoinitiators for Free-Radical Polymerization, *Progress in Polymer Science*, 17, 953-1044.

- [20] **Hageman, H.J.** (1985), Photoinitiators for Free-Radical Polymerization, *Progress in Organic Coatings*, 13, 123-150.
- [21] **Monroe, B.M. and Weed, G.C.** (1993), Photoinitiators for Free-Radical-Initiated Photoimaging Systems, *Chemical Reviews*, 93, 435-448.
- [22] **Davidson, R.S.** (1983), in *Advances in Physical Chemistry*, D. Bethel and V. Gold, Editors. Academic Press: London. p. 1.
- [23] **Ledwith, A., Bosley, J.A., and Purbrick, M.D.** (1978), Exciplex Interactions in Photoinitiation of Polymerization by Fluorenone-Amine Systems, *Journal of the Oil & Colour Chemists Association*, 61, 95-104.
- [24] **Ledwith, A. and Purbrick, M.D.** (1973), Initiation of Free-Radical Polymerization by Photoinduced Electron-Transfer Processes, *Polymer*, 14, 521-522.
- [25] **Jauk, S. and Liska, R.** (2008), Photoinitiators with Functional Groups 9: New Derivatives of Covalently Linked Benzophenone-Amine Based Photoinitiators, *Journal of Macromolecular Science Part a-Pure and Applied Chemistry*, 45, 804-810.
- [26] **Catalina, F., Tercero, J.M., Peinado, C., Sastre, R., Mateo, J.L., and Allen, N.S.** (1989), Photochemistry and Photopolymerization Study on 2-Acetoxy and Methyl-2-Acetoxy Derivatives of Thioxanthone as Photoinitiators, *Journal of Photochemistry and Photobiology a-Chemistry*, 50, 249-258.
- [27] **Peinado, C., Catalina, F., Corrales, T., Sastre, R., Amatguerri, F., and Allen, N.S.** (1992), Synthesis of Novel 2-(3'-Dialkylaminopropoxy)-Thioxanthone Derivatives - Photochemistry and Evaluation as Photoinitiators of Butyl Acrylate Polymerization, *European Polymer Journal*, 28, 1315-1320.
- [28] **Balta, D.K., Temel, G., Aydin, M., and Arsu, N.** (2010), Thioxanthone Based Water-Soluble Photoinitiators for Acrylamide Photopolymerization, *European Polymer Journal*, 46, 1374-1379.
- [29] **Temel, G. and Arsu, N.** (2007), 2-Methylol-Thioxanthone as a Free Radical Polymerization Initiator, *Journal of Photochemistry and Photobiology a-Chemistry*, 191, 149-152.
- [30] **Karasu, F., Arsu, N., Jockusch, S., and Turro, N.J.** (2009), Mechanistic Studies of Photoinitiated Free Radical Polymerization Using a Bifunctional Thioxanthone Acetic Acid Derivative as Photoinitiator, *Macromolecules*, 42, 7318-7323.
- [31] **Balta, D.K., Karasu, F., Aydin, M., and Arsu, N.** (2007), The Effect of the Amine Structure on Photoinitiated Free Radical Polymerization of Methyl Methacrylate Using Bisketocoumarin Dye, *Progress in Organic Coatings*, 59, 274-277.
- [32] **Polykarpov, A.Y., Hassoon, S., and Neckers, D.C.** (1996), Tetramethylammonium Tetraorganylborates as Coinitiators with 5,7-Diiodo-3-Butoxy-6-Fluorone in Visible Light Polymerization of Acrylates, *Macromolecules*, 29, 8274-8276.

