

**SYNTHESIS AND CHARACTERIZATION OF A NOVEL TRIPTYCENE
TYPE PHOTO-CROSSLINKER**

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**TRİPTİSİN ESASLI FOTO-ÇAPRAZBAĞLAYICININ SENTEZİ VE
KARAKTERİZASYONU**

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FOREWORD

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Chemistry

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ABBREVIATIONS

| | |
|------------------------|--------------------------------------|
| THDA | : Triptycene hydroquinone diacrylate |
| HDA | : Hydroquinone diacrylate |
| HEA | : 2-hydroxyethyl acrylate |
| HEMA | : 2-hydroxyethyl methacrylate |
| GMA | : Glycidyl methacrylate |
| TH | : Triptycene hydroquinone |
| DMPA | : 2,2-dimethoxy-2-phenylacetophenone |
| DMA | : Dynamic Mechanical Analyzer |
| DSC | : Differential Scanning Calorimetry |
| NMR | : Nuclear Magnetic Resonance |
| UV | : Ultra Violet |
| T_g | : Glass transition temperature |
| IMFV | : Internal Molecular free Volume |
| PI | : Photoinitiator |
| S | : Photosensitizer |
| R_p | : Rate of polymerization |
| THF | : Tetrahydro furan |
| RT | : Room temperature |
| ET₃N | : Triethyl amine |

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SYNTHESIS AND CHARACTERIZATION OF A NOVEL TRIPTYCENE TYPE PHOTO-CROSSLINKER

SUMMARY

Triptycene molecules are relatively high molecular weight compounds possessing three aromatic rings in the structure and incorporated into polymers in order to improve their mechanical strength and thermal stability. In this study, we describe synthesis and use of novel triptycene type crosslinker in free radical photoinduced curing applications. Thus, formulations containing monofunctional (meth)acrylates monomers, a crosslinker and a photoinitiator, namely, 2,2-dimethoxy-2-phenylacetophenone (DMPA) was irradiated at 350 nm.

Triptycene type crosslinker was synthesized with several steps. Firstly, Diels-Alder addition of 1,4-benzoquinone to anthracene, followed by the treatment of the resulting compound with HBr was performed to produce triptycene hydroquinone (TH). Secondly, TH was acylated to result triptycene hydroquinone diacrylate (THDA) which has two diacrylate terminals attached to triptycene framework via para positions of benzene ring. Therefore, the novel crosslinker THDA is a difunctional monomer with two diacrylate groups and it can be used as a crosslinker in photoinduced curing applications. NMR technique was used to characterize the novel crosslinker THDA. Hydroquinone diacrylate (HDA) was used in similar photoinduced reactions as an analog crosslinker allowing comparison with THDA. Photo-differential scanning calorimetry (photo DSC) experiments were carried on so as to demonstrate the curing behavior of the formulations. Concentration of crosslinker was increased gradually to gain insight into the effect of the crosslinker ratio in kinetics of photopolymerization. Crosslinking behavior of THDA was compared with that of the conventional analog crosslinker HDA. Higher rate of polymerizations and faster auto-accelerations were attained when THDA was used in the formulations or when the crosslinker percentages in formulations were increased. The results revealed that THDA is an efficient crosslinker for UV curable formulations with the potential interlocking behavior for the improved thermal and mechanical properties of the final products.

TRİPTİSİN ESASLI FOTO-ÇAPRAZBAĞLAYICININ SENTEZİ VE KARAKTERİZASYONU

ÖZET

Triptisin molekülü göreceli olarak yüksek molekül ağırlığına sahip üç benzen halkasının birbirine paralel ve 120 derece açıyla bisikloktan merkez iskeletine bağlandığı bir geometriye sahiptir. Son zamanlarda yapılan araştırmalar triptisinin polimer yapısına katıldığında polimerin mekanik ve ısıl özelliklerini geliştirdiğini ispatlamıştır. Bu çalışmada, triptisin yapısı içeren yeni bir çaprazbağlayıcının sentezi ve foto başlatıcılı kürleştirme uygulamalarında kullanımı incelenmiştir. Bu bağlamda tek-işlevsel metakrilat veya akrilat monomeri, çapraz bağlayıcı ve foto başlatıcı içeren formülasyonlar hazırlanmıştır. Foto başlatıcı olarak 2,2-dimetoksi-2-fenilasetofenon (DMPA) kullanılmış, reaksiyon esnasında 350 nm UV ışığa maruz bırakılmıştır.

Triptisin esaslı çaprazbağlayıcı sentezi bir kaç basamakta gerçekleştirilmiştir. Öncelikle antrasen ve benzokinon bileşiklerinin Diels-Alder katılması ve ardından HBr ile indirgenmesiyle triptisin hidrokinon (TH) sentezlenmiştir. Daha sonra TH bileşiği akrilol klorürle açillenecek triptisin hidrokinon diakrilat (THDA) oluşturulmuştur. THDA iki adet akrilat terminali içerdiği için foto başlatıcılı serbest radikalik polimerizasyon formülasyonlarında iki-işlevsel monomer (çaprazbağlayıcı) görevi görebilir. THDA molekülünün karakterizasyonu NMR yöntemiyle yapılmıştır. THDA molekülü için analog bileşik hidrokinon diakrilat (HDA) olarak belirlenmiştir.

Formülasyonların kürleşme davranışları foto tarayıcı kalorimetre (foto DSC) ile ölçülmüştür. Formülasyonlarda çaprazbağlayıcı konsantrasyonları kademeli olarak artırılmış ve çaprazbağlayıcı oranının artmasının fotopolimerizasyon kinetiğine etkisi incelenmiştir. Triptisin içeren çaprazbağlayıcının davranışları hidrokinon içeren analog çaprazbağlayıcının davranışları ile karşılaştırılmıştır. Çaprazbağlayıcı konsantrasyonu artırıldığında ya da triptisin esaslı çaprazbağlayıcı içeren formülasyonlar kullanıldığında daha yüksek polimerizasyon hızları ve daha hızlı oto-akselerasyon değerleri gözlenmiştir. Sonuçlar THDA'nın ultra viole kürleşme sistemlerinde etkin bir çaprazbağlayıcı görevi üstlendiğini göstermektedir. Aynı zamanda, THDA çentik kitlenmesi gibi bir potansiyele sahip olduğu için oluşan çapraz bağlı polimerin mekanik ve ısıl özelliklerini geliştirmesi beklenmektedir.

1. INTRODUCTION

1.1 Background

Iptycenes are widely used in many applications related to polymer technologies. They have specific three dimensional scaffold in which arene rings held together with a bicyclo[2,2,2]octane central unit [1].

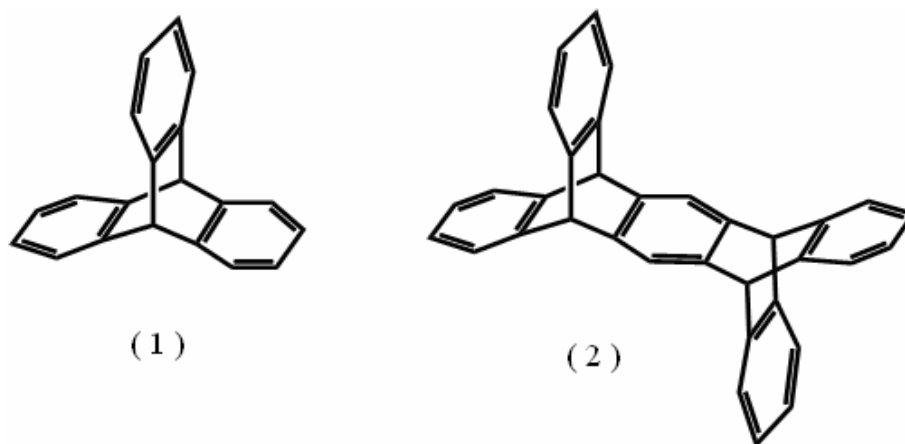


Figure 1.1 : Structures of two iptycenes: triptycene (1) and pentyptycene (2).

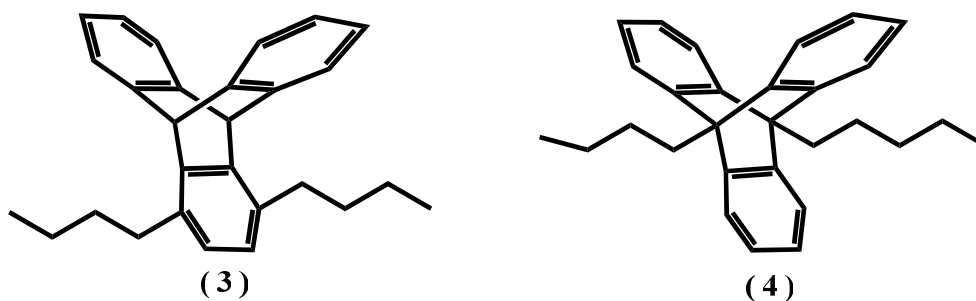


Figure 1.2 : Schematic of two possible incorporations of triptycene into the backbone of a polymer: benzene (3) versus bridgehead (4).

In cases iptycene units are incorporated in conjugated polymers, such polymers exhibit high stability and amplified fluorescent character playing a crucial role in sensory of nitroaromatic explosives at gaseous phase [2]. Analyte molecules in vapor

phase diffuse into polymer medium and interact with pentiptycene units (Figure 1.3). This interaction quenches the fluorescent character of conducting polymer. Thus sensory of nitroaromatic explosives becomes possible.

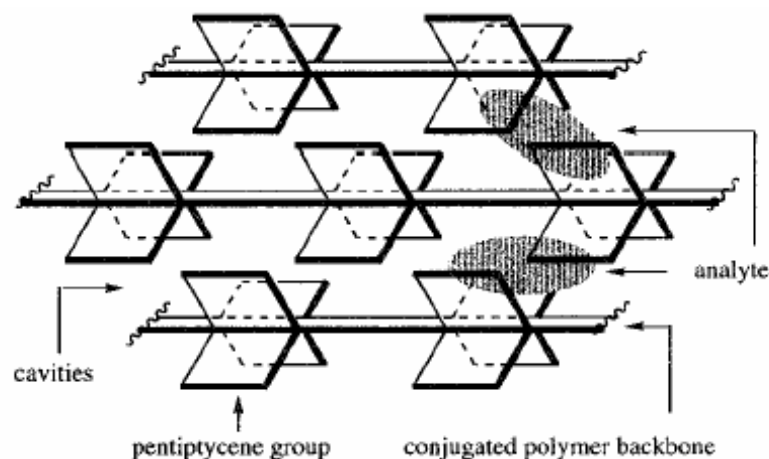


Figure 1.3 : Depiction of analyte diffusion and binding from. The analyte particles occupy the cavities created by the iptycene units [2].

