İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

NEW INITIATING SYSTEMS FOR FREE RADICAL PHOTOPOLYMERIZATION

Ph.D. Thesis by

Mehmet Atilla TAŞDELEN

Department: Polymer Science and Technology

Programme: Polymer Science and Technology

OCTOBER 2008

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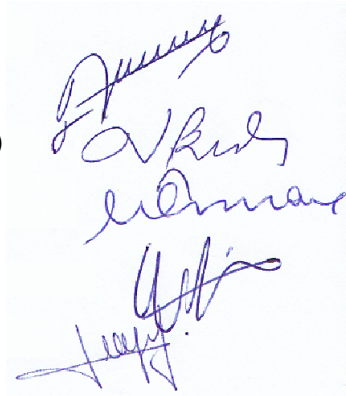
Supervisor (Chairman) :   **Prof.Dr. Yusuf YAĞCI**

Members of the Examining Committee :   **Prof.Dr. Niyazi BIÇAK (İ.T.U.)**

Prof.Dr. Ümit TUNCA (İ.T.U.)

Prof.Dr. Nergis ARSU (Y.T.U.)

Prof.Dr. Duygu AVCI (B.U.)

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

SERBEST RADİKAL FOTOPOLİMERİZASYONUNDA YENİ BAŞLATICI SİSTEMLER

DOKTORA TEZİ

Mehmet Atilla TAŞDELEN

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Diğer Jüri Üyeleri :	**Prof.Dr. Niyazi BIÇAK (İ.T.Ü.)**
	Prof.Dr. Ümit TUNCA (İ.T.Ü.)
	Prof.Dr. Nergis ARSU (Y.T.Ü.)
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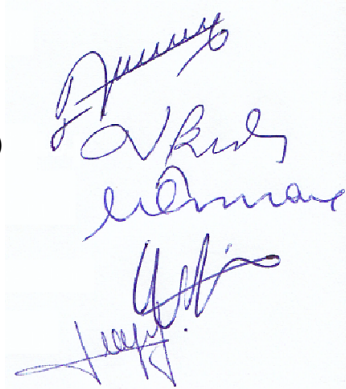
EKİM 2008

ACKNOWLEDGEMENTS

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^{1}H-NMR	: Hydrogen Nuclear Magnetic Resonance Spectroscopy
FT-IR	: Infrared Spectrophotometer
UV	: Ultra Violet
GPC	: Gel Permeation Chromatography
DSC	: Differential Scanning Calorimetry
GC-MS	: Gas Chromatography Mass Spectrometry
DLS	: Dynamic Light Scattering
TEMPO	: 2,2,6,6-Tetramethylpiperidine-*N*-oxyl
CH_2Cl_2	**:** Dichloromethane
$CDCl_3$	**:** Deuterated chloroform
THF	: Tetrahydrofuran
MMA	: Methyl Methacrylate
HEMA	**:** 2-Hydroxyethyl Methacrylate
PPI	: Poly(propylene imine)
PAMAM	: Poly(amido amine)
ISC	: Inter System Crossing
NMP	: Nitroxide Mediated Polymerization
PS	: Photosensitizer
PEO	: Poly(ethylene oxide)
PI	: Photoinitiator
COI	: Coinitiator
DMPA	: 2,2-Dimethoxy-2-phenyl acetophenone
BP	: Benzophenone
TX	: Thioxanthone
ITX	: 2-Isopropyl thioxanthone
CTX	: 2-Chlorothioxanthone
CQ	: Camphorquinone
St	: Styrene
DAEMA	: 2-(Dimethylamino)ethyl Methacrylate
TEA	: Triethylamine
TMEDA	: *N,N,N',N'*-Tetramethyl Ethylene Diamine
NDMA	: *N, N*-Dimethylaniline
DMEA	: *N,N*-Dimethylethanolamine
EA	: Ethanolamine
PA	: Propylamine
EAEPA	: 2-(2-Phosphono-ethoxymethyl)-acrylic acid ethyl ester
DEBAAP	: *N,N*-Diethyl-1,3-bis(acrylamido)propane
P-a	: Benzoxazine
B-a	: Bisbenzoxazine
N-a	: Naphtoxazine
BD	: Benzodioxinone

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LIST of SYMBOLS

λ	: Wavelength
$h\nu$	: Radiation
$R^{\cdot}$	: Radical
mW	: Miliwatt
nm	: Nanometer
E	: Excitation energy
h	: Planck's constant
l	: Light path length
C	: Concentration
A	: Absorbance
ε	: Molar extinction coefficient
k	: Rate constant
$\Phi_{R^{\cdot}}$	: Quantum yield of radical formation
Φ_P	: Quantum yield of photoinitiation
f_P	: Initiation efficiency of photogenerated radicals
I_a	: Intensity of radiation absorbed by the system
I_o	: Intensity of radiation falling on the system
l	: Optical path length in Beer Lambert law
[S]	: Concentration of the absorbing molecule in Beer Lambert law
E_T	: Triplet energy
F	: Faraday constant
$E_{\frac{1}{2}}^{ox}$ (D/D$^{+\cdot}$)	: Oxidation potential of donor
$E_{\frac{1}{2}}^{red}$ (A/A^{-})	: Reduction potential of acceptor
E_{PS}	: Singlet state energy of the photosensitizer
ΔE_c	: Coulombic stabilization energy
ΔG	: Gibbs Energy Change
Å	: Angström
ppm	: Parts per million
K	: Kelvin
^{o}C	: Celsius
N	: Normality
M	: Molarity
T_g	: Glass-transition temperature
M_n	: The number average molecular weight
M_w	: The weight average molecular weight
M_w/M_n	: The molecular weight distribution
(c)	: Conversion
t	: Time
ΔH_t	: Reaction heat evolved at time t
ΔH_0^{theory}	: Theoretical heat for complete conversion

NEW INITIATING SYSTEMS FOR FREE RADICAL PHOTOPOLYMERIZATION

SUMMARY

Photopolymerization is one of the most rapidly expanding processes for materials production. Applications of photopolymerization are being further developed and provide a number of economic advantages over the usual thermal operations: solvent-free formulations, low energy input, room temperature treatment and low costs. During the past decade photopolymerization has been practically applied in variety of areas, including printing inks, adhesives, surface coating, printing plates and microelectronics. Photoinitiated radical polymerization may be initiated by both α-cleavage (*Type I*) and hydrogen abstraction type (*Type II*) initiators. Because the initiation is based on a bimolecular reaction, *Type II* photoinitiators are generally slower than *Type I* photoinitiators, which are based on unimolecular formation of radicals. However, recent research interest has focused on *Type II* photoinitiators because of their better optical absorption properties in the near-UV spectral region. Upon photolysis, photoexcited sensitizer undergoes electron transfer reaction followed by hydrogen abstraction leading to the formation of two radicals: a radical produced from the carbonyl compound (ketyl-type radical) and another radical derived from the hydrogen donor. The photopolymerization of vinyl monomers is usually initiated by the radical produced from the hydrogen donor. For efficient polymerization, the bimolecular H-abstraction reaction must compete with other side reactions, such as non-reactive quenching (i.e., through energy transfer) of the photoexcited initiator by monomer or oxygen. These systems are therefore more sensitive to oxygen, and polymerization in air may lead to relatively low curing rates. The selection of a coinitiator (H-donor) is undoubtedly of great importance. Tertiary amines are more reactive co-initiators than are alcohols or ethers. However, the practical application of amines suffers from their usage in large amounts which is particularly important for curing applications since formulations containing amine at high concentrations causes a decrease in the pendulum hardness of the cured films due to the plasticizing effect of amines. In addition, the amine tends to cause discolorations, and is known to be both toxic and mutagenic.
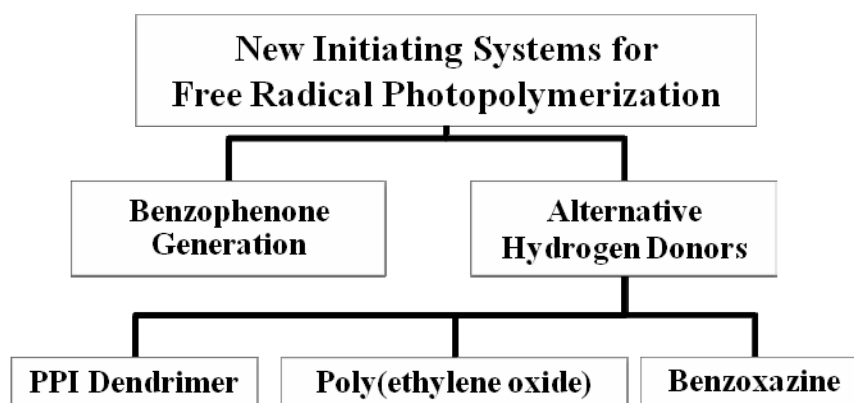
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│    Free Radical Photopolymerization │
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│ Benzophenone │   │  Alternative │
│  Generation  │   │Hydrogen Donors│
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│ PPI Dendrimer│ │Poly(ethylene oxide)│ │ Benzoxazine │
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In this thesis, we describe two strategies for overcoming these limitations by benzophenone generation from structurally designed benzodioxinones and using alternative co-initiators including poly(propylene imine) dendrimer, poly(ethylene oxide) and benzoxazine.

In the first strategy, we report a new photoinitiating system for free radical polymerization based on generation of benzophenone by photolysis of benzodioxinone. In this initiating system, benzophenone, actual photoinitiator, is formed only after photodecomposition of benzodioxinone. The subsequent step is the usual radical formation by the hydrogen abstraction of photoexcited benzophenone from a hydrogen donor. One obvious advantage of this method is the improved shelf life of curing formulations in which the photoinitiator benzophenone is photochemically masked and liberated only after photolysis. We have also demonstrated a novel photoinduced simultaneous polymerization and cross-linking of 2-hydroxy methyl methacrylate by using specially designed benzodioxinones. These molecules have the ability to generate initiating species as well as cross-linking agents that brings out photoinduced polymer network formation.

In the second strategy, to decrease toxicity and improve the polymerization process, alternative hydrogen donors such as, nonvolatile poly(propylene imine) (PPI) dendrimers, biocompatible poly(ethylene oxide)s (PEO) and thermally curable benzoxazine monomers have been tested. Three generations of PPI dendrimers were used as hydrogen donors in Type II photoinitiated free radical polymerization of methyl methacrylate by using one of the following photosensitizers; benzophenone and thioxanthone. The effect of generation number of the PPI dendrimer on photoinitiation efficiency and molecular weight of the resulting polymers was investigated. The location of hydrogen donating sites was evaluated by photolysis studies in the absence of monomer by using a stable radical namely, 2,2,6,6-tetramethylpiperidine-*N*-oxyl free radical (TEMPO) and showed that hydrogen abstraction occurs from the inner tertiary amino groups of PPI dendrimer. Hydrogen donating capability of PEO in *Type II* photoinitiated free radical polymerization was demonstrated by polymerization and spectroscopic studies. The effect of molecular weight of PEO on the photoinitiation efficiency was investigated. Photolysis of

solutions containing benzophenone and PEO in the presence of TEMPO revealed that photoexcited benzophenone readily abstracts hydrogen from methylene groups present in PEO backbone. Potential use of the photoinitiating system in dental formulations was also demonstrated. Thermally curable benzoxazine monomers were used as hydrogen donors in *Type II* photoinitiated free radical polymerization of methyl methacrylate by using one of the following photosensitizers; benzophenone, camphorquinone and thioxanthone derivatives. The postulated mechanism is based on the intermolecular reaction of the excited photosensitizer with the tertiary amino moiety of the ground state benzoxazine and a subsequent hydrogen abstraction reaction. The resulting aminoalkyl radicals initiate the polymerization. The incorporation of benzoxazine groups into polymers is demonstrated by spectroscopic methods.

SERBEST RADİKAL FOTOPOLİMERİZASYONUNDA YENİ BAŞLATICI SİSTEMLER

ÖZET

Fotopolimerizasyon bilimi, uygulama alanlarındaki artış nedeniyle, gerek endüstri gerekse akademik çalışmalarda gittikçe artan bir öneme sahip olmaktadır. Fotopolimerizasyon, termal polimerizasyona göre bir çok üstün özellik gösterir. Bunlar, düşük enerji tüketimi, oda sıcaklığında sertleşme, çözücüsüz ortamda polimerleşme, uygulanacak yüzey alanı ve uygulama süresinin kontrol edilebilmesi gibi sıralanabilir. Bu üstün özellikler, fotopolimerizasyonun kaplama, yapıştırıcı, kontakt lens ve diş hekimliği gibi bir çok uygulamada kullanımını sağlar. Basitçe ışıkla başlatılmış polimerizasyon reaksiyonlarına, fotopolimerizasyon denir. Fotobaşlatıcılar, radikal oluşturma mekanizmalarına göre (*I.Tip*) ve (*II.Tip*) fotobaşlatıcılar olmak üzere iki ayrı sınıfa ayrılır. Birinci tip fotobaşlatıcılar, radikal vermek üzere doğrudan fotoparçalanmaya uğrayan, çeşitli fonksiyonel gruplar içeren aromatik karbonil bileşikleridir. İkinci tip sistemlerde, polimerizasyonun başlaması hidrojen verici molekül üzerinde oluşan radikaller vasıtasıyla gerçekleşirken, etkin olmayan ketil radikalleri birbirleriyle birleşerek ortamdan kaybolur. Radikal üretimi iki molekülün etkileşimi sonucu olan, *II. Tip* fotobaşlatıcılar, tek molekülün parçalanarak radikal oluşturduğu *I. Tip* fotobaşlatıcılara göre daha yavaş çalışmaktadır. Diğer yandan*, II. Tip* fotobaşlatıcılar daha iyi optik özelliklere sahip olduklarından, düşük enerjili ışık kaynaklarıyla çalışma imkanı sunmaktadırlar. Ayrıca *I. Tip* fotobaşlatıcılarla elde edilen polimerler, ışığa mağruz kaldıklarında α-bölünme mekanizması sonucu, uçucu yan ürünler meydana getirirler. Oluşan bu ürünler kötü kokuya sebebiyet verir. Bu açıdan bakıldığında, *II. Tip* 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, *II. Tip* fotobaşlatıcılar daha çok tercih edilir. Etkili bir başlatma olabilmesi için, hidrojen koparma reaksiyonu diğer yan reaksiyonlarla (uyarılmış fotobaşlatıcıların enerjilerini oksijen yada monomere aktarmasıyla enerjinin boşa harcanması) yarışabilmelidir. Bu sebepten dolayı *II. Tip* serbest radikal fotopolimerizasyonu oksijene karşı yüksek seviyede duyarlıdır. Hidrojen verici grupların seçimi bu sistemde büyük önem kazanmıştır. İkinci tip 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.

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│     Serbest Radikal Fotopolimerizasyonunda    │
│           Yeni Başlatıcı Sistemler            │
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        │                           │
┌───────────────┐         ┌─────────────────────┐
│   Benzofenon  │         │  Alternatif Hidrojen │
│    Üretimi    │         │   Verici Bileşikler  │
└───────────────┘         └─────────────────────┘
                    │             │              │
        ┌──────────────────┐ ┌───────────────┐ ┌─────────────┐
        │  PPI Dendrimer   │ │ Poli(etilen oksit)│ │ Benzoksazin │
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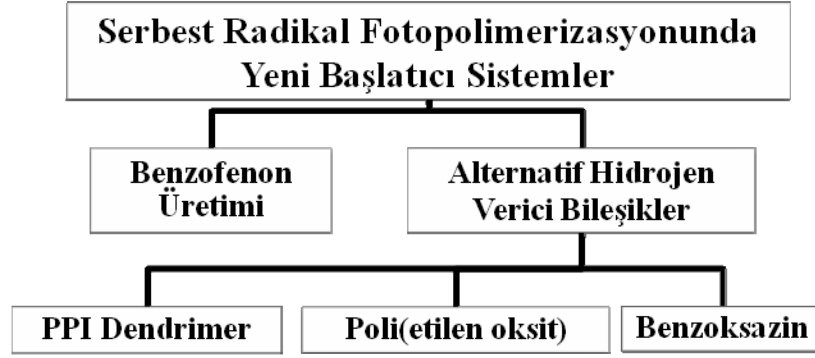
Bu tezde, yukarıdaki olumsuzlukları ortadan kaldırmak için benzofenon üretimi ve alternatif hidrojen verici moleküllerin kullanımına dayalı iki farklı strateji izlenmiştir.

İlk strateji, ışığa duyarlı benzodioksinon bileşiklerinin fotopolimerizasyonda kullanımı üzerine kurulmuştur. Benzodioksinon bileşikleri ışıkla uyarıldıkları zaman ortama benzofenon verirler, benzofenon da eğer ortamda hidrojen verici bileşik varsa, amin ve eter gibi, serbest radikal polimerizasyonunu başlatır. Bu sistemin avantajı ortama benzofenonun yavaş yavaş salınmasıdır. Ayrıca çapraz bağlı polimer sentezinde benzodioksinon bileşiklerinin kullanımı incelenmiştir. Mevcut araştırmalar, benzodioksinonun fotolizi sonucu oluşan ikinci ürün ketenin, çok reaktif olduğunu, ortamdaki hidroksil bileşiği ile reaksiyona girerek yüksek verimle ester oluşturduğunu göstermiştir. Bu teoriden yola çıkarak sentezlenmiş bisbenzodioksinon bileşiği ile hidroksi fonksiyonlu monomerin hidrojen verici moleküller varlığında fotolizi sonucu eş zamanlı polimerizasyon ve çapraz bağlanma reaksiyonlarının gerçekleşmesiyle çapraz bağlı polimerlerin tek kademede sentezlenmesi sağlanmıştır.

İkinci strateji *II. Tip* serbest radikal fotopolimerizasyonda tersiyer aminlere alternatif olarak uçucu olmayan poli(propilen imin) (PPI) dendrimeri, biyouyumlu poli(etilen oksit) (PEO) ve ısısal olarak sertleşebilen benzoksazin bileşiklerinin kullanılmasına dayanmaktadır.

İlk bölümde metil metakrilatın *II. Tip* serbest radikal fotopolimerizasyonunda hidrojen verici grup olarak PPI dendrimerinin kullanımı incelenmiştir. Polimerizasyonda benzofenon, kamforkinon ve tiyoksanton türevleri fotouyarıcı olarak kullanılmıştır. PPI dendrimerlerin yapısının polimerizasyona ve elde edilen polimerlerin molekül ağırlığına etkisi ayrıca gözden geçirilmiştir. PPI dendrimer ve benzofenon çözeltisi monomersiz ortamda bir radikal tutucu (2,2,6,6-tetrametilpiperidinil-1-oksi, TEMPO) varlığında fotolize uğratılmıştır. Bu işlem sonunda TEMPO molekülü dendrimere bağlanmaktadır. Böylelikle uyarılmış benzofenon molekülünün PPI dendrimerin iç yapısındaki tersiyer aminlerden hidrojen koparttığı spektroskopik olarak kanıtlanmıştır.

İkinci bölümde, PEO'in *II. Tip* serbest radikal fotopolimerizasyonunda hidrojen verme kabiliyeti polimerizasyon ve spektroskopik yöntemlerle aydınlatılmıştır.

PEO'in molekül ağırlığının ve fotobaşlatma etkisi ayrıca incelenmiştir. PEO ve benzofenon çözeltisi monomersiz ortamda TEMPO varlığında fotolize uğratılmaktadır. Bu işlem sonunda TEMPO molekülü PEO'e bağlanmaktadır. Böylelikle uyarılmış benzofenon molekülünün PEO'in anazinciri üzerindeki metilen gruplarından hidrojen koparttığı kanıtlanmıştır. Ayrıca PEO'in diş dolgusu formülasyonundaki potansiyel kullanımı da gösterilmiştir.

Son bölümde, ısısal olarak sertleşebilen benzoksazinlerin *II. Tip* serbest radikal fotopolimerizasyonunda hidrojen verici bileşik olarak kullanımı incelenmiştir. Kabul edilen mekanizmaya göre fotouyarıcılar düşük enerji seviyesindeki benzoksazinlerin amin gruplarıyla moleküller arası etkileşim sonucu hidrojen kopartarak radikaller oluştururlar. Benzoksazinin amin gruplarına komşu alkiller üstünde oluşan radikaller ancak polimerizasyonu başlatabilirler. Polimerlerizasyonun benzoksazinle başlatıldığı spektroskopik yöntemlerle kanıtlanmıştır.

1. INTRODUCTION

Photoinitiated free radical polymerization has been widely used in research and industrial applications during the past few decades. Photopolymerization offers compelling advantages over traditional thermal polymerization, including low energy consumption, room temperature curing, spatial and temporal control of initiation, and solvent-free polymerization. These advantages have lead to tremendous growth in the use of photopolymerization in a variety of applications, including coatings on a variety of substrates, adhesives, flexographic printing plates, soft contact lenses, and dental materials.

Photoinitiated radical polymerization may be initiated by both cleavage (*Type I*) and H-abstraction type (*Type II*) initiators. Because of their vital role in photopolymerization, photoinitiators are the subject of particularly extensive research. Most of this research has focused on *Type I* photoinitiators, which upon irradiation which undergo an α-cleavage process to form two radical species. *Type II* photoinitiators are a second class of photoinitiators and are based on compounds whose triplet excited states are reacted with hydrogen donors thereby producing an initiating radical (reaction 1.1). Because the initiation is based on bimolecular reaction, they are generally slower than *Type I* photoinitiators which are based on unimolecular formation of radicals. On the other hand, *Type II* photoinitiators possess better optical absorption properties in the near ultraviolet spectral region. Moreover *Type I* compounds give raise to volatile photodecomposition products due to the cleavage mechanism adding to migration the problem of release of odour. In this respect the *Type II* photoinitiators have a more favorable profile because the ketyl radical either is re-oxidized back to the ketone or gives rise to recombination products with formation of higher molecular weight derivatives with a lower volatility than parent compounds.

Typical *Type II* photoinitiators include benzophenone, thioxanthones, benzil, and quionones while alcohols, ethers, amines and thiols are used as hydrogen donors. The

selection of a coinitiator (hydrogen donor) is undoubtedly of great importance. Tertiary amines are more reactive co-initiators than are alcohols or ethers.

$$Ph_2C=O \xrightarrow{h\nu} {}^3[Ph_2C=O]^* \xrightarrow{R-H} Ph_2\overset{\bullet}{C}-OH + \boxed{R^\bullet} \tag{1.1}$$
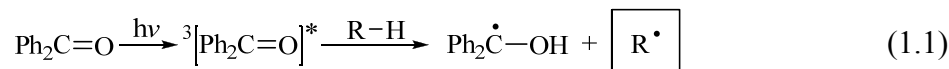
In many curing applications of fully formulated mixtures usually all the initiators are added in the solid form or in a concentrated solution at the beginning of the polymerization and immediately initiates the polymerization when exposed to the light. This is one of the prerequisite for a rapid curing. However, in turn such formulations may not exhibit a good shelf life due to the initiation on storage. In *Type II* photoinitiating system, the unreacted photoinitiator and amine coinitiator, as well as the photolysis products, tend to cause discoloration of the cured composite. Furthermore, the practical application of amines suffers from their usage in large amounts which is particularly important for curing applications since formulations containing amine at high concentrations causes a decrease in the pendulum hardness of the cured films due to the plasticizing effect of amines. In addition, the amine is known to be both toxic and mutagenic.

In this thesis, we describe two strategies for overcoming these limitations by benzophenone generation from structurally designed benzodioxinones and using alternative coinitiator including poly(propylene imine) dendrimers, poly(ethylene oxide)s and benzoxazines.

Benzodioxinones are relatively new photosensitive compounds which form salicylate esters when irradiated in the presence of alcohols and phenols. The acylation occurs under neutral conditions and is tolerant to a wide range of sterically hindered alcohols (reaction 1.2). One obvious advantage of this method is the improved shelf life of curing formulations in which the photoinitiator benzophenone is photochemically masked and liberated only after photolysis. It has also been shown that functional groups of photolysis product can be used in self-cross-linking of monofunctional monomers.

$$(1.2)$$
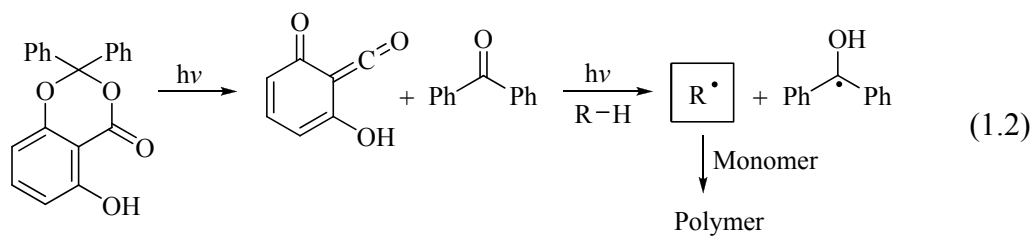
In order to decrease toxicity and improve the polymerization process, we have also tested several alternative hydrogen donors such as, nonvolatile multifunctional poly(propylene imine) dendrimers, biocompatible poly(ethylene oxide)s, and thermally curable benzoxazine monomer in *Type II* photoinitiating system to find a substitute for the tertiary amines.

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.

2.1.1. Photoinitiated Free Radical Polymerization

Photoinitiated free radical polymerization consists of photoinitiation (reactions 2.1a-c), propagation, chain transfer, and termination (reactions 2.1d-f). 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.

$$PI \xrightarrow{h\nu} PI^* \qquad \textbf{(Absorption)} \qquad (2.1a)$$

$$PI^* \longrightarrow R_1^\bullet + R_2^\bullet \qquad \textbf{(Radical Generation)} \qquad (2.1b)$$

$$R_1^\bullet + M \longrightarrow R_1\text{-}M^\bullet \qquad \textbf{(Photoinitiation)} \qquad (2.1c)$$

Photoinitiation 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. Repeated addition of monomer units to the chain radical produces the polymer backbone (propagation).

Chain transfer also takes place, that is, growing chains are terminated by hydrogen abstraction from various species (e.g., from solvent) and new radicals capable of initiating other chain reactions are formed.

$$R_1\text{-}M^{\bullet} + M \longrightarrow R_1\text{-}MM^{\bullet}$$
$$R_1\text{-}MM^{\bullet} + (n-2)M \longrightarrow R_1\text{-}M_n^{\bullet}$$
$$\left.\right\} \text{ (Propagation)} \qquad (2.1d)$$

$$R_1\text{-}M_n^{\bullet} + R\text{-}H \longrightarrow R_1\text{-}M_n\text{-}H + R^{\bullet}$$
$$R^{\bullet} + M \longrightarrow R\text{-}M^{\bullet}$$
$$\left.\right\} \text{ (Transfer)} \qquad (2.1e)$$

$$R_1\text{-}M_n^{\bullet} + R_1\text{-}M_m^{\bullet} \longrightarrow R_1\text{-}M_{n+m}\text{-}R_1$$
$$R_1\text{-}M_n^{\bullet} + R_2^{\bullet} \longrightarrow R_1\text{-}M_n\text{-}R_2$$
$$R_1\text{-}M_n^{\bullet} + R_1\text{-}M_m^{\bullet} \longrightarrow R_1\text{-}M_n + R_1\text{-}M_m$$
$$R_1\text{-}M_n^{\bullet} + R_2^{\bullet} \longrightarrow R_1\text{-}M_n + R_2$$
$$\left.\right\} \text{ (Termination)} \qquad (2.1f)$$
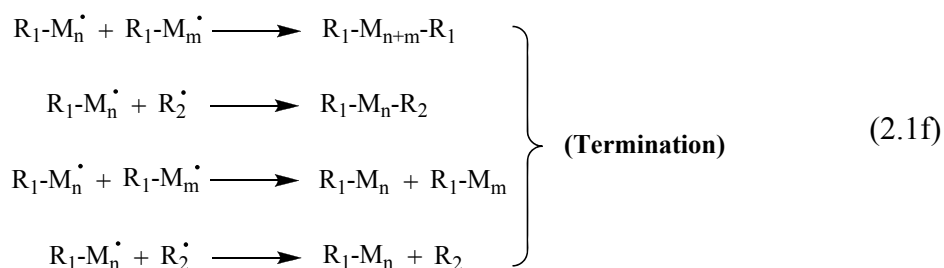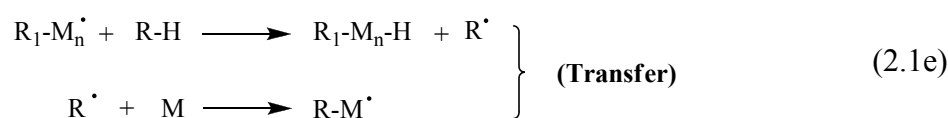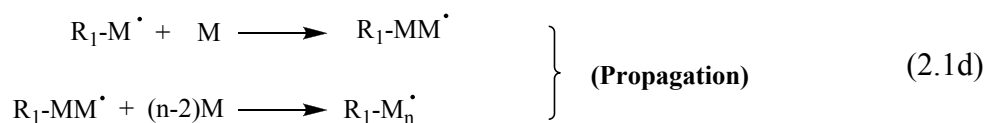
Finally, chain radicals are consumed by disproportionation or recombination reactions. Termination can also occur by recombination or disproportionation with any other radical including primary radicals produced by the photoreaction.

2.1.1.1. Absorption of Light
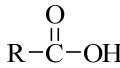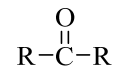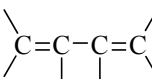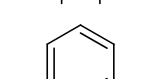
Photochemistry is concerned with chemical reactions induced by optical radiation [1-3]. The radiation is most often ultraviolet (200–400 nm) or visible (400–800 nm) light but is sometimes infrared (800–2500 nm) light.

Absorption of a photon of light by any compound causes electronic excitation. The energy causing excitation, E, is described by $E = hc/\lambda$ where h is Planck's constant, c is the speed of light, and , is the wavelength of the exciting light. Light absorption is described by $A = \varepsilon C l$, where ε is the molar absorptivity (extinction coefficient), C is the concentration of the species, and l is the light path length.

The extinction coefficient, a constant for a compound at a specific wavelength, is an experimental measure of the probability of absorption at that wavelength. The magnitude of the extinction coefficient depends upon the compound's chromophore, the chemical moiety responsible for the absorption of light. Typical chromophores contain unsaturated functional groups such as $C=C$, $C=O$, NO_2, or $N=N$ [1, 4]. Table 2.1 lists some chromophores, their wavelength of maximum absorption, and the

extinction coefficient at this wavelength [1, 4]. These values are qualitative because chromophore absorption is highly dependent upon neighboring substituent. For example, the absorption maximum and extinction coefficient of conjugated dienes are known to be influenced by the number of conjugated double bonds, alkyl substituent, and ring structure [4].

Table 2.1 Local wavelength of maximum absorption and associated extinction coefficient for typical chromophores

Chromophore	λ_{max} (nm)	ε_{max}
$\backslash\;\;/$ C=C $/\;\;\backslash$	195	10,000
—C≡C—	195	2,000
—N=N—	345	10
NO_2	270	18.6
S=O	210	1500
O ‖ R−C−OH	205	60
O ‖ R−C−R	190 280	900 15
$\backslash\;\;\;\;\;\;\;\;/$ C=C−C=C $/\;\|\;\;\|\;\backslash$	215	20,000
⬡	185 200 255	60,000 8,000 200

2.1.1.2. Photoinitiation

a) Radical Generation by Monomer Irradiation

Some monomers can generate radical species via absorption of light. Two possibilities are suggested for photoinitiation of polymerization by photosensitive monomers. As shown in reaction 2.2, the biradical formed by a photoinduced cyclization or a simple alpha-cleavage of monomer may be responsible for initiating polymerization.

$$M \overset{h\nu}{\underset{h\nu}{<}} \boxed{\cdot M \cdot} \quad \boxed{R_1^{\cdot}} \;+\; \boxed{R_2^{\cdot}} \tag{2.2}$$
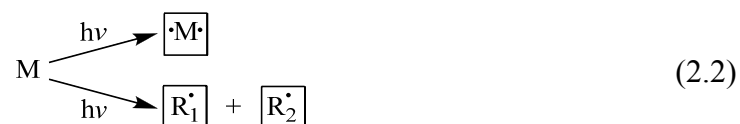
These species can react with intact monomer molecules and thus leading to growing chains. Readily commercially available monomers which undergo polymerization and copolymerization through UV irradiation to some extent are listed in Table 2.2 [5, 6].