- [33] Shi, J.M., Zhang, X.P., and Neckers, D.C. (1992), Xanthenes - Fluorone Derivatives .1, *Journal of Organic Chemistry*, 57, 4418-4421.
- [34] Shi, J.M., Zhang, X.P., and Neckers, D.C. (1993), Xanthenes - Fluorone Derivatives .2, *Tetrahedron Letters*, 34, 6013-6016.
- [35] Tanabe, T., Torresfilho, A., and Neckers, D.C. (1995), Visible-Light Photopolymerization - Synthesis of New Fluorone Dyes and Photopolymerization of Acrylic-Monomers Using Them, *Journal of Polymer Science Part a-Polymer Chemistry*, 33, 1691-1703.
- [36] Valdesaguilera, O., Pathak, C.P., Shi, J., Watson, D., and Neckers, D.C. (1992), Photopolymerization Studies Using Visible-Light Photoinitiators, *Macromolecules*, 25, 541-547.
- [37] Aydin, M., Arsu, N., and Yagci, Y. (2003), One-Component Bimolecular Photoinitiating Systems, 2 - Thioxanthone Acetic Acid Derivatives as Photoinitiators for Free Radical Polymerization, *Macromolecular Rapid Communications*, 24, 718-723.
- [38] Cokbaglan, L., Arsu, N., Yagci, Y., Jockusch, S., and Turro, N.J. (2003), 2-Mereapthioxanthone as a Novel Photoinitiator for Free Radical Polymerization, *Macromolecules*, 36, 2649-2653.
- [39] Aydin, M., Arsu, N., Yagci, Y., Jockusch, S., and Turro, N.J. (2005), Mechanistic Study of Photoinitiated Free Radical Polymerization Using Thioxanthone Thioacetic Acid as One-Component Type II Photoinitiator, *Macromolecules*, 38, 4133-4138.
- [40] Balta, D.K., Arsu, N., Yagci, Y., Jockusch, S., and Turro, N.J. (2007), Thioxanthone-Anthracene: A New Photoinitiator for Free Radical Polymerization in the Presence of Oxygen, *Macromolecules*, 40, 4138-4141.
- [41] Yilmaz, G., Aydogan, B., Temel, G., Arsu, N., Moszner, N., and Yagci, Y. (2010), Thioxanthone-Fluorenes as Visible Light Photoinitiators for Free Radical Polymerization, *Macromolecules*, 43, 4520-4526.
- [42] Turro, N.J. (1978). *Modern Molecular Photochemistry*. Menlo Park, CA: University Press.
- [43] Rehm, D. and Weller, A. (1970), Kinetics of Fluorescence Quenching by Electron and H-Atom Transfer, *Israel Journal of Chemistry*, 8, 259-&.
- [44] Jakubiak, J. and Rabek, J.F. (1999), Photoinitiators for Visible Light Polymerization, *Polimery*, 44, 447-461.
- [45] Koleske, J.V. (2002), *Radiation Curing of Coatings*, ASTM International, West Conshohocken, Pa.
- [46] Roffey, C.G. (1989), *Photopolymerization of Surface Coatings*, Wiley, New York.

- [47] **Bellobono, I.R. and Zeni, M.** (1986), Kinetic-Study of Photoinduced Polymerization of Diallyl Oxydiethylene Dicarboxylate [Diethylene Glycol Bis(Allylcarbonate)], *Makromolekulare Chemie-Rapid Communications*, 7, 733-738.
- [48] **Yao, H.W., Huang, M.J., Chen, Z.Y., Hou, L.S., and Gan, F.X.**, (2002), Optimization of two-monomer-based photopolymer used for holographic recording, *Materials Letters*, 56, 3-8.
- [49] **Garcia, C., Fimia, A., and Pascual, I.**, (2001), Holographic behavior of a photopolymer at high thicknesses and high monomer concentrations: mechanism of photopolymerization, *Applied Physics B-Lasers and Optics*, 72, 311-316.
- [50] **Villegas, L., Encinas, M.V., Rufs, A.M., Bueno, C., Bertolotti, S., and Previtali, C.M.**, (2001), Aqueous photopolymerization with visiblelight photoinitiators: Acrylamide polymerization photoinitiated with a phenoxazine dye/amine system, *Journal of Polymer Science Part a Polymer Chemistry*, 39, 4074-4082.
- [51] **White, L.A., Hoyle, C.E., Jonsson, S., and Mathias, L.J.**, (2002), Bulk freeradical photopolymerizations of 1-vinyl-2-pyrrolidinone and its derivatives, *Journal of Polymer Science Part a-Polymer Chemistry*, 40, 694-706.
- [52] **Jacobine, A.F., Glaser, D.M., Grabek, P.J., Mancini, D., Masterson, M., Nakos, S.T., Rakas, M.A., and Woods, J.G.**, (1992), Photocrosslinked Norbornene Thiol Copolymers - Synthesis, Mechanical-Properties, and Cure Studies, *Journal of Applied Polymer Science*, 45, 471-485.
- [53] **Kaur, M. and Srivastava, A.K.** (2002), Photopolymerization: A Review, *Journal of Macromolecular Science-Polymer Reviews*, C42, 481-512.
- [54] **Kutal, C., Grutsch, P.A., and Yang, D.B.** (1991), A Novel Strategy for Photoinitiated Anionic-Polymerization, *Macromolecules*, 24, 6872-6873.
- [55] **Palmer, B.J., Kutal, C., Billing, R., and Hennig, H.** (1995), A New Photoinitiator for Anionic Polymerization, *Macromolecules*, 28, 1328-1329.
- [56] **Yamaguchi, Y. and Kutal, C.** (2000), Benzoyl-Substituted Ferrocenes: An Attractive New Class of Anionic Photoinitiators, *Macromolecules*, 33, 1152-1156.
- [57] **Yamaguchi, Y., Palmer, B.J., Kutal, C., Wakamatsu, T., and Yang, D.B.** (1998), Ferrocenes as Anionic Photoinitiators, *Macromolecules*, 31, 5155-5157.
- [58] **Encinas, M.V., Rufs, A.M., Norambuena, E., and Giannotti, C.** (1997), P-Nitroacetanilide in the Presence of Triethylamine as a Photoinitiator System for Vinyl Polymerization, *Journal of Polymer Science Part a-Polymer Chemistry*, 35, 3095-3100.
- [59] **Fouassier, J.P.** (1995), *Photoinitiation, Photopolymerization and Photocuring: Fundamentals and Applications*. Munich: Hanser Publishers.