Iptycenes are also utilized to produce low dielectric constant polymeric materials having improved thermal stability and high T_g [3]. Paddlewheel configuration of the three arene blocks brings high degree of internal molecular free volume (IMFV) to iptycene structure [4]. In LC (liquid crystal) applications by means of minimization IMFV, more proper and compact alignment of crystals occurs, because of decrease in aspect ratio (length/width) [5].

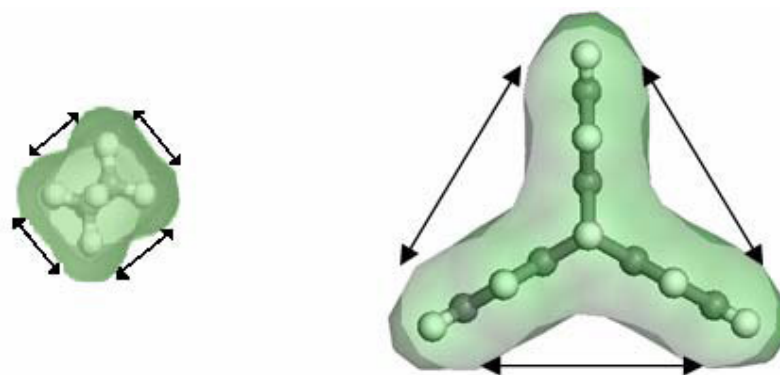


Figure 1.4 : Face views of space-filling models of ethylene (left) and triptycene (right) showing the contrast in IMFV. The triptycene has significantly sized cavities; whereas, the ethylene does not [5].

Discretely incorporation of triptycene (the simplest iptycene) units into polymer backbone creates molecular barbed wires (Figure 1.5) having enhanced lateral interactions by virtue of occupation of triptycene cavities with neighboring polymer chain in order to minimize the free energy arose from IMFV of triptycene [6].

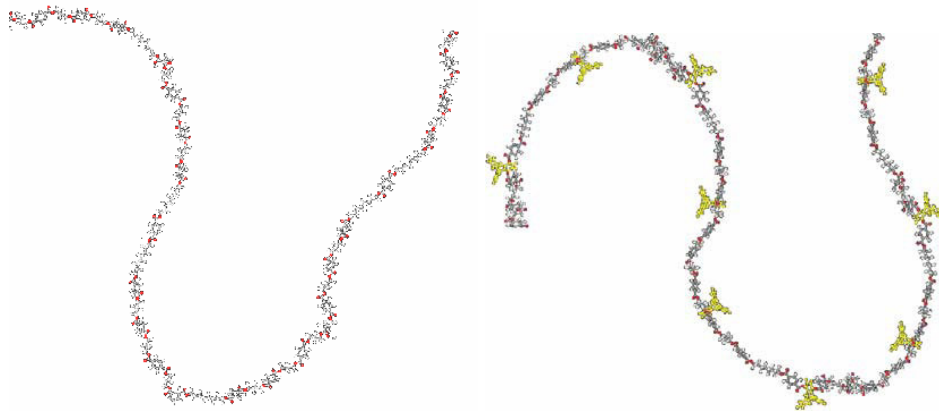


Figure 1.5 : Schematics of the typical “smooth” polymer chain contour and “molecular barbed wire” generated by the incorporation of triptycene units (yellow) [6].

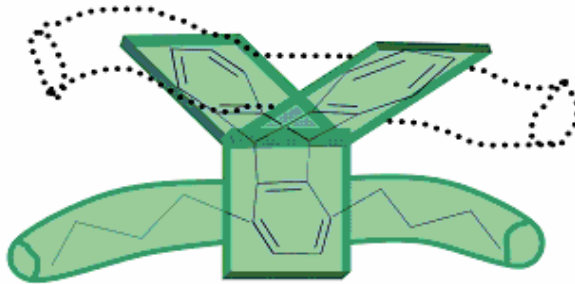


Figure 1.6 : A neighboring polymer chain can slide into the open triptycene cavity in order to minimize IMFV (and thus, the total free volume of the system). Once occupied, the polymer chain can thread along the triptycene cavity during deformation [6].

If a strain applies on polymer, adjacent chain begins to thread into the cavity until two opposite triptycene units meet and interlock (figure 1.7). These two interactions, threading and interlocking enhances ductility and stiffness of polymer simultaneously [4]. However, possibility of threading and interlocking reduces when

polymer backbone closely constructed by branched or bulky groups in place of a simple alkyl chain.

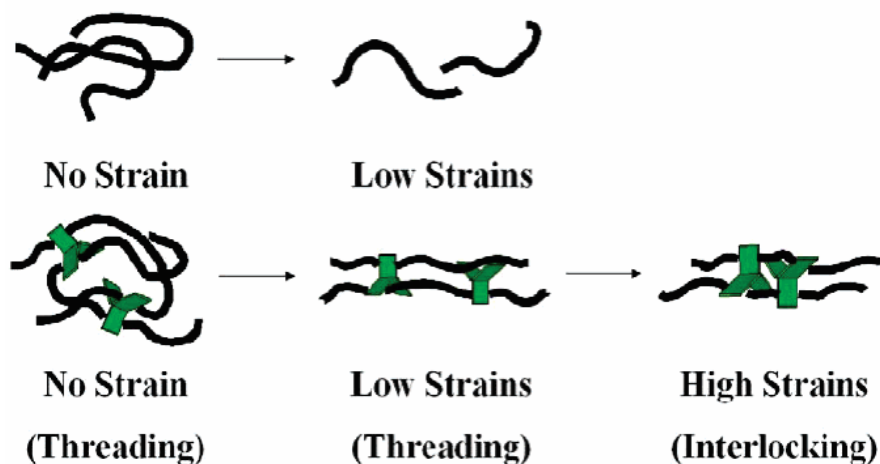


Figure 1.7 : Schematic of the new types of interactions (“threading” and “interlocking”) induced by the triptycene unit and the minimization of IMFV (bottom). The same polymer without triptycene relies on entanglements and will fail at early strains if there are poor lateral interactions (top) [4].

1.2 Starting Point

In addition to enhancement of mechanical performance of a polymer comprising triptycene, improvement in thermal properties such as glass transition and decomposition temperature is also remarkable [4,7]. Increase in performance of both thermal stability and mechanical strength may present some advantages in crosslinked networks derived by photo initiated free radical polymerization.

Triptycene can be placed either along polymer chain or as a crosslinker in these networks. In particular, the simple triptycene hydroquinone scaffold may be modified as a crosslinker. In this manner, a novel triptycene based difunctional crosslinker including acrylate functionalities was synthesized in order to use in free radical photo induced polymerization.

The photo induced (radiation curable) polymerization technique is rapid, durable and utilized to form crosslinked systems possessing high thermal permanence and mechanical strength and resistance to solvents [8,9]. Studies on kinetics of radiation curable polymerization may provide sort of predictions on some thermal and mechanical behaviors of cured systems [10,11]. Commonly acrylate or methacrylate resins are available for radiation curable coatings based on crosslinked networks.

2. PHOTOPOLYMERIZATION

Photopolymerization is one of the most interesting study field including many of practical applications encouraging scientist to be more enthusiastic to develop plenty of research topics on it. Photopolymerizations are light-induced reactions that convert a liquid monomer into a solid polymer. 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

In photoinduced polymerization, absorbed light directly or indirectly causes generation of a species, which is able to initiate polymerization of the polymerizable constituents, monomers or oligomers [12]. The photoabsorbing molecule is either the photoinitiator or some part of the photoinitiation system. A photoinitiator or photoinitiator system is known to be a compound or combinations of molecules which, when exposed to radiation, initiate much more rapidly polymerization than in their absence. Indeed, the polymerization would not occur without a photoinitiator system. Most photoinitiation processes involve a uni- or bimolecular process. This applies to free radical. In order to prevent misunderstanding, it is convenient to define some terms will be used in the text.

Photoinitiator: A molecule which absorbs energy of radiation, either directly or indirectly and consequently initiates polymerization. During the irradiation its concentration in the system is depleted. In many cases, other molecules are present which participate in the photoinitiation process or sequence of the process. These molecules are known as coinitiator or sensitizer (photosensitizer) by the means of their role [12].

Coinitiator: A molecule which is part of bimolecular initiating system. It does not directly absorb energy of radiation, but aids to initiate polymerization.

Sensitizer: A molecule, which absorbs energy and then transfers it to another molecule, usually the photoinitiator, which yields the primary reactive species. A sensitizer is usually dispensable, whereas coinitiator is mandatory for initiation to occur.

Absorption characteristics of the photoinitiation system can be shifted by using also a sensitizer. This shift is usually towards longer wavelengths (red-shift or bathochromic shift) to decrease energy cost and increase efficiency of the system [12]. Photoinitiators can be combined with others to induce bathochromic shift. One of these combined photoinitiators acts as a sensitizer. The formation of excited bimolecular complexes is the other possible mechanism for initiation system. Excited state complexes are generated from excitation of a ground state complex, directly by absorption, or from complex formation of an excited state molecule with a ground state molecule. The coinitiator may be a molecule, which activates excited state formation or may be a ground state molecule. In excited state complexes, there are several reactions which may potentially occur. The coinitiator can act as an electron acceptor or an electron donor. The molecule, in turn, is oxidized or reduced, so mechanism is known as electron transfer. Finally, either the oxidized or reduced molecule becomes active initiating species. The complex can undergo other possible processes, such as energy transfer, fragmentation, or extraction of an atom (like hydrogen).

2.1 Photoinduced Free-Radical Polymerization

Radical photopolymerization of vinyl monomers played an important role in the early development of polymerization. One of the first procedures for polymerizing vinyl monomers was the exposure of monomer to sunlight. Blyth and Hoffman [13] reported on the polymerization of styrene by sunlight more than 150 years ago. Today photoinitiated free-radical polymerization and crosslinking of multifunctional vinyl monomers and oligomers (prepolymers) in particular, has currently a lively commercial interest on account of its potential in a large number of applications.

The photoinitiator, or more generally the photoinitiating system is considered as an essential ingredient of all UV-curable (crosslinkable) compositions. Light induced radical polymerization, particularly curing by ultraviolet light, is by far the most important application of radiation curing and the development and introduction of new radical photoinitiators, both as experimental and as commercial products, have proceeded at breath taking pace during the last decade. The developments in the field of photoinitiators are stimulated by following factors [12].