Table 2.2 Photosensitive monomers

Allyl methacrylate	Methyl methacrylate
Barium acrylate	1,6-hexanediol diacrylate
Cinnamyl methacrylate	Pentaerythritol tetramethacrylate
Diallyl phthatlate	Styrene
Diallyl isophtalate	Tetraethylene glycol dimethacrylate
Diallyl terephthalate	Tetrafluoroethylene
2-Ethylhexyl acrylate	N-Vinylcarbazole
2-Hydroxyethyl methacrylate	Vinyl cinnamate
2-Hydroxypropyl acrylate	Vinyl 2-furoate
N,N'Methylenebisacrylamide	Vinyl 2-furylacrylate

On the other hand, radical generation via irradiation of vinyl monomer does not play a role due to regarding technical applications such as very low efficiency of radical formation and usually unsatisfactory absorption characteristics. For example, styrene irradiated at 313 nm produces small amounts of polystyrene in addition to larger amounts of styrene oligomers [1].

b) Radicals via Photoinitiators

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

Compounds which undergo unimolecular bond cleavage upon irradiation as shown in reaction 2.3 are termed "*Type I* photoinitiators".

$$\text{PI} \xrightarrow{\text{h}\nu} (\text{PI})^* \xrightarrow[\text{fragmentation}]{\substack{\text{unimolecular} \\ \text{reaction}}} \boxed{R_1^\bullet} + \boxed{R_2^\bullet} \qquad (2.3)$$
$$\text{free radicals}$$
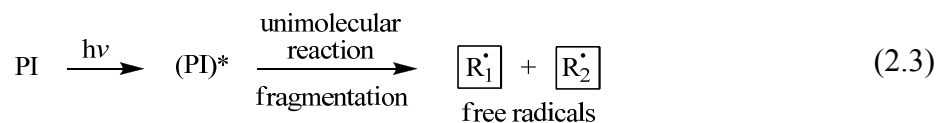
If the excited state photoinitiator interacts with a second molecule (a coinitiator) to generate radicals in a bimolecular reaction as shown in reaction 2.4, the initiating system is termed a "*Type II* Photoinitiator".

$$\text{PI} \xrightarrow{\text{h}\nu} (\text{PI})^* + \text{COI} \xrightarrow[\substack{\text{hydrogen} \\ \text{abstraction}}]{\substack{\text{bimolecular} \\ \text{reaction}}} R_1^\bullet + \boxed{R_2^\bullet} \qquad (2.4)$$
$$\text{free radicals}$$
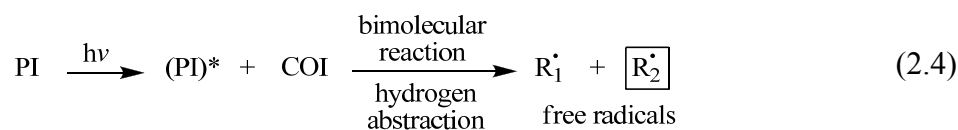
Efficient photoinitiators of both classes are known and find everyday usage. *Type I* photoinitiators are highly reactive UV photoinitiators, but are less frequently used in

visible light curing systems. *Type II* photoinitiators are versatile initiators for UV curing system and visible light photoinitiators belong almost exclusively to this class of photoinitiators.

2.1.1.3. *Type I* Photoinitiators (Unimolecular Photoinitiator Systems)

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 (reaction 2.5). The fragmentation that leads to the formation of radicals is, from the point of view of chemical kinetics, a unimolecular reaction (Eq:2.1).

$$PI \xrightarrow{h\nu} PI^* \xrightarrow{k} R_1^{\bullet} + R_2^{\bullet} \qquad (2.5)$$
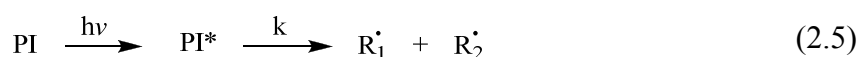
$$\frac{d[R_1^{\bullet}]}{dt} = \frac{d[R_2^{\bullet}]}{dt} = k\,[PI^*] \qquad (Eq:2.1)$$

The number of initiating radicals formed upon absorption of one photon is termed as quantum yield of radical formation ($\Phi_{R^{\bullet}}$) (Eq:2.2).

$$\Phi_{R^{\bullet}} = \frac{\text{Number of initiating radicals formed}}{\text{Number of photons absorbed by the photoinitiator}} \qquad (Eq:2.2)$$

Theoretically, cleavage type photoinitiators should have a $\Phi_{R^{\bullet}}$ 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:

$$f_P = \frac{\text{Number of chain radicals formed}}{\text{Number of primary radicals formed}} \qquad (Eq:2.3)$$

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

$$\Phi_P = \Phi_{R\bullet} \times f_P \qquad \text{(Eq:2.4)}$$

Regarding the energy necessary, 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.

$$\text{R}^1 = \text{H, Alkyl, substituted Alkyl, } \text{R}^2 = \text{H, Alkyl, substituted Alkyl}$$
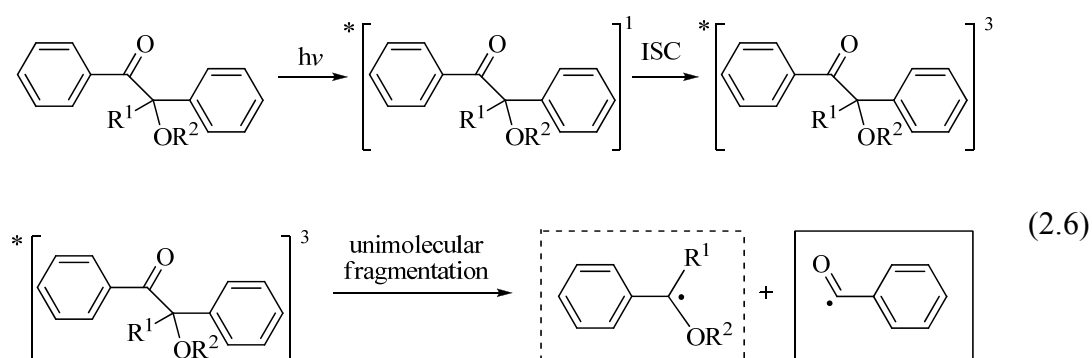
Type I photoinitiators which undergo a direct photofragmentation process (α or less common β cleavage) upon absorption of light and formation of initiating radicals capable of inducing polymerization. As illustrated in reaction 2.6, the photoinitiator is excited by absorption of ultraviolet light and rapid intersystem crossing to the triplet state. In the triplet state, the bond to the carbonyl group is cleaved, producing an active benzoyl radical fragment and another fragment. The benzoyl radical is the major initiating species, while, in some cases, the other fragment may also contribute to the initiation. The most efficient *Type I* initiators are benzoin ether derivatives, benzil ketals, hydroxylalkylphenones, α-aminoketones and acylphosphine oxides (Table 2.3) [7-10].
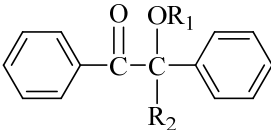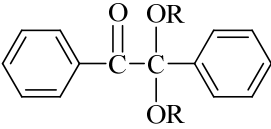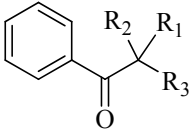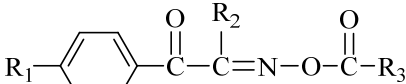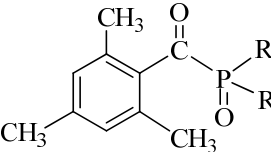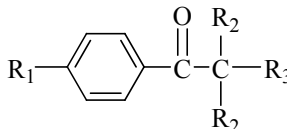
a) Benzoin Derivatives

Benzoin and its derivatives are the most widely used photoinitiators for radical polymerization of vinyl monomers. As depicted in Reaction 8.8, they undergo α-cleavage to produce benzoyl and α-substituted benzyl radicals upon photolysis.

The importance of these photoinitiators derives from the following: they possess high

absorptions in the far UV region (λ_{max} = 300–400 nm, $\varepsilon_{max} \geq$ 100–200 l mol^{-1} cm^{-1}), high quantum efficiencies for radical generation [11, 12] and a relatively short lived triplet state [13].

Table 2.3 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$_3$H$_7$, CH$_2$	365
Acetophenones	R_1 = OCH$_3$, OC$_2$H$_5$ R_2 = OCH$_3$, H R_3 = C$_6$H$_5$, OH	340
Benzyl oximes	R_1 = H, SC$_6$H$_5$ R_2 = CH3, C$_6$H$_{13}$ R_3 = C$_6$H$_5$, OC$_2$H$_5$	335
Acylphosphine Oxides	R = C$_6$H$_5$ or OCH$_3$	380
Aminoalkyl phenones	R_1 = SCH$_3$, morpholine R_2 = CH3, CH$_2$Ph or C$_2$H$_5$ R_3 = N(CH$_3$)$_3$, morpholine	320

Regarding the photochemistry of benzoin derivatives, starting from excited triplet states populated after intersystem crossing, Norrish *Type I* bond scission is the main chemical reaction occurring under various experimental conditions [14-17]. In the consequence of this bond cleavage, benzoyl and ether radicals are formed. In the

absence of monomer, hydrogen abstraction takes place leading to benzaldehyde, benzil, and pinacol derivatives [15, 16]. The reactivity of benzoyl and benzyl ether radicals were found to be almost the same provided the concentration of radicals is low and that of monomer high. On the other hand, if the concentration of radicals is high and that of monomer low, benzoyl radicals are more reactive toward monomer molecules present than the ether radicals [11, 17, 18].

The photoinduced α-cleavage reaction is not or only very little affected by triplet quenchers including styrene, owing to the short lifetime of the excited triplet state [19]. This circumstance makes benzoin photoinitiators particularly useful for industrial applications involving styrene monomer. Regarding practical applications, it has to be mentioned that benzoin derivatives are only storable for limited time at ambient temperature (i.e., they slowly but steadily decompose thermally during storage).

b) Benzil Ketals

Benzilketals are another important class of photoinitiators developed for free radical vinyl polymerization. Benzilketals exhibit higher thermal stability than benzoin compounds due to the absence of thermally labile benzylic hydrogen. The most prominent member of this class is the commercially used 2,2- dimethoxy-2-phenyl-acetophenone (DMPA). Indeed, this initiator shows an excellent efficiency in photopolymerizations and is at the same time easy to synthesize. Other benzilketals are also suitable initiators but do not reach the price performance ratio of DMPA.

Like benzoin ethers, benzilketals undergo α-cleavage whereby a benzoyl radical and a dialkoxybenzyl radical is formed (reaction 2.7). Although the benzoyl radicals are, as explained earlier, vigorously reacting with olefinic bonds of vinyl monomers, dialkoxybenzyl radicals were found to be of low reactivity. Actually, one of seven dialkoxy benzyl radicals formed is found to be incorporated into the polymer chain during the photopolymerization of methyl methacrylate initiated by DMPA. However, to what extent this portion of dialkoxy benzyl groups is caused by termination instead of initiation remains unclear. Dimethoxybenzyl radicals undergo a fragmentation yielding methyl radicals [20, 21], which act as additional initiating species in radical vinyl polymerization [22, 23].

$$(2.7)$$
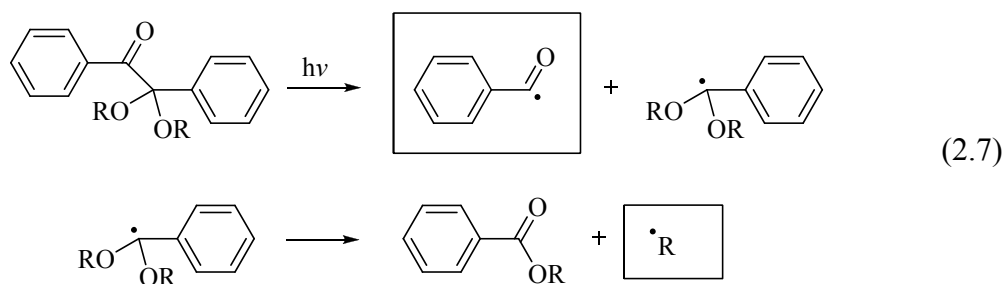
c) Acetophenones

α-Substituted acetophenones are another important class of photoinitiators used in various applications of free radical polymerizations [20]. These initiators exhibit excellent initiator properties especially in micellar solutions [24]. The most prominent example of this class of photoinitiators is the commercially available α,α-diethoxyacetophenone; furthermore 1-benzoylcyclohexanol and 2-hydroxy-2-methyl-1-phenylpropanone are initiators with good properties. Besides high efficiency of acetophenones include high storage stability and little tendency toward yellowing. Regarding photochemistry, both *Type I* and *Type II* bond ruptures were evidenced [22]. However, only the α-cleavage (*Type I*) gives initiating radicals: benzoyl radicals directly formed upon the light-induced α-cleavage and ethyl radicals, generated in a subsequent thermal fragmentation reaction (2.8).

$$(2.8)$$
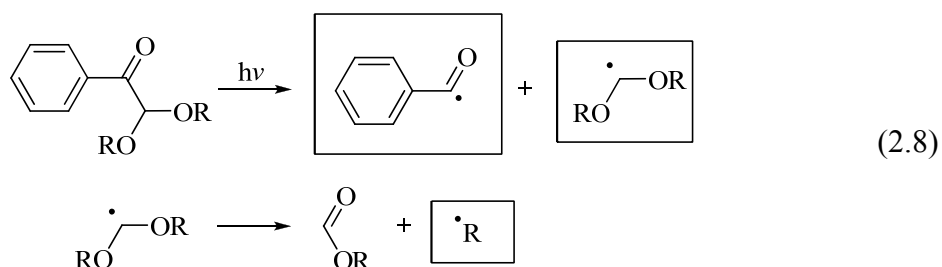
d) Aminoalkyl Phenones

α-Aminoalkyl phenones have recently been developed for the use in pigmented photopolymerizations. These compounds possess better absorption characteristics than many other aromatic ketone photoinitiators and are, therefore, quite amenable to practical applications where irradiation at longer wavelengths is desired. There is no doubt that α-aminoalkylphenones undergo α-cleavage to yield initiating benzoyl radicals and other carbon centered radicals [25, 26]. By means of thioxanthone as triplet sensitizer the sensitivity of the initiating formulation can be extended to the near UV or even visible region of the spectrum [27, 28]. Recently, ammonium group

containing benzoin ethers have turned out to be efficient, water-soluble photoinitiators in the polymerization of trimethylolpropane triacrylate.

e) Benzyl Oximes

o-Acyl-α-oximino ketones are known to undergo cleavage with high quantum efficiency [29] and have been used as photoinitiators for acrylates and unsaturated polyesters [29, 30]. Besides benzoyl radicals, phenyl radicals are produced in a secondary reaction. Both radical types are reactive in initiation. The most prominent example of these initiators is O-benzoyl-α-oximino-1-phenyl-propane-1-one, the reaction of which is illustrated in reaction 2.9.

(2.9)
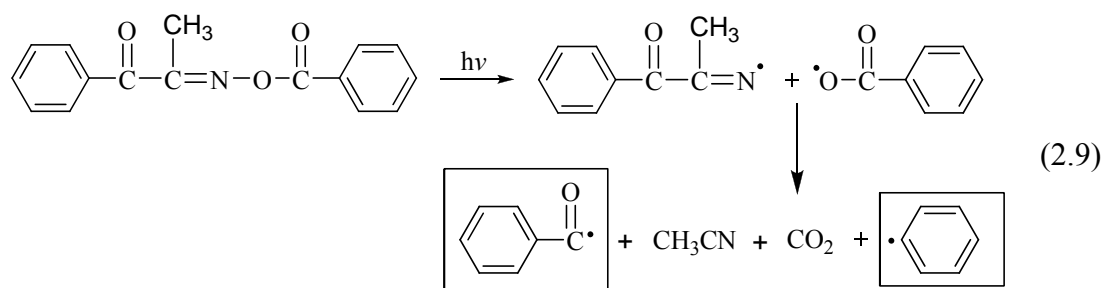
Although these compounds absorb more strongly in the near UV than most of the other aromatic photoinitiators, their use as photoinitiators is limited, because they are thermally not very stable. The relatively weak N-O bond dissociates both photochemically and thermally at moderate temperatures.

f) Acylphosphine Oxide and Its Derivatives

Acylphosphine oxides and acylphosphonates with different structures have been used as photoinitiators for free-radical initiated photopolymerization. Long wavelength absorption characteristics make these compounds particularly useful for the polymerization of titanium dioxide pigmented formulations containing acrylate or styrene type monomers and of glass fiber reinforced polyester laminates with reduced transparency [31-36]. These initiators are thermally stable up to 180 °C and no polymerization takes place when the fully formulated systems are stored in dark. Moreover, very little yellowing occurs in coatings cured with acylphosphine oxides. With respect to the storage of curing formulations and the actual curing, it has to be taken into account that acylphosphine oxides may react with water, alcohols, or amines, as well as what leads to the cleavage of the C-P bond. By introducing bulky

groups in *ortho*-position of the benzoyl group, the solvolysis is significantly slowed down. Furthermore, these substituents seem also to be able to increase the tendency for α-scission.

$$(2.10)$$
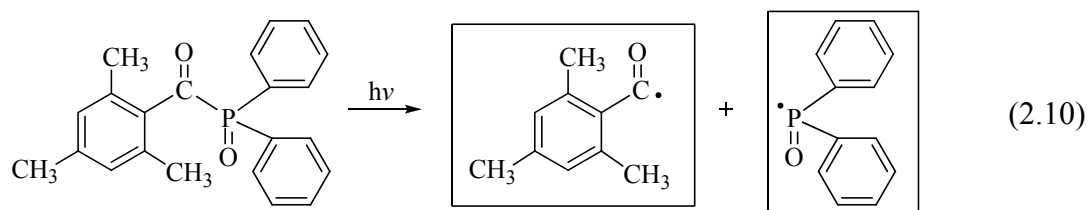
Extensive investigations [35] on the photochemistry of acylphosphine oxides revealed that they do undergo α-cleavage with fairly high quantum yields (reaction 2.10). Furthermore, it was found that the phosphonyl radicals formed are highly reactive toward vinyl monomers where rate constants of radicals generated from photoinitiators with various monomers are compiled. Notably, dialkoxyphosphonyl radicals are highly reactive toward monomers. For carbon centered benzoyl radicals significantly lower rate constants are detected. The excellent reaction efficiency of phosphonyl radicals is attributed to the high electron density at the phosphorous atom and the pyramidal structure of the radicals providing more favorable streric conditions for the unpaired radical site to react with monomers.

g) Aminoalkyl Phenones

α-Hydroxy alkylphenone is another photoinitiator containing benzoyl groups that has found practical application in many vinyl polymerizations [37]. This initiator has both a high light sensitivity and good thermal stability. Furthermore, coatings prepared using α-hydroxy alkylphenone do show only very little yellowing, what makes these compounds particularly suitable for clear coatings. Another striking advantage is that α,α′-dilalkyl hydroxyphenones are liquid at room temperature and are of relatively low polarity. Therefore, they are easy to dissolve in non-polar curing formulations.

Regarding the photochemistry of α-hydroxy alkylphenones, α-scission is the dominating reaction starting from the first excited triplet state. Although the reactivity of benzoyl radicals toward monomers is of no doubt, the question whether the hydroxyalkyl radical is able to initiate polymerization is not entirely elucidated. However, for 1-hydroxycyclohexylphenyl ketone (see reaction (2.11) initiated

15

polymerization of methyl 2-*tert*-butyl acrylate, it has been shown by analysis of photolysis products that hydroxyalkyl radicals add to the double bond of the monomer.

$$(2.11)$$
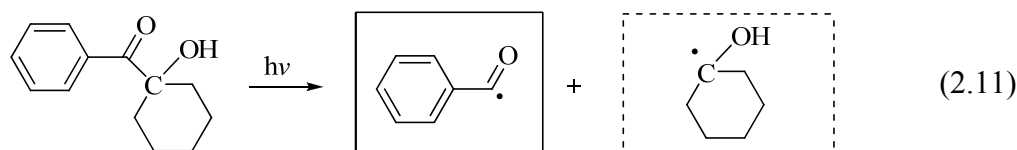
2.1.1.4. *Type II* Photoinitiators (Bimolecular Photoinitiator Systems)

Bimolecular photoinitiators are so-called because two molecular species are needed to form the propagating radical: a photoinitiator that absorbs the light and a co-initiator that serves as a hydrogen or electron donor. These photoinitiators 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 co-initiator to produce initiating radicals (reactions 2.12). In this case, radical generation follows 2nd order kinetics (Eq:2.5).

$$PI \xrightarrow{h\nu} PI^* + COI \xrightarrow{k} R_1^{\bullet} + R_2^{\bullet} \qquad (2.11)$$
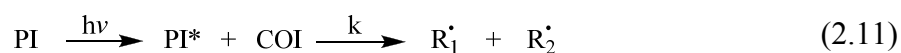
$$\frac{d[R_1^{\bullet}]}{dt} = \frac{d[R_2^{\bullet}]}{dt} = k[PI^*][COI] \qquad (Eq:2.5)$$
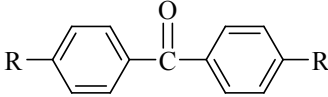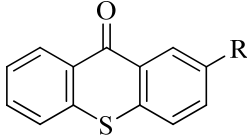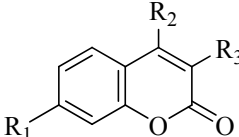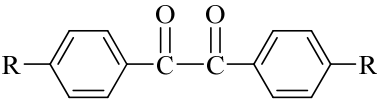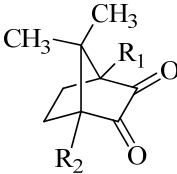
In these systems, photons are absorbed in the near UV and visible wavelengths. Free radical active centers are generated by hydrogen abstraction or photo-induced electron transfer process aforementioned.

(1) Hydrogen abstraction. Photoinitiators that proceed via a hydrogen abstraction mechanism are exemplified by combination of benzophenone and a hydrogen donor (reaction 2.13). When R-H is an amine with transferable hydrogen, benzophenone undergoes an electron transfer followed by a hydrogen abstraction to produce an initiating species and semipinacol radical. The semipinacol radical does not efficiently initiate polymerization and typically react with other radicals in the system as a terminating species causing a reduction in the polymerization rate.

R = amines, alcohols, ethers, thiols

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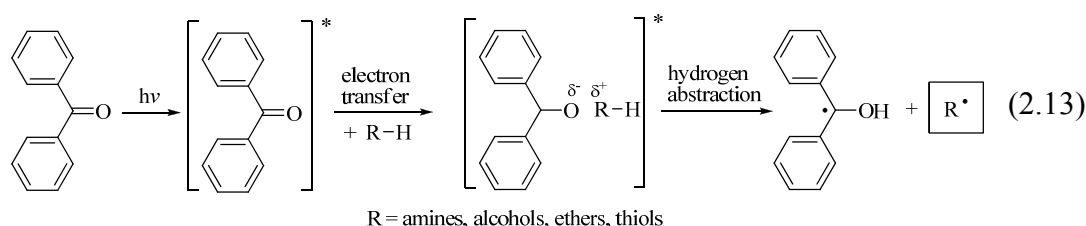
Photosensitizers of *Type II* system including benzophenones, thioxanthones, camphorquinones, benzyls, and ketocoumarins are listed in Table 2.4.

Table 2.4 Structures of typical *Type II* photosensitizers

Photosensitizers	Structure	λ_{max} (nm)
Benzophenones	R = H, OH, N(C$_2$H$_5$)$_2$, C$_6$H$_5$	335
Thioxanthones	R = H, Cl, isopropyl	390
Coumarins	R$_1$ = N(C$_2$H$_5$)$_2$, 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) Benzophenones

Hydrogen abstraction by the excited triplet manifold of benzophenone [38], which is populated with quantum yields close to unity, from tertiary amines (*N*-methyldiethanol amine) is depicted in reaction 2.13. The carbon centered radical stemming from the amine is able to initiate free radical polymerizations of suitable monomers. α-Aminoalkyl radicals are especially suitable for the polymerization of acrylates [39] and are less efficient for styrene polymerization, which is explainable in terms of triplet quenching by styrene. The ketyl radicals add scarcely to olefinic double bonds due to resonance stabilization and for steric reasons, but instead undergo recombination and disproportionation reactions. Furthermore, they may act

as chain terminators in the polymerization leading to ketyl moieties incorporated into polymer chains and relatively short chains [40]. To avoid chain termination by ketyl radicals, additives such as onium salts [41-43] or certain bromo compounds [44] have turned out to be useful. These additives react with the ketyl radicals thus suppressing chain termination. In the case of onium salts, phenyl radicals, which initiate polymerizations instead of terminating growing chains, are produced by the interaction of ketyl radicals with salt entities. Thus, the overall effect of these additives is an enhancement in polymerization rate.

Recently, benzophenone based initiators with hydrogen donating amine moieties covalently attached via an alkyl spacer were introduced as photoinitiators for vinyl polymerization [45-48]. Though also following the general scheme of *Type II* initiators, the initiation is a monomolecular reaction, because both reactive sites are at the same molecule. Hydrogen transfer is suspected to be an intramolecular reaction.

b) Thioxanthones

Thioxanthones in conjunction with tertiary amines are efficient photoinitiators [49] 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. The reaction mechanism has been extensively investigated by spectroscopic and laser flash photolysis techniques [50-52]. It was found that the efficiency of thioxanthones in conjunction with tertiary amines is similar to that of benzophenone/amine systems. The most widely used commercial derivatives are 2-chlorothioxanthone and 2-isopropylthioxanthone. A great advantage is that thioxanthones are virtually colorless and do not cause yellowing in the final products.

Interestingly, when *N*-ethoxy-2-methylpyridinium salt is added to the mixture consisting of monomer (methyl methacrylate) and thioxanthone, a significant enhancement of the polymerization rate is detected [53]. This effect has been attributed to a reaction of ketyl radicals stemming from thioxanthone with the pyridinium salt, which leads to the generation of initiating ethoxy radicals.

18

c) Coumarins

In conjunction with tertiary amines, ketocoumarines act as highly efficient *Type II* photoinitiating systems [9, 54, 55]. The spectral sensitivity of this system can be tuned to various wavelengths of the visible part of spectrum by selection of suitable substituents. Moreover, the substitution pattern determines whether the coumarin acts as electron donor or as electron acceptor. 3-Ketocoumarins with alkoxy substituents in the 5- and 7-position show good absorption in the near UV and are excellent electron acceptors. Regarding co-initiators, alkyl and aryl amines are most suitable.

d) Benzil and Quinones
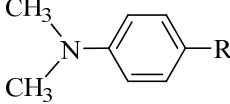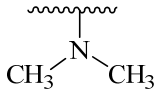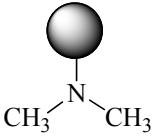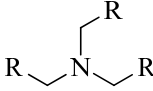
Benzil and quinones, such as 9,10-phenanthrene quinone and camphor quinone in combination with hydrogen donors, can be used as photoinitiators both in the UV and visible region [40, 56]. Photopolymerization of methyl methacrylate using benzil was elaborately studied by Hutchiso et al.[40]. They have observed a threefold increase in the polymerization rate when a hydrogen-donating solvent, such as tetrahydrofuran, was used in the system indicating the importance of hydrogen abstraction.

Amines, such as dimethylaniline and triethylamine, are also used as co-initiators for free radical polymerizations [57]. In these cases, initiating radicals are supposedly generated through exciplex formation followed by proton transfer. The low order of toxicity of camphorquinone and its curability by visible light makes such systems particularly useful for dental applications [58, 59]. It is noteworthy that the reactivity is relatively low, owing to a low efficiency in hydrogen abstraction reactions. This circumstance has prevented the use of quinones in other applications.

f) Hydrogen Donors

The co-initiators such as an amine, ether, thiol or alcohol with an abstractable α-hydrogen are also classified in Table 2.5.

Table 2.5 Structures of typical *Type II* hydrogen donors

Hydrogen Donors	Structure
Aliphatic Amines	$R_1 = C_2H_5$, CH_3, $CH(CH_3)_2$ $R_2 = C_2H_5$, C_2H_4OH, $CH(CH_3)_2$ $R_3 = C_2H_5$, C_2H_4OH, $CH(CH_3)_2$
Aromatic Amines	$R = H$, $COOH$, $COOCH_2CH_3$, $COOC_8H_{17}$
Polymeric Amines	polymer = poly(methyl methacrylate)s, polyacrylates or polyurethanes
Dendrimeric Amines	core = polyglycerols or poly(propylene imine)s
Acrylated Amines	R = acrylates or methacrylates
Alcohols	$R-OH$ R = isopropyl, hydroxyethyl methacrylate
Ethers	$R-O-R$ R = tetrahydrofuran, benzodioxole poly(ethylene oxide), poly(propylene oxide), poly(tetrahydrofuran)
Thiols	$R-SH$ R = benzimidazole, benoxazole, benzthiazole, thioxanthone

f.1) Amines

Tertiary amines are commonly employed as co-initiators in *Type II* systems because of the ease of formation of the α-amino alkyl radicals [60, 61], their high reactivities toward double bonds of the monomers and the ability of tertiary amines to reduce oxygen inhibition [62, 63]. The efficiency of amines both as co-initiators as well as oxygen scavengers depends on their structure [64-66]. To be effective in accelerating the polymerization in air, amines have to be able to sustain the chain reaction

involving the reaction of α-aminoalkyl radicals with oxygen (reaction 2.14).

$$R_1\text{-}N\text{-}\overset{\cdot}{C}H\text{-}R \;+\; O_2 \;\longrightarrow\; R_1\text{-}N\text{-}CH\text{-}R$$ with R_2 groups and $OO^{\cdot}$

(2.14)
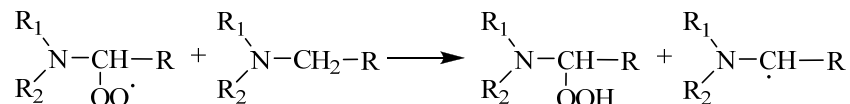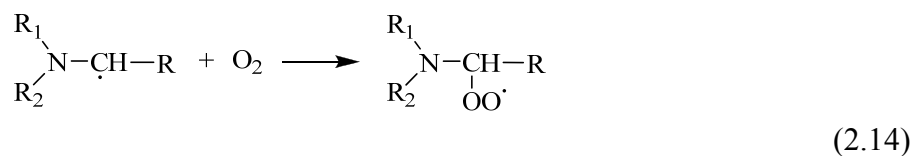
However, amines have some disadvantages: they tend to impart yellowing to the UV-cured products; they increase the product's hydrophilicity; and they may cause corrosion of the substrates [7, 60]. In addition, aromatic amines (commonly used in photocurable dental fillings as co-initiators for camphorquinone [59, 67, 68] are suspected to be mutagenic [59, 69].

Although, in general, amines accelerate the polymerization process in air, in an inert atmosphere, they can exert a retarding effect resulting from chain-transfer reactions and slow re-initiation (reaction 2.15) by stabilized α-amino alkyl radical [65, 70-72].