- [60] **Yagci, Y. and Mishra, M.K.** (1998), *Handbook of Radical Vinyl Polymerization*. New York: Marcel Dekker, Inc.
- [61] **Yagci, Y.** (2006), Photoinitiated Cationic Polymerization of Unconventional Monomers, *Macromolecular Symposia*, 240, 93-101.
- [62] **Cho, J.D. and Hong, J.W.** (2005), Curing Kinetics of UV-Initiated Cationic Photopolymerization of Divinyl Ether Photosensitized by Thioxanthone, *Journal of Applied Polymer Science*, 97, 1345-1351.
- [63] **Sangermano, M., Malucelli, G., Bongiovanni, R., Priola, A., Annby, U., and Rehnberg, N.** (2002), Cationic Photoinitiated Copolymerization of 1-Propenyl-Vinyl Ether Systems, *European Polymer Journal*, 38, 655-659.
- [64] **Turro N.J.** (1991), *Modern molecular chemistry*. Mill Valley: University Science Books.
- [65] **Decker C, Jenkins A.D.** (1985), *Macromolecules*, 18:2141.
- [66] **Gou L, Coretsopoulos C.N, Scranton A.B.** (2004), *J Polym Sci, Part A: Polym Chem*, 42:1285.
- [67] **Pappav P.** (1992), *Radiation curing, science and technology*. New York: Plenum Press.
- [68] **Fouassier J.P, Rabek J.F.** (1993), *Radiation curing in polymer science and technology*. London: Elsevier Applied Science.
- [69] **Roffery C.G.** (1982), *Photopolymerization of surface coatings*. New York: Wiley Interscience.
- [70] **Fouassier J.P.** (1995), *Photoinitiation photopolymerization and photocuring; fundamentals and applications*. Munich: Hanser Publishers.
- [71] **Miller, C.W., Hoyle, C.E., Jonsson, S., Nason, C., Lee, T.Y., Kuang, W.F., Viswanathan, K.** (2003), N-vinylamides and reduction of oxygen inhibition in photopolymerization of simple acrylate formulations. *ACS Symp. Ser.*, 847, 2-14.
- [72] **R.S. Davidson,** (1993), The role of amines in UV-curing, in: J.P. Fouassier, J.F. Rabek (Eds.), *Radiation Curing in Polymer Science and Technology: Polymerisation Mechanisms*, vol. III, Elsevier Applied Science, London, p. 153.
- [73] **C. Decker, J. Faure, M. Fizez, L. Rychla.** (1979), *Photogr. Sci. Eng.* 23 (3) 137.
- [74] **C. Decker.** (1979), *Makromol. Chem.* 180 2027.
- [75] **M. Awokola, W. Lenhard, H. Löffler, C. Flosbach, P. Frese.** (2002), *Prog. Org. Coat.* 44, 211.
- [76] **D.A. Bolon, K.K. Webb.** (1978), *J. Appl. Polym. Sci.* 22 (9) 2543.

- [77] **E. Selli, I.R. Bellobono.** (1993), Photopolymerization of multifunctional monomers: kinetic aspects, in: J.P. Fouassier, J.F. Rabek (Eds.), Radiation Curing in Polymer Science and Technology: Polymerisation Mechanisms, vol. III, *Elsevier Applied Science*, London, p. 1.
- [78] **F.R. Wight.** (1978), *J. Polym. Sci.: Polym. Lett. Ed.* 16 121.
- [79] **R. Müller.** (2001), in: Proceedings of the RadTech Europe Conference, *Polymer Reviews*, C42, 481-512.
- [80] **Hubbell, J.A., Thomas, S.N., Swartz, M.A.** (2009), *Nature*, 462, 449-460.
- [81] **Willner, I.** (2002), *Science*, 298, 2407-2408.

## **CURRICULUM VITAE**

**Name Surname:** Faruk OYTUN  
**Place and Date of Birth:** Çanakkale – 06.12.1989  
**Address:** İstanbul Teknik Üniversitesi, Fen Edebiyat Fakültesi,  
Kimya Bölümü, 34469, Maslak, İstanbul  
**E-Mail:** faruk2561@hotmail.com  
**B.Sc.:** Pamukkale University

## **PUBLICATIONS/PRESENTATIONS ON THE THESIS**

- Faruk Oytun, Muhammet U. Kahveci, Yusuf Yağcı. Sugar Overcomes Oxygen Inhibition in Photoinitiated Free Radical Polymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, 2012 DOI: 10.1002/pola.26554.
- Poster Presentation in IUPAC World Polymer Congress, Blacksburg, VA, USA, 2012