- There is the continuous improvement of photoinitiators for existing applications such as coatings, inks, photoresists, printing plates or adhesives. Since there is no single photoinitiator, which can meet the particular requirements of all these applications, there is a tendency to develop tailor-made products for each of these technologies.
- The adoption of radiation curing by new technologies requires new types of photoinitiators to fulfill specific demands.

2.1.1 Stages of Free-Radical Polymerization

A typical free-radical polymerization comprises four elementary steps (Figure 2.1):

- 1) initiation
- 2) propagation
- 3) chain transfer
- 4) termination

The first step, *initiation* is decomposition of the initiator molecule into primary radicals R'. In photoinitiated polymerization, this step may be considered as generation of radicals as a result of absorption of incident light by photoinitiators and following primary photochemical reactions. The actual initiation occurs when free radical react with a monomer. After the initiation step, the classical picture of radical polymerization is valid for the photoinitiated polymerization process. The *propagation* or growth reaction consists of the (rapid) addition of monomer molecules to the radical species to produces the polymer backbone. In this step reaction is repeated many times. Usually, it occurs in head-to-tail fashion, because the free radical formed is more stable. However, as with initiation, alternatives are possible and head-to-head, tail-to-head, and tail-to-tail modes occur, usually to minor extents. In *termination*, growth of polymer chains is brought to an end by the

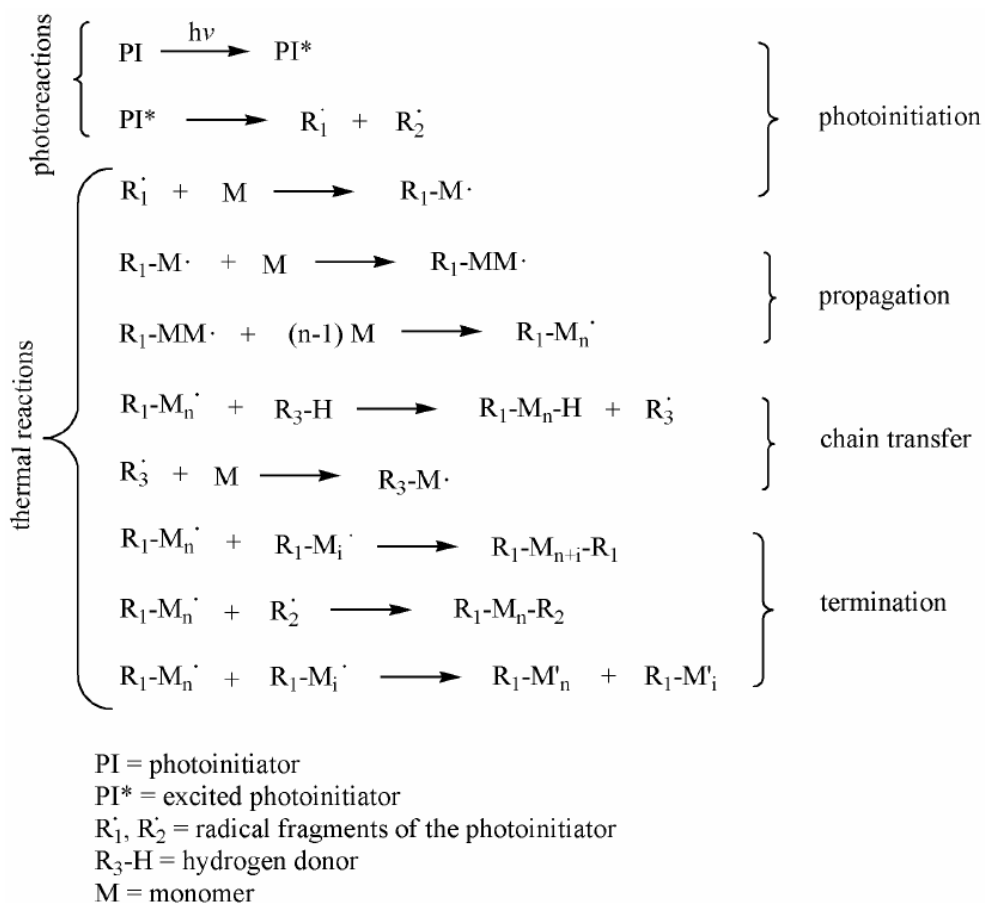


Figure 2.1: Various steps in a photoinitiated free-radical polymerization

destruction of propagating radicals. Normally, in the absence of retarding species that destroy growing radicals, chain termination occurs by bimolecular interaction of radicals [12].

2.1.2 Free-Radical Initiated Acrylate/Methacrylate Systems

The most widely used UV curable radical-initiated systems are based on acrylate unsaturation, with the general formula $H_2C=CR-COOR'$ (if $R = H$, the monomer is an acrylate, if $R = CH_3$, it is a methacrylate). Methacrylates are less reactive than acrylates, but are less toxic and cause less skin irritation than acrylates. The curing reaction of acrylates is typical of vinyl monomers [12]. Therefore, the degree of double bond conversion is the measure of the degree of cure. The best results are obtained when using oligomers as binders and monomers as reactive thinners. Examples of difunctional and polyfunctional acrylates are shown in Table 2.1. A partial list of most common acrylate oligomers follows.

Table 2.1: Examples of difunctional and multifunctional acrylates used in UV curing

| Monomer | Type of Main Chain | Functionality | Abbreviation | Molecular Weight | Viscosity, mPa.sec at 25°C |
|------------------------------------|----------------------|---------------|--------------|------------------|----------------------------|
| 1,6-hexanediol diacrylate | Linear hydrocarbon | 2 | HDDA | 226 | 5–10 |
| Tripropyleneglycol diacrylate | Branched ether | 2 | TPGDA | 300 | 10–20 |
| Dipropyleneglycol diacrylate | Branched ether | 2 | DPGDA | 242 | 8–12 |
| Trimethylolpropane triacrylate | Branched hydrocarbon | 3 | TMPTA | 296 | 50–150 |
| Pentaerythritol triacrylate | Branched hydrocarbon | 3 | PETA | 298 | 350–700 |
| Ditrimethylolpropane tetraacrylate | Branched ether | 4 | DTMPTA | 438 | 450–900 |
| Dipentaerythritol pentaacrylate | Branched ether | 5 | DPEPA | 525 | 14000 |

Epoxy acrylates. The most widely used oligomers are aromatic and aliphatic epoxy acrylates. Epoxy acrylates are highly reactive and produce hard and chemically resistant films. The polymerization of monoacrylates produces linear polymers, whereas diacrylates produce branching, and higher-functionality acrylates give rise to cross-linked structures. Cured materials are useful as coatings and adhesives on rigid substrates such as metal cans and paneling, or as binders in composites. The epoxy component contributes to adhesion to nonporous substrates and enhances chemical resistance of the film.

Urethane acrylates. Urethane acrylates are formed by the reaction of isocyanates with hydroxy-functional acrylate monomers. After UV cure, they produce tough, flexible materials that exhibit good abrasion resistance.

Polyester acrylates. Acrylated polyesters are prepared by reacting the OH group of polyesters with acrylic acid or hydroxy acrylate with acid groups of the polyester structure. Polyester acrylates are often low-viscosity resins requiring little or no monomer. They produce coatings and adhesives dominated by the polyester structure used in the oligomer. They are used for pressure-sensitive adhesives and also for strong rigid adhesives for metal-to-metal bonding. Amino-modified polyester acrylates show a high reactivity and low skin irritation.

Silicone acrylates. Acrylated organopolysiloxanes, which exhibit excellent release properties, are used as release coatings on papers and films. The silicone structure provides flexibility and resistance to heat, moisture, radiation degradation and shear forces.

Polyether acrylates. Polyether acrylates are produced by esterification of polyetherols with acrylic acid. They have a very low viscosity and do not require reactive thinners. Amino-modified polyether acrylates have a higher reactivity and low skin irritation, similar to polyester acrylates. Solid urethane and polyester acrylates can be used as main components of radiation curable powders. Together with suitable unsaturated polyesters, powders are formed that give low film flow temperatures and allow separating of film formation from curing. This technology has been used successfully in powder coating of wood and plastics [12].

2.2 Ultra-Violet Radiation

Electromagnetic radiation (or light) can be used as the energy source for a variety of processes involving functional monomers, oligomers and polymers. In these processes, it is utilized mainly to effect the formation of new chemical bonds [14]. The light used in polymeric systems typically has wavelengths ranging in the ultraviolet spectral range extending from 200 to 400 nm, although, in some special cases, it may include wavelength in the visible range up to 750 nm. Xenon lamps provide significant emissions in the 450 to 550 nm range. Because the energy of radiation increases with increasing frequency (or decreasing wavelength), radiation with short waves contains a large amount of energy.

This energy is capable of bringing about certain chemical reactions in a system that is sensitive to light (i.e., the system can absorb light) and the absorbed energy can then generate species that are capable of initiating polymerization or cross-linking reactions. For the most part, UV radiation is used to convert reactive liquid monomers and oligomers to solids. This process essentially involves polymerization and sometimes polymerization and cross-linking simultaneously. Monomers and oligomers with the functionality of two form linear polymers, whereas multifunctional polymers (with functionality of more than two) yield three-dimensional cross-linked networks. Cross-linking imparts solvent resistance, increases hardness and improves heat resistance. The main practical utility of these

reactions is in curing coatings and inks and in photo-imaging. Cross-linking of already existing polymers is also a viable process and is currently a very active field of research [14].

2.2.1 Basic Concepts

The processes of photochemistry are the same for polymers and small molecules. The *Grotthus-Draper Law* states that no photochemical reactions can occur unless a photon of light is absorbed. This means, for example, that many commercial plastics transparent in the near UV can undergo photodegradation only as a result of the absorption of light by impurities. The intensity of any light absorbed by a light-absorbing species (chromophores) follows Lambert-Beer's Law:

$$I = I_0 10^{-\epsilon cd} \quad (2.1)$$

where I_0 is the intensity of the incident light I is the intensity of transmitted light

ϵ is the molar extinction coefficient ($\text{cm}^{-1} \text{mol}^{-1}$) c is the concentration of absorbing species d is the optical path length

Absorbance A (or optical density) is defined as $-\log(I/I_0)$, then $A = \epsilon cd$.

Typical chromophoric groups for UV light are $\text{C} = \text{O}$, ROOH and aromatic groups. These extend the absorption of monomers, oligomers and polymers into the UV light range. Figure 2.2 shows an energy-level (Jablonski) diagram for a ketone, a common chromophore in polymers. Several intramolecular processes are shown competing with photochemical reactions, including reemission of a photon as fluorescence or phosphorescence, radiationless decay to the ground state and crossing from one excited state to another [14].