(2.15)
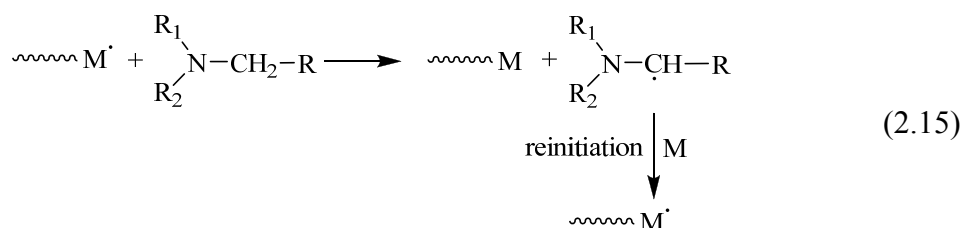
Monovinyl monomers containing aliphatic tertiary amino groups have found application in dental composites. They are used as co-monomers, which can act also as co-initiators [73, 74].

f.2) Ethers

The effect of the either group is less pronounced. The introduction of polyether groups into the polymer backbone has been reported to increase the rate of polymerization in air considerably, presumably through enhanced chain transfer of the hydrogen atoms in the α-position to the ether oxygen to peroxy radicals, similar to amine-containing systems [60, 75, 76].

(2.16)

21
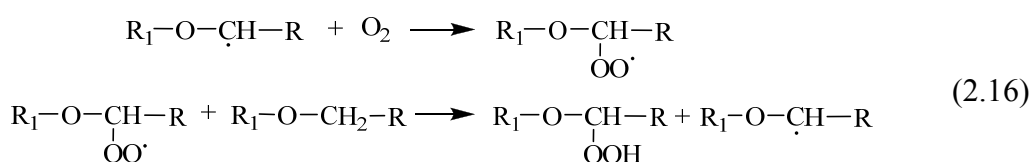
However, such monomers undergo oxidation during storage or at higher polymerization temperatures, which complicates the polymerization kinetics [77]. The oxygen containing polymers are more susceptible to swelling in water than analogous polymers without ether groups [77].

An addition of polyethers such as poly(ethylene oxides) and poly(propylene oxides) reduces the sensitivity of the polymerization to the reactions toward oxygen inhibition. Moreover, because the rate constant for hydrogen abstraction from ethers is $\sim 2 \times 10^5$ $M^{-1} s^{-1}$ whereas addition of a benzoyl radical to an acrylate is $\sim 10^5$ to 10^6 $M^{-1} s^{-1}$, hydrogen abstraction may readily compete with the addition of initiator radical to monomer provided that the concentration of ether groups is high enough [64].

Aliphatic ethers may also be used as co-initiators in *Type II*-initiating systems, but their ability to reduce excited states is much lower than that of amines. For instance, the quenching rate constant of benzophenone triplet by ethers is $\sim 10^6$ $M^{-1} s^{-1}$ [78] and by aliphatic amines $\sim 10^9$ $M^{-1} s^{-1}$ [78]. Hydrogen abstraction from ethers by an excited photoinitiator occurs directly and is not preceded by an electron transfer step.

f.3) Sulfides

The influence of sulfides on photopolymerization has been studied less extensively. The introduction of aliphatic sulfide groups into an acrylate-based, UV-curable formulation both as an additive and as a part of a monomer may be advantageous for the polymerization product. First, it will improve the thermal resistance of the resulting product since aliphatic sulfides are known thermo-oxidative stabilizers [79]. Moreover, the presence of the sulfide groups in the polymerization product can improve its hydrophobic properties [77, 80]. Finally, the sulfide group increases the refractive index of the polymer due to the high polarizability of the sulfur atom [80].

Similar to amines, aliphatic sulfides may serve as hydrogen donors for *Type II* initiators (e.g. quenching rate constant of benzophenone triplet by alkyl sulfides [81] is $\sim 10^7$ x 10^9 $M^{-1} s^{-1}$). Sulfides of various structures (simple sulfides, cyclic dithioacetals, sulfur-containing alcohols, ester [82, 83], amino acids, carboxylic acids [84, 85] were tested as co-initiators for benzophenone and its derivatives.

Sulfides can also act as oxidizable compounds for the reduction of oxygen inhibition [80, 83]. They may consume oxygen in [75, 76] and in thick layers, their activity reaches that of aliphatic amines [80]. Their activity in photopolymerizations ranges from low to high, depending on their hydrogen-donating abilities (reaction 2.17).

$$R_1-S-\overset{.}{C}H-R \ + \ O_2 \ \longrightarrow \ R_1-S-\underset{\underset{OO^.}{|}}{C}H-R$$

$$R_1-S-\underset{\underset{OO^.}{|}}{C}H-R \ + \ R_1-S-CH_2-R \ \longrightarrow \ R_1-S-\underset{\underset{OOH}{|}}{C}H-R + R_1-S-\overset{.}{C}H-R \qquad (2.17)$$
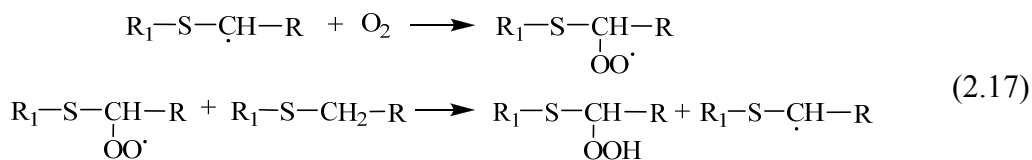
However, due to occurrence of chain-transfer reactions sulfides may also exert a retarding effect on the polymerization, especially at higher temperatures and in an inert atmosphere. They can also undergo photolysis during the photoinitiation and the radicals formed can additionally initiate the polymerization (reaction 2.18). Generally, the observed effect of sulfides is a result of accelerating and retarding processes occurring simultaneously and their relationship and the extent of the effect depend on the reaction conditions and on the sulfide structure [80].

$$R_1-S-R \ \xrightarrow{h\nu} \ \overset{.}{R_1} \ + \ ^.S-R \ \xrightarrow[M]{initiation} \ \text{\textwave} M^. \qquad (2.18)$$
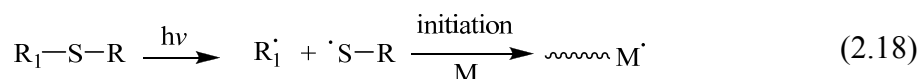
The effect of the sulfide group becomes more complex when the thioether linkage is built into a di(meth)acrylate monomer [77]. In this case, an enhancement of the cross-link density will occur and also such factors as the improved flexibility of the chain connecting the two unsaturations [77, 86] and the lower reactivity of the sulfur-containing macroradical [87] may affect the course of the polymerization.

(2) 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 (reactions 2.19).

$$PS \xrightarrow{h\nu} PS^*$$

$$PS^* + A \longrightarrow PS^{\cdot+} + A^{\cdot-} \longrightarrow R_1^\cdot + R_2^\cdot \qquad (2.19)$$

$$PS^* + D \longrightarrow PS^{\cdot-} + D^{\cdot+} \longrightarrow R_1^\cdot + R_2^\cdot$$
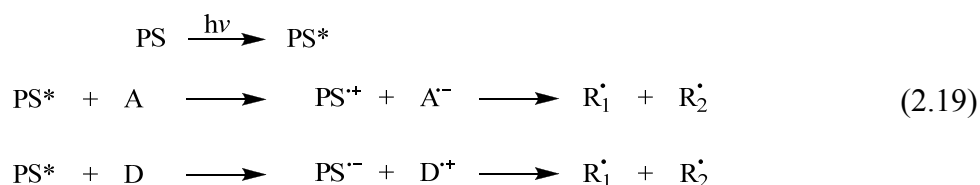
The electron transfer is thermodynamically allowed, if Gibbs Energy Change (ΔG) calculated by the Rehm-Weller equation (Eq:2.6) [119] is negative.

$$\Delta G = F\ [E\tfrac{1}{2}ox\ (D/D^{+\cdot}) - E_{\frac{1}{2}}^{red}\ (A/A^{\cdot})] - E_{PS} + \Delta E_c \qquad (Eq{:}2.6)$$

where, F = Faraday constant,
$E_{\frac{1}{2}}^{ox}\ (D/D^{+\cdot})$ = oxidation potential of donor,
$E_{\frac{1}{2}}^{red}\ (A/A^{\cdot})$ = reduction potential of acceptor,
E_{PS} = Singlet state energy of the photosensitizer,
ΔE_c = 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. Co-initiators, 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) [88-91]. 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 [88]. Either mechanism will result in the formation of a free-radical active center capable of initiating a growing polymer chain.

2.1.1.5. Monomers
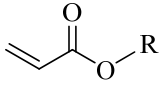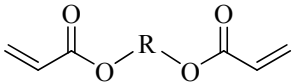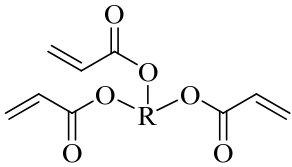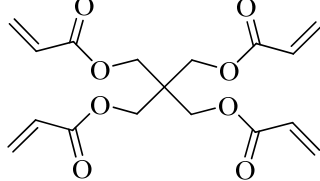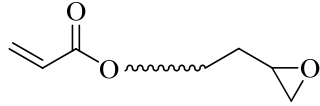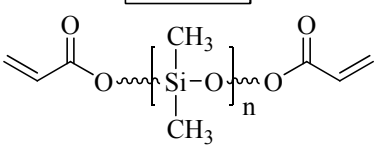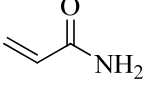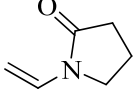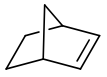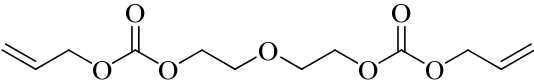
Unsaturated monomers, which contain a carbon–carbon double bond (C=C), are used extensively in free radical photopolymerizations. The free-radical active center reacts with the monomer by opening the C=C bond and adding the molecule to the growing polymer chain. Most unsaturated monomers are able to 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. The generalized structure of these monomers is shown in Table 2.6. These monomers have very high reaction rates, with acrylates having an even faster reaction rate than their methacrylate counterparts [92]. 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 [92, 93]. 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 [94]. Acrylamide is used in stereo lithography and to prepare holographic materials [95-97]. N-vinylpyrrolidinone is copolymerized with acrylates and methacrylates for cosmetic and biomedical applications [98]. Norbornene is copolymerized with thiols for optical fiber coatings [99].

Table 2.6 Chemical structures of free radical polymerizable monomers

Monomers	Structure
Methyl acrylate, Ethyl acrylate, Butyl acrylate, 2-Hydroxyethyl acrylate, 2-Ethylhexyl acrylate	$R = CH_3, C_2H_5, C_2H_4OH, C_4H_9$
1,4-Butanediol diacrylate, Neopentyl glycol diacrylate, 1,6-Hexanediol diacrylate, 1,10-Decamethylene diol diacrylate, Diethylene glycol diacrylate, Dipropylene glycol diacrylate, Tetraethylene glycol diacrylate Tripropylene glycol diacrylate	$R = C_4H_8, C_5H_{10}, C_6H_{12}, C_{10}H_{20},$ $C_4H_8O, C_6H_{12}O, C_8H_{16}O_3, C_9H_{18}O_2$
Glycerol triacrylate Trimethylolethane triacrylate Trimethylolpropane triacrylate Pentaerythritol triacrylate	$R = C_3H_5, C_5H_9, C_6H_{11}, C_5H_9O$
Pentaerythritol tetraacrylate	
Epoxy acrylates	
Urethane acrylates	polyurethane
Polyester acrylates	polyester
Polyether acrylates	polyether
Silicone acrylates	CH_3 $Si-O$ n CH_3
Acryl amide	NH_2
N-vinylpyrrolidinone	
Norbornene	
Diallyldiglycolcarbonate	

2.1.2. Photocrosslinking

The field of photocrosslinking of monomers, oligomers, and polymers has grown into an important branch of polymer science. It constitutes the basis of a considerable number of commercial applications, not only in conventional areas of thin layer materials, such as coatings, inks, photoresists, adhesives, photoimaging, and photolithography, but also in new domains using photocrosslinked polymeric materials in thick layers, such as insulating materials on wire and cable, hot water pipe, shrinkage tube and hose, and foams. The amount of research on this subject is increasing rapidly. Many publications and reviews concentrate on photocuring and photopolymers [1, 7, 61, 93, 100-115].

The term *photocrosslinking of polymer* is defined as the process whereby light (UV, visible, or laser light) is used to induce the crosslinking of preexisting high polymers. This means that light irradiation of polymers carrying more than two reactive groups per chain (or of blends with a photoinitiator or a sensitizer) initiates crosslinking to a three-dimensional network structure. The reaction may also occur with an added crosslinking reagent which carries two or more functional groups per molecule. Photocuring is not a synonym of photocrosslinking since the former includes photopolymerization of monofunctional monomers, particularly in polymer materials with no photocrosslinkable functional groups.

2.1.2.1. Photocrosslinkers

Di- and polyfunctional monomers act as crosslinkers. Acrylates of alkylene glycol, trimethylol propane and pentaerythritol, triallyl cyanurate, and triallyl isocyanurate are most widely used (reaction 2.20).

(2.20)
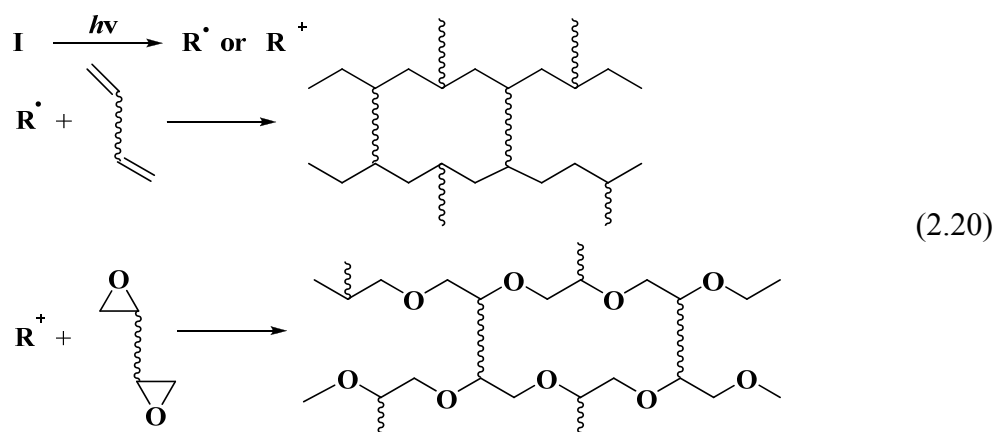
2.1.2.2. Photocrosslinkable Polymers

Photocrosslinkable polymers possess functional groups which can undergo light-induced reactions to form a crosslinked polymer directly. Photocrosslinkable polymers can be classified as follows:

• polymers bearing functional groups which crosslink by themselves under photoirradiation: photoinitiators or photosensitizers may be added but other crosslinking agents or polymerizable monomers are not necessary, and the functional group is either a photopolymerizable group or a one-to-one coupling group;

• polymers blended with photoinitiator: this is shown in photoinitiated crosslinking of polyethylene described in a later section (a multifunctional crosslinker may be added to enhance the crosslinking efficiency);

• polymers mixed with crosslinkers: as the classic bichromate process shows, the functional groups are activated by contact with a photoexcited crosslinker or the photodecomposition products of a crosslinker (a photoinitiator may be added); and

• polymers synthesized in the presence of polyfunctional monomers via radical, ionic, or polyaddition reactions (a photocrosslinking composition is obtained): in practice, a sensitizer is indispensable.

The applicability of the four processes depends on the photocrosslinkable polymeric material itself, the required properties of the photocrosslinked products, and the workability. For example, in photocrosslinking of polyethylene, a photoinitiator such as benzophenone must be added because there are no chromophoric groups in the polyethylene chain and the latter type process has to be applied.

The most important commercially and the simplest systems in this group are polymers with cinnamate or chalcone structures either as pendant groups or in the polymer backbone that undergo photocycloaddition. Poly(vinyl cinnamate) is one of the best known examples of a material which becomes insoluble through photocycloaddition. Crosslinking involves the dimerization by reaction of the photoactivated cinnamate group with a second cinnamate group in the ground state. The result is the formation of a substituted cyclobutane ring of truxillic ester type (reaction 2.21) [116].

$$\text{(2.21)}$$
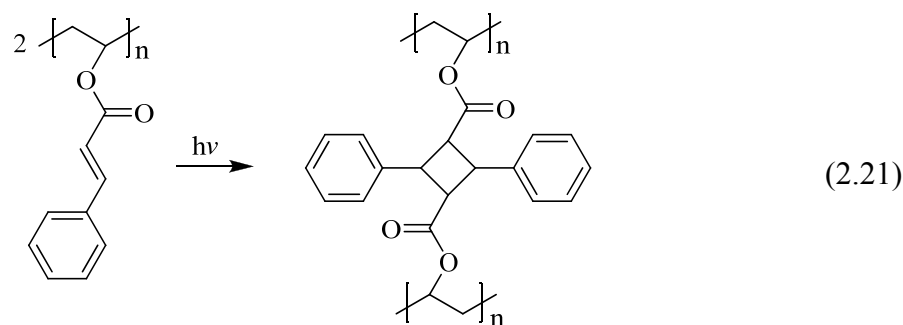
2.1.2.3. Photoinitiated Radical Reactions

In this system, a photoinitiator is added to the polymer or grafted onto the polymer chains [117-123]. Excitation of the photoinitiator under light yields reactive radicals which initiate subsequent reactions in the polymer matrix and produce crosslinks between two macromolecular chains. The pure polymer may be photocrosslinked. But even with a limited quantity of photoinitiator either blended in or grafted onto the polymer, we obtain a considerable enhancement of the crosslinking reaction.

2.1.2.4. Thiol-ene Reactions

Thiol-ene polymerizations are reactions between multifunctional thiol and ene (vinyl) monomers that proceed via a step growth radical addition mechanism. Initiation is achieved through generation of radical centers, the most common method being photoinitiation of the radical centers.

The generally accepted mechanism of the thiol-ene system was proposed by Kharasch *et. al.*[124]. In this regard, it is worth mentioning the pioneering work of Morgan *et. al.*[125] who used benzophenone to absorb light and initiate the polymerization of the radical chain process via a hydrogen abstraction reaction involving the excited benzophenone and a ground state thiol. Excited benzophenone abstract a hydrogen from a thiol monomer, generating thiyl radical that can either propagate or terminate. It is important to note that after generation of an initial thiyl radical species the thiol-ene propagation basically involves a free radical addition step followed by a chain transfer step and effectively produces addition of a thiol across a carbon-carbon double bond (reaction 2.22). The photocrosslinking of two component systems, such as thiols/acrylates, have rapidly expanded starting from the 1970s until now [126].

29

(2.22)
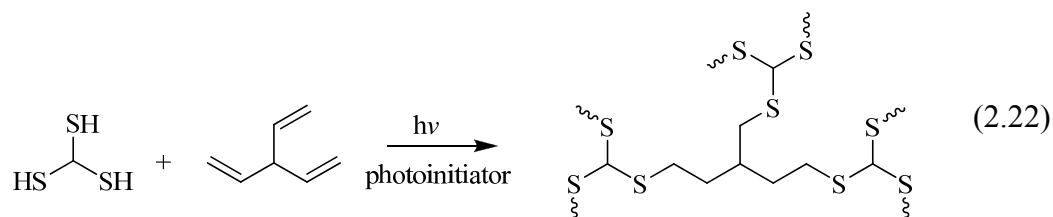
Jacobine has described many photocrosslinkable systems based on a polythiol plus a polyene (a polyunsaturated co-reactant) [127]. This reaction corresponds to the addition of a thiol group on an ethylenic double bond in a photocrosslinkable system consisting of a polythiol plus a polyene. Crosslinking can take place directly by irradiating with a suitable wavelength if the polythiol or the polyene, or both, has functionality, or in the presence of a photoinitiator such as an aromatic ketone compound.

2.2. Ketenes

Ketene is a linear molecule. The carbonyl (C=O) bond of ketene (C=C=O) is 1.16 Å in length, which is shorter than that of C=O (1.22 Å) in aldehyde and ketone. The shorter C=O bond of ketene implies an increase of the "triple bond" character. This increase in triple bond character results from the relative importance of the resonance structure A over the two others (B and C) (reaction 2.23)[128].

(2.23)
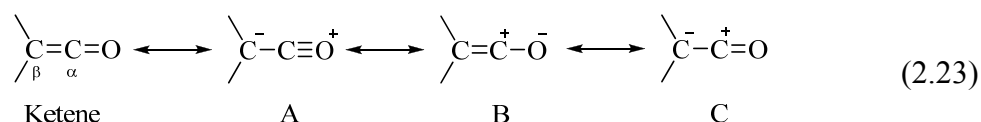
2.2.1. Preparation of Ketenes

Ketenes are versatile, well-known substrates in organic synthesis. Their cumulated double bond structure imparts a unique spectrum of reactivity, and gives rise to a large number of mechanistically interesting transformations. There are many ways [129] to synthesize ketenes through thermolytic, and photolytic reactions (Table 2. 7). Most ketenes cannot be isolated due to their high reactivity. Hence, the formation of ketene is usually demonstrated via a trapping experiment and by isolating the products from its reactions with alcohol and cyclopentene [130].

The dehalogenation of 2-haloacyl halides in the presence of activated zinc is the oldest [131] and the most widely used method to generate ketenes [132-134]. The

first ketene, diphenyl ketene, was prepared by Hermann Staudinger using dehalogenation of α-bromodiphenylacetyl bromide [131]. This method gives excellent yields for stabilized ketenes. Metal anions such as manganese pentacarbonyl and chromium tetracarbonyl nitrosyl have also been shown to be effective in dehalogenation [135-137].

Dehydrohalogenation of acyl halides involved the elimination of hydrogen halide using a tertiary amine [138-140]. The initial step of the reaction is the formation of an acylammonium salt [141-143]. However, the use of tertiary amine may lead to other products [144, 145]. Monoalkylketenes cannot be prepared by this method since they dimerize in the presence of triethylamine hydrochloride. The dehydrochlorination of acyl chloride is also effected with a metal catalyst [146, 147].

Table 2.7 Synthetic pathways for ketene formation

Dehalogenation	$Ph-\underset{\underset{Ph}{|}}{\overset{\overset{Br}{|}}{C}}-\overset{\overset{Br}{|}}{C}=O \xrightarrow{Zn} \underset{Ph}{\overset{Ph}{>}}C=C=O$
Dehydrohalogenation	$R_1-\underset{\underset{R_2}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{Br}{|}}{C}=O \xrightarrow{NEt_3} \underset{R_2}{\overset{R_1}{>}}C=C=O$
Wolff rearrangement	$Ph-\overset{\overset{O}{||}}{C}-\overset{\overset{N_2}{||}}{C}-CH_3 \xrightarrow{\Delta\ or\ h\nu} Ph-\overset{\overset{O}{||}}{C}-\ddot{C}-CH_3 \longrightarrow \underset{H_3C}{\overset{Ph}{>}}C=C=O$
Dehydration of carboxylic acid	$CH_3-\overset{\overset{O}{||}}{C}-OH \xrightarrow[-H_2O]{\Delta} \underset{H}{\overset{H}{>}}C=C=O$
Decomposition of acetic acid	$CH_3-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow[-CH_3COOH]{\Delta} \underset{H}{\overset{H}{>}}C=C=O$
Decomposition of cyclic ketone	cyclohexanone $\xrightarrow{h\nu}$ $\longrightarrow$ $CH_3\text{-}\!\!\!\!-\!\!\!\!-\!\!\!\!\overset{}{\underset{\underset{H}{|}}{C}}\!\!=\!C\!\!=\!O$
Decomposition of alkynyl ether	$CH_3-\overset{\overset{O}{||}}{C}\!\!\equiv\!\!-O \xrightarrow{-CH_2=CH_2} CH_3-\overset{\overset{O}{||}}{C}-\overset{\overset{H}{|}}{C}=C=O$
From cyclobutanone	$\square\!\!=\!O \xrightarrow{\Delta} \underset{H}{\overset{H}{>}}C=C=O\ +\ CH_2=CH_2$

The preparative value of the Wolff rearrangement reaction arises from the reactivity and ready accessibility of α-diazocarbonyl. The rearrangement can be triggered thermally [148], photochemically [149, 150] or by metal catalysts [151]. The Wolff rearrangement provides a very versatile method for the preparation of ketenes with a wide variety of structural types. However, side reactions such as C-H

insertion by the carbene intermediate [152] or fragmentation of the ketene [153] is more likely to occur in a thermal or catalyzed reaction than in a photochemical one. Alkyl ketenes can be obtained by reaction of carboxylic acid over alkali metal-exchange zeolite [154]. Direct dehydration of a carboxylic acid also leads to the formation of ketene [155]. Alkyl ketenes [156] and the parent ketene [157, 158] are also produced by pyrolysis of acid anhydride. Photochemical decomposition of cyclic ketones provides ketenes via a biradical [159, 160]. Most of the reactions are carried out in alcoholic solvents, and as a result the ketene is converted to the ester [161-163].

Ketenes can also be obtained by thermolysis of alkynyl ethers [164-166]. The main drawback of this route is the availability and stability of the alkynyl ether under the reaction conditions [167].

Ketene is also produced by reverse [2+2] or [4+2] cycloaddition reaction. Thermal decomposition of cyclobutane-1,3-dione (ketene dimer) regenerates ketene. The photochemical decomposition also leads to ketene but lower yields are obtained due to side reactions [168]. Cyclobutanone and cyclobutenone produce ketenes by thermolysis [169-171] or photolysis [172]. The cleavage is thought to proceed via a biradical, but alternative paths cannot be excluded [173].

2.2.2. Reactions of Ketenes

Ketenes are very reactive towards both unsaturated compounds and nucleophiles [174]. However, the [2+2] cycloaddition of ketene is by far the most synthetically useful reaction of ketenes. Additions of alcohol, amine or acid are not usually used in synthesis as the corresponding ester, amide or anhydride can be obtained by simpler methods.

2.2.2.1. Cycloaddition Reaction

Ketenes react with unsaturated compounds to produce the [2+2] cycloadduct. Ketenes react with carbon-carbon double [175-177] and triple [178-180] bond to from cyclobutanone and cyclobutenone respectively. Ketenes also react with carbonyl [181], imine [182-184] and azo compound [185, 186] to yield four-membered cyclic 2-oxetanones, 2-azetidinones and diazetidinones, respectively

(Table 2.8). The cyclobutanones formed by the reaction of a ketene with cyclopentadiene were found to be versatile intermediates [187] in the synthesis of tropones [188]. Ring contraction of α-halocyclobutanone produces cyclopropanes [189]. Decarbonylation of β-lactone yields alkenes [190].

Table 2.8 [2+2] Cycloaddition reactions of ketenes with unsaturated compounds

Alkene	$\underset{Ph}{\overset{Ph}{C}}=C=O$ + ⌃ ⟶ Ph—☐(O) + Ph—☐(O)
Alkyne	$\underset{H_3C}{\overset{H_3C}{C}}=C=O$ + C_2H_5O—≡ ⟶ H_3C—☐(CH₃, O, C₂H₅O)
Carbonyl	$\underset{H_3C}{\overset{H_3C}{C}}=C=O$ + $Cl-\overset{O}{\overset{\|}{C}}-Cl$ ⟶ H_3C—☐(CH₃, O, Cl, Cl)
Imine	$\underset{H}{\overset{RO}{C}}=C=O$ + $R_2-N=CH-R_1$ ⟶ RO—☐(H, O, R₁, N—R₂)
Azo compound	$\underset{Ph}{\overset{Ph}{C}}=C=O$ + $\underset{}{\overset{Ph}{N}}=N-R$ ⟶ Ph—☐(O, R—N–N–Ph) + Ph—☐(O, Ph—N–N–R)
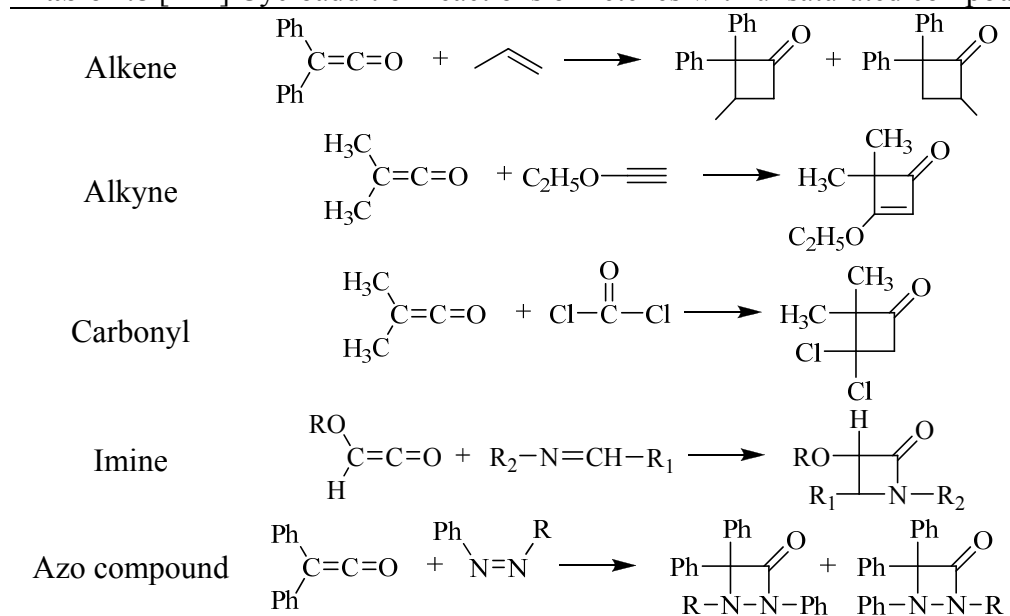
The [2+2] cycloaddition is the predominant cycloaddition reaction of ketenes. However, in few cases ketene is the dienophile in [4+2] cycloaddition in reactions with selected dienes or β-unsaturated ketones [191]. The [4+2] cycloaddition is a more common reaction for vinyl- [192] and oxo-ketene [193] (reaction 2.24).

$$\text{(cyclopentane ring with } C=O, O) + O=C=N-R \longrightarrow \text{(bicyclic ring with } O, N-R, O, O) \qquad (2.24)$$
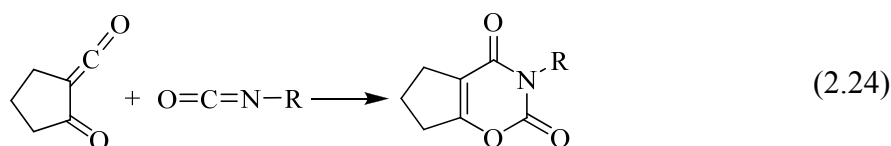
2.2.2.2. Nucleophilic Addition Reaction

Ketenes also react with nucleophiles such as hydride [194], water [195], alcohols[196-199], amines [200-202] and amides [203] to give the corresponding enol, ester, amide or imide (Table. 2.9). Intramolecular hydride attack occurs in 4-methylvinyl ketenes to form the corresponding aldehyde [204]. The addition of alcohol was synthetically useful in the preparation of an unsaturated ester from vinyl ketene [205]. Reaction with amines has been used in the synthesis of indolizidine and quinolizidine [206].

Table 2.9 Nucleophilic addition reactions of ketenes

Hydride	Ph, R C=C=O →(1. LiAlH₄ / 2. Me₃SiCl)→ Ph, R / OSiMe₃, H + Ph, R / H, OSiMe₃
Water	(ketene, Ph chain) C=O →(H₂O)→ COOH (chain, Ph)
Alcohol	Ph C=O, OCH₃, OH → (8-membered lactone ring with Ph, O, CH₃O)
Amine	C=O, NH₂, R, Ph, Ph → (pyrrolidinone NH, R, Ph, Ph)
Amide	(aryl) C=C=O, N-H-R, O → (isoquinolinedione, N-R, O, O)

The nucleophilic attack also occurs at the carbonyl carbon atom of the ketene. Electronic and steric effects of the ketene substituents were rationalized by an in-plane attack [130]. When amine was used as a nucleophile, a zwitterionic intermediate has been observed by NMR spectroscopy [207].

2.2.2.3. Electrophilic Addition Reaction

Electrophilic addition on ketenes occurs with protons [207] and metal alkoxides [208] (reaction 2.25). Addition of carboxylic acid [209, 210], phosphoric acid [211] and sulfonic acid [212] to ketenes produces mixed anhydrides.

Protonation

$$CH_2=C=O \quad \xrightarrow{H^+} \quad CH_3-\overset{+}{C}=O$$

(2.25)
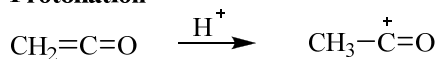
Reaction with metal alkoxides

$$CH_2=C=O \quad \xrightarrow{R_nMOR} \quad R_nMCH_2-\overset{+}{C}=O \quad \xrightarrow{\bar{O}R} \quad R_nMCH_2-\overset{O}{\overset{\|}{C}}-OR$$
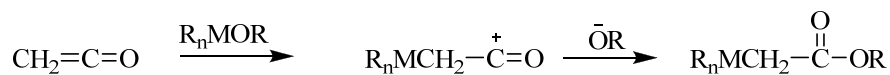
2.2.2.4. Radical Addition Reaction

Radical additions to ketenes have been studied with the hydroxyl radical [213]. The hydroxyl radical addition occurs on either carbon of the ketene and is followed by bond cleavage (reaction 2.26).

34

$$CH_2=C=O \xrightarrow{\cdot OH} HOCH_2-\overset{\cdot}{C}=O \longrightarrow HO\overset{\cdot}{C}H_2 + CO$$

$$CH_2=C=O \xrightarrow{\cdot OH} \overset{\cdot}{C}H_2-\underset{\underset{OH}{|}}{C}=O \longrightarrow CH_3-\underset{\underset{\overset{\cdot}{O}}{||}}{C}=O \longrightarrow \overset{\cdot}{C}H_3 \qquad (2.26)$$
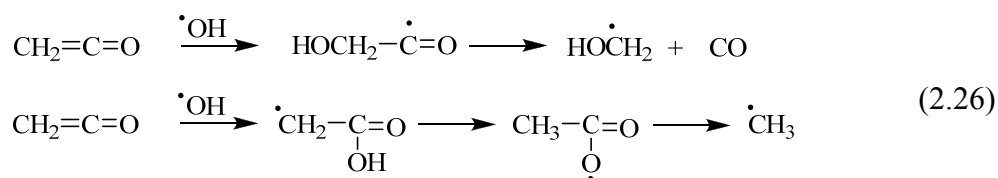
2.2.3. Polymerization of Ketenes

Polymers derived from ketenes were first observed by Wedekind [214] and by Staudinger [215, 216], and this provided an impetus for the further development of polymer chemistry. The formation of high polymers from ketenes was examined systematically by Natta, et al., and this work has been reviewed [217, 218]. Types of ketene polymers include those formed by 1,2-additions of the C=C bonds and of the C=C bonds, which are polyketones and polyacetals, respectively, and polyesters 3 that have both types of linkages. All three have been prepared from dimethylketene ($Me_2C=C=O$) by appropriate choice of catalyst and solvent (reaction 2.27-29) [217]. The formation of polyketone by polymerization of diphenylketene with aluminium tribromide in toluene was proposed to involve formation of enolate, which added diphenylketene while polyacetals was formed from diphenylketene by butyllithium in ether. The formation of polyester took place when aluminium triethyl in toluene was used as the catalyst [217, 219-221].

$$(2.27)$$

polyketones

$$(2.28)$$

polyacetals

$$(2.29)$$

polyesters
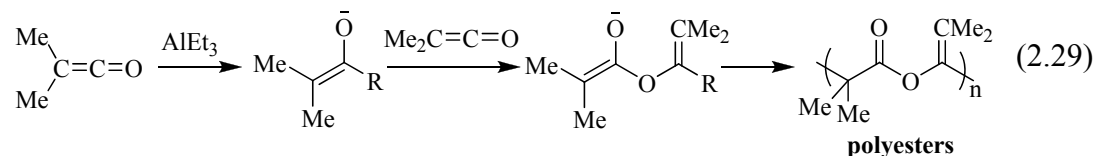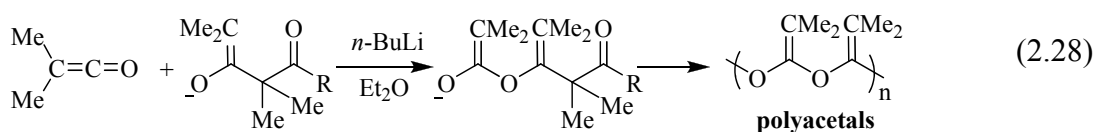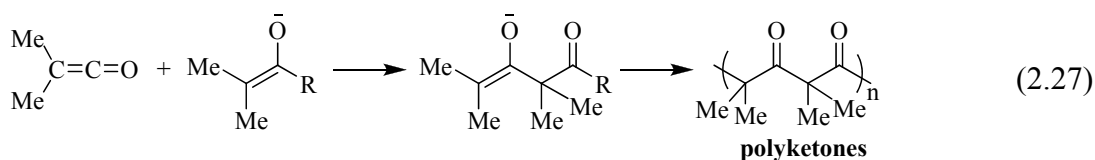
Ketene was polymerized by lanthanum triisopropoxide, probably in a process involving a lanthanum enolate. This species served to initiate methyl methacrylate polymerization [222]. This catalyst also formed a copolymer of diethylketene and methyl methacrylate [222]. Cationic polymerization of dimethylketene has been reported [223, 224], as well as radiation cryopolymerization of ketene, which was proposed to proceed by an anionic mechanism. Diphenylketene has also been

polymerized using ethyllithium or *t*-butyllithium [225]. Ketenes also form copolymers with other carbonyl compounds or with isocyanates [226, 227].

(2.30)
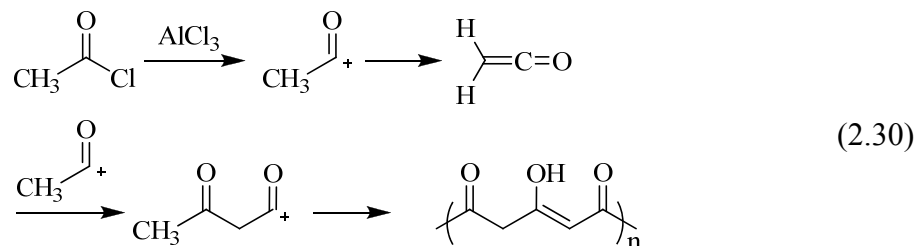
Polyketene, the polymer of ketene, was formed by the reaction of acetyl chloride with aluminium trichloride, and was proposed to result from deprotonation of the acylium ion forming to ketene, which then reacted with acylium ion forming to 1,3-dioxobutanylium, followed by addition of ketene monomers leading to polyketene (reaction 2.30) [228]. Polyketene has also been formed by acid polymerization of the ketene acetal followed by mild hydrolysis of the resulting acetal [229]. Polyketene was found to be extensively enolized, with interesting conducting properties [230].

Ketoketenes formed by photolysis of 2-diazo-1,3-diketones in diethyl ether polymerize to polyesters (reaction 2.31) [231]. A variety of polymers have been prepared from carbon suboxide [232]. Carbon suboxide spontaneously forms a low molecular-weight polymer.

(2.30)
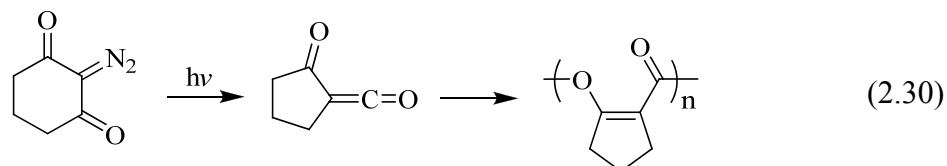
2.2.4. Ketenes from Dioxinones

The chemistry of dioxinone, a convenient precursor for acetylketene, has been the subject of a short review [233]. Dioxinone is a product of the reaction of diketene and acetone, and forms acetylketene and acetone on thermolysis (reaction 2.31). Even though the preparation of diketene in acetone was used on a large scale in industry, the formation of dioxinone was not recognized for a long time [234].

(2.31)
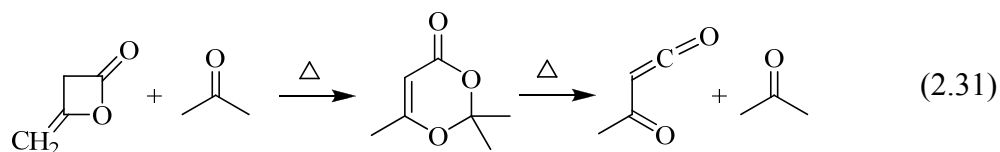
Dioxinones cleave on thermolysis or photolysis, with formation of an acylketene and a ketone [235]. Pyrolysis of dioxinone at 180–240 ^{o}C and trapping of the product in an argon matrix at 5–12 K showed the presence of acetylketene and acetone by FT-IR (equation 2) [236]. Ketenyl bands at 2135 and 2142 cm^{-1}suggested the presence of both the s-cis and s-trans conformations of 2. Dimerization of acetylketene proceeded by a [4+2] cycloaddition to form aromatic product (reaction 2.32) [236]. The stereochemistry of dioxinone formation has been studied by computational methods [237].

(2.32)
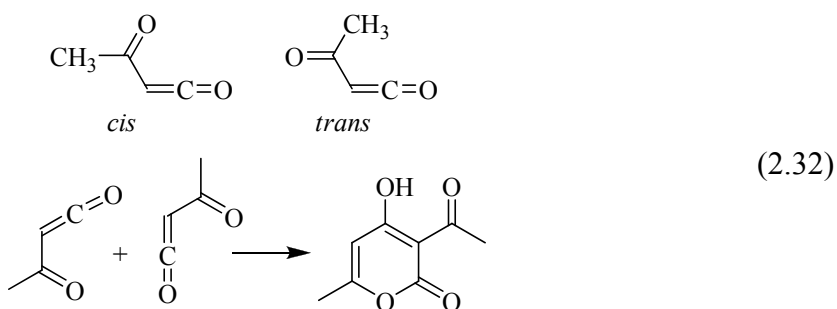
A variety of substituted acylketenes have been prepared from dioxinones, including halo derivatives haloacylketenes from halodioxinones, and these were trapped with dimethylcyanamide to give halooxazinones (reaction 2.33) [238, 239]. It was noted that the chloroketene formed more readily than the fluoro compound, and this is consistent with the known destabilization of ketenes by fluorine. Tri-fluoromethyl dioxinones gave the a-trifluoromethyl ketenes, which were trapped by benzyl alcohol (reaction 2.34) [240].

(2.33)

(2.34)
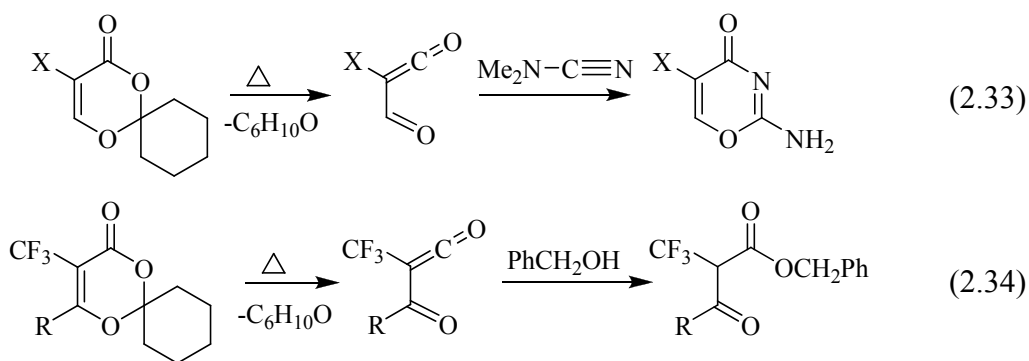
Dioxinones with side chains bearing nucleophilic groups form acylketenes, which cyclize by intramolecular attack (reaction 2.35) [198]. This reaction was also used to prepare eight-membered rings [241] and other medium ring-sized lactones [242, 243].

(2.35)
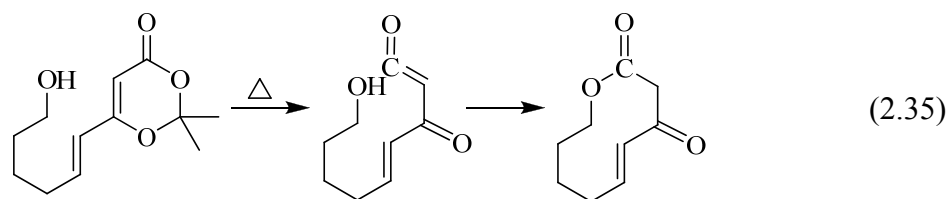
Thermolysis of acyldioxinone, forming diacetylketene in the presence of phenylisocyanate, gave [4+2] cycloaddition forming oxazinones (reaction 2.36) [244].

(2.36)
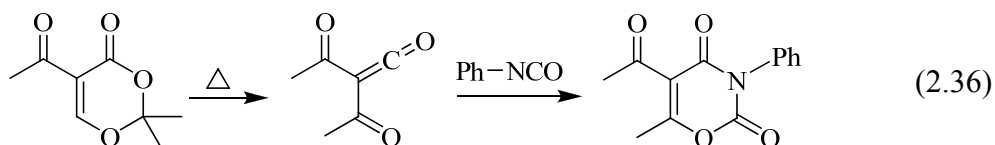
Photolysis of the dioxinone with 248 nm light provided a convenient source of the ketene for measurement of the rate of hydration (reaction 2.37) [245].

(2.37)
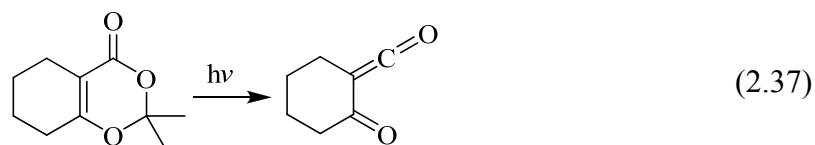
2.3. Dendrimers

Dendrimers are tree-like compounds. They have very unique structural features, such as many branches, high symmetry, monodispersity, globular shape, and void space in the interior [246]. Compared to the well known behavior of linear macromolecules, dendrimers have very low intrinsic viscosity because of the high density of atoms in a limited volume [247]. The properties of dendrimers are very different from those of small organic molecules and those of linear macromolecules because they are determined mostly by the terminal functional groups [248].

Since the first synthetic dendrimer was reported in 1978, [249] this kind of materials has attracted great attention of researchers in different fields. During the1980-90's, researchers made great efforts to synthesize new families of dendrimers with higher generations. Poly(amido amine) (PAMAM) and poly(propylene imine) (PPI) dendrimers are the most common and are commercially available. Hydrophobically modified PAMAM and PPI dendrimers are amphiphiles and have received extensive attention because of their unique behavior at the air/water and air/solid interfaces. In the last few years, interest in the application of these materials has risen rapidly. So

far, dendrimers have found applications in medicinal chemistry, high-performance polymers and separation agents, catalysis, energy transfer and other fields [250].

The synthesis of dendritic macromolecules is unlike the synthesis of regular polymers. Perfect dendrimers are synthesized by a two-step repetitive synthetic approach, are ideally branched and have the same chain lengths. Regular polymers usually are synthesized by chain or step polymerization. Two major approaches, convergent and divergent synthesis, are employed to prepare dendrimers as illustrated in Figure 2.1 [246, 251, 252].
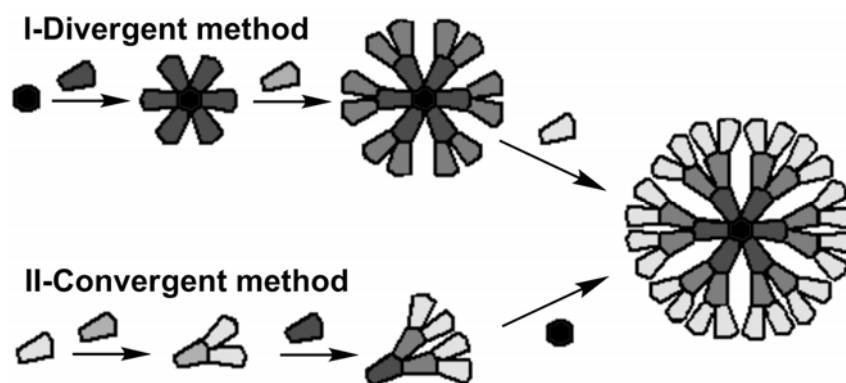
Figure 2.1 The two major synthesis methods of dendrimer

2.3.1. Divergent Synthesis

The divergent method is an "inside out" method. In this strategy, a dendrimer begins with a core molecule and grows outwards toward the periphery from the core. The reactive groups on the dendrimer surface react with monomer units to grow a new generation to the dendrimer in a stepwise manner as shown Figure 2.1. Thus, the number of coupling reactions increases exponentially with each successive generation. In this way dendrimers can be constructed step by step until spatial crowding prevents further reactions of the end functional groups [253].

This synthesis method allows easy analysis of lower generation materials after each step of the reaction. However, higher generation dendrimers synthesized by the divergent approach often contain structural defects because the reactions between end functional groups and monomers become more difficult with the increasing surface congestion of the dendrimers. Examples of this synthetic method can be found in the work of Meijer, [254] Tomalia, [255] Diederich [256] and Newkome [257]. The synthesis of poly(propylene imine) dendrimers will be addressed in detail

(Meijer's and Worner's work) [254, 258].

2.3.2. Convergent Synthesis

In contrast to the divergent method, the convergent method is an "outside in" strategy. The convergent approach prepares dendrimers from the periphery toward the core. In this method, different individual dendrimer branches (wedges or dendrons) are synthesized first. When the growing dendrons are large enough, several dendrons are tied to a suitable core to build up a new complete dendrimer. The starting blocks end up being on the periphery of dendrimers, while the succeeding blocks take the position of a focal point. Hawker and Frechet reported the first example of convergent method to synthesize polybenzyl ether dendrimers (reaction 2.38) [252, 259].

$$(2.38)$$
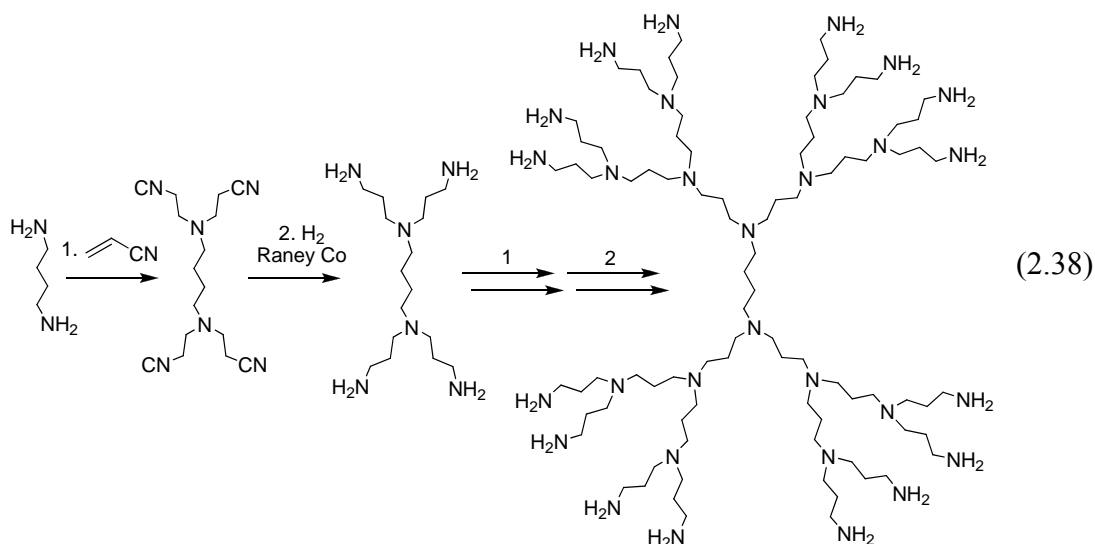
In their work, two iterative synthetic steps were employed: (1) a benzyl bromide group of a dendritic synthon was used to alkylate phenolic hydroxyl groups, (2) carbon tetrabromide was used to convert a benzylic alcohol group of the higher generation dendron to a benzylic bromide. The highest generation synthesized is the sixth generation. Other examples of the convergent strategy come from Miller, [260] Stoddart, [261] Wolf [262] and Yoshida [263]. The advantage of convergent growth over divergent growth stems from the fact that convergent synthesis gives more homogeneous and defect-free dendrimers,

The commercially available PPI family dendrimers are synthesized by the divergent approach [254, 258]. A short view of the synthesis is given in the following

paragraph because of its importance in this thesis. The synthesis starts from a 1, 4-diaminobutane core as shown in Scheme 2.38. It proceeds as a series of two repetitive reactions: a Michael addition reaction of amino groups to acrylonitrile, followed by reduction of the nitriles to primary amines. The nitrile-ended materials are denoted as "half-generation" and the "full-generation" amine-terminated dendrimers are considered as generation. So far, the highest generation synthesized is the fifth generation. Although only 23% of the fifth generation PPI dendrimers are perfect due to the steric problem on the surface of the higher generation dendrimers, this is the highest known for any 64-end-group dendrimers synthesized by a divergent method [250]. Nevertheless, the polydispersity of PPI dendrimers is still very low compared to hyperbranched polymers.

The molecular weight and the number of terminal groups increase exponentially with the dendrimer increasing generation. But the dendrimer diameter does not increase exponentially, it increases near linearly. This fact leads the density of dendrimer end groups to increase nonlinearly: the higher the dendrimer generation, the more densely packed the surface. Table 2.10 shows general properties of PPI dendrimers related to the dendrimer generations [254, 258].

Another consequence of the exponential growth pattern of dendrimers is a change of shape with generation. As the dendrimer generation increases, the dendrimer becomes more crowded, and the shape changes from an open expanded configuration to a spherical or globular structure.

Table 2.10 General features of poly(propylene imine) dendrimers

Generation	End Groups	Tertiary Amines	Molecular Weight[a]	Diameter (nm)[b]	End groups/surface area(1/nm2)
1	4	2	317	0.9	0.39
2	8	6	773	1.4	0.32
3	16	14	1687	1.9	0.35
4	32	30	3514	2.4	0.44
5	64	62	7168	2.8	0.65

[a]Molecular weight is based on perfect dendrimers.
[b]The dimensions of PPI were determined by small-angle neutron scattering [264].

2.3.3 Modification of Poly (propylene imine) Dendrimers

As mentioned above, the terminal groups of PPI dendrimers are amines and most modifications take place at the end groups. Some modifications also happen at core

and branch points since the interior amines are tertiary amines.

2.3.3.1 Chain End Modifications (Exterior Modification)

Amine groups can react with many different organic groups [265] (reactions 2.39). The consequent products such as polynitriles, polyesters, polyamides, and perfluorinated dendrimers have been studied and applied in a variety of fields.

(2.39)
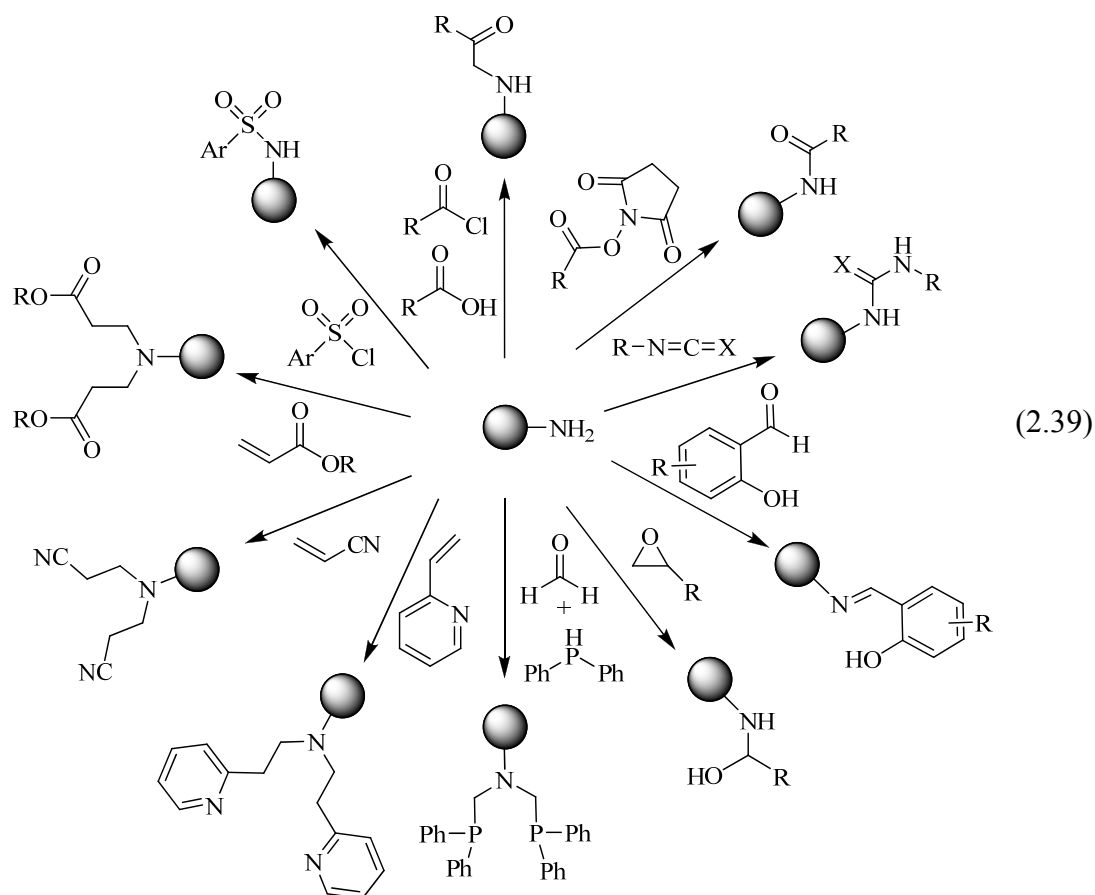
2.3.3.2 Chain End and Branch Point Modification (Complete Modification)

In addition to modification of the exterior, it is also possible to modify the interior of PPI-dendrimers by quaternizing the internal tertiary amines to generate multiple cationic ammonium sites. Elissen-Roman has presented complete quaternization of PPI dendrimers (modified at the exterior and quaternized at interior) [266-268]. Meijer and coworkers also introduced several PPI dendrimers modified at both the exterior and the interior with the aim to make water soluble, hydrolytically stable and non-toxic transfection agents [269].

In the work, the end groups of PPI dendrimers were modified with acetyl or with triglycol gallate (PEG-like) groups which keep water solubility and produce non-

toxic species. The PPI dendrimers were modified at the interior by reacting internal tertiary amines with methyl iodide to construct a micro-environment with multiple quaternary charge sites. The number of charge sites is between 2 and 60 with the variation of dendrimer generation. The higher local concentration of charge (cationic) sites means the better capability of forming complexes with DNA and other multi-anionic species such as RNA.

2.3.3.3 Core and Branch Point Modifications (Interior Modifications)

Due to greater steric hindrance and less reactivity than the chain ends, core and branch point modifications are not as common as chain end modifications. Because the properties of dendrimers are mainly determined by the end groups, core and branch point modifications are less attractive. In order to successfully internally modify dendrimers, chain end reactions should be blocked by using protecting groups to make internal sites selectively available or prepare the PPI dendrimers by using a new amine source.

2.3.4 Applications of Dendrimers

Due to their structural features such as high branches, symmetry, globular shape, dendrimers have potential applications in a wide range of areas. These include drug delivery, molecular recognition, [253] chemical sensors, medical diagnostic agents, high-performance polymers, catalysts, [270] and building blocks of supermolecules, just name a few. There are many review articles [250, 271, 272] and books [246, 264] published since the first report of successful synthesis of dendritic molecules.

PAMAM and PPI dendrimers and their derivatives have been studied as potential transfection agents for gene delivery, because this kind of dendrimers are positively charged and can bind DNA in a physiological environment [269]. For instance, plain and quaternized PPI dendrimers favored to target gene to the liver [268].

However, their toxicity in cell cultures, their binding capabilities to DNA and their transfection efficiency are big concerns. According to Malik et al. [273], the terminal or surface groups of dendrimers determine the toxicity of the overall dendritic structure; therefore it is very promising to chemically modify the surface of dendrimers to create delivery systems with low toxicity, good water solubility, and

improved hydrolytic stability [269].

PAMAM and PPI dendrimers have been employed as cross-linking agents to modify the commercially available polyimides [274-276]. Sirkar and co-workers [277] opened a new door of research and development of dendrimer-modified membrane materials. They developed a high-performance CO_2 selective poly(vinylidene fluoride) flat membrane by using PAMAM as a carbon dioxide selective molecular gate.

Dendrimers are promising materials for hosting catalytically active metal nanoparticles for the following reasons: (1) fair uniformity of composition and structure, (2) excellent stability of the nanoparticles by encapsulation without agglomeration during reactions, (3) good retention of the nanoparticles by steric effects with metal active surface, (4) good flexibility of the dendrimer periphery to tailor solubility of the nanocomposite, and (5) the outstanding ability of the branches to selectively control the access of small molecules to the encapsulated nanoparticles. These materials have been demonstrated to be very good homogeneous catalysts for the electrochemical reduction of oxygen [278-282].

Dendrimers can be artificial light-harvesting systems because of their unique structures: (1) an energy gradient for the funneling process because of tree-like structure, (2) the number of peripheral absorbing units that grows exponentially with increasing generation, and (3) the relatively short distance between the core and the periphery [283]. One example of photonic molecular assemblies in which light absorption is followed by nearly quantitative energy transfer have been reported by Moore and coworkers [284]. They reported that energy was transferred through the dendrimer to a core chromophore in a host-guest system.

Dendrimers are significantly different from linear polymers. They have numerous beneficial properties, such as variable size and conformation, high structural and chemical homogeneity, high functionality and binding density, as well as controllable degradation; therefore, it is expected those unique properties should be used in a variety of applications.

2.4. Poly(ethylene oxide)

PEO is a water-soluble, thermoplastic polymer produced by the heterogeneous polymerization of ethylene oxide [285]. The white, free-flowing polymer is synthesized by the following reaction:

$$\text{ethylene oxide} \xrightarrow{\text{catalyst}} \text{poly(ethylene oxide)} \qquad (2.40)$$
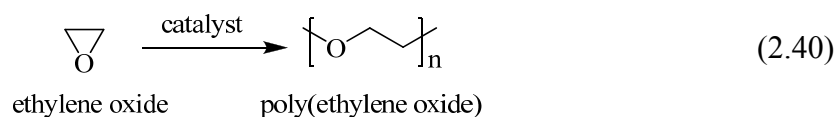
PEO is available in a broad range of molecular weight grades, from as low as 100 to over 7×10^6. Although most commonly known as PEO, they are occasionally referred to as poly(ethylene glycol) or polyoxyethylene.

2.4.1. Physical Properties

At molecular weights of 10^5–10^7, PEO forms a highly ordered structure. This has been confirmed by ^{1}H-NMR and X-ray diffraction patterns and by the sharpness of the crystalline melting point (62–67 °C). However, the highest degree of crystallinity (ca 95%) is obtained at a molecular weight of 6000. The polymer chain contains seven structural units per fiber identity period (1.93 nm) [286].

The temperature, T_g, of poly(ethylene oxide) has been measured over the molecular weight range of 10^2–10^7 [287, 288]. These data indicate a rapid rise in the transition temperature to a maximum of −17 °C for a molecular weight of 6000. The highest percentage of crystalline character develops at that molecular weight. Beyond this point, chain entanglement reduces crystallinity.

PEO is completely soluble in water at room temperature. However, at elevated temperatures (>98 °C) the solubility decreases. It is also soluble in several organic solvents, particularly chlorinated hydrocarbons. Aromatic hydrocarbons are better solvents for PEO at elevated temperatures.

Significant use properties of PEO are complete water solubility, low toxicity, and unique solution rheology, complexation with organic acids, low ash content, and thermoplasticity.