The ground states of almost all organic compounds have all electron spins paired. Absorption of a photon promotes an electron from the singlet state S_0 to a high energy singlet state $S_1, S_2 \dots S_n$, numbered in the order of increasing energy above the ground state. A change in the spin state of an electronically excited molecule, called *intersystem crossing*, produces triplet species $T_1, T_2 \dots T_n$ with two unpaired spins. A triplet state is always lower in energy than the corresponding singlet state. Singlet states may emit light and return to the ground state.

To put it simply:

- The absorption of a photon by a chromophore brings about a transition into the excited singlet state.
- Generally, the excited molecule has two possibilities to emit the absorbed energy: It can either return into the ground state by emitting energy by fluorescence or can cross over to the excited triplet state.
- Molecules in the triplet state are biradicals, which can, if the energy is high enough for breaking a bond, form free radicals. The free radicals can then initiate the polymerization and/or cross-linking reaction.

The main decay processes to the ground state shown in Figure 2.2, which is essentially an energy diagram for the different electronic states, are:

❖ Radiative processes:

- Absorption: $S_0 + h\nu \rightarrow S_1$
- Fluorescence: $S_1 \rightarrow S_0 + h\nu'$
- Phosphorescence: $T_1 \rightarrow S_0 + h\nu''$

where h is the Planck's constant and ν , ν' , and ν'' respective frequencies of the absorbed or emitted light.

❖ Radiationless processes:

- Internal conversion: $S_1 \rightarrow S_0 + \text{heat}$
- Intersystem crossing: $T_1 \rightarrow S_0$ or $S_1 \rightarrow T_1$

The result of a photochemical reaction involving monomers, oligomers and polymers depends on the chemical nature of the material, wavelength of the light and the other components of the system. Ultraviolet, visible and laser light can polymerize functional monomers, crosslink or degrade polymers, particularly in the presence of oxygen. As pointed out at the beginning of this chapter, we will be focusing on the reactions, which lead to useful products [14].

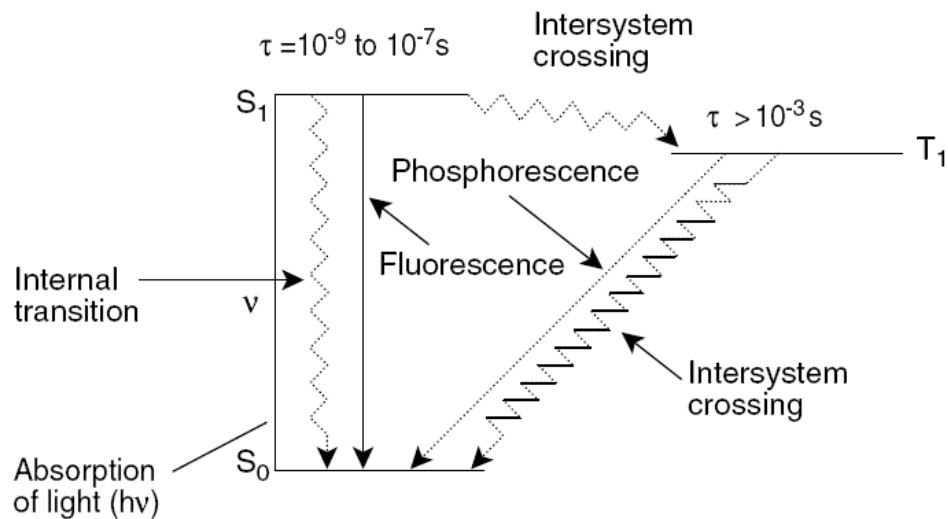
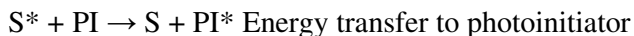
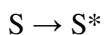
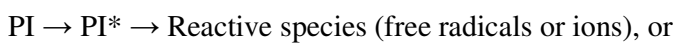


Figure 2.2: Primary processes occurring in the excited state of a UV radical initiator

2.3 Photoinitiators and Photosensitizers

Essentially two types of compounds are used in the UV curing process to absorb the light and generate reactive species. These are photoinitiators and photosensitizers. A *photoinitiator* (PI) is a compound-generating reactive species that will initiate polymerization or cross-linking. A *photosensitizer* (S) is a compound that will energize certain species that will, in turn, lead to production of reactive species [14]. It is a molecule that usually absorbs light at longer wavelengths and transfers energy to a photoinitiator to generate free radicals or ions.



Thus, photosensitizers are useful mainly by being capable of extending the spectral sensitivity of certain photoinitiators under specific conditions. The function of a photoinitiator is:

- Absorbing the incident UV radiation
- Generation of reactive species (free radicals or ions)
- Initiation of photopolymerization

In UV curing process, photons from the UV source are absorbed by a chromophoric site of a molecule in a single event. The chromophore is a part of the photoinitiator. The light absorption by the photoinitiator requires that an emission light from the light source overlap with an absorption band of the photoinitiator. The photon absorption follows Lambert-Beer's Law (see earlier part of this section). The number of photons I presents at depth l from the surface is given as a function of the optical absorbance, A , normalized to the initial number of photons I_0 :

$$\log(I_0/I) = A = \epsilon [PI] l \quad (2.2)$$

Where $[PI]$ is the concentration of photoinitiator. The quantity l is also termed the *photon penetration path*.

In general, upon exposure to UV radiant energy, a photoinitiator can generate free radicals or ions, as pointed out earlier. These are generated at a rapid rate and their depth profile corresponds to the inverse photon penetration profile. Similar to electron penetration, the final cure profile often deviates from the initial radical or ion distribution because they can live much longer than the exposure time. Depending on the type of reactive species generated upon exposure to UV light, photoinitiators are classified as free radical, cationic and anionic [14].

2.4 Free Radical Photoinitiators

The UV curing of certain monomers, such as acrylate, methacrylate and maleate/vinyl ether systems, is initiated by free radicals. In all practical cases, the initiating radicals are generated from electronically excited photoinitiator molecules. A photoinitiator molecule is excited into the singlet state by the absorption of a photon. The formation of a radical occurs via a triplet state. Radical formation occurs via two possible reaction sequences that are designated as Type I and Type II reactions. In Type I reaction, the photoinitiator triplet state decays into a radical pair by homolytic decomposition and directly forms radicals capable of initial polymerization. The absorbed radiation causes bond breakage to take place between a carbonyl group and an adjacent carbon. In Type II reaction, triplet states of ketones possessing an α hydrogen preferably react with suitable hydrogen-donating compounds by hydrogen abstraction. The resulting radical pair can be generated either by a homolytic

cleavage of the R-H bond or via an intermediate charge transfer complex followed by proton transfer. The lifetime of the excited initiator species is very short, generally less than 10^{-6} s. During this time, it can be partitioned essentially between two processes: (1) It can decay back to the original state with emission of light and heat or (2) yield a reactive intermediate (free radical or ion) that, in turn, can react with another free radical or initiate polymerization of a monomer.

Free-radical photoinitiators are classified by their chemical nature as Type I and Type II, but a few systems with different chemistry, e.g., borate salt initiators, depend on inter- or intramolecular electron transfer and do not fit into either category [14].

2.4.1 Type I Photoinitiators

Type I initiators are compounds that upon irradiation undergo a homolytic cleavage reaction (α - or β -cleavage) to generate two radicals (Figure 2.3).

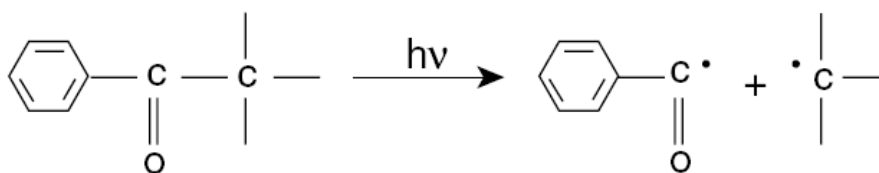


Figure 2.3: Homolytic cleavage reaction of a Type I initiator

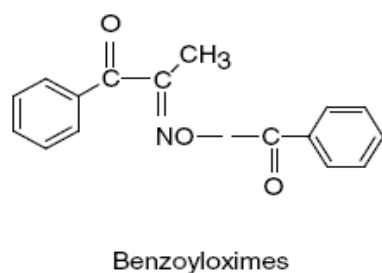
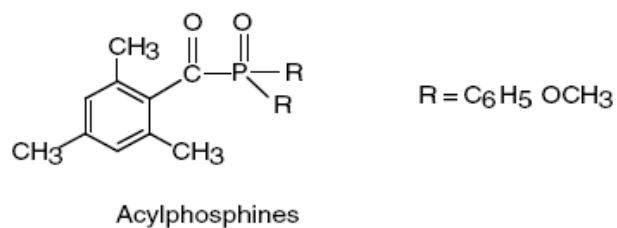
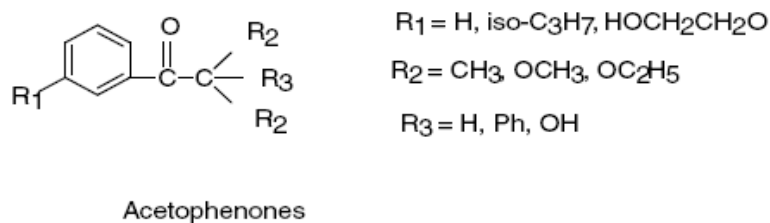
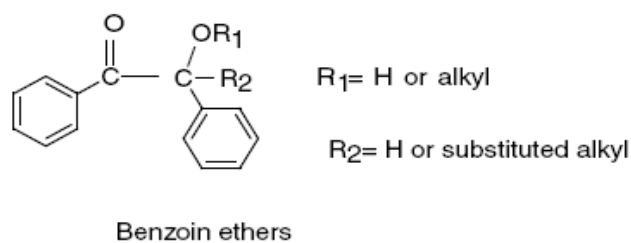
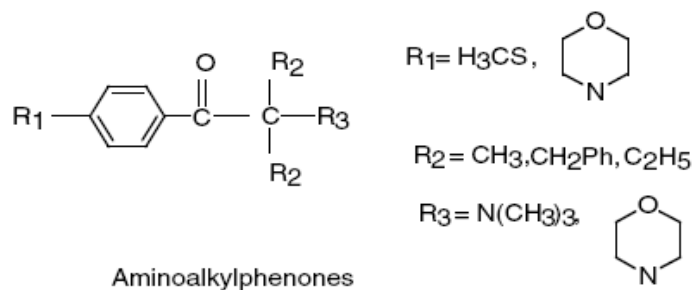
The chromophore in this type of photoinitiator is frequently an aromatic carbonyl. The benzoyl radical is the major initiating species, while, in some cases, the other fragment may also contribute to the initiation. The most efficient Type I initiators are benzoin ether derivatives, benzil ketals, hydroxylalkylphenones, α -aminoketones and acylphosphine oxides. Substituents on the aromatic carbonyl influence the absorption.