PEO is safely used in numerous pharmaceutical and personal care applications. PEO shows low order toxicity in animal studies by all routes of exposure. Because of their

high molecular weight, they are poorly adsorbed from the gastrointestinal tract and are completely and rapidly eliminated [289]. PEO is not skin irritants or sensitizers, nor do they cause eye irritation. Considerable interest has been shown in PEO for diverse applications in food, drug, and cosmetic products.

2.4.2. Irradiation and Crosslinking

Exposure of PEO to ionizable radiation (gamma irradiation, electron beam, or ultraviolet light) can result in molecular weight breakdown or cross-linking, depending on the environmental conditions. If oxygen is present, hydroperoxides are formed and chain scission leads to an overall decrease in molecular weight. However, in the absence of oxygen, cross-linking becomes the preferred reaction [290]. The resulting polymer network exhibits hydrogel properties of high water capacity [291, 292]. Studies of the cross-linking mechanism and structure of the cross-linked polymer indicate that a complex network of cross-linked chains of varying lengths is present [293-296]. When the cross-linking is performed in solution, the cross-links can be both intermolecular and intramolecular; the overall structure of the crosslinked polymer is the combined result of chain scission, intramolecular bonding, and intermolecular bonding.

2.4.3. Uses

Poly(ethylene oxide)s are used in a number of industries and in a variety of end uses [297]. The polymers often are used as additives, and small amounts impart special characteristics to a product.

The end uses include binders for ceramic green ware, wood products and artifact preservation, sizings, adhesives, surfactants, chromatography, water treatment and flocculation, hydrodynamic drag-reduction agents; functional fluids such as metal-working lubricants, hydraulic fluids, drilling fluids, metal-cleaning formulations, and quenchants; flocculants, thermal sportswear, personal care products such as lotions, lipsticks, chopsticks, ointments, shaving creams, adhesives, and skin lubricants; pharmaceutical products such as suppositories, enzyme modifiers, emollients, tablet and specialty coatings, and binders; textile-manufacture products such as dye assistants, antistatic agent additives, fiber lubricants, wastewater flocculants; and

many others. The association complexes briefly described above is used in adhesives, microencapsulation, controlled release of pharmaceuticals, and medical devices.

2.5. Benzoxazines

Benzoxazine chemistry has been discovered around for more than 60 years since the first work reported by Holly and Cope in 1944; [298] however, the use of benzoxazines as precursors for a class of thermosetting phenolic resins with useful mechanical and thermal properties has not been recognized until recently [299, 300]. Polybenzoxazines exhibit (i) near zero volumetric change upon curing, (ii) low water absorption, (iii) for some polybenzoxazines T_g much higher than cure temperature, (iv) high char yield, (v) no strong acid catalysts required for curing, (vi) release of no toxic by-product during curing. Enormous design flexibility which permits tailoring the properties of the cured materials is offered by the molecular structure of polybenzoxazines for wide range of applications [301].

2.5.1. Monomer Synthesis

Benzoxazine monomers are typically synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution method or solventless method. Using various types of phenols and amines, having different substitution groups attached, various types of benzoxazine monomer can be synthesized. These substituting groups can provide additional polymerizable sites and also affect the curing process. In order to obtain polymeric materials, with desired properties, by tailoring the benzoxazine monomer with different functionality and a wide variety of monomers can be synthesized by using appropriate chosen phenol and amine.

2.5.1.1. Mono-functional Benzoxazine Monomers

Holly and Cope [298] first reported the condensation reaction of primary amines with formaldehyde and substituted phenols for the synthesis of well-defined benzoxazine monomers. According to the reported procedure, this reaction was performed in a solvent in two-steps. Later, Burke found that the benzoxazine ring reacts preferentially with the free *ortho* positions of a phenolic compound and forms

a Mannich bridge [302]. The synthetic procedure of the Mannich condensation for benzoxazine synthesis in a solvent proceeds by first addition of amine to formaldehyde at lower temperatures to form an *N,N*-dihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and *ortho* position of the phenol at the elevated temperature to form the oxazine ring [303] (reaction 2.41).

$$2CH_2O + RNH_2 \longrightarrow HO\diagdown\diagup N \diagdown\diagup OH \longrightarrow \quad (2.41)$$
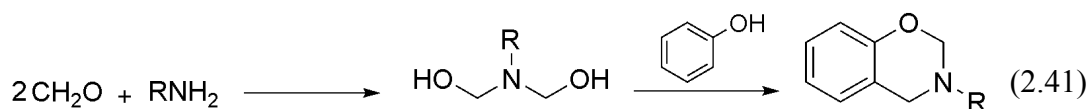
2.5.1.2. Di-functional and Multifunctional Benzoxazine Monomers

Curing of mono-functional benzoxazines with phenol resulted in the formation of only oligomeric structures with average molecular weight around 1000 dalton. Thus, no materials could be made from this approach since the thermal dissociation of the monomer competed with chain propagation reaction so that high molecular weight linear structures were unobtainable [304]. Hemvichian *et al.* have reported that the reduction of reactivity is due to the hydrogen bonding formation. Such phenomenon was observed in the temperature range below where reverse Mannich reaction occurs in benzoxazine chemistry [305]. To overcome this limitation, Ishida and coworkers [306, 307] have developed a new class of difunctional or multifunctional benzoxazine monomers, and their curing into phenolic materials with the ring opening reactions being initiated by dimers and higher oligomers in the resin composition. The main constituent of the resulting products was a monomer with difunctional benzoxazine ring structures at both ends of the bisphenol A. The rest of the composition consisted of a mixture of dimers and oligomers, with both benzoxazine rings and free phenol structures, as detected by ^{1}HNMR, FTIR and GPC. It was observed that, the composition of the products is, to a large extent, dependent on the polarity of the solvent. This synthetic method consists of a few simple steps and can easily provide different phenolic structures with wide design flexibility.

Similar type of difunctional benzoxazine was prepared using aniline instead of methyl amine [308, 309] and the pure monomer was referred as B-a and oligomers were as oligo-B-a. The structures of oligo-B-a and B-a were analyzed by ^{1}H-NMR measurements. The overall synthetic procedure is shown in reaction 2.42 [308]. To

achieve successful processing, cure kinetics of this material was investigated by using DSC, which indicated that the curing of benzoxazine precursors is an auto-catalyzed reaction until vitrification is occurred, and diffusion begins to control the curing process afterwards [309].

(2.42)
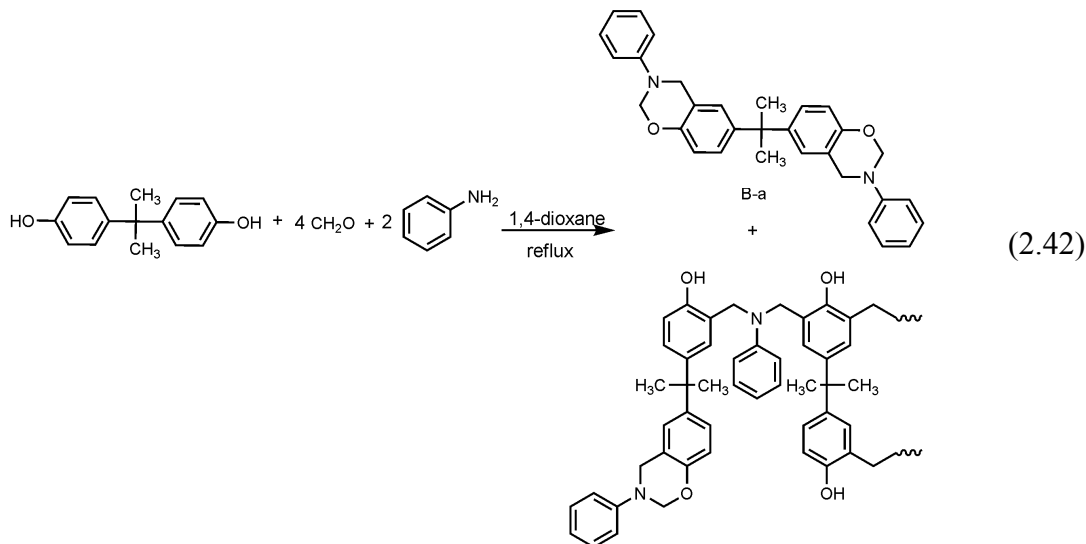
2.5.2. Polymerization of Benzoxazines

To understand the polymerization reaction mechanism of benzoxazines, understanding of the chemical structure of its oxazine ring is very important. A single crystal X-ray crystallographic study revealed that the preferential conformation of a mono-oxazine ring containing benzoxazine is a distorted semi-chair structure, with the nitrogen and the carbon between the oxygen and nitrogen on the oxazine ring sitting, respectively, above and below the benzene ring plane. The resulting ring strain from this molecular conformation helps this type of six-membered ring to undergo ring-opening reaction under specific conditions. In addition, due to their high basicity (by Lewis definition) both the oxygen and the nitrogen of the oxazine ring can act as potential cationic polymerization initiation site and makes the ring very likely to open via a cationic mechanism [310, 311]. The electron charge calculation after energy minimization predicts that oxygen might be the preferred polymerization site over nitrogen due to its high negative charge distribution (O, -0.311; N, -0.270).

The ring opening reaction of the benzoxazine was first reported by Burke and coworkers [303]. In the reaction of 1,3- dihydrobenzoxazine with a phenol, having both *ortho* and *para* position free, it was found that aminoalkylation occurred

49

preferentially at the free *ortho* position to form a Mannich base bridge structure, along with small amount reaction at *para* position. To explain this *ortho* preferency formation of a intermolecular hydrogen-bonded intermediate species was proposed. Riese *et al*. also observed the high reactivity of the *ortho* position when following the kinetics of mono-functional benzoxazines with 2,4-di-*tert*-butylphenol catalyst [304]. The typical method of polymerization of benzoxazine monomers is thermal curing without using any catalyst [309, 312-314]. It should be emphasized that the polymerization mechanism of benzoxazine resins is still not well established.

2.5.2.1. Cationic Polymerization of Benzoxazines

From the investigations on use of various cationic, anionic and radical initiators it has been proposed that the ring opening polymerization of the benzoxazine proceeds through a cationic mechanism [310, 311, 315, 316]. McDonagh and Smith reported that 3,4-dihydro-2H-1,3-benzoxazine exhibits ring/chain tautomerism when protonated, by migration of the proton from the nitrogen to the oxygen atom, and thereby produce iminium ions in the chain form [317]. Ring opening mechanism by protonation of the oxygen atom to form an iminiumion, followed by electrophilic aromatic substitution, as shown in reaction 2.43 was proposed by Dunkers and Ishida [318].

(2.43)
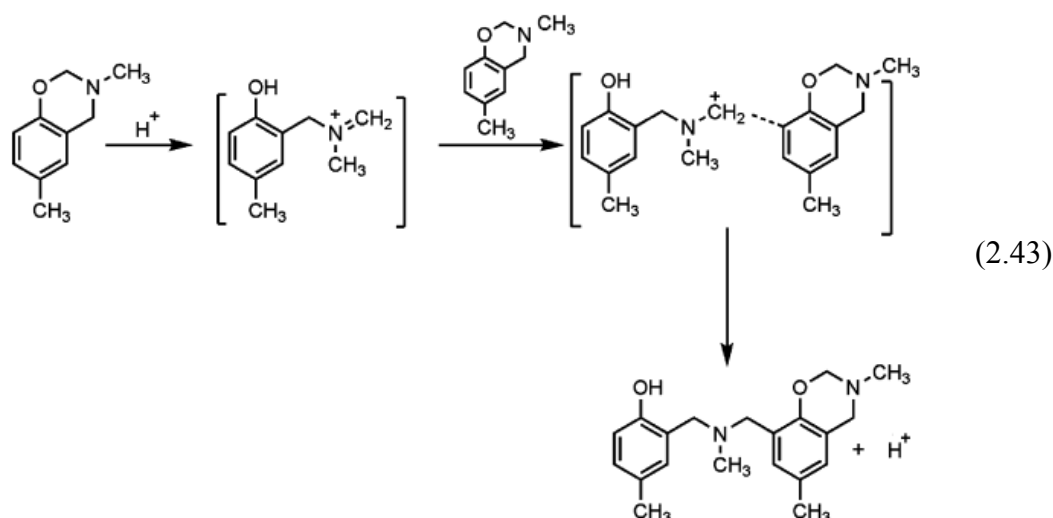
In the presence of strong organic acid, such as trifluroacetic acid, benzoxazine monomer converts to polybenzoxazine immediately at low temperatures after ring opening. The formation of the iminium ion as intermediate was proposed, because trifluoroacetic acid can provide a counter ion, capable of existing in the ionic form rather than the covalent form and can give stability of the intermediate. As the curing

temperature increases, side reactions also took place, which also leads to curing.

But when sebacic acid, a weak acid, was used as catalyst, the polymerization reaction was slow in the early stage of the reaction. The ring opening polymerization of benzoxazines when catalyzed by a weak carboxylic acid was proposed to be an auto-accelerated reaction, where aminomethyl ester species were initially formed as an intermediate.

2.5.2.2. Thermal Polymerization of Benzoxazines

A cross-linked network structured polybenzoxazines, with higher T_g and degradation temperature, can be obtained when difunctional or multifunctional benzoxazines undergo polymerization. The polymeric structures form due to curing of mono-functional and difunctional benzoxazines are shown below in reaction 2.44 and 2.45 [319]. Obviously, difunctional benzoxazines derived from diamines are expected to undergo similar cross-linking [320, 321].

$$(2.44)$$

$$(2.45)$$
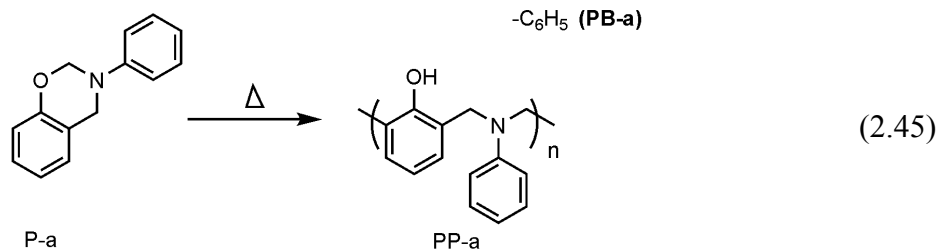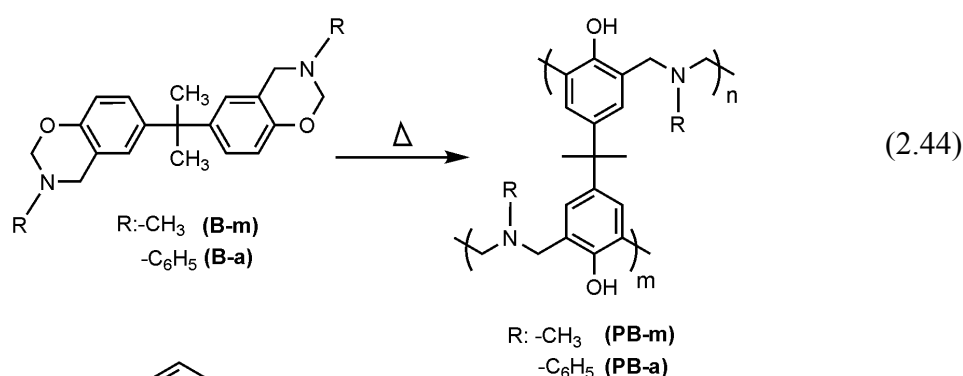
In the DSC thermogram of a mono-functional benzoxazine, P-a, a sharp exotherm was observed with onset and maximum temperatures of the exotherm at 202 and 230 ^{o}C respectively, corresponding to the ring-opening polymerization. The amount of exotherm for benzoxazine was 62 cal/g. In case of difunctional benzoxazine, DSC showed an exotherm on with onset at 223 ^{o}C and maximum at 249 ^{o}C corresponding to the ring-opening polymerization of benzoxazine. The amount of exotherm for bisbenzoxazine was 79 cal/g [319].

3. EXPERIMENTAL WORK

3.1. Materials and Chemicals

3.1.1. Monomers

Styrene (St, 99%, Aldrich)

It was passed through a basic alumina column to remove the inhibitor before use.

Methyl methacrylate (MMA, 99%, Aldrich)

It was passed through a basic alumina column to remove the inhibitor before use.

2-Hydroxyethyl methacrylate (HEMA, 96%, Acros)

It was passed through a basic alumina column to remove the inhibitor before use.

2-(Dimethylamino)ethyl methacrylate (DAEMA, 98%, Aldrich)

It was passed through a basic alumina column to remove the inhibitor before use.

3.1.2. Solvents

Diethyl ether (J.T. Baker)

It was dried with calcium chloride and distilled over sodium wire.

Dichloromethane (J.T. Baker)

It was first washed with conc. sulfuric acid until the acid layer remained colorless, and then with water, followed by another washing with 5% sodium hydroxide (aq.) and finally with water again. It was dried with calcium chloride and distilled over calcium hydride. It was stored over molecular sieves for use as a solvent in the photopolymerization experiments.

Tetrahydrofuran (THF, 99.8%, J.T.Baker)

(a) It was used as eluent for chromatography as received (High Performance Liquid Chromatography Grade).

(b) For use in the chemical reactions, it was dried and distilled over benzophenone/sodium.

n-Hexane (Aldrich)

It was used without further purification.

Acetonitrile (Aldrich)

It was used as received.

N,N-Dimethyl acetamide (Aldrich)

It was used as received.

Methanol (Technical)

It was used for the precipitation of polymers without further purification.

3.1.3. Other Chemicals

Benzophenone (BP, 99%, Acros)

It was used after being recrystallized from ethanol.

Thioxanthone (TX, 97%, Aldrich)

It was used after being recrystallized from ethanol.

2-Chlorothioxanthone (CTX, Ward Blenksop)

It was used after being recrystallized from ethanol.

2-Isopropyl thioxanthone (ITX, Ward Blenksop)

It was used after being recrystallized from ethanol.

Camphorquinone (CQ, 98%, Fluka)

It was used as received.

Triethylamine (TEA, 98%, J.T. Baker)

It was distilled over calcium hydride prior to use.

***N, N*-Dimethylaniline (NDMA, 98%, Fluka)**

It was distilled over calcium hydride prior to use.

Propylamine (PA, 98%, Acros)

It was distilled over calcium hydride prior to use.

***N, N, N', N'*-Tetramethylethylenediamine (TMEDA, 99%, Acros)**

It was distilled over calcium hydride prior to use.

***N,N*-Dimethylethanolamine (DMEA, 99%, Acros)**

It was distilled over calcium hydride prior to use.

Ethanolamine (EA, 99%, Acros)

It was distilled over calcium hydride prior to use.

Poly(propyleneimine) dendrimers (PPI, Aldrich)

Third through fifth generation amine terminated poly(propylene mine) dendrimers (PPI-16, PPI-32 and PPI-64; 16, 32 and 64 for generations 3, 4 and 5, respectively) were used without further purification.

2,2,6,6-Tetramethylpiperidine-N-oxyl free radical (TEMPO, 99%, Aldrich)

It was used without further purification.

Poly(ethylene oxide) (PEO, Hoechst AG, Frankfurt Germany)

PEOs with different molecular weight were used without further purification.

2-(2-Phosphono-ethoxymethyl)-acrylic acid ethyl ester (EAEPA, IVOCLAR VIVADENT AG)

It was used without further purification.

_N,N_-Diethyl-1,3-bis(acrylamido)propane (DEBAAP, IVOCLAR VIVADENT AG)

It was used without further purification.

3.2. Equipment

3.2.1. Photoreactor

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

3.2.2. 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.

3.2.3. Infrared Spectrophotometer (FT-IR)

FT-IR spectra were recorded on a Perkin Elmer FTIR Spectrum One B spectrometer.

3.2.4. UV-visible Spectrophotometer

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

3.2.5. Gel Permeation Chromatography (GPC)

a) Gel permeation chromatography (GPC) analyses were performed with a set up consisting of a Waters 410 Differential Refractometer, a Waters 515 HPLC Pump and an apparatus equipped with three Waters ultrastyragel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min. Molecular

weights were calculated on the basis of a calibration curve recorded with mono disperse polystyrene standards.

b) Gel permeation chromatography (GPC) analyses were measured on a Shimadzu system equipped with a SCL 10A system controller, a LC-10AD pump, a RID-10A refractive index detector, a SPD-10A UV detector and both a PSS Gram30 and a PSS Gram1000 column in series, whereby *N, N*-dimethyl acetamide with 5 mmol LiCl was used as eluent at 1mL/min flow rate and the column oven was set to 60 ^{o}C. The molecular weight and the molecular weight distribution of the prepared polymers were calculated by using poly(methyl methacrylate) standards.

3.2.6. Differential Scanning Calorimeter (DSC)

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

3.2.7. Gas Chromatography Mass Spectrometry (GC-MS)

GC-MS measurements were performed by using Thermo Finnigan Trace DSQ instrument equipped with Zebron ZB-5MS capillary GC column (5% silarylen, 95% polydimethylsiloxane).

3.2.8. Dynamic Light Scattering (DLS)

Dynamic light scattering measurements were done at 25 ^{o}C using Malvern Nano-S particle size analyzer. The PPI-n-PMMA polymers were dissolved in *N,N*-dimethyl acetamide at a concentration of 1 mg/mL. Hundred measurements each having 10 s correlation times were recorded for each sample.

3.3. Preparation Methods

Benzodioxinone and derivatives were kindly synthesized by Volkan KUMBARACI. Their synthesis procedures are given below.

3.3.1. Synthesis of (5-hydroxy-2,2 diphenyl-4H-benzo[d][1,3]dioxin-4-one) (<u>1</u>)

Benzodioxinone compound was synthesized according to the literature procedure

[322]. Thus, to a flask containing 2, 6-dihydroxybenzoic acid (5.0 g, 16 mmol) and 4-4-dimethylaminopyridine (0.192 g, 1.6 mmol), ethylene glycol dimethyl ether (20 mL) and benzophenone (4.37 g, 24 mmol) were added. This solution was cooled to 0 °C under nitrogen followed by the drop wise addition of thionyl chloride (1.74 mL, 24 mmol). The reaction was brought to room temperature and stirred for 18 h after which the volatiles were removed via nitrogen flushing while under vacuum. When the volume was reduced by approximately 50%, the remaining solution was purified by flash chromatography (5/95, ethyl acetate/hexane) and afforded 3.6 g (35%).

^{1}H-NMR (CDCl$_3$): δ= 10.13 (d, J = 4.8, 1H, OH), 7.53−7.62 (m, 4H, Ar), 7.29−7.41 (m, 7H, Ar), 6.64 (d, J = 8.4, 1H, Ar), 6.54 (d, J = 8.4, 1H, Ar).

FT-IR: 3240, 1694, 1633, 1587, 1471, 1342, 1225, 1110, 697 cm^{-1}.

UV (CH$_2$Cl$_2$): λ$_{max.}$, nm (ε, l mol^{-1} cm^{-1}); 327 (3295).

3.3.3. Synthesis of (5-(9-(4-oxo-2,2-diphenyl-4H-benzo[d][1,3]dioxin-5-yloxy) nonyloxy)-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one) (**3**)

Bisbenzodioxinone was synthesized as described previously [324]. The crosslinker bisbenzodioxinone was synthesized by a three-step procedure. First, the phenolic benzodioxinone, 5-hydroxy-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one (**1**), was synthesized as described above. In the second step, it was converted to bromononyl derivative (**2**) by etherification reaction according to the procedure given below:

(3.1)
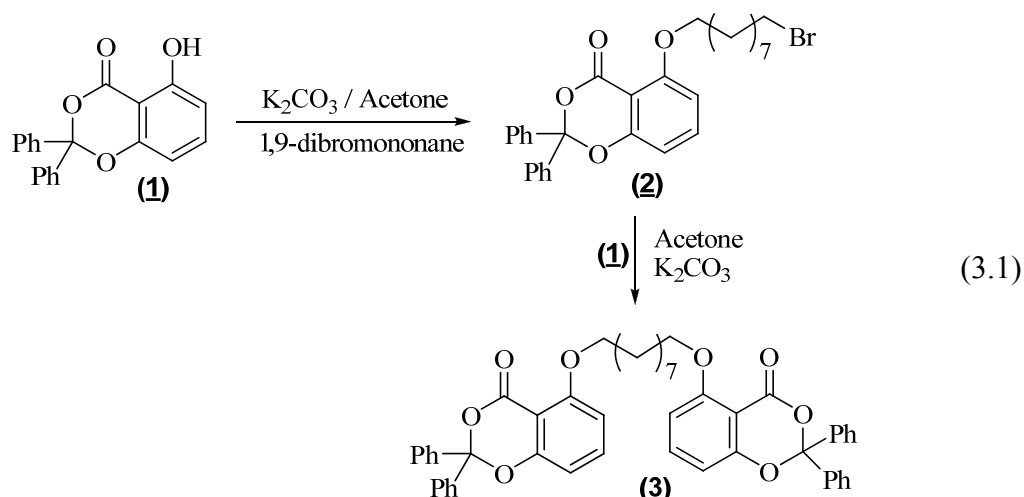
A solution of above obtained benzodioxinone, (**1**), (0.6 g, 1.88 mmol) and anhydrous potassium carbonate (5 g) in acetone (25 mL) were stirred for three hours. After that time, 1,9-dibromononane (2.5 mL, 12 mmol) was added and the mixture was heated

at reflux temperature for 16 hours. The reaction was diluted with ether (100 mL), filtered through a pad of celite, and concentrated on the rotary evaporator. After the volume was reduced to app. 50%, remaining solution was purified by column chromatography (over silicagel 20 % ethyl acetate/hexane) and afforded the desired bromononyl benzodioxinone (**2**) 0.7 g (71%).

^{1}H-NMR (CDCl$_3$): δ= 7.59-7.58 (dd, *J=8.1*, J=2.3, 4H, Ar), 7.56-7.55 (m, 1H, Ar), 7.38-7.28 (m, 6H, Ar), 6.72-6.69 (d, *J=8.1*, 1H, Ar), 6.50-6.47 (d, *J=8.3*, 1H, Ar), 3.95 (t, *J=6.7*, 2H, CH$_2$O), 3.39 (t, *J=6.6*, 2H, CH$_2$Br), 1.86-1.64 (m, 4H, CH$_2$), 1.43-1.25 (m, 10H, CH$_2$).

In the final step, similar etherification procedure was applied. For this purpose, a solution of above obtained bromononyl derivative of benzodioxinone (**2**), (0.6 g, 1.88 mmol) and anhydrous potassium carbonate (5 g) in acetone (25 mL) were stirred for three hours. After that time, phenolic benzodioxinone (**1**), (0.7g, 1.33 mmol) was added and the mixture was heated at reflux temperature for 16 hours. The reaction was diluted with ether (100 mL), filtered through a pad of celite. Acetone was removed on the rotary evaporator, after that residue washed with petroleum ether, then remaining residue was purified by column chromatography (over silicagel 20 % ethyl acetate/hexane) and afforded bisbenzodioxinone (**3**), 0.6 g (59%) m.p.;138-141 °C.

^{1}H-NMR (CDCl$_3$): δ= 7.59-7.58 (dd, *J=8.1, J=2.3*, 8H, Ar), 7.41-7.28 (m, 10H, Ar), 6.72-6.69 (d, *J=8.3*, 2H, Ar), 6.52-6.49 (d, *J=8.7*, 2H, Ar), 3.96 (t, J=6.7, 4H, CH$_2$O), 1.86-1.74 (m, 4H, CH$_2$), 1.43-1.22 (m, 10H, CH$_2$).
^{13}C-NMR (CDCl$_3$): 160.2, 156.9, 138.8, 135.4, 127.9, 127.7, 127.6, 127.4, 125.4, 107.9, 105.8, 104.7, 103.6, 68.5, 68.3, 52.7, 30.7, 28.3, 28.2, 28.0, 27.7, 24.6
FT-IR: 3059 (w, phenyl), 2927-2853 (s, Aliphatic), 1749 (vs, C=O), 1608 (s, C=C), 1508 (s, C=C), 1247 (vs, C-O), 1083 (vs. O-C-O), 694 (vs, C=C) cm^{-1}.
UV (THF): λ$_{max}$., nm (ε, l mol^{-1} cm^{-1}); 318 (8780), 256 (10760), 232 (15180).

3.3.4. Synthesis of 7-(2-bromoethoxy)-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one (5)

The model compound 7-(2-bromoethoxy)benzodioxinone (**5**) was synthesized by a two-step procedure. First, the phenolic benzodioxinone, 7-hydroxy-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one (**4**), was synthesized. In the second step, it was converted

to bromononyl derivative by etherification reaction according to the procedure given below:

$$(3.2)$$
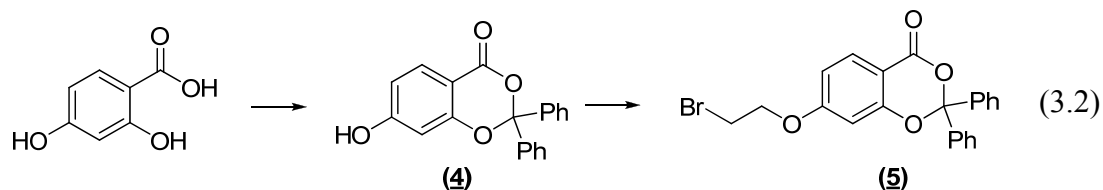
Trifluoroacetic acid (12 mL) and trifluoroacetic anhydride (10 mL) mixture was added to a round bottom flask containing 2,4- dihydroxybenzoic acid (2.5 g, 16.2 mmol, 1 eq) and benzophenone (4.4 g, 24.4 mmol, 1.5 eq) at 0°C, under nitrogen. The reaction was warmed to room temperature and then stirred for 24 h. The slightly yellow homogeneous mixture was concentrated and the residue was dissolved in toluene (40 mL) and concentrated again. This operation was repeated 3 times. The crude residue was purified by column chromatography. (silicagel, 30 % ethyl acetate/hexane) to yield 0.9 g (17 %). m.p.:63-65 ^{o}C.

^{1}H-NMR (CDCl$_3$): δ= 10.43 (s, 1H, OH), 7.60-7.54 (dd, J=7.4, J=1.4, 4H, Ar), 7.35-7.31 (m, 6H, Ar), 7.71 (d, J=8.7, 1H, Ar), 6.63 (s, 1H, Ar), 6.52 (d, J=8.6, 1H, Ar).
FT-IR: 3230, 2975, 1687, 1612, 1594, 1491, 1447, 1240, 1121, 960, 750 cm^{-1}
 UV (CH2Cl2): λ$_{max.}$, nm (ε, l mol^{-1} cm^{-1}); 303 (8932), 263(18470), 229 (21869).

In the final step, similar etherification procedure was applied. A solution of benzodioxinone (**4**) (0.7 g, 2.2 mmol) and anhydrous potassium carbonate (5 g, 36.2 mmol) in acetone (25 mL) were stirred for three hours. After that time, 1,2-dibromoethane (0.6 mL, 6.6 mmol) was added and the mixture was heated at reflux temperature for 16 hours. The reaction was diluted with ether (100 mL), filtered through a pad of celite, and concentrated on the rotary evaporator. After the volume was reduced to app. 50%, remaining solution was purified by column chromatography (over silicagel 30 % ethyl acetate/hexane) and afforded the desired bromoethoxy benzodioxinone (**5**). Then, 7-(2-bromoethoxy)-benzodioksinone (2) recrystallized from carbon tetrachloride to yield 0.2 g (21%). m.p.:143-145 ^{o}C.

^{1}H-NMR (CDCl$_3$): δ= 7.76 (d, J=8.7, 1H, Ar), 7.59 -7.56 (m, 4H, Ar), 7.36-7.31 (m, 6H, Ar), 6.62 (s, 1H, Ar), 6.57 (d, J=8.6, 1H, Ar), 4.31 (t, J=6.2, 2H, CH2O), 3.63 (t, J=6.1, 2H, CH2 Br).
FT-IR: 3059, 2920, 1723, 1615, 1581, 1444, 1263, 1165, 959, 760 cm^{-1}
 UV (CH2Cl2): λ$_{max.}$, nm (ε, l mol^{-1} cm^{-1}); 296 (5110), 263(13122), 229 (20055).