2.4.2 Type II Photoinitiators

A large number of aromatic ketones (benzophenone, substituted benzophenones, benzils, fluorenone, xanthone and thioxantones) will act as Type II initiators, with their performance being dramatically enhanced by the use of tertiary amine synergists [14]. There are essentially two classes of amine synergists, aliphatic and aromatic, with different characteristics and uses. Aliphatic amines are transparent

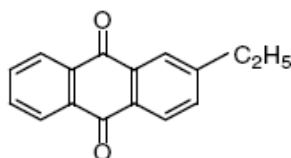
down to about 260 nm and, consequently, a coating containing such amine can be cured with UV light down to that wavelength.

Table 2.2: Type I photoinitiators

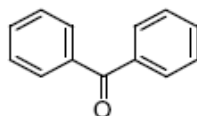


Aromatic amine synergists display strong absorption around 300 nm and consequently screen much of the UV light. Therefore, in cures with benzophenone it is best to use an aliphatic amine, whereas thioxanthenes, because of their strong absorption at wavelengths greater than 340 nm, can be used successfully with an aromatic amine. Combinations of Type I and Type II photoinitiators are used to reduce air inhibition in the absence of amines. Possible explanation of the synergistic effect is that the photocleavage of the Type I initiator yields free radicals that react with oxygen to generate peroxy-radicals (R-O-O •). These radicals are poor initiators for the usual radical polymerization, but they abstract hydrogen from monomers and oligomers, which regenerates radicals (chain process). Oxygen depletion enhances the effectiveness of Type II initiators as energy-transfer agents for decomposing hydroperoxides into alkoxy (RO •) and hydroxy (HO •) radicals. In contrast to peroxy radicals and hydroxy radicals, they are highly effective initiators for acrylate polymerization. In the overall process, oxygen is used to produce initiating radicals. Some examples of Type II and Type I photoinitiators are shown in Tables 2.2 and 2.3 respectively.

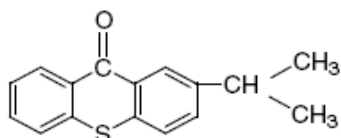
Table 2.3: Type II photoinitiators



Anthraquinones



Benzophenone



2-Isopropyl thioxanthone(ITX)

3. PHOTOPOLYMERIZATION KINETICS

As mentioned before photoinduced polymerization is a rapidly expanding technology resulting from its main advantages: the process is solvent-free, energy efficient and generally economical. It has found extensive application for producing photoactive polymer-based systems used in the coating industry, paints or printing inks, adhesives, composite materials and dental restorative formulations. Its unique feature “occurrence of polymerization only in illuminated areas” enables the generation of high-resolution images for the production of printing plates, optical discs and microcircuits. More recently, applications for this technology have included three-dimensional stereolithography and holographic recordings. Acrylate-based resins (Figure 3.1) are the most widely used light-curable systems because of the high reactivity of the acrylate monomers [15].

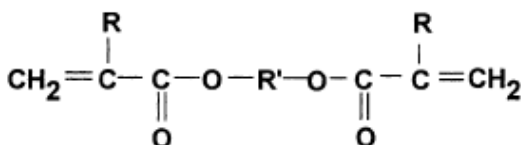


Figure 3.1: General formula of diacrylate crosslinker

UV-irradiation in the presence of a suitable photoinitiator is one of the most efficient methods for the generation of highly cross-linked polymers from multifunctional monomers. Polymerizations can be carried out under a wide range of conditions, including variations in monomer structures, the number and type of reactive functional groups, temperature, atmosphere, irradiation rate and photoinitiator type [15]. Because of the importance of free-radical photopolymerizations of multifunctional monomers and the effect of the polymer structure on material properties, it is necessary to study the influence of reaction conditions and monomer structure on the polymerization kinetics.

3.1 Linear vs. Crosslinking Systems

3.1.1 Linear systems

From the point of view of elementary reaction steps, free-radical crosslinking polymerization does not differ from the linear polymerization of monovinyl compounds and involves initiation, propagation, chain transfer and termination, where transfer and termination can occur by several mechanisms [15]. However, the kinetics of network formation show special features arising from the participation of a multi-unsaturated monomer and is complicated by other factors not observed in linear polymerizations. The next subsections give short characteristics concerning linear and crosslinking polymerizations. It is generally accepted that in free-radical polymerization, two mechanisms are responsible for the formation of dead polymer: chain transfer (to monomer, polymer, solvent, initiator or an additive) and bimolecular termination. Termination leads to the loss of two reactive centers via recombination and disproportionation and is a highly exothermic reaction. The process is second order in relation to the total concentration of radicals:

$$R_t = -\frac{d[P']}{dt} = 2k_t[P']^2 \quad (3.2)$$

Where R_t is the termination rate, k_t the termination rate coefficient (the sum of the rate coefficients of recombination and disproportionation) and $[P']$ is the total radical concentration. Free radical termination is a diffusion-controlled process.

The most important effect of diffusion control for the termination process is the gel effect (auto-acceleration) observed in concentrated systems. Figure 3.2 shows typical kinetic curves for a mono (meth)acrylate: polymerization rate (R_p) as a function of time (t), degree of double bond conversion (p) as a function of time and $R_p = f(p)$.

For the bulk polymerization of methyl methacrylate (MM), autoacceleration sets in at about 20-25%, causing a rapid increase in the polymerization rate despite monomer consumption. At still higher conversions, the gel effect appears to stop and R_p reaches its maximum value, R_p^{\max} : Then the reaction proceeds with decreasing rate reaching either complete monomer consumption or limited conversion due to vitrification. The most important parameters, which characterize these curves are: R_p^{\max} , t_{Rm} the time needed to reach R_p^{\max} , p_{Rm} the conversion at R_p^{\max} , and p^f the final

degree of double bond conversion that can be reached under given conditions.

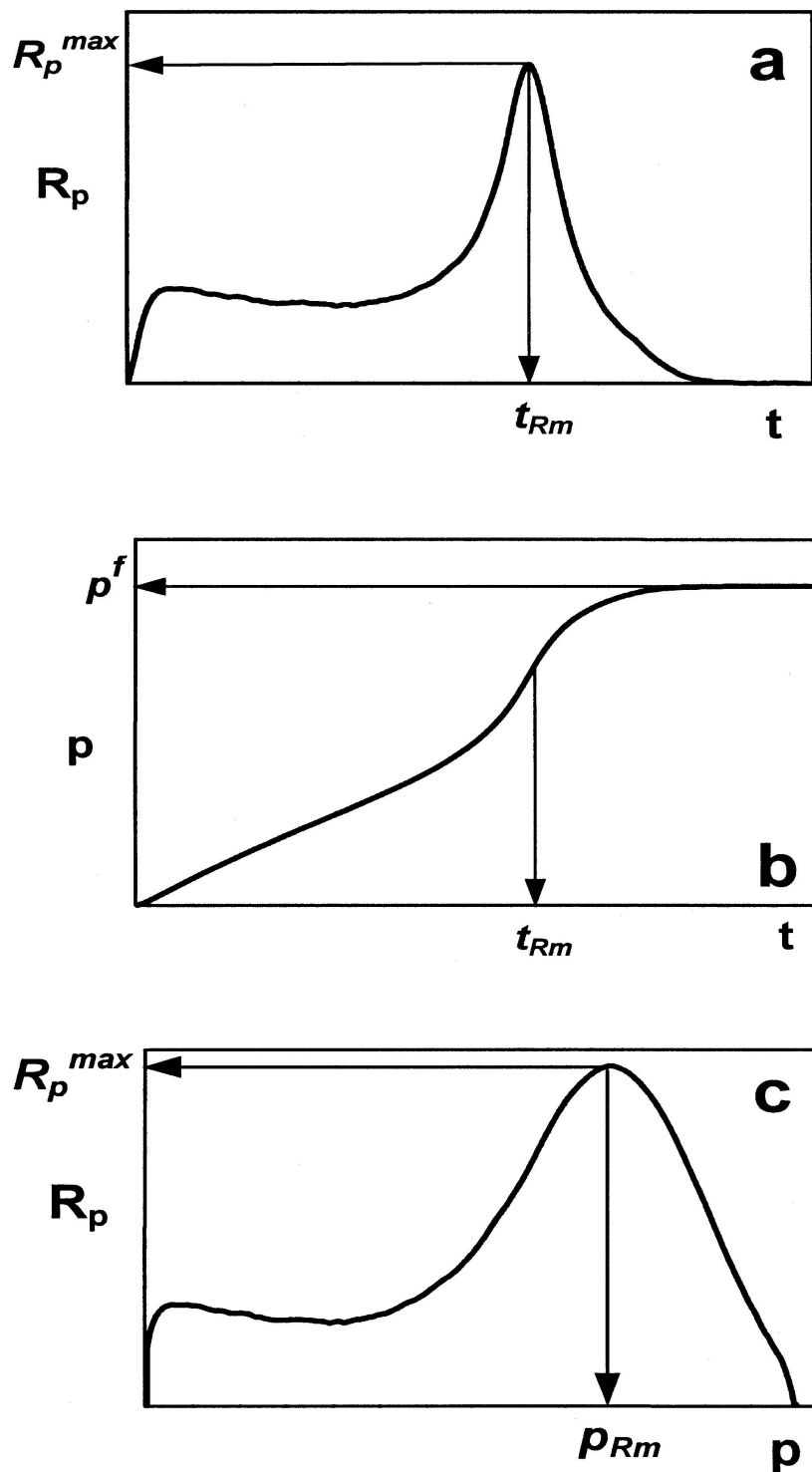


Figure 3.2: Typical shapes of kinetic curves for the polymerization of a monomethacrylate monomer: (a) polymerization rate as a function of irradiation time; (b) conversion of double bonds as a function of time; (c) polymerization rate as a function of double bond conversion [15].

As mentioned earlier, the rate determining process for termination is diffusion, both translational (diffusion of center-of-mass of a polymer coil) and segmental (a segmental reorientation of the two macroradicals so that the two radical ends are sufficiently close for chemical reaction and form a radical-radical encounter pair). Each type of diffusion is affected differently by the extent of conversion. Translational diffusion, which is chain-dependent, decreases as the reaction proceeds due to an increasing viscosity of the system. Segmental diffusion is chain-length independent, and increases due to the decreasing size of polymer coils [15].