3.3.5. Synthesis of Benzoxazine (P-a)

The general procedure is as follows [307]; 18.6 g (0. 2 mol) aniline is added slowly to the flask containing 12.0 g (0.4 mol) *p*-formaldehyde, keeping the temperature below 10 °C in ice bath. The mixture is stirred for 10 min, 18.8 g (0.2 mol) phenol is added to the mixture. Then the flask heated up to 100 °C for one and half an hour. The content of the flask is dissolved in ethyl ether. The ether solution was washed several times with 1 N sodium hydroxide solution and deionized water, respectively. Organic layer was dried with anhydrous sodium sulfate and diethyl ether was evaporated to yield light yellow viscous liquid. Solid product was formed after applying vacuum at 50 °C in 24 h. (Yield: 65%)

3.3.6. Synthesis of Naphtoxazine (N-a)

The general procedure is as follows [325]; a 100 ml round-bottomed flask, equipped with magnetic stirrer and a reflux condenser, placed in ice bath, was charged with *p*-formaldehyde (0.03 mol) and aniline (0.015 mol). 2-Naphthol (0.015 mol) was subsequently added to the mixture. The flask is then placed in an oil bath which is heated to 110 °C and the mixture was maintained at that temperature for 3 h. At the end of the reaction the mixture was diluted with dichloromethane and washed successively several times with 0.1 N sodium hydroxide and diluted acetyl hydroxide solution. It was, then neutralized with distilled water. Organic layer was dried with anhydrous sodium sulfate and dichloromethane was evaporated to yield naphtoxazine. (Yield: 56%)

3.3.7. Synthesis of Bisbenzoxazine (B-a)

Synthesis of bisbenzoxazine was performed as follows [306]; to 100 mL of 1,4-dioxane, aniline (40.0 mmol, 3.72 g), 4,4'-Isopropylidenediphenol (40.0 mmol, 9.13 g), and *p*-formaldehyde (160 mmol, 4.80 g) were added and refluxed for 3 days. The reaction mixture was filtered and 1, 4-dioxane was evaporated under vacuum. Resulting oily product was dissolved in chloroform and washed five times with 40 mL 0.1 N sodium hydroxide aqueous solution and distilled water, respectively. Then, the chloroform solution was dried with anhydrous sodium sulfate. Removal of solvent by evaporation afforded orange yellow oil. (Yield: 60%)

3.3.8. General Procedure for Photopolymerization

Monomer (MMA) either in bulk form or in solution with dichloromethane, sensitizer (benzophenone, thioxanthone or camphorquinone), and coinitiator (benzoxazine, PPI dendrimer or PEO) were put into a Pyrex tube, degassed with nitrogen, and irradiated at room temperature in a photoreactor (Rayonet) equipped with 16 lamps and emitting light nominally at 350 nm. In the case of sensitization with thioxanthone and benzoxazine coinitiator, a cupric sulfate aqueous solution was used as the photofilter in order to avoid the absorption of benzoxazine. At the end of irradiation, the content of the tube was dissolved in dichloromethane followed by precipitation in 10-fold excess methanol. Finally, the solid polymer was collected by filtration and dried overnight at reduced pressure. Conversions were determined gravimetrically.

3.3.9. Real-Time Infrared Spectroscopy Studies of Photopolymerization

Typical procedure: A solution of bisbenzodioxinone (5 mM), 2-hydroxyethyl methacrylate (HEMA, 4000 mM) and triethyl amine (TEA 15 mM) or 2-dimethylamino ethyl methacrylate (DAEMA, 15 mM) in 1 mL dichloromethane were put in sodium chloride window with dry nitrogen.

The samples were placed in the compartment of a Fourier transform infrared spectrometer and were simultaneously exposed to a UV photolyzing light and an IR analyzing light beam. The photolyzing light was generated by a Rayonet merry-go-round photoreactor equipped with 16 lamps emitting nominally at $\lambda > 300$ nm with a light intensity of 3×10^{-3} mW cm^{-2} as measured by Delta ohm HD-9021 power meter. At the end of the given time, cross-linked polymers were recovered by removing solvent under reduced pressure.

3.3.10. Photo-DSC Studies of Polymerization

Photo-DSC was conducted on a modified Perkin Elmer Diamond DSC equipped with a home-made aluminum cylinder. UV light (320–500 nm) was applied by a light guide (OmniCure Series 2000) with a light intensity of 18.40 mW·cm^{-2} at the level of the surface of the cured samples. The mass of the samples was 8 mg, and the measurements were carried out in an isothermal mode at 30 $^{\circ}$C under a nitrogen flow

of 20 mL·min^{-1}.

A dental primer formulation consisting of 40% EAEPA [molecular weight of EAEPA = 238 g·mol^{-1}, theoretical enthalpy of EAEPA (ΔH_{0E}) = 62,900 J·mol^{-1}], 20% DEBAAP [molecular weight of DEBAAP = 238 mol·g^{-1}, theoretical enthalpy of DEBAAP (ΔH_{0D}) = 120,600 J·mol^{-1}], and 40% water was used as a standard resin. The mass of the samples was 7.5 ± 0.5 mg, and a PI concentration of 0.022 mmol·g^{-1} CQ was used for standard conditions. In all cases, an equimolar amount of a co-initiator was used.

3.3.11. Photografting of 7-(2-Bromoethoxy)-benzodioxinone onto Poly(hydroxymethyl methacrylate-*co*-methyl methacrylate)

Typical procedure: A solution of 7-(2-bromoethoxy)-benzodioxinone (35 mM) and P(HEMA-*co*-MMA) which synthesized as described previously[324] (33 g/L) in dichloromethane were put in pyrex tube and filled with dry nitrogen prior to irradiation from photoreactor equipped with 16 lamps emitting nominally at λ > 300 nm. At the end of given time, modified copolymers were recovered by precipitation of the irradiated solutions into 10-fold excess hexane and dried in vacuum.

3.3.12. Model Study of Capping Photochemically Generated Radicals onto Dendrimer with TEMPO Radical and Subsequent Nitroxide Mediated Polymerization

Photosensitizer (benzophenone, 0.03 g, 75×10^{-3} mol L^{-1}) in CH$_2$Cl$_2$ (2 mL) solution, hydrogen donor (dendrimer (PPI-16), 0.08 g, 2.5×10^{-3} mol L^{-1}) and TEMPO (75×10^{-3} mol L^{-1}) were put into a Pyrex tube, degassed with nitrogen and irradiated in the absence of monomer for 1.5 h at room temperature. The residue was purified by pouring the dendritic TEMPO intermediate in CH$_2$Cl$_2$ into *n*-hexane three times. This way, the low molecular weight by-products and the remaining TEMPO and benzophenone were removed. After drying in a vacuum oven at room temperature for 24 h, dendritic TEMPO intermediate was obtained in 81% yield. In the subsequent step, dendritic TEMPO intermediate (0.04 g, 3×10^{-3} mol L^{-1}) in DMSO (1 mL), monomer (St, 1 mL, 4.3 mol L^{-1}) were added into tube and polymerization was carried out at 125 °C for 22.5 h via nitroxide mediated

polymerization. At the end of reaction, the mixture was diluted with THF and precipitated in excess *n*-hexane. The solid was collected after filtration and dried at room temperature in a vacuum overnight. Polymer was obtained in 19% yield.

3.3.13. Model Study of Capping Photochemically Generated Radicals onto Poly(ethylene oxide) with TEMPO Radical and Subsequent Nitroxide Mediated Polymerization

Photosensitizer (BP, 0.028 g, $75 \cdot 10^{-3}$ mol·L^{-1}) in CH$_2$Cl$_2$ (2 mL) solution, hydrogen donor (PEO, 0.27 g, $75 \cdot 10^{-3}$ mol·L^{-1}) and TEMPO (0.024 g, $75 \cdot 10^{-3}$ mol·L^{-1}) were put into a Pyrex tube, degassed with nitrogen and irradiated in the absence of monomer for 1.5 h at room temperature. The residue was purified by pouring the polymeric TEMPO intermediate in CH$_2$Cl$_2$ into *n*-hexane three times. This way, the low molecular weight by-products and the remaining TEMPO and BP were removed. After drying in a vacuum oven at room temperature for 24 h, polymeric TEMPO intermediate was obtained in 75% yield. In the subsequent step, polymeric TEMPO intermediate (0.084 g, 0.022 mol L^{-1}) in dimethyl sulfoxide (1 mL), monomer (St, 1 mL, 4.3 mol L^{-1}) were added into tube and polymerization was carried out at 125 ^{o}C for 18 h via NMP. At the end of reaction, the mixture was diluted with THF and precipitated in excess n-hexane. The solid was collected after filtration and dried at room temperature in a vacuum overnight. Polymer was obtained in 36% yield (M_n = 12500, M_w/M_n = 1.64).

3.3.14. Thermal Curing of Benzoxazine End-functionalized Poly(methyl methacrylate)

A clear solution of 1 g of benzoxazine end-functionalized poly(methyl methacrylate) and 2 g of monofunctional benzoxazine in THF was prepared. This solution was charged into a glass mold. The solvent was evaporated in a preheated air oven (90 ^{o}C), after which the temperature of the oven was increased up to 200 ^{o}C and the sample was left inside for 1 h. The mold was then cooled to room temperature and the sample was removed from the mold.

4. RESULTS AND DISCUSSION

4.1. New Photoinitiating Systems Based on Benzophenone Generation

Benzophenone and its derivatives are the most widely used bimolecular photoinitiators in industry due to their low cost despite their relatively low reactivity and hardness of cured films. Benzophenone combined with tertiary amines is commonly used in curing formulations. In many curing applications of fully formulated mixtures, usually all the initiator is added in the solid form or in a concentrated solution at the beginning of the polymerization and it immediately initiates the polymerization when exposed to the light. This is one of the prerequisite for a rapid curing. However, in turn such formulations may not exhibit a good shelf life due to the initiation on storage.

$$(4.1)$$
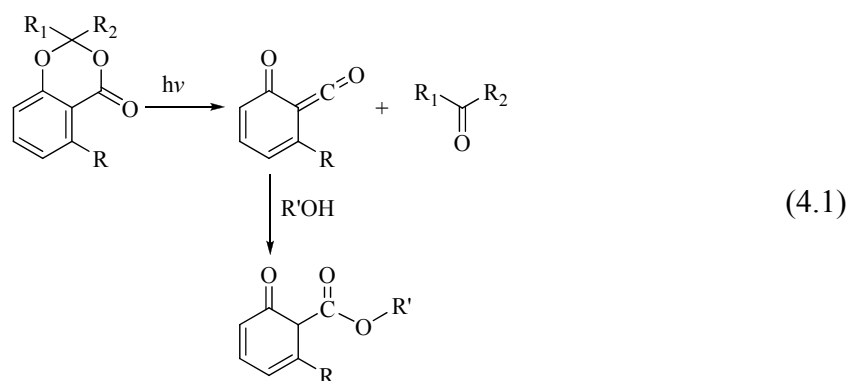
Benzodioxinones are relatively new photosensitive compounds which form salicylate esters when irradiated in the presence of alcohols and phenols (reaction 4.1). The acylation occurs under neutral conditions and is tolerant to a wide range of sterically hindered alcohols [326]. Generation of benzophenone as photoinitiators from benzodioxinones may increase shelf life at the expense of initiation ability. In this system[327], benzophenone, actual photoinitiator, is formed only after photodecomposition of benzodioxinone. The subsequent step is the usual radical formation by the hydrogen abstraction of photoexcited benzophenone from a hydrogen donor such as amines and ethers. It has also been shown that functional

groups of photolysis product can be used in self-cross-linking of monofunctional monomers.

4.1.1. Photochemically Masked Benzophenone: Photoinitiated Free Radical Polymerization by Using Benzodioxinone

A new photoinitiating system for free radical polymerization by using benzodioxinone as photochemically masked benzophenone was presented. For this purpose, first UV spectral change of benzodioxinone on irradiation was investigated. As shown in Figure 4. 1, upon irradiation, the absorption at 325 nm which belongs to the benzodioxinone rapidly diminishes while the absorption at about 360 nm corresponding to benzophenone increases.
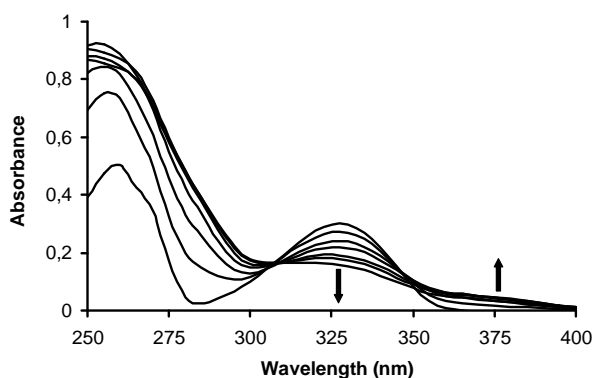
Figure 4.1 Typical UV spectral change of benzodioxinone on irradiation at $\lambda = 350$ nm under nitrogen in CH_2Cl_2.

This was further substantiated by finding that benzophenone is formed during the irradiation of benzodioxinone in CH_2Cl_2. After irradiation the products were analyzed by GC-MS. Figure 4. 2 shows a plot of the benzodioxinone to benzophenone concentrations versus irradiation time.
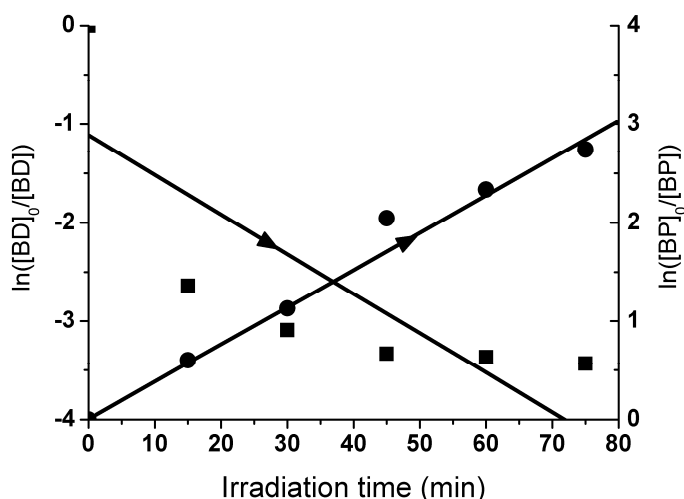
Figure 4.2 Plot of concentration of benzodioxinone (■) and benzophenone (●) vs irradiation time in CH_2Cl_2.

The next question concerns whether benzophenone thus formed undergo reactions on irradiation to generate reactive species and consequently initiate the polymerization. Indeed, methyl methacrylate (MMA) containing benzodioxinone and one of the following compounds; triethylamine (TEA), *N,N*-dimethyl ethanol amine (DMEA), and tetrahydrofuran (THF) is converted into poly(methyl methacrylate) (PMMA) upon irradiation with UV light at $\lambda_{inc.}$ = 350 nm. The excited triplet of benzophenone, which is populated by the successive absorption of the ground state benzophenone formed in the first stage, abstracts hydrogen from the hydrogen donor, i.e., TEA. The carbon-centered radicals stemming from the amine are able to initiate free radical polymerization of MMA (reaction 4.2). α-Amino radicals are especially suitable for the polymerization of acrylates and methacrylates [39].

$$(4.2)$$
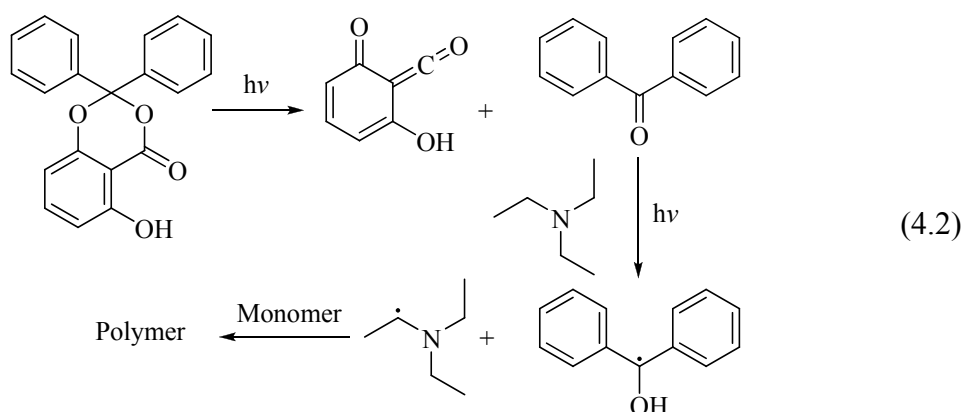
Table 4.1 lists the polymerization results of MMA by using benzodioxinone in conjunction with different hydrogen donors. The results indicate the crucial effect of the hydrogen donors. In the absence of hydrogen donor, polymerization was not

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initiated. It is known [6] that excited carbonyl triplet states are usually by two or three orders of magnitude more reactive toward tertiary amines than toward alcohols and ethers. Thus, TEA and DMEA were found to be very efficient in the generation of the initiating radicals. Notably, another hydrogen donor ethanol amine (EA) is not efficient in the process. This behavior may be explained by less favored hydrogen abstraction from primary amines and the participation of EA in the simultaneous salicylate ester formation. The hydroxyl group of EA reacts with ketene according to the reaction 5 and possible hydrogen abstraction from the alcoholic site is precluded. These reasons may also account for the observed relatively high molecular weight and polydispersity. For comparison, photopolymerizations by using directly added benzophenone in combination with respective hydrogen donors are also included. As can be seen, in the case of TEA, benzophenone system is less efficient while EA readily initiates the polymerization.

Table 4.1 Photoinitiated free radical polymerization of methyl methacrylate at room temperature in CH_2Cl_2 for 120 minute at $\lambda=350$ nm

Run	Photosensitizer[a]	H-donor[b]	Conv. (%)	M_n^c	M_w/M_n^c
1	BD	TEA	18	16500	1.3
2	BD	-	-	-	-
3	BD	DMEA	13	19800	1.4
4	BD	THF[d]	7	33000	1.8
5	BD	EA	1	55700	2.4
6	BP	TEA	7	14900	1.5
7	BP	EA	10	15500	1.3

Acrynonym: BD; benzodioxinone, BP; benzophenone, TEA; triethyl amine, DMEA; *N,N*-dimethyl ethanolamine, EA; ethanol amine, THF; tetrahydrofuran
[a][PS]= 2.5 x 10^{-3} mol L^{-1}
[b][H-donor]= 7.5 x 10^{-3} mol L^{-1}
[c]determined by GPC according to polystyrene standards.
[d]polymerization was performed in neat THF ([THF] = 6.16 mol L^{-1}]).

In this initiating system, benzophenone, actual photoinitiator, is formed only after photodecomposition of benzodioxinone. The subsequent step is the usual radical formation by the hydrogen abstraction of photoexcited benzophenone from a hydrogen donor. Thus, the time between adding the initiator and the actual initiation can be chosen. This circumstance enables such initiators to be applied for curing formulations, where the curing (polymerization or crosslinking) of a coating may be initiated at exactly the time desired and with the curing rate intended.

4.1.2. Photoinduced Cross-linking Polymerization of Monofunctional Vinyl Monomer without Conventional Photoinitiator and Crosslinker

The photoinitiated polymerization of acrylates and methacrylates is one of the most efficient and facile processes for the rapid production of polymeric crosslinked materials, especially materials with tailor-made properties and ambient temperature operations [328, 329]. Therefore, this technique is widely employed in coating industries in which a high demand is put on mechanical properties as well as on the optical properties of the materials. The strategies for photoinduced cross-linking can be broadly classified into two main approaches, (i) one-stage crosslinking of multifunctional monomers or copolymerization with difunctional monomers [330-332], (ii) two-stage cross-linking via prepolymers possesing photosensitive sites. The latter is less used due to the limited number of available photosensitive groups with high cross-linking efficiency. Considerable attention has been given to the polymers with cinnamate [116, 333-336], chalcone [116, 337], stilbene [338-340], maleimide and anthracene [341] pendant groups which undergo photoinduced cross-linking via cycloaddition reactions. Among the acrylic and methacrylic monomers, 2-hydroxyethyl methacrylate (HEMA) receives special interest due to its hydrophilic nature, which in the cross-linked form (hydrogel) provides the possibility to absorb a significant amount of water while maintaining a distinct three dimensional structure (insoluble). Cross-linked polymeric materials prepared from HEMA are widely used for biomedical and pharmaceutical applications. Several techniques have been used to prepare HEMA based cross-linked polymers. All the employed techniques involved either the use of bifunctional comonomers or chemical cross-linking reaction of the linear polymer though the hydroxyl groups present in the structure.

Various photoinitiator systems continue to be developed and investigated for photocuring and crosslinking of monomers and polymer materials. The monomers most widely used for photopolymerization processes are acrylates. The reason is that they polymerize rapidly and, by introducing chemical modifications in the ester group, materials with very different properties may be obtained without sacrifing too much polymerization rate. Methacrylates generally polymerize more slowly but, due to the stiffer main chain, yield harder products. The crosslinked homo and copolymers of HEMA have been widely studied and applied as biomaterials in the form of

homogeneous transparent gels. They are usually prepared in bulk, or in solution polymerization in the presence of free radical initiators and crosslinking agents. In our work, upon irradiation of bisbenzodioxinones, bisketene and the corresponding benzophenone are formed concomitantly. The excited triplet of benzophenone, which is populated by the successive absorption of the ground state benzophenone formed in the first stage, abstracts hydrogen from the hydrogen donors. The carbon-centered radicals stemming from the amine are able to initiate free radical polymerization of HEMA. At the same time, photocrosslinking occurs via inter-chain ester formation through the reaction of bisketene formed simultaneously with hydroxyl groups of HEMA or the corresponding growing polymer as depicted in reaction 4.3.

(4.3)
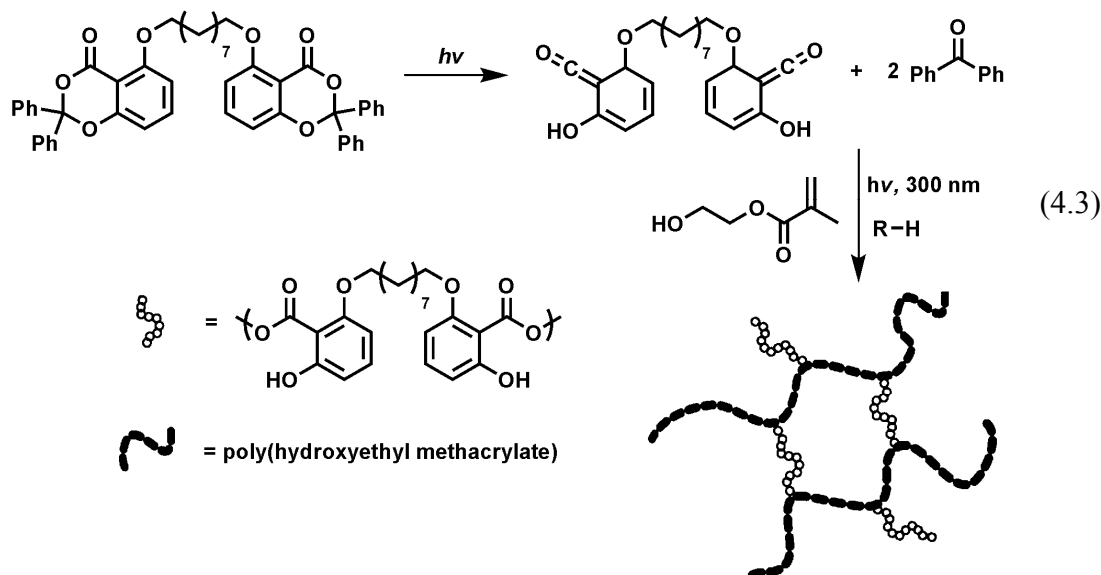
In addition to the visual observation of the viscosity increase and gelation of the dichloromethane solutions containing HEMA and bisbenzodioxinone in the presence of hydrogen donors such as triethylamine (TEA) or 2-dimethylamino ethyl methacrylate (DAEMA) under UV light at $\lambda > 300$ nm, cross-linking reaction was followed by real time FT-IR spectroscopy (Figure 4.3). The reaction profile of the system was monitored by the changes of the intensity of double bond bands. It is found that the intensity of the absorbance peak at 815 cm^{-1} (C=C–H twisting), and 1638 cm^{-1} (C=C stretching) decreases with increasing time of exposure to UV irradiation. Another peak at 1163 cm^{-1} due to (–CO–O– stretching) absorbance is designated as the reference peak for its invariability [342] during photopolymerization. Thus, the percentage of conversion (c) of C=C bond can be calculated according to the following

equation using integrated intensity at 1625 cm^{-1} (using 810 cm^{-1}, similar results can also be obtained):

(c) = 100 x (1- $A_t S_0 / A_0 S_t$)   (Eq:4.1)

where A_t and A_0 are the areas of the 1638 cm^{-1} or 815 cm^{-1} peaks and S_t, S_0 the areas of 1163 cm^{-1} peak at time t, and t=0, respectively. From the results in Figure 4.3, it is obvious that the methacrylate double bonds decrease rapidly.
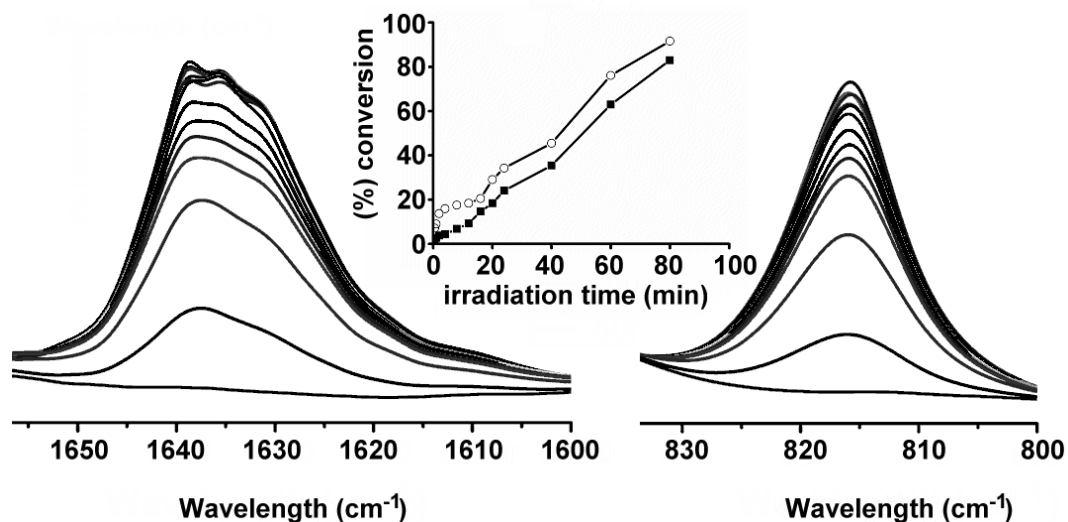
Figure 4.3 Representation of the decrease of the acrylate bands of HEMA at 1638 (a) and 815 (b) cm^{-1} followed by real time FT-IR spectroscopy during photopolymerization. Inner figure: Real time FT-IR kinetic profiles demonstrating the photoinduced polymerization of HEMA initiated by bisbenzodioxinone with triethyl amine (■) or DAEMA (○).

Measuring changes in the characteristic monomer IR absorption bands, allows the direct monitoring of polymerization process continuously. Based on the data calculated by equation 4.1, the conversion curves under polychromatic light, are plotted in Figure 4.3 for the mixture of HEMA and bisbenzodioxinone with two hydrogen donors (TEA and DAEMA). The conversion profiles for both hydrogen donors clearly show that more than 80 % of double bonds undergo polymerization within 80 minutes. It is interesting to note the slightly higher reactivity observed with DAEMA. This is probably due to the fact that DAEMA contains hydrogen donating sites as well as polymerizable methacrylate group. Thus DAEMA both initiates and participates in the polymerization as a co-reactant. This system has the advantage of being the part of the cross-linked network and avoids potential consequences in bio and food packing applications where it is necessary to prevent low molecular weight contaminants from migration.

The polymerization of the mono methacrylate HEMA by the radicals, produced from the photochemical decomposition of benzodioxinone and subsequent hydrogen abstraction, leads to only linear polymers being formed, whereas the bisketenic intermediates, formed in parallel, give rise to the cross-linked structures through ester formation with the hydroxyl groups. This step of the process was also investigated with FT-IR spectroscopy. The reaction of hydroxyl groups was followed by the change of the O-H band at 3600-3200 cm^{-1}. As can be seen from Figure 4.4, where the partial IR spectral changes of the formulation containing benzodioxinone, HEMA and TEA are recorded, the intensity of the band decreased with the irradiation time until 30% of hydroxyl groups are consumed and thereafter leveled off (Figure 4.3). This observations confirm that the cross-linking reaction has taken place with some hydroxyl groups along the poly(hydroxyethyl methacrylate) (PHEMA) backbone formed. It is also noted that there are some hydroxyl groups unreacted which have not been reacted with keten groups. This may be due to the steric reasons as HEMA polymerizes fast and OH groups in the backbone are too close to hinder the access to some of the OH groups, thus preventing ester formation from occurring at all possible sites. However, about 30 % conversion of hydroxyl groups would still yield the desired network formation.
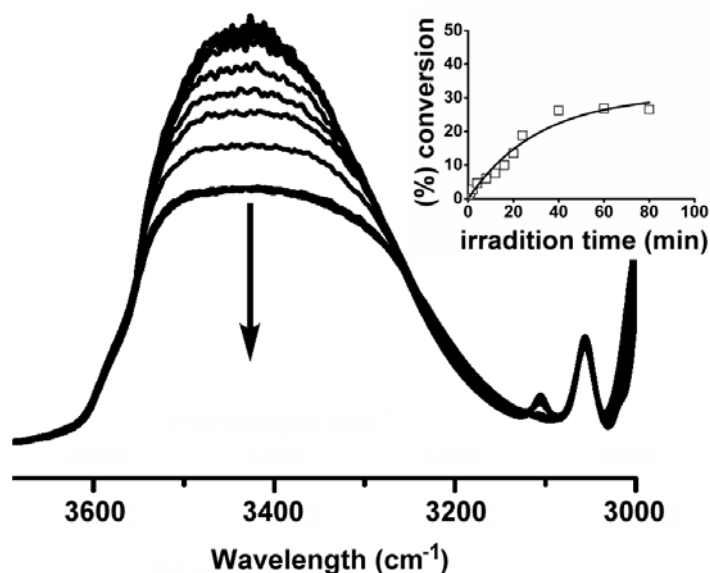
Figure 4.4 Representation of the decrease of the hydroxy bands of HEMA at 3200-3600 cm^{-1} followed by real time FT-IR spectroscopy during photopolymerization

The model compound, namely 7-(2-bromoethoxy)-benzodioxinone has strong structural characteristics and photolysis under similar experimental conditions and

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yields soluble side chain modified polymers which can be analyzed with spectral methods (reaction 4.4).
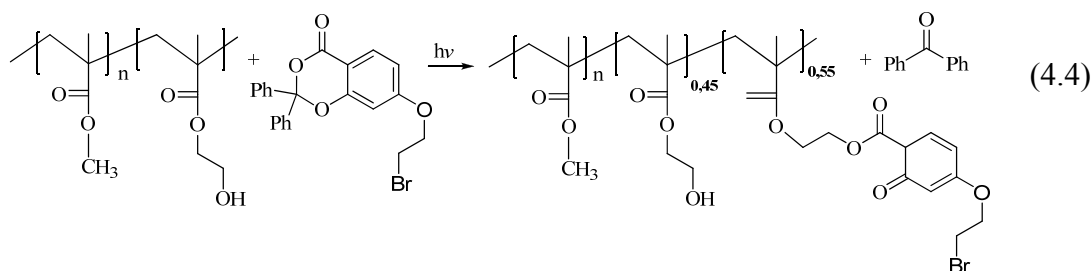
The appearance of the peaks belonging to the aromatic protons at 7-8.2 ppm in the ^{1}H-NMR spectrum of the irradiated polymer is a typical indication for the analogous cross-linking through ester formation (Figure 4.5). Moreover, aromatic ester could clearly be observed in the FT-IR spectrum of the cross-linked polymer (Figure 4.6). The new three bands at 1608 and 1580, and 1655 cm^{-1} observed in IR spectrum of the cured film represents the aromatic and ester groups that exist in the network structure.
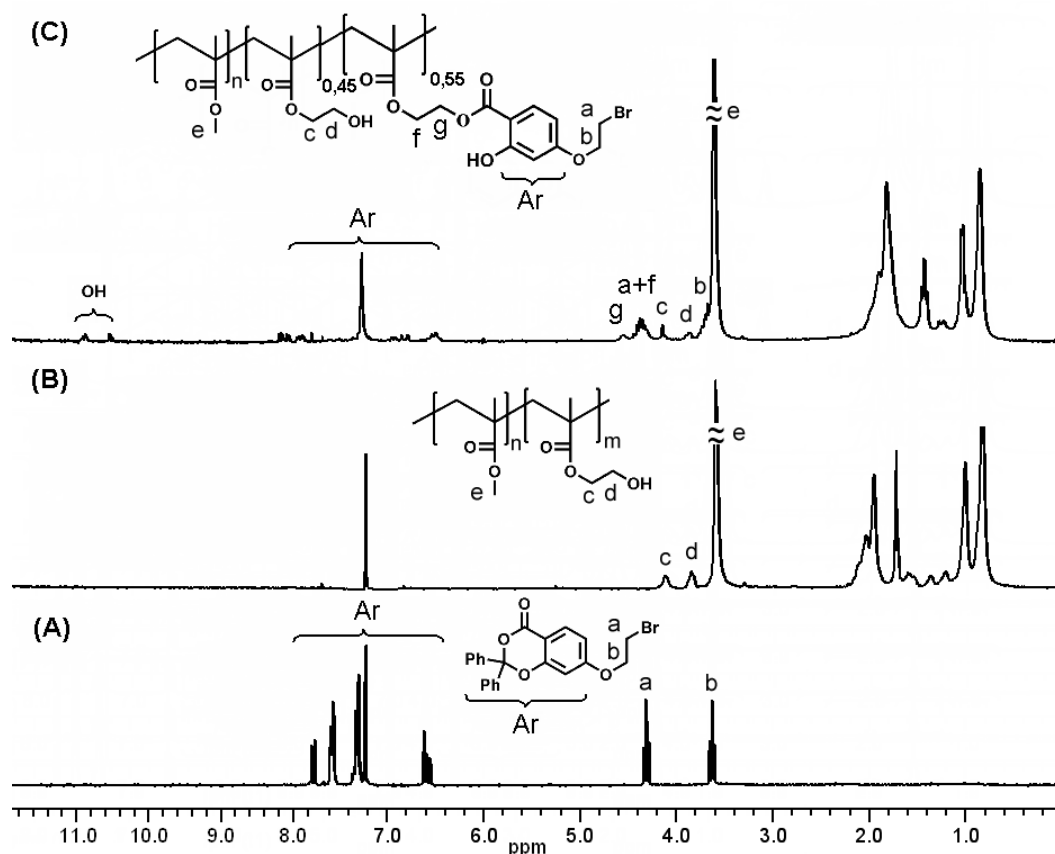
Figure 4.5 ^{1}H-NMR spectra of 7-(2-bromoethoxy) benzodioxinone (A), P(HEMA-co-MMA) copolymer (B) and their photolysis product (C).