3.1.2 Conversion dependence of the rate coefficients in linear systems

Changes in the kinetic coefficients can result from changes in the diffusivities of monomer and polymer molecules as the polymerization develops. When the increase in segmental diffusion is exactly counterbalanced (or almost counterbalanced) by the decrease in translational diffusion, k_t remains constant or moderately decreases as conversion increases. At some point, translational diffusion begins to control the termination and rapid autoacceleration (gel effect) occurs. Termination becomes increasingly slower and the termination rate constant k_t decreases several orders of magnitude. At still higher conversions, the gel effect appears to stop. This shows that the termination mechanism controlled by translational diffusion has changed and is now again chain-length independent. This new controlling mechanism is reaction diffusion. The change in the termination mechanism from one controlled by translational diffusion to another controlled by reaction diffusion occurs near the maximum polymerization rate. The region of slower change occurs for monomers conversions ranging from about 30-50% up to about 70-80%.

The monomers, which show this type of behavior for their termination rate coefficients, were classified by Buback et al. as class “B” (MM, styrene). Class “A” monomers, of which butyl acrylate is typical, seem to lack the first plateau region and translational diffusion is the rate controlling step from the very beginning of the polymerization process. Reaction diffusion controlled termination begins earlier, for instance at 10% conversion for butyl acrylate [15, 16].

3.2 Crosslinking Systems

Although network formation by free-radical polymerization of multi unsaturated

monomers displays special features of linear polymerization, primarily the occurrence of the autoacceleration, there exists several main differences arising from the existence of more than one double bond in the monomer molecule. Figure 3.3 shows reactions leading to network formation [15].

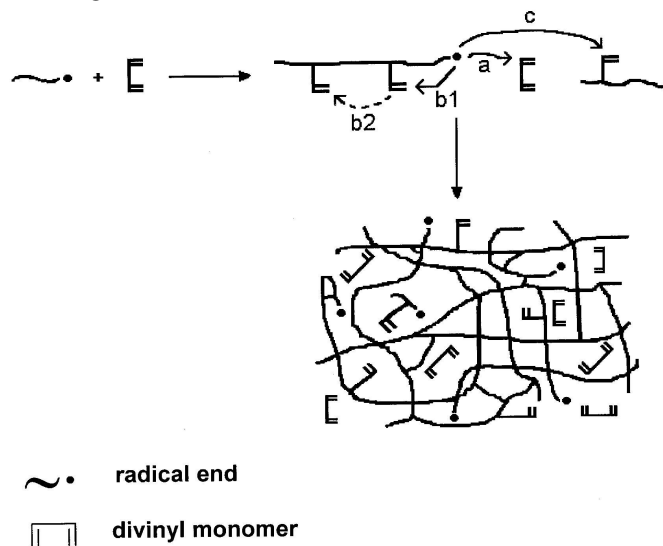


Figure 3.3: Network formation [15]

Monomer molecules are first incorporated into polymer chains as units containing pendant bonds. Further propagation can proceed by addition of the next monomer molecule (path a) and by intramolecular (path b) or intermolecular (path c) attack of the radical site on the pendant double bond. Path b is a cyclization reaction (intramolecular crosslinking), whereas path c, intermolecular crosslinking, leads to network formation. The apparent reactivity of pendant double bonds on the same chain is initially enhanced as compared to monomeric double bonds due to their larger concentration near the radical site. This leads to extensive cyclization and formation of compact structures “microgels”. These compact, internally crosslinked molecules are formed at the beginning of polymerization. Cyclization causes a delay in the gel point conversion, which is up to 2–3 orders of magnitude higher compared to the theoretical value for a ring-free system. Many of the unreacted pendant double bonds become entrapped in the microgel regions and their apparent reactivity decreases due to steric hindrance (thermodynamic excluded volume effect). Further reaction (macrogelation) occurs by the chemical joining of microgel particles. Such a view of network formation was proposed for the homopolymerization of multi-unsaturated monomers and their copolymerization with mono-unsaturated monomers. The formation of microgels is the reason for network inhomogeneity and

this can lead to a significant reduction in the mechanical strength of the polymer network when compared to a homogeneous network [15].

Cyclization can proceed if chain flexibility allows for ring formation. A very stiff bridge between two unsaturations will prevent intramolecular crosslinking. Cyclization is also difficult when the connecting bridge is very long, as for α,ω -unsaturated monomers.

Topological factors and vitrification both limit final conversion of double bonds to well below 100%. Fully cured networks can be formed only with oligomers that have relatively long flexible spacers between acrylate functionalities. Network formation highly affects the termination process. As the large polymer, chains become entangled or crosslinked in the network, center-of-mass diffusion is dramatically suppressed. Polymer radicals can still approach each other mainly through segmental diffusion or by propagation. As the reaction proceeds and crosslink density increases, the movement of radical sites by propagation reactions becomes much faster compared to segmental diffusion. Thus, reaction diffusion becomes the dominating termination mechanism from the relatively low conversion degrees [15].

Due to these reaction trends, polymer radicals can be broadly classified into three populations: (i) free radicals that are not attached to the network; (ii) radicals attached to the loosely crosslinked portion of the network so that they are spatially restricted but still mobile; and (iii) trapped radicals that are surrounded by dead polymer chains and unable to react further. Within very densely crosslinked parts of the network, the latter are eliminated from further propagation, and radical trapping may be considered as an additional means of radical deactivation. Thus, one may consider two types of termination reactions:

the usual bimolecular interaction of polymer radicals (bimolecular termination):



with bimolecular termination rate coefficient k_t^b ;

and a first-order process involving only one polymer radical (monomolecular termination):



with monomolecular termination rate coefficient k_t^m .

The way by which the termination in the polymerizing crosslinking system occurs will depend mainly on the degree of double bond conversion and the reaction conditions, including monomer structure (crosslink density), temperature, etc. It should be noted, however, that whereas bimolecular termination is irreversible, the radicals eliminated by the monomolecular process can be reactivated by an increase in network mobility, e.g. by a temperature rise. An alternative path for termination, when bimolecular termination is strongly suppressed, involves chain transfer. This reaction provides additional mobility to the radical sites on the network, reducing the lifetime of the radicals and hence reducing the rate of polymerization [15].

The restriction of the mobility of macroradicals by network formation from the very beginning of the polymerization is the main cause for another phenomenon: the onset of autoacceleration in the initial stages of polymerization. Typical kinetic curves for a dimethacrylate monomer are shown in Figure 3.4.

For di(meth)acrylate monomers, the polymerization rate reaches its maximum between 20 and 40% conversion. Note that the maximum on the $R_p = f(t)$ curve corresponds to an inflection point on the $p = f(t)$ curve. The decrease of R_p after R_p^{max} may result from such factors, as: a decrease in monomer concentration, difficulties in monomer diffusion through the solidifying medium, reduced mobility of unreacted pendant double bonds and decreasing dissociation efficiency of the photoinitiator in the viscous medium (cage effect). The gel point, that is the stage when microgels join together to form one huge molecule, can occur at conversions, as low as 1–2% [15].

When comparing the linear and cross-linked systems, one can see that although the dependence of the rate coefficients on the degree of conversion is qualitatively similar in both cases, network formation causes the reaction diffusion mechanism to be much more pronounced in crosslinked systems and setting in at lower conversions. The changes in k_t and k_p (rate coefficient of propagation) occurring with conversion increase depend not only on the type but also on the number of functional groups in the monomer molecule and on the nature of the polymerization conditions.

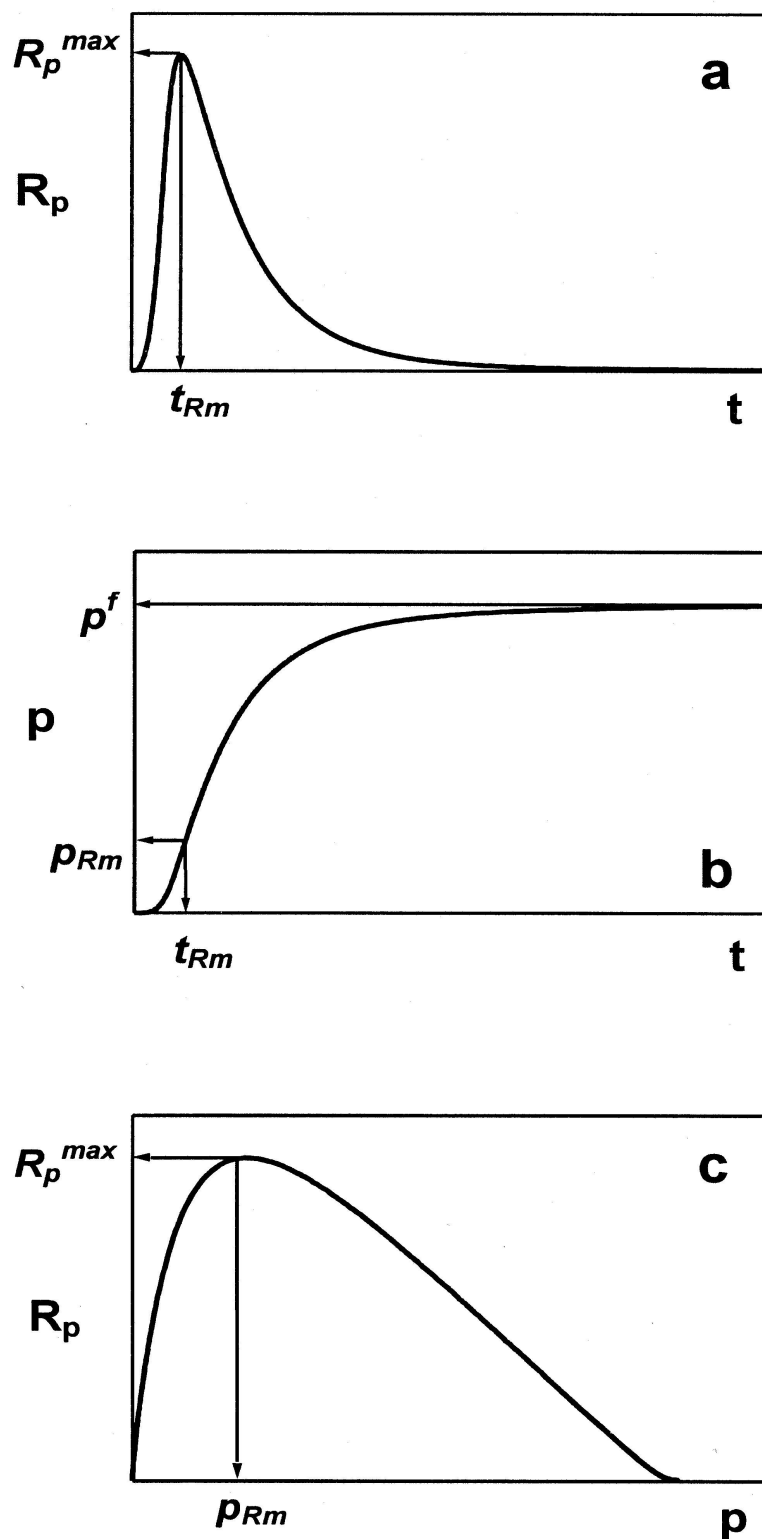


Figure 3.4: Typical shapes of kinetic curves for a dimethacrylate polymerization: (a) polymerization rate as a function of irradiation time; (b) conversion of double bonds as a function of time; (c) polymerization rate as a function of double bond conversion [15].

4. EXPERIMENTAL

4.1 Materials

4.1.1 For polymerization

Mono functional monomers, glycidyl methacrylate (2,3-Epoxypropyl methacrylate) GMA (merck), 2-hydroxyethyl acrylate HEA (aldrich) and 2-hydroxyethyl methacrylate HEMA (aldrich) were used as purchased. Radicalic photo-initiator 2,2-dimethoxy-2-phenylacetophenone DMPA (across organics) was also used without any additional treatment.

4.1.2 For difunctional monomer synthesis

Acryloyl chloride (aldrich), hydroquinone (fluka), hydrogen bromide HBr (merck) and p-benzoquinone (fluka) were utilized without any purification. Anthracene (fluka) was purified via recrystallization from xylene.

4.2 Equipments

4.2.1 Photo-DSC

Perkin Elmer Diamond photo-DSC device was utilized for photo induced curing experiments. The photo-DSC equipment consists of Photocalorimeter accessory and basic Diamond DSC instrument.

The photocalorimeter accessory kit includes:

- All parts to extend the Diamond DSC capabilities for photo curing studies
- A curing device with a 200W mercury lamp and a bandwidth filter of 250 to 450nm. (Exfo OmniCure 2000)
- A high power fiber light guide with dual leg configuration, 3mm tip diameter, 1500 mm length
- A Trigger box for accurate shutter control

4.2.2 NMR

NMR spectra of synthesized compounds were derived using by Bruker 250 MHz AC Aspect 3000 NMR device.

5. RESULTS AND DISCUSSIONS

A novel triptycene based crosslinker triptycene hydroquinone diacrylate was synthesized and characterized so as to use in free-radical photo induced polymerization systems. Photo-polymerizations were performed using monofunctional monomers glycidyl methacrylate (GMA), 2-hydroxyethyl acrylate (HEA) and 2-hydroxyethyl methacrylate (HEMA) with difunctional monomers (crosslinkers) hydroquinone diacrylate (HDA) as model compound (non-triptycene analog) and new synthesized one triptycene hydroquinone diacrylate (THDA). 2,2-dimethoxy-2-phenylacetophenone (DMPA) was used as photo-initiator in formulations. Photo-polymerization kinetics was analyzed for different compositions of monofunctional monomers and crosslinkers by using photodifferential scanning calorimeter (photo-DSC). Each monofunctional monomer was reacted with varied percentages of a difunctional monomer HDA and THDA respectively to observe the influence of triptycene based crosslinker on rate of polymerization and characteristics of cured polymer.

5.1 Preparation of Crosslinkers

5.1.1 Synthesis of HDA

Though hydroquinone diacrylate is commercially available, it was simply synthesized by acylation of hydroquinone with acryloyl chloride.

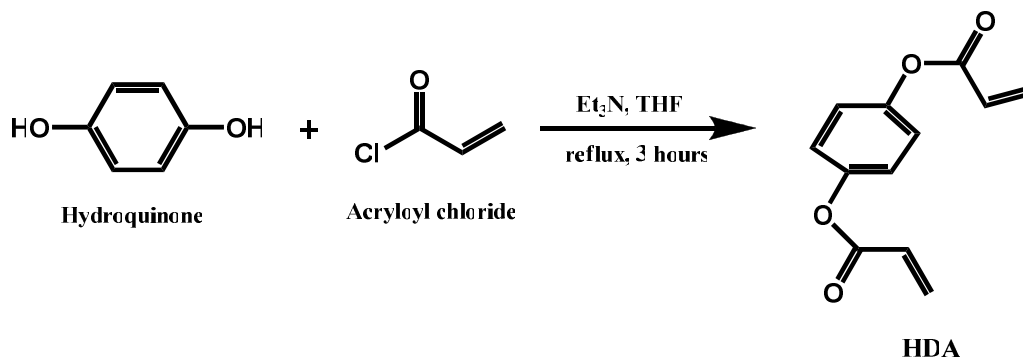


Figure 5.1: Synthesis of HDA

5.1.2 Synthesis of Triptycene Hydroquinone

In order to obtain triptycene hydroquinone diacrylate at the beginning triptycene hydroquinone (TH) should be synthesized. TH was prepared by following synthesis route described by P. Bartlett et al [1] (Figure 5.2). At the first step 10 gr anthracene was recrystallized from xylene and dissolved with 7 gr p-benzoquinone in 150 ml xylene. Diels-Alder reaction taken place in 250 ml rounded flask at reflux temperature under nitrogen atm for 3 hours. Pale yellow crystals were collected and recrystallized from xylene. At the second step 10 gr product of first step was dissolved in 70 ml glacial acetic acid and 4 drops of 40% HBr was added to solution. Reaction was carried on for an hour at reflux temperature. TH crystals were filtered and collected with high yield (93%).

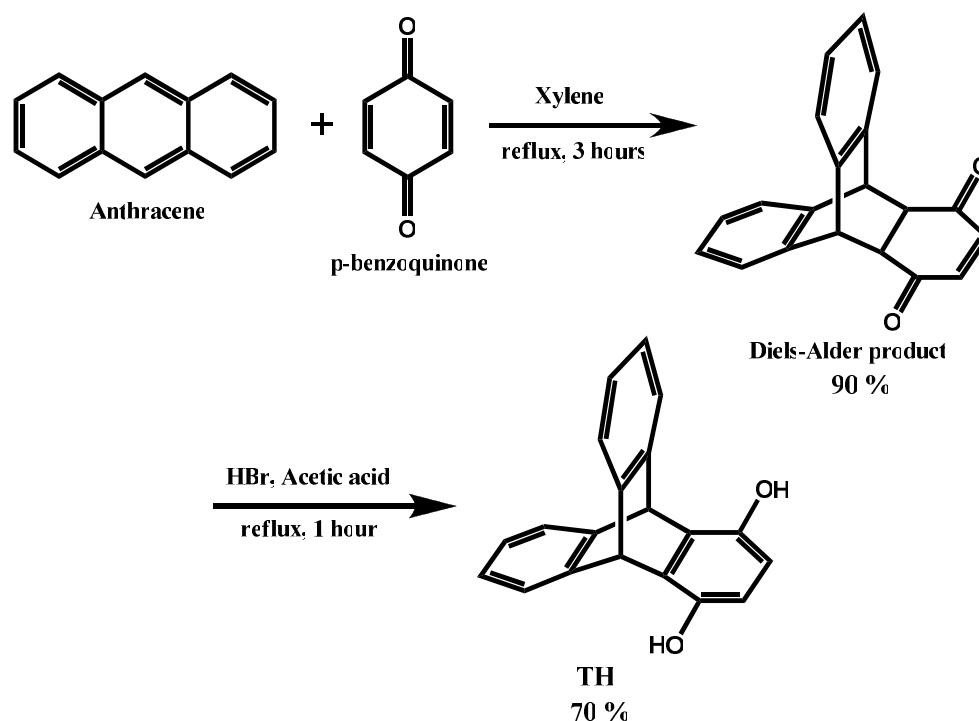


Figure 5.2: Synthesis route for Triptycene hydroquinone (TH)

5.1.3 Synthesis of THDA

2 gr TH and 4 ml triethyl amine dissolved in 50 ml THF using 100 ml two necked flask. 1,3 ml (2,3 molar equivalent) acryloyl chloride was added drop by drop and suddenly transparency of reaction mixture turn to cloudy white color. Reaction was lusted for 3 hours at RT and under N₂ atm. Reaction mixture was taken to separatory funnel. After work up, organic phase was separated and THDA was purified by

means of liquid chromatography using silica gel as the adsorbent.. THDA was obtained as white crystals (mp: 196 °C) with 70% yield. Synthesis route of THDA is summarized in Figure 5.3.

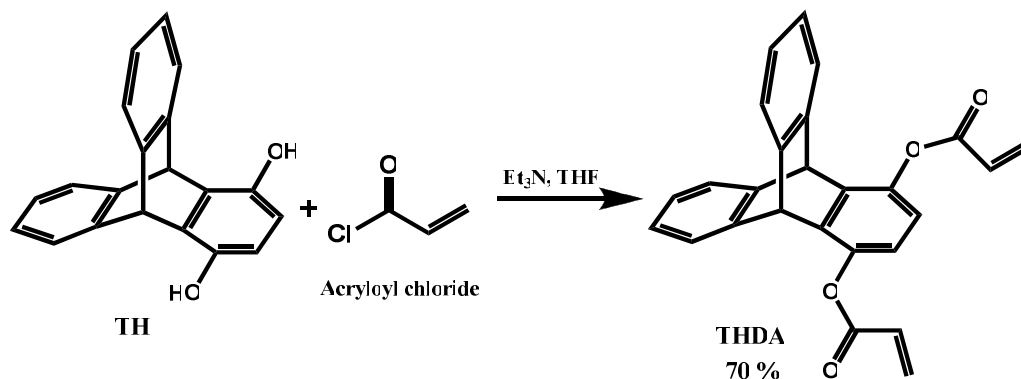


Figure 5.3: Synthesis of Triptycene hydroquinone diacrylate (THDA)

5.2 Characterization of THDA

Comparison of ^1H NMR spectra of TH and THDA are presented in Figure 5.4. Signified **a**, **b**, **c** and **d** hydrogens have specific peaks belong to TH. **e** represents diol hydrogens in TH spectrum and it inherently disappears at THDA spectrum.