A novel photoinduced simultaneous polymerization and cross-linking of monovinyl monomers containing pendant hydroxyl groups by using specially designed

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benzodioxinones have been presented. These molecules have the ability to generate initiating species as well as cross-linking agents that brings out photoinduced polymer network formation. The present method may provide a basis for coating a surface with layers from monovinyl monomers and is potentially useful for the preparation of hydrogels for use in bio applications.
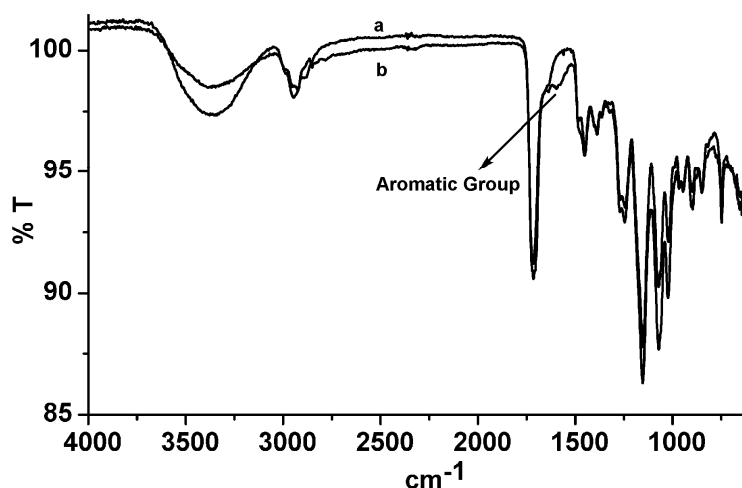
Figure 4.6 FT-IR spectra of homo PHEMA (a) and crosslinked product of photolysis of HEMA and bisbenzodioxinone (b).

4.2. New Photoinitiating Systems Based on Alternative Hydrogen Donors

In curing applications, *Type II* photoinitiators exhibit several disadvantages. This systems concerns high usage of high volatile and odorous amines as hydrogen donors [343]. Much research has been put into the development of alternative hydrogen donors. Polymer-bound tertiary amines have also been developed as low volatile amine [344, 345]. However, they exhibit a lower photoinitiating activity when compared to systems in which non-polymer-bound tertiary amines have been employed [346, 347]. In the second part of thesis, we investigate new photoinitiating systems to demolish these disadvantages by using alternative hydrogen donors, such as, nonvolatile, multifunctional poly(propylene imine) dendrimer and biocompatible poly(ethylene oxide)s. In addition we will also use thermally curable benzoxazine monomer as a hydrogen donor to obtain functional polymers and new materials.

4.2.1. Poly(propylene imine) Dendrimers as Hydrogen Donor in *Type II* Photoinitiated Free Radical Polymerization

Dendrimers are highly branched, well-defined architectures with a number of interesting characteristics [348]. Their nanoscale structures have a variety of potential applications in the fields of coatings, chemical sensors, catalytic nanoreactors, drug delivery systems and liquid crystalline dendrimers [250]. The poly(propylene imine) dendrimer (PPI) was chosen for many reasons, including their high density interior and exterior amine groups [349] they could act as hydrogen donors for *Type II* photoinitiated free radical polymerization.

The use of tertiary amines in *Type II* initiating systems is not limited only to their hydrogen donation capability. They are added to UV-curing formulations also for ameliorating the inhibiting action of atmospheric oxygen. The photoinitiation efficiency of aromatic carbonyl/amine systems is highly dependent on the structures of the amine.
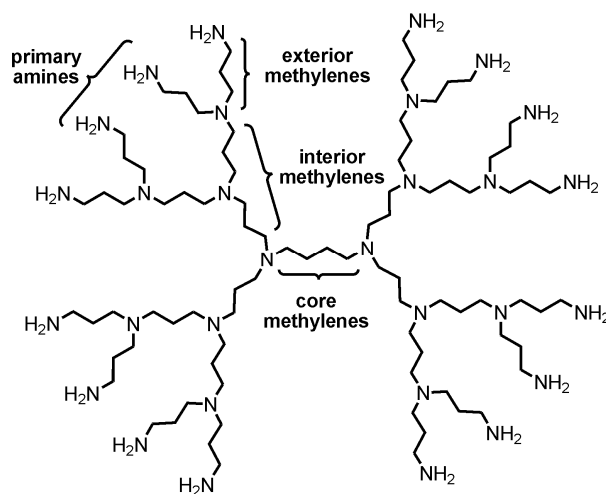
Poly(propylene imine) dendrimers, the periphery of the dendritic unit is filled with primary amine groups, while all the branching points, in the interior of the dendrimer, are occupied by tertiary amine, which are well-known effective quenchers for photosensitizers, via exciplex formation [350-353] (Scheme 2). Recently, Yin et. al. synthesized thioxanthone end functional poly(propylene imine) dendrimer which can initiate methacrylate [354, 355] and acrylamide [356] polymerizations. These investigations did answer the question whether the hydrogen abstraction occurred via intra or intermolecular processes and, whether photoexcited thioxanthone prefers to abstract hydrogen from outer or inner amine methylenes.

Therefore, photopolymerization studies by using externally added aromatic carbonyl compounds in the presence of three generations of PPI dendrimers were performed in order to provide information that would be useful in confirming the efficiency of the initiating system and validity of the proposed mechanism. Additionally, primary amino functions present in the periphery of the dendritic units may also participate in the hydrogen abstraction reactions. This study has been performed with the goal of obtaining information on the influence of the amine structure of the dendrimers that condition the photoinitiation efficiency. The results indicate that methylene hydrogenes adjacent to tertiary amino groups reacts more readily with photoexcited aromatic carbonyl compounds to generate initiating free radicals than with those of the primary amino groups present in the periphery of the dendritic units.

Several experiments on the photopolymerization of MMA in the presence of benzophenone and three different generations of PPI dendrimers were performed. The mechanism involves hydrogen abstraction by the photoexcited benzophenone from exterior methylenes of dendrimer. The carbon centered radicals stemming from these methylenes are able to initiate the free radical polymerization of MMA (reaction 4.5). The results are collected in Table 4. 2. A control experiment in the absence of dendrimer under identical experimental conditions was also carried out. In this case, there was no considerable amount of PMMA precipitated.

(4.5)
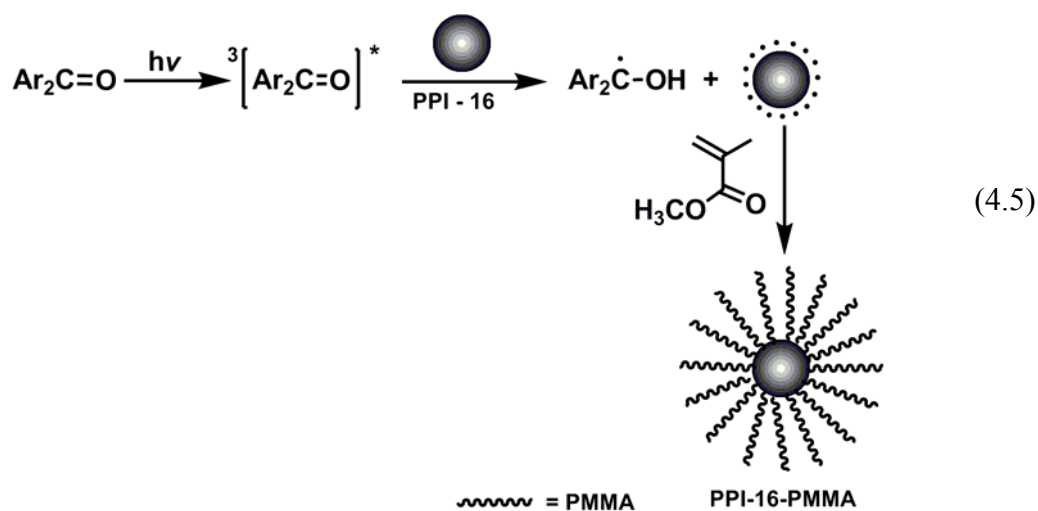
Thioxanthone appeared to be a more efficient photosensitizer and polymers were partially insoluble indicating possible propagating radical interactions within the interior of the dendrimers. For comparison, polymerization with conventionally used linear amines namely, propyl amine (PA), triethyl amine (TEA) and *N,N,N',N'-*

tetramethyl ethylene diamine (TMEDA) were also included. It is interesting to note that dendrimers regardless of the generation number exhibit the higher initiation efficiency as co-initiator than the linear amines in the polymerization under the same experimental conditions. It is also noted that, the conversion of MMA increases in the order of PPI-16 < PPI-32 < PPI-64. The larger local amine concentration accelerate the hydrogen abstraction between the excited state BP and dendrimers to generate a larger amount of radicals, which results in the higher conversion of MMA polymerization. The decrease of the molecular weights of the resulting polymers by the generation numbers is also confirms this statement.

Table 4.2 Photoinitiated free radical polymerization of methyl methacrylate at room temperature in CH_2Cl_2 for 90 minute at $\lambda = 350$ nm

Run	PS^b	$H-donor^c$	Con. (%)	$Mn,_{GPC}{}^a$	Mw/Mn^a
PPI-16-PMMA	BP	PPI-16	26	93600	2.2
PPI-32-PMMA	BP	PPI-32	33	66000	2.8
PPI-64-PMMA	BP	PPI-64	36	66400	3.8
PPI-32-PMMA-TX	TX	PPI-32	43	insoluble	-
TMDEA-PMMA	BP	TMEDA	28	26600	1.7
TEA-PMMA	BP	TEA	22	3700	1.9
PA-PMMA	BP	PA	14	6600	3.1
PMMA	BP	-	-	-	-

^{a} estimated by GPC based on poly(methyl methacrylate) standards.
^{b} [PS]= 75 x 10^{-3} mol L^{-1}
^{c} [H-donor]= 2.5 x 10^{-3} mol L^{-1}

In order to give more insight to the polymerization mechanism, similar photolysis was performed in the presence of a stable radical, 2,2,6,6-tetramethyl-1-piperidinyl-1-oxy (TEMPO), in the absence of the monomer. By utilizing TEMPO in the photolysis, alkoxyamine with TEMPO coupled to dendrimer was synthesized. Hydrogen abstraction between photoexcited benzophenone and methylene groups of the dendrimers yields radicals which are quickly trapped by the nitroxide radicals to give consequently alkoxyamine functional dendrimers as depicted in reaction 4.6. Figure 4.7 gives the ^{1}H-NMR spectra of poly(propylene imine) dendrimer (A) before and (B) after capping with TEMPO. In the ^{1}HNMR spectrum of PPI-16 (Figure 4.7A), there are 6 different peaks, which belong to 11 unique methylenes groups (the exterior methylenes (**9-11**), interior methylenes (**3-8**), core methylenes (**1-2**)), and end functional amine group [357]. After capping with TEMPO, the new proton signals from TEMPO methylenes and methenes appears at 0.8-1.0 ppm (18) and 1.2 ppm (**19**). The exterior methylenes proton signals of dendrimer (**11, 9**) shifted to 3.6-

3.8 ppm clearly (Figure 4.7B) proved that TEMPO moieties were incorporated into the dendrimer. Herein, the reactions of primary amines with the acrylate groups via Michael addition should be considered. However, resulting secondary or tertiary amines may also act as hydrogen donor. Therefore, this side reaction does not bring any disadvantages to system.

$$Ar_2C=O \xrightarrow{h\nu} {}^3\left[Ar_2C=O\right]^* \xrightarrow{PPI-16} Ar_2\dot{C}-OH \; + \quad\quad (4.6)$$

(4.7)

ᴡᴡᴡᴡ = PSt   PPI-16-PSt
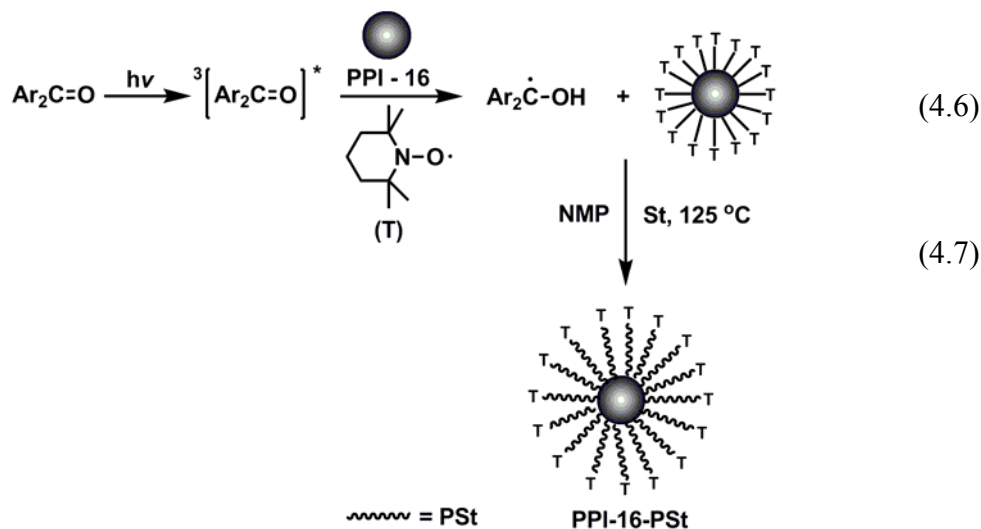
Similar to previous reports [358-361] alkoxyamine incorporated polymers were used successfully as a polymeric initiator for nitroxide mediated radical polymerization of styrene to afford star polymers (reaction 4.7).
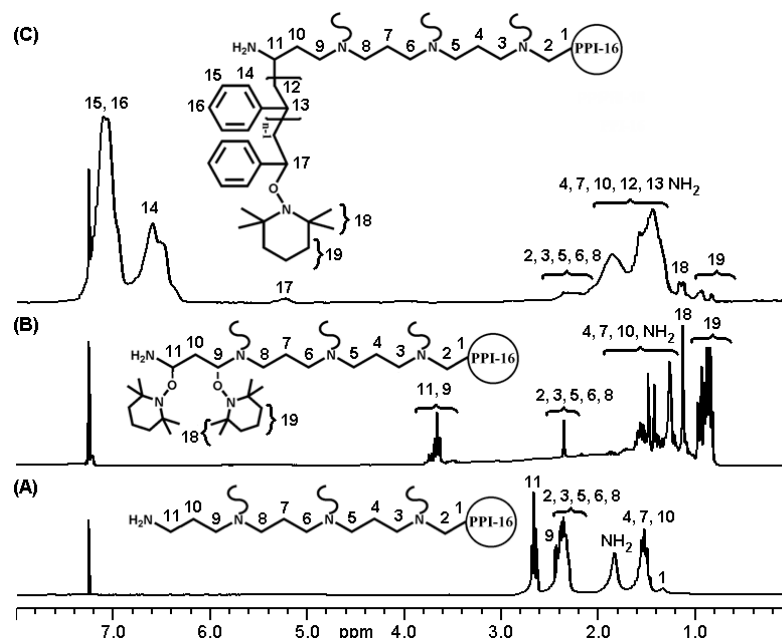
Figure 4.7 ^{1}HNMR spectra of PPI-16 dendrimer (A) after capping with TEMPO (B) and dendrimer-star polymer (C) in CDCl$_3$.

Subsequent bulk polymerization of styrene using above functionalized dendrimer was carried out at 125 °C. The ^{1}H NMR spectrum of the resulting dendrimer-star

polymer (Figure 4.7C) shows that both repeating polystyrene (such as 6.2–7.2 ppm (**14-16**) attributed to the aromatic protons and 1.2-1.8 ppm (**12, 13**) methlyenes and methenes protons) and dendrimer units are present. The exterior methylenes groups (**9, 11**) protons of dendrimer are overlapped with the characteristic signals of the polystyrene. The interior methylenes protons signals of the dendrimer (**2, 3, 5, 6, and 8**) and characteristic protons of the TEMPO group (**18, 19**) are still visible at 2.1-2.3 and 0.8–1.2 ppm. Moreover, the proton from the last unit of the polystyrene block, near the oxygen atom of the TEMPO moiety (**17**), gave a signal that can be identified at 5.2 ppm.

The glass transition temperatures (T_g) of polymers were determined by DSC under a nitrogen atmosphere. It is indicated that the glass transition temperature (T_g) was a function of backbone depending on the structure, the number of end-groups, and the number of crosslinks or branching points. For the dendrimers, the increase in the number of end-groups lowers the glass transition temperature, while the opposite effect was observed with the number of branch points and the polarity of the end group [362-364]. It is well known that homopolymerization by using conventional linear amines yields linear polymers. However, the utilization of dendrimers as hydrogen donor is expected to give branched and star shaped structures as a consequence of the photoinitiation mechanism. As can be seen from Table 4. 3, the T_gs of dendrimer-star polymers are significantly different from those of analogous linear polymers obtained by using conventional amines such TMEDA. Notably, no obvious difference in T_gs of polymers is observed.

Table 4.3 Glass transition temperatures[a] (T_g) of the polymers obtained by using PPI dendrimers and *N,N,N',N'*-tetramethyl ethylene diamine as hydrogen donors in the photopolymerization

Polymer	Hydrogen Donor	T_g (°C)
TMEDA-PMMA	TMEDA	81.5
PPI-16-PMMA	PPI-16	127.7
PPI-32-PMMA	PPI-32	128. 4
PPI-64-PMMA	PPI-64	129.2

[a]Determined by DSC under nitrogen at a heating rate of 10 °C/min.

Particle size measurements by dynamic light scattering (DLS) provided further information on the polymerization. All the polymers independent of the generation number showed two dominant sizes below a particle diameter of 500 nm. The intensities and the sizes corresponding to the DLS peaks scattered in time around an

average value. 100 measurements of 10 s correlation time each were taken for each sample. Figure 4.8 shows the hydrodynamic diameter of the particles as a function of the measurement number for PPI-16-PMMA (#: 1-100), PPI-32-PMMA (#: 101-200) and PPI-64-PMMA (#: 201-300). The average diameter values for the smaller particle sizes (squares) were 20.9 ± 0.5 nm for n = 16, 29.7 ± 1.5 nm for n = 32 and 24.5 ± 1.4 nm for n = 64. The existence of no significant change in these values from 3 to 5 generations indicates that they correspond to the diameter of the individual particles.

The measured hydrodynamic radius values (~10-15 nm) are consistent with the measured molecular weights (66000-94000 g/mole) of the PMMA polymers and indicate that the PMMA chains have partially stretched conformations in N, N-dimethyl acetamide between that of a globule and a fully stretched chain. Although the measured molecular weight of PMMA produced by using PPI-16 was 1.4 times those of the polymers from PPI-32 and PPI-64, no significant increase in the hydrodynamic radius was observed for PPI-16-PMMA. This can be interpreted as smaller tendency for stretching of PPI-16-PMMA chains due to smaller surface density of NH_2 functional groups on PPI-16. This is also consistent with the large scatter in agglomerate sizes for PPI-16-PMMA.
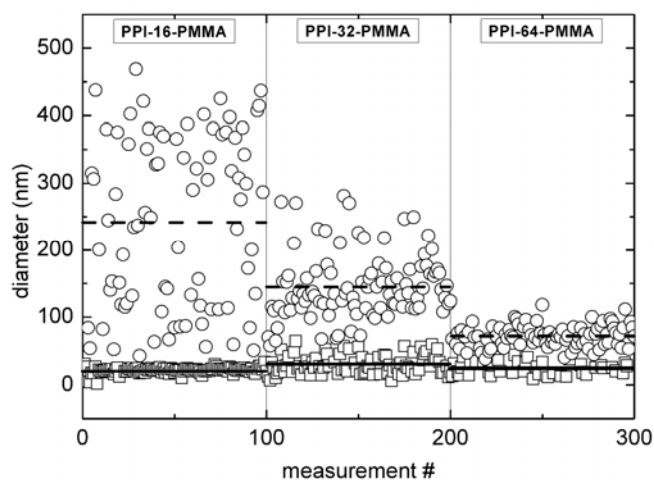
Figure 4.8 Particle diameters as a function of measurement number for PPI-n-PMMA polymers in N, N-dimethyl acetamide. The solid lines indicate the average values.

The average values of the DLS peaks corresponding to the larger particle diameter (circles) were 242.0 ± 14.0 nm for n = 16, 145.8 ± 4.9 nm for n = 32 and 71.7 ± 1.7 nm for n = 64. The significant scattering in the diameter indicates that this peak

corresponds to the agglomeration of the individual particles. Both the scattering of the data and the average diameter values decreased with increasing n from 16 to 64. This is due to the stabilization of the individual particles by the PMMA molecules. Doubling the number of NH_2 functional groups does not change the core diameter of PPI dendrimer significantly (an increase of only 0.4 nm in hydrodynamic radius [365]), but this doubles the surface density of the radicals and thus the surface density of PMMA chains. The repulsive steric interactions of denser PMMA chains prevent the agglomeration of the individual particles into larger aggregates. As a result, while the agglomerate sizes scattered between 45 to 500 nm for PPI-16-PMMA, the scattering range decreased to 40-120 nm in the case of PPI-64-PMMA.

In conclusion, PPI dendrimers can be used as hydrogen donors in *Type II* photoinitiators for free radical polymerization. It was found that their initiation efficiency is better than those of conventional amines such as TMDEA. Based on the model studies by using a radical scavenger, the hydrogen abstraction occurs from the tertiary amino groups present in the interior. *T*g and particle size determination of the resulting polymers revealed the presence of nearly stretched polymer chains around the dendrimers.

4.2.2. The Use of Poly(ethylene oxide) as Hydrogen Donor in *Type II* Photoinitiated Free Radical Polymerization

PEO and its derivatives are finding a rapidly expanding range of chemical, biomedical applications resulting from their low cost and useful properties, such as solubility in aqueous and organic solvent [366]. Recently it has been shown that PEO films can be effectively cross-linked in the solid state or aqueous solution by UV irradiation in the presence of photoinitiators such as benzophenone [367, 368]. Cross-linked polymer based on PEO form an essential class of new materials with number of applications, such as drug delivery system, membranes, wound dressing. In this section, we investigated the possibility of using PEO as latent hydrogen donor for photoexcited aromatic carbonyl compounds further expanding the hydrogen donation concept to polymeric structures.

In a previous study [369] PEO-macroinimer (*macro*molecule-*ini*tiator-mono*mer*) of the following structure, possessing both polymerizable and radical generation sites

was used for the formation of hydrogels of various swelling capacities and moduli of elasticity.
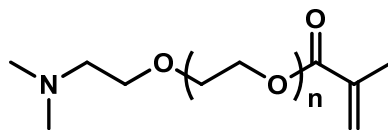
Hydrogen abstraction from one of the methyl groups adjacent to the amino group by a photoexcited benzophenone molecule [370, 371] leads to the formation of macroinimer and ketyl radicals, where the latter radical is known to undergo radical coupling and is thus, ineffective in initiating the polymerization reactions. It became evident that the hydrogen abstraction also occurs from PEO itself without the requirement of additional hydrogen donors. Thus, a portions of the initially difunctional macroinimer becomes trifunctional as a result of the hydrogen abstraction reaction from either terminal amino groups or PEO backbone, which seems to be responsible for the formation of an infinite network in the reaction system.

Table 4.4 Comparison of initiator efficiency in photoinitiated free radical polymerization of MMA[a]

Run	PS	[PS] mol×L^{-1}	[PEO][b] mol×L^{-1}	Conversion (%)[c]	M_n[d]	M_w/M_n[d]
P-1	BP	$5×10^{-3}$	$5×10^{-3}$	47	58800	1.9
P-2	BP	$5×10^{-3}$	$10×10^{-3}$	30	48000	1.8
P-3	BP	$10×10^{-3}$	$5×10^{-3}$	50	46000	1.8
P-4	TX	$5×10^{-3}$	$5×10^{-3}$	31	53700	2.5
P-5	ITX	$5×10^{-3}$	$5×10^{-3}$	46	55600	2.0
P-6	BP	$5×10^{-3}$	-	-	-	-

[a]polymerization time =90 min.
[b]M_{nPEO} =1800, M_w/M_n =1.06
[c]overall MMA conversion
[d]estimated by GPC based on polystyrene standards.

These observations prompted us to perform independent detailed investigations to confirm hydrogen abstraction reactions between photoexcited various aromatic carbonyl compounds acting as *Type II* photoinitiators and PEO. Thus, PEO with various molecular weights was used as a hydrogen donor for the polymerization of MMA in the presence BP. The results are compiled in (Table 4.4). For comparison, photopolymerizations by using either TX or ITX are also included. As can be seen, BP is not an efficient photoinitiator in the absence of the co-initiator, PEO. The presence of PEO is important for effective photoreduction and photopolymerization.

As can be seen from the data presented in Table 4.5, the chain length of the PEO affects the overall conversion of MMA. When the molecular weight of PEO is increased, the conversion decreases significantly which may be attributed to the limited mobility. The interaction of photoexcited sensitizer with hydrogen donating PEO is suppressed at more viscous media. The overall reaction pathway is depicted in reaction 4.8.

(4.8)
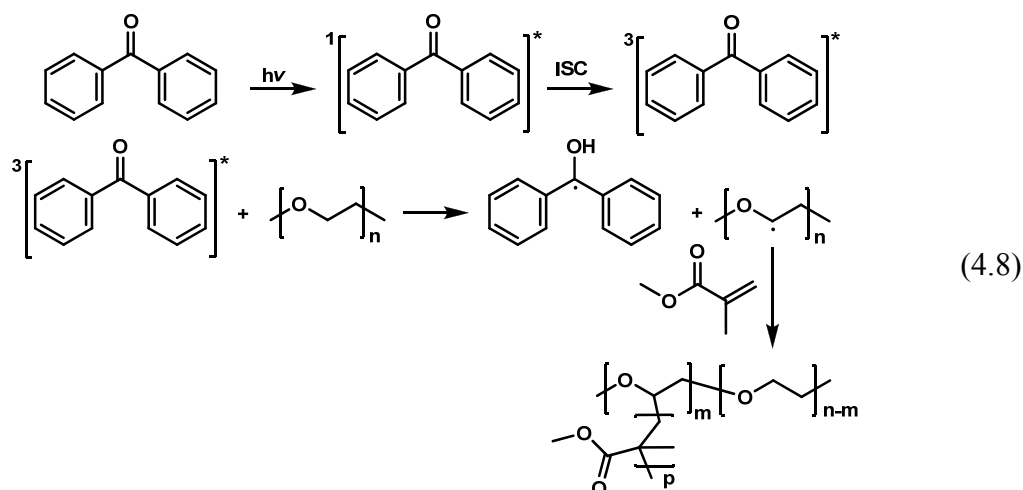
Notably, one of the consequences of the hydrogen abstraction from PEO is the formation of graft copolymers, since initiating radicals are generated on the backbone of PEO. This was confirmed by the molecular weight increases observed in all cases as well as the spectral evidences. For example the IR spectra of the resulting polymers possess both characteristic ester carbonyl and main chain ether bands at 1730 cm^{-1} and 1100 cm^{-1}, respectively.

Table 4.5 Comparison of molecular weight of PEO in photoinitiated free radical polymerization of MMA[a]

Run	M_{nPEO}	M_w/M_{nPEO}	Conversion (%)[c]	M_n[d]	M_w/M_n[d]
P-7	1300	1.01	99	120000	2.1
P-8	1500	1.02	72	87000	2.0
P-9	1800	1.06	47	59000	1.9
P-10	4500	1.44	3	32000	2.0
P-11	7000	1.22	12	25000	1.9

[a] $[PS = (BP)] = 5 \cdot 10^{-3}$ mol L^{-1}, polymerization time = 90 min.
[b] $[PEO] = 5 \cdot 10^{-3}$ mol L^{-1}
[c] Overall methyl methacrylate conversion
[d] Estimated by GPC based on polystyrene standards.

To confirm further, the hydrogen donating capability of PEO spectroscopically, we performed a model study by using a typical radical scavenger, namely TEMPO in the

same photoinduced process in the absence of monomer. The photochemically generated radicals are readily scavenged by TEMPO (reactions 4.9 and 4.10). ^{1}H-NMR spectra of the initial PEO and the reaction products are presented in Figure 4.9A. As can be seen, the characteristic protons of PEO appear at 3.6 ppm ($-O-CH_2-$) (Figure 4.9A). After scavenging with TEMPO some portion of these peaks shifted to 3.9 and 4.4 ppm ($-O-CH-$ and $-CH_2-O$ protons, respectively) (Figure 4.9B). The characteristic protons of the TEMPO moiety are also visible at 0.9, 1.2 and 1.3 ppm.

$$(4.9)$$

$$(4.10)$$
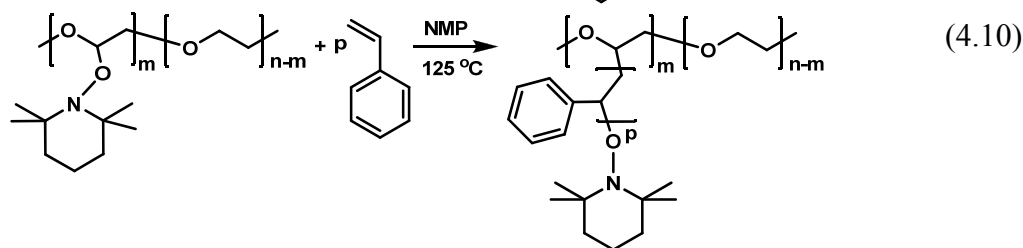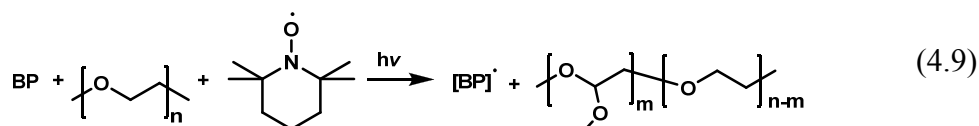
Similar to literature reports [358-361, 372] TEMPO incorporated polymers were used successfully as a polymeric initiator for NMP of St to afford graft copolymers. Experimentally subsequent bulk polymerization of styrene using above functionalized dendrimer was carried out at 125 $^{\circ}$C. The ^{1}H NMR spectrum of the resulting graft copolymer (Figure 4.9C) exhibits in addition to the precursor PEO repeating polystyrene (such as 6.2–7.2 ppm attributed to the aromatic protons and 1.2–1.8 ppm methylenes and methenes protons) and PEO.
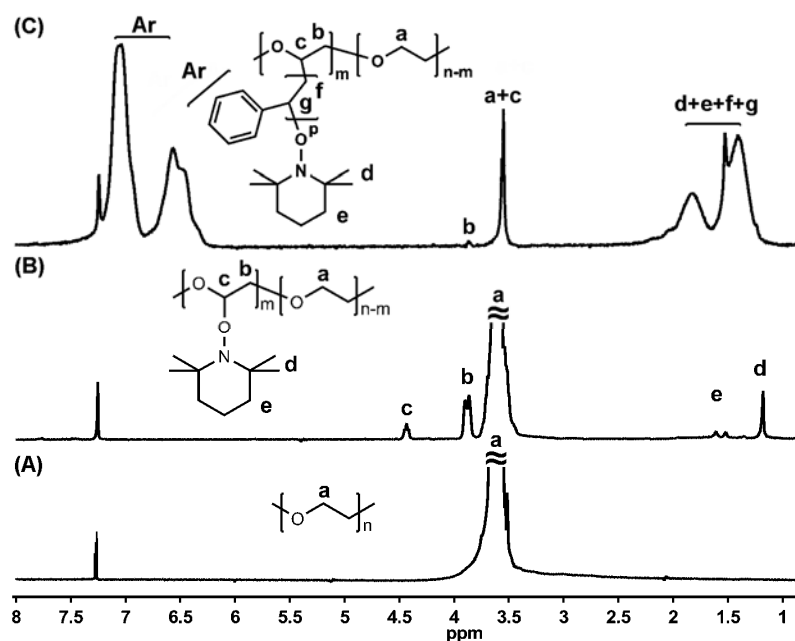
Figure 4.9 ^{1}H-NMR spectra of a) PEO, b) TEMPO functionalized PEO and c) poly(ethylene oxide-g-styrene) in CDCl$_3$.

Figure 4.10 shows the GPC traces of the initial PEO and of the polymer obtained by photoinitiation. The GPC traces of the graft copolymers are shifted to higher molecular weights and no significant amounts of unreacted starting PEO remained in the analyzed materials. In this connection, it should be pointed out that the unreacted PEO is soluble in methanol and removed during precipitation. Moreover, the traces corresponding to the graft copolymer is unimodal. This observation clearly indicates that all of the initiator was implied in the copolymerization reactions, and no significant homopolymerization processes occurred.
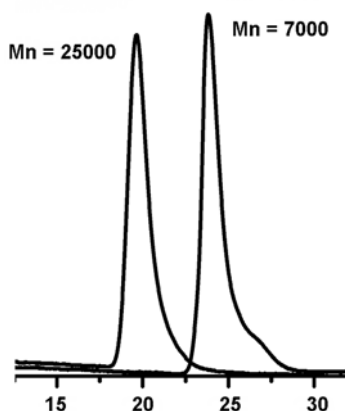
Figure 4.10 GPC traces of a) PEO, b) poly(ethylene oxide-g-methyl methacrylate)

For the evaluation of the hydrogen donation of PEO in the dental formulations, photo DSC experiments using the water-borne primer formulation consisting of a mixture

of EAEPA, DEBAAP, and water (2:1:2) was used [73, 373]. To investigate the influence of the molecular weight PEO, CQ (0.022 mmol·L⁻¹) and PEO (0.022 mmol·L⁻¹) concentration were used. For comparison, a second set of formulation was prepared with a CQ/NDMA in a concentration as usually applied under practical conditions. Photo-DSC plots of these experiments are shown in Figure 4.11. Figure 4.12 displays a plot of the conversion vs. irradiation time derived from Figure 4.11. By integrating the area under the exothermic peak, the conversion of the acrylate groups (*c*) or the extent of the reaction was determined according to equation 4.2.

$$(c) = \Delta H_t / \Delta H_0^{theory} \qquad\qquad\qquad\qquad \text{(Eq:4.2)}$$

where ΔH_t is the reaction heat evolved at time t, and ΔH_0^{theory} is the theoretical heat for complete conversion.
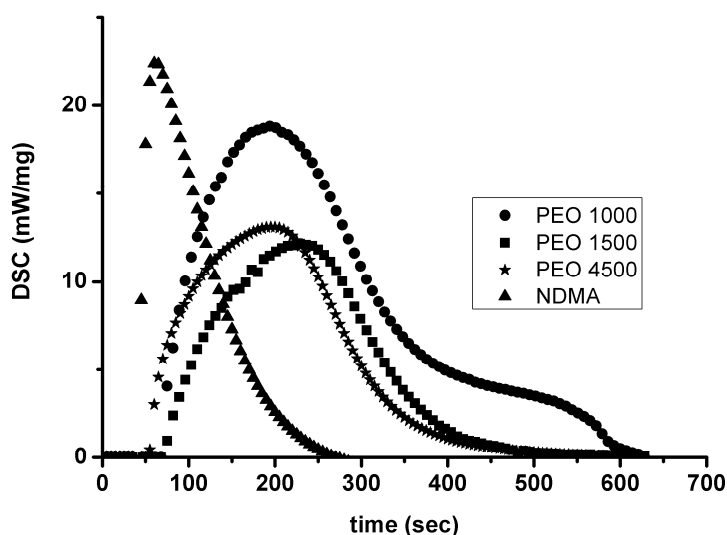
Figure 4.11 Photo-DSC of dental formulations with *N, N*-dimethylaniline and different molecular weight PEOs as hydrogen donor, cured at 30 °C by UV light with an intensity of 18.4 mW cm⁻².

By changing the molecular weight of PEO, usually applied for dental formulations (40% 2-(2-phosphono-ethoxymethyl)-acrylic acid ethyl ester (EAEPA), 20% *N, N*-diethyl-1,3-bis(acrylamido)propane (DEBAAP), and 40% water) the same tendency but with slightly decreased photoreactivity was found comparing to CQ/NDMA system (Figure 4.11). However, the calculated data clearly show no significant decrease in the final conversion with PEO instead of NDMA as the co-initiator (Figure 4.12).
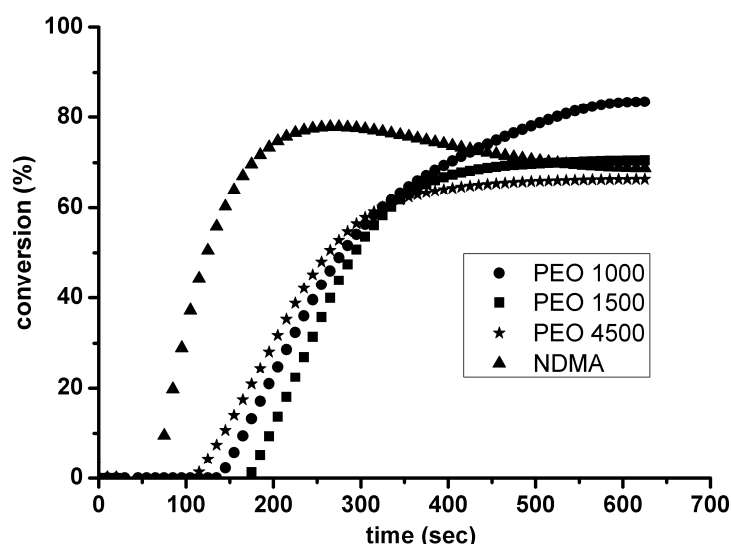
Figure 4.12 Time vs. Conversion for polymerization of different dental formulations calculated from Figure 4.11 data according to equation 4.2.

It has been shown that PEO can act as a hydrogen donor for *Type II* photoinitiation. The obvious advantage of this initiation is the elimination of amine based hydrogen donors and to provide alternative hydrogen donors with easily availability and non-toxicity. Moreover, the water solubility of PEO provides the use of initiating system in water-borne formulations. The initiating system can also be used in photografting for the preparation of amphiphilic copolymers.

4.2.3. Photoinitiated Free Radical Polymerization Using Benzoxazines as Hydrogen Donors

Polybenzoxazines are class of phenolic polymers formed by thermal ring-opening of the corresponding benzoxazines without any catalyst (reaction 4.11) [306].

(4.11)
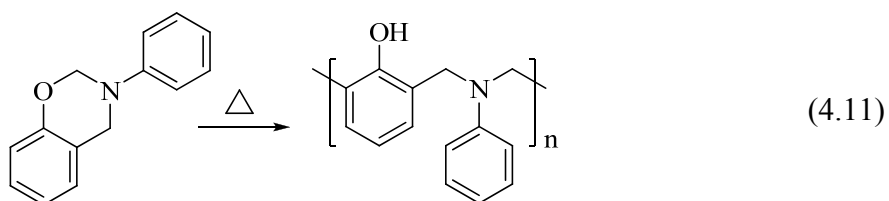
These polymers and their derivatives are of great interest for different scientific and industrial fields due to their superior mechanical and physical properties together with unusual thermal properties [301]. Benzoxazines can also be polymerized by cationic conventional [310] and onium salt photo-initiators [374]. However, the structures of the resulting polymers are complex and strongly related to with the ring opening process of the protonated monomer either at the oxygen or nitrogen atoms

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[374]. We have recently reported several routes to incorporate these interesting benzoxazine structures into polymer chains [375-377].

Within the scope of this thesis, we investigated the use of benzoxazine as hydrogen donor in conjunction with aromatic carbonyl photosensitizers in photoinitiated free radical polymerization. The photoinitiation efficiency of aromatic carbonyl/amine systems is highly dependent on the structures of the amine and tertiary amines [378] with hydroxyalkyl substituents were found to be the most suitable co-initiators. Depending on the substituents, dialkyl aniline derivatives are also used in these systems. Besides the oxazine ring, benzoxazines possess substituted dimethyl aniline groups in the structure.
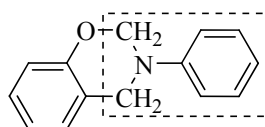
It seemed, therefore, appropriate to test whether they would also act as hydrogen donor in photoinitiated free radical polymerization using aromatic carbonyl sensitizers. For this purpose, the reactions of benzoxazine with excited states of benzophenone (BP), thioxanthone (TX), 2-chloro-thioxanthone (CTX), 2-isopropyl-thioxanthone (ITX) and camphorquinone (CQ) were studied. In ground state, benzophenone absorbs the light at the wavelengths where benzoxazine (P-a) also has significant spectral response (Figure 4.13) and can not be used as photosensitizer in the system.
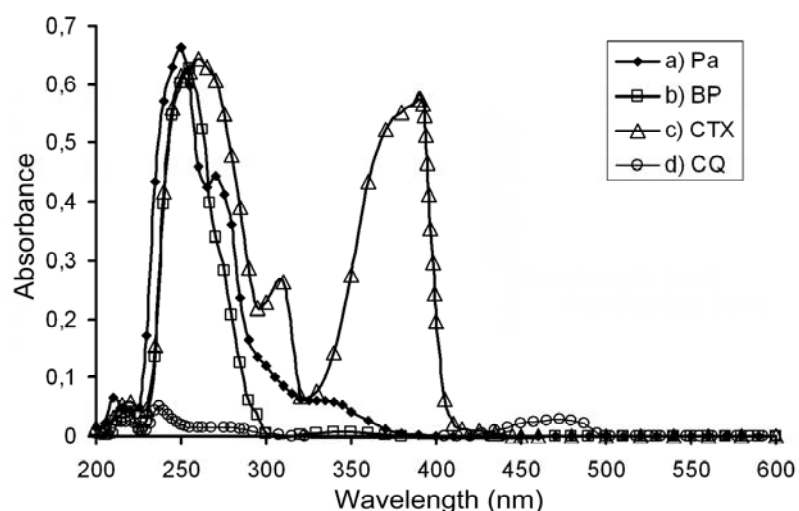
Figure 4.13 Optical absorption spectra of benzoxazine (a), and photosensitizers; BP (b), CTX (c) and CQ (d) in CH_2Cl_2. The concentration of all compounds is 1 x 10^{-5} M.

At the wavelength chosen for the polymerization, $\lambda > 350$ nm, TX and derivatives strongly absorb and P-a is virtually transparent. Incident light is almost absorbed by these photosensitizers. The polymerization of methyl methacrylate (MMA) was served as probe for the conversion of P-a into species capable of initiating free radical polymerization. Typical results are presented in Table 4.6. It should be pointed out that all sensitizers are ineffective for initiating polymerizations in the absence of P-a. Notably CTX acts the most efficient sensitizer. For comparison, polymerization with conventionally used amine hydrogen donor namely, triethyl amine (TEA) was also included. It is interesting to note that P-a exhibits almost the same initiation efficiency as co-initiator with TEA in the polymerization under identical experimental conditions. It is know that the efficiency of the deactivation of TX excited states is strongly related to the oxidation potential of the amine used[23] and P-a has a similar oxidation potential ($E_{ox} = 1.55$ V)[21] to those of the aliphatic amines ($E_{ox} = 0.6$-1.5 V)[23]. When naphtoxazine is used in the system, a relatively low conversion was attained which may be due to the interference of the absorption of the naphtyl group with that of the photoinitiator CTX.

Table 4.6 Photoinitiated free radical polymerization[a] of methyl methacrylate at room temperature in bulk or in CH_2Cl_2 for 120 min at $\lambda > 350$ nm.

Run	PS	[PS] (mol L^{-1})	H-donor	[H-donor] (mol L^{-1})	Conv. (%)	M_n[d]	M_w/M_n[d]
1	CTX	(5 x 10^{-3})	P-a	(15x10^{-3})	13	23000	2.1
2	CQ	(5x10^{-3})	P-a	(15x10^{-3})	11	58000	2.5
3	TX	(5 x 10^{-3})	P-a	(15x10^{-3})	12	33000	3.3
4	CTX	(10x10^{-3})	P-a	(30x10^{-3})	9.7	15000	1.6
5	ITX	(10x10^{-3})	P-a	(30x10^{-3})	8.8	20000	2.5
6	CTX	(5 x 10^{-3})	P-a	(15x10^{-3})	8.8	13000	1.3
7	CTX	(5 x 10^{-3})	B-a	(15x10^{-3})	22,4	14500	1.7
8	CTX	(5 x 10^{-3})	TEA	(15x10^{-3})	10	21000	1.5
9	CTX	(5 x 10^{-3})	N-a	(15x10^{-3})	6	20000	2.2

[a]interference filter : Cupric sulfate aqueous solution
[b]in bulk, [Monomer = 9.13 mol L^{-1}]
[c]in CH_2Cl_2 solution, [Monomer = 4.57 mol L^{-1}]
[d]determined from GPC measurement.

The initiating action of P-a is based on electron transfer followed by hydrogen abstraction, resulting in the formation of benzoxazine radical analogous to TX-amine systems according to the following reactions (Scheme 2).

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(4.12)
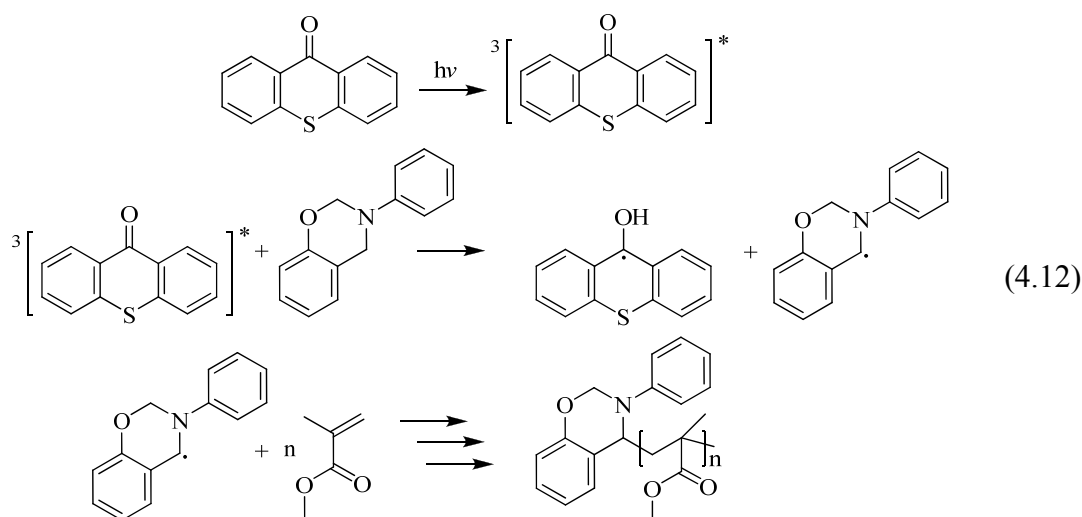
Figure 4.14 shows a Stern-Volmer plot of the quenching of the TX fluorescence by P-a. The linear relationship between the fluorescence intensity and P-a concentration is strong evidence for the interaction of excited TX with Pa.

Support for the proposed mechanism depicted in reaction 4.12 was readily obtained by ^{1}H-NMR analysis of the polymers formed. As can be seen from Figure 4.15, the spectrum of the corresponding poly(methyl methacrylate) PMMA obtained by using TX as photosensitizer and P-a as a hydrogen donor and purification by several precipitation presents not only the specific signals of PMMA, but also chemical shifts belonging to the P-a moiety. Notably, while the protons at 5.2 ppm (N-CH$_2$-O) remains at the same position, the protons at 4.6 ppm (N-CH$_2$-Ph) disappears. In fact, after hydrogen abstraction and addition of the monomer, the latter protons are expected to shift to 3.6 ppm where the signal overlaps with O-CH$_3$ protons of PMMA. This result indicates that hydrogen abstraction occurs dominantly at the carbon atom of N-CH$_2$-Ph. This is expected since hydrogen abstraction in this case would lead to the formation of more stable benzylic radicals. Moreover, the agreement of the number average molecular weight ($M_{n,HNMR}$ =14000), calculated by using the value of the integral of N-CH$_2$-O in comparison with the integrals of O-CH$_3$ protons of PMMA, with that obtained by GPC measurement ($M_{n,GPC}$ =13000, Table 4.6, Run 6)is an additional evidence for the proposed mechanism.

$$y = 57{,}308x + 0{,}9981$$
$$R^2 = 0{,}9999$$
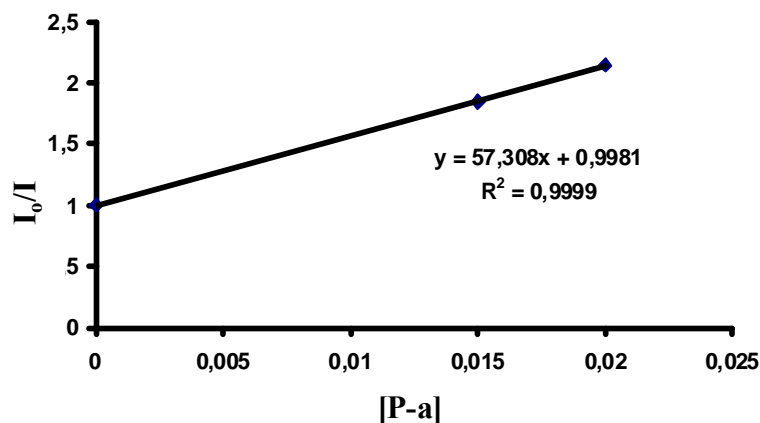
Figure 4.14 Stern-Volmer plot of the quenching of CTX fluorescence $(1 \times 10^{-3}\ M)$ by benzoxazine in CH_2Cl_2. (Excitation wavelength 395 nm).

Complete curing of thick free radical UV-curable coatings is rather difficult. One possible pathway in tackling this dilemma is the use of dual curing techniques involving two steps such as UV-irradiation induced radical generation followed by thermal curing to improve the surface and interior curing. In this context, the covalent attachment of P-a moieties into polymers by means of the described photoinitiating system may be particularly useful for deep curing of thick films. In order to confirm this possibility, we have performed DSC studies.
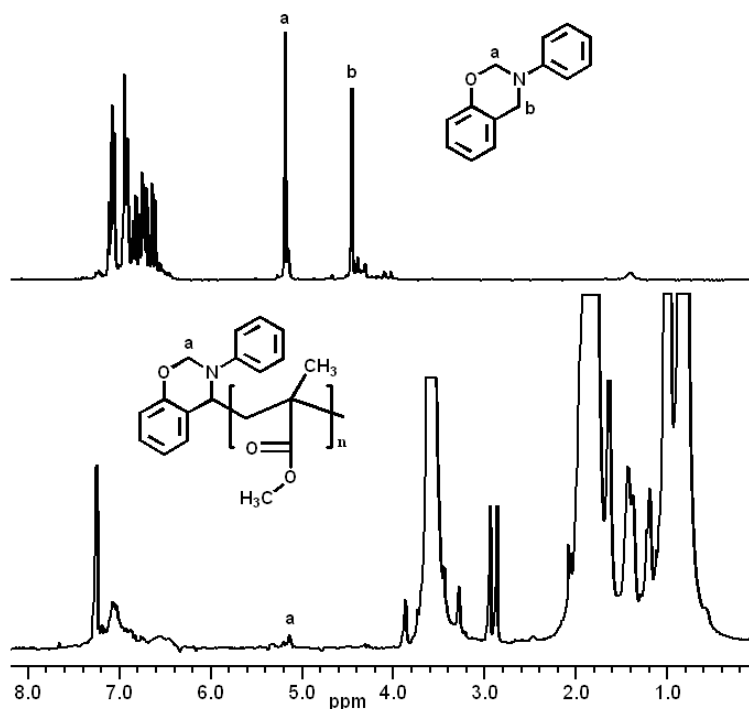
Figure 4.15 ^{1}H-NMR spectra of benzoxazine (a) and PMMA obtained by using CTX and benzoxazine in $CDCl_3$.

As stated previously, benzoxazine groups are expected to undergo ring opening

polymerization. Because of the polymeric nature, the ring opening process could not be monitored by the exothermic peak observed in DSC thermograms. In this connection, it should be pointed out that the benzoxazine functional poly(ε-caprolactone) does also not exhibit the exotherms that observed with low molecular weight benzoxazines. Therefore, the thermal curability of the benzoxazine groups was indirectly demonstrated. For this purpose bisbenzoxazine (B-a) of the following structure was cured by heating at 200 ^{o}C for 1 h in the presence of PMMA-P-a (reaction 4.13).

(4.13)

R: PMMA or H
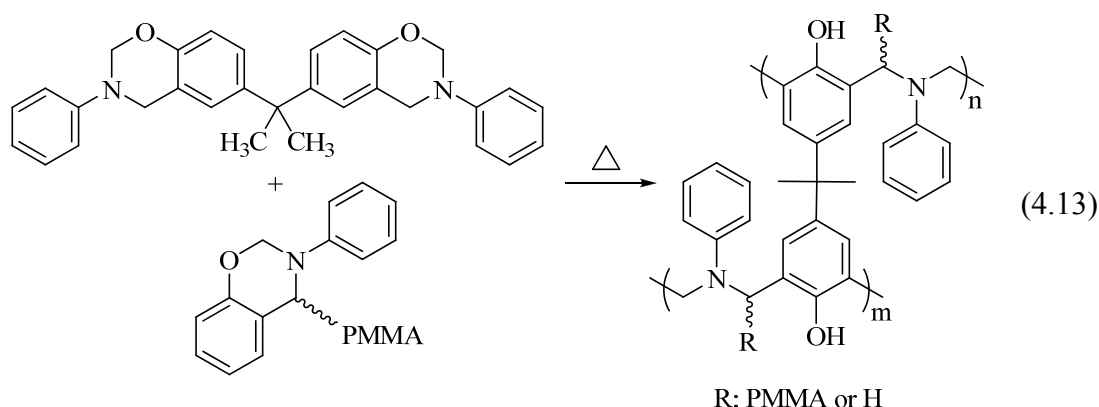
Extraction with tetrahydrofuran, which is solvent for PMMA, did not remove any polymer from the resulting product. Moreover, as can be seen from the FT-IR spectrum of the cured product (Figure 4.16b), in the addition to the stretching carbonyl band at 1721 cm^{-1}, the phenolic O-H band at 3387 cm^{-1} is evidencing both ring opening of benzoxazine groups and chemically incorporated PMMA chains.
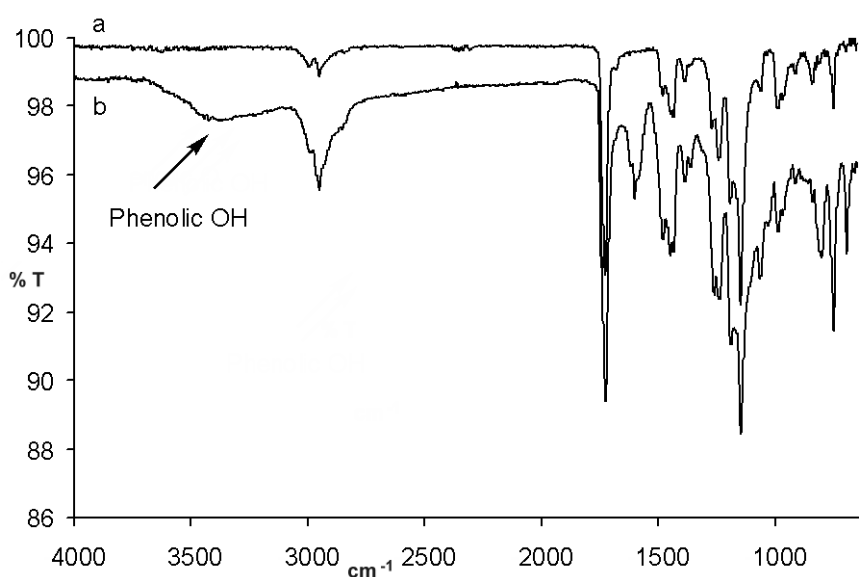
Figure 4.16 FT-IR spectra of PMMA-benzoxazine before (a) and after thermal curing in the presence of bisbenzoxazine (b).

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In conclusion, although the mechanistic details remain to be evaluated, it is clear that photoinitiation of free radical polymerization using P-a can efficiently be achieved at wavelengths of $\lambda > 350$ nm with aid of aromatic carbonyl photosensitizers. Work in progress is directed at further understanding the initiating mechanism by laser flash photolysis studies together with the use of formulations containing multifunctional monomers for deep curing applications.

5. CONCLUSION

Two different strategies for the *Type II* photoinitiation system based on benzophenone generation from benzodioxinone and using alternative hydrogen donors have been investigated in this thesis.

The first strategy consists of benzodioxinone and hydrogen donors such as triethylamine and tetrahydrofuran. A feasible mechanism involves photochemically generated benzophenone from benzodioxinone and subsequent hydrogen abstraction of photoexcited benzophenone from hydrogen donors to yield radicals capable of initiating polymerization of MMA.

A novel photoinduced simultaneous polymerization and cross-linking of hydroxy methyl methacrylate by using specially designed benzodioxinones was also demonstared. These molecules have the ability to generate benzophenone species as well as cross-linking agents that brings out photoinduced polymer network formation.

The second strategy rely on using several alternative hydrogen donors namely poly(propylene imine) dendrimers, poly(ethylene oxide) and benzoxazines for efficient photoinitiating systems.

Three generations of poly(propylene imine) dendrimers, were used as hydrogen donors in photoinitiated free radical polymerization of methyl methacrylate. The effect of generation number of the dendrimer on photoinitiation efficiency and molecular weight of the resulting polymers was investigated. Glass transition temperatures and particle size measurements of the resulting polymers indicated the presence of nearly stretched polymer chains around the dendrimers.

The location of hydrogen donating sites was evaluated by photolysis studies in the absence of monomer by using a stable radical namely, 2,2,6,6-tetramethylpiperidine-N-oxyl free radical (TEMPO) and showed that hydrogen abstraction occurs from the inner tertiary amino groups. The TEMPO attached dendrimers were further used in the nitroxide mediated radical polymerization (NMP) of styrene to yield star

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polymers.

Hydrogen donating capability of poly(ethylene oxide) in *Type II* photoinitiated free radical polymerization was demonstrated by polymerization and spectroscopic studies. The effect of molecular weight of PEO on the photoinitiation efficiency was investigated.

Photolysis of solutions containing benzophenone and PEO in the presence of TEMPO revealed that photoexcited benzophenone readily abstracts hydrogen from methylene groups present in PEO backbone. It was demonstrated that such photoinitiating system can be converted to a versatile grafting process. PEO possessing photochemically attached TEMPO units initiates the NMP of styrene upon heating at 110 ^{O}C leading to the formation of poly(ethylene oxide-*g*-styrene) graft copolymer.

Potential use of the photoinitiating system in dental formulations was also demonstrated. The polymeric nature, water solubility and biocompatibility of PEO make an effective synergist in dental formulations.

The benzoxazines possessing substituted dimethyl aniline group in the structure which were shown to act as hydrogen donor in photoinitiated free radical polymerization of methyl methacrylate. The postulated mechanism is based on the intermolecular reaction of the excited photosensitizer with the tertiary amino moiety of the ground state benzoxazine and a subsequent hydrogen abstraction reaction. The resulting aminoalkyl radicals initiate the polymerization.

The described photoinitiating system may be useful particularly for deep curing of thick films via a two-step procedure. During the photopolymerization, the benzoxazine ring structure was conserved and may undergo subsequent thermal ring opening reaction to yield polymers with high crosslink density. The double cure involving photo and thermal systems is expected to provide complete curing of free radical formulations which can not be achieved under normal circumstances because of oxygen inhibition and screening effect.

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AUTOBIOGRAPHY

Mehmet Atilla Taşdelen was born in Gaziantep in 1979. He graduated from Bayraktar High School in 1996. In the same year, he was admitted to Ege University, Department of Chemistry.

After his graduation in 2000, he was accepted as a M.Sc. Student to Istanbul Technical University, Institute of Science, Polymer Science and Technology Programme where he obtained M.Sc. degree in 2002

He was registered as a Ph.D. student to Istanbul Technical University, Polymer Science and Technology Program in 2002. In his Ph.D period, he worked as a visiting scientist supported by TUBITAK-R2214 Programme through a doctoral fellowship at the Ghent University, Department of Chemistry for 6 months in 2007.

He is co-author of the following 24 scientific papers published / submitted in international journals and 9 chapters in several books.

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