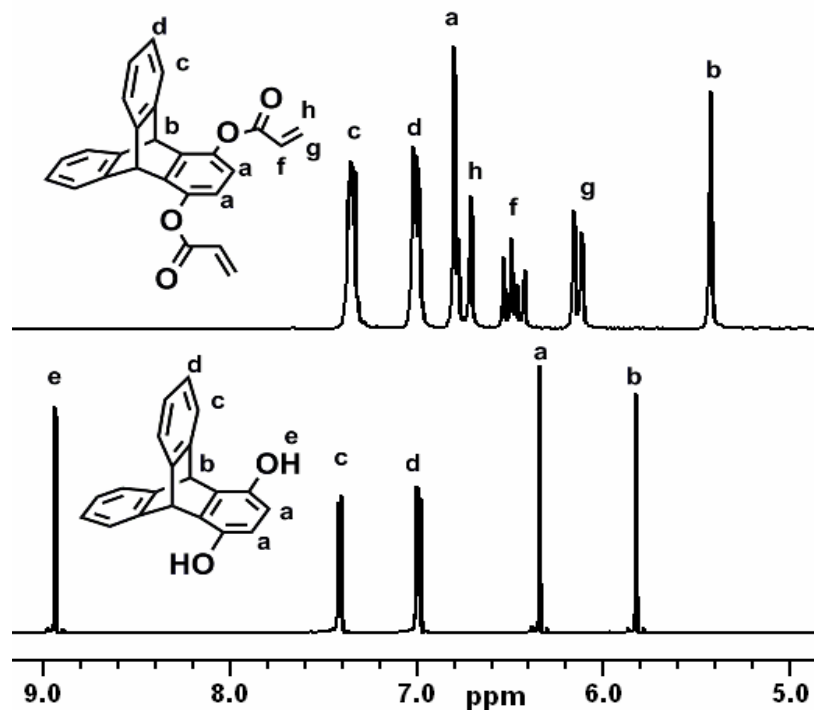


Figure 5.4: NMR spectra of THDA and TH

Furthermore **h**, **f** and **g** peaks refer to acrylic hydrogens appearing between **a** and **b**. Integration and splitting of peaks also pertain to corresponding structures

5.3 Photoinduced Curing Formulations

Solvent-free formulations were prepared to investigate effect of THDA compare to analog crosslinker HDA. Besides, influences of various crosslinker concentrations and the case absence of crosslinker were also analyzed. Molar percentage of crosslinkers in formulations were determined with respect to solubility of THDA in monofunctional monomers. THDA dissolves in GMA better than in HEMA and HEA. In formulations highest molar percentages were used as much as possible, for instance at most 3% crosslinker molar ratio was obtained in GMA case. All formulations were listed in table 1, table 2 and table 3 for GMA, HEMA and HEA respectively. For all formulations 1% molar ratio of photoinitiator DMPA was used.

Table 5.1: Formulations for GMA

| | sample a | sample a1 | sample a2 | sample a3 | sample a4 | sample a5 | sample a6 |
|--------|----------|-----------|-----------|-----------|-----------|-----------|-----------|
| THDA % | - | 1 | 2 | 3 | - | - | - |
| HDA % | - | - | - | - | 1 | 2 | 3 |
| GMA % | 100 | 99 | 98 | 97 | 99 | 98 | 97 |

Table 5.2: Formulations for HEMA

| | sample b | sample b1 | sample b2 |
|--------|----------|-----------|-----------|
| THDA % | - | 1 | - |
| HDA % | - | - | 1 |
| HEMA % | 100 | 99 | 99 |

Table 5.3: Formulations for HEA

| | sample c | sample c1 | sample c2 |
|--------|----------|-----------|-----------|
| THDA % | - | 1 | - |
| HDA % | - | - | 1 |
| HEA % | 100 | 99 | 99 |

5.4 Photo-DSC Experiments

Photo-DSC measurements were performed using Perkin-Elmer Photo-DSC equipped by mercury lamp source of 250-400 nm range UV light. For each experiment, around 3 mg of samples were taken into aluminum pans. Photo-DSC measurements were carried on at 30 °C under nitrogen purge. All samples irradiated for 10 minutes since light shutter opening. Before the shutter opening 30 seconds offset was programmed to respite system to reach thermal equilibrium. Mainly instantaneous rate of polymerizations are determined upon dividing instantaneous heat flow (releasing from photoinduced reaction) by ΔH_P (enthalpy of polymerization). ΔH_P is simply calculated for each sample by sum of acrylic and methacrylic double bonds' molar enthalpies multiply by their molar ratio in formulations. ΔH methacrylate and ΔH acrylate were taken 55000 and 80500 J/mol respectively. Instantaneous conversion values may be calculated sum of area under rate of polymerization curve. Conversion curves were determined by integration of rates curves.

5.5 Photo-DSC Results

5.5.1 GMA formulations

Rate of polymerizations versus time curves for GMA-THDA formulations are displayed in Figure 5.5. One by one *sample a* (GMA-THDA-%0), *sample a1* (GMA-THDA-%1), *sample a2* (GMA-THDA-%2) and *sample a3* (GMA-THDA-%3) are shown together for comparison. Similar to THDA, photopolymerization rates of HDA containing formulations are plotted in Figure 5.6. Faster auto-accelerations and higher maximum rate of polymerization values were observed for both HDA and THDA cases when crosslinker concentrations increased gradually. The reason is that rise in crosslinker concentration causes more network formations leading reaction to become more diffusion controlled. Besides plateau regions before onset of autoacceleration became narrower especially in the case of *sample a3* GMA including 3% THDA.

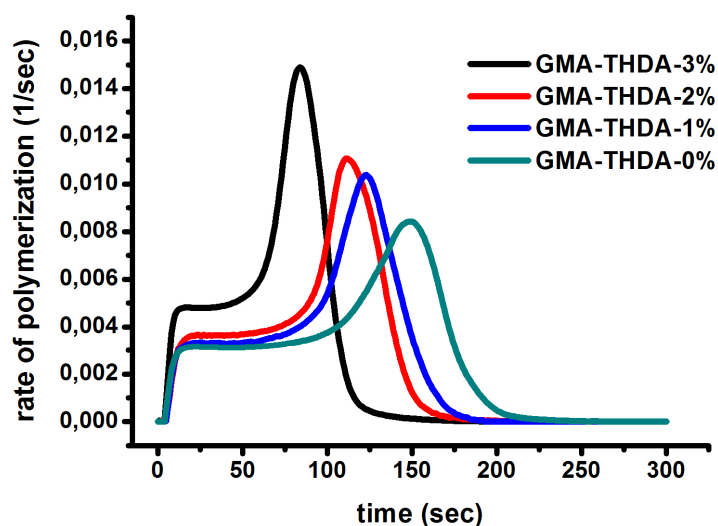


Figure 5.5: Rate vs. time plots for GMA-THDA formulations

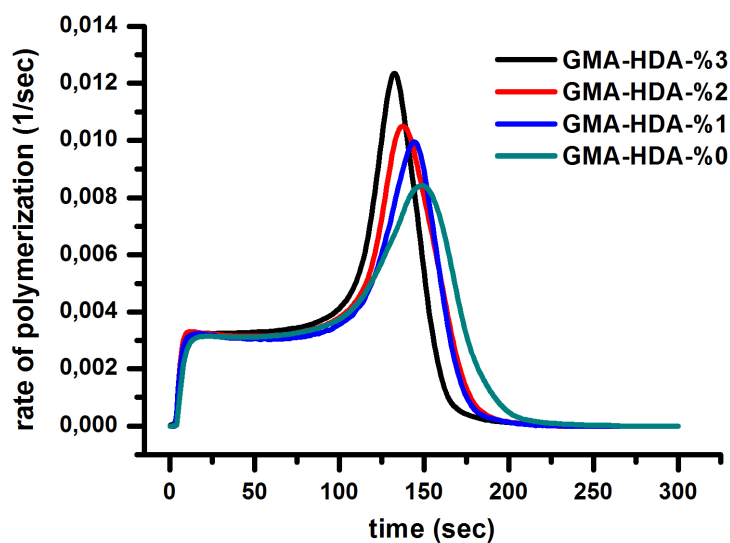


Figure 5.6: Rate vs. time plots for GMA-HDA formulations

Distinctively THDA creates much faster rates than HDA, this is clearly shown in Figure 5.7 where photopolymerization rates of *sample a* (GMA without difunctional monomer), *sample a3* (GMA-THDA-3%) and *sample a6* (GMA-HDA-3%) are plotted. It may be due to reaction tends to be under control of diffusion in earlier stages of polymerization for *sample a3* because of lack mobility of network coil centers. Because of their denticulated structure, both entangled or crosslinked THDA units induce formation of rough (barbed) coil networks while polymerization.

Diffusion or mobility of the rough coils is more suppressed than smoother ones, which are formed with HDA.

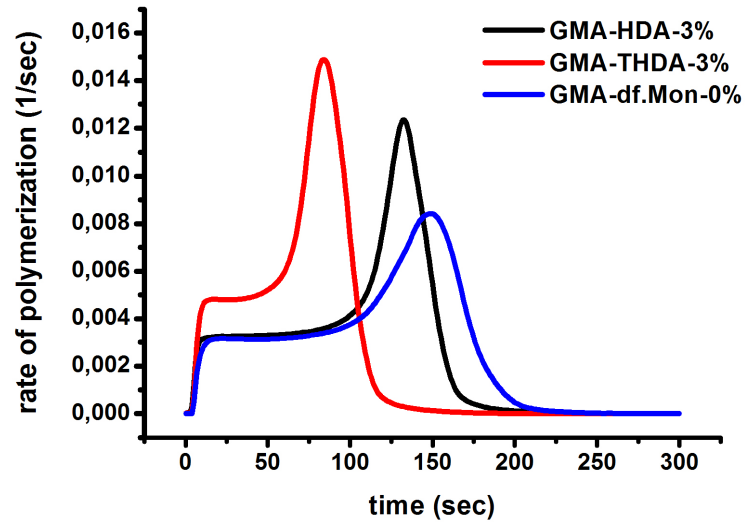


Figure 5.7: Rate vs. time plots for GMA-3% crosslinker formulations

Narrower plateau and faster autoacceleration of sample a3 could be based on T_g of formed GMA-THDA crosslinked polymer is higher than T_g of GMA-HDA. Melting point of HDA is much lower than THDA (88 °C and 196 °C respectively). Higher melting point of THDA may provoke higher glass transition temperature of formed polymer.

As it is seen in Figure 5.8, Figure 5.9 and Figure 5.10 conversions slightly decrease when crosslinkers are added to formulations. There is no clear difference between THDA and HDA according to their influence on final conversions. The reason could be that limited occurrence of microgelation at the beginning of the reaction in cases crosslinker comprising formulations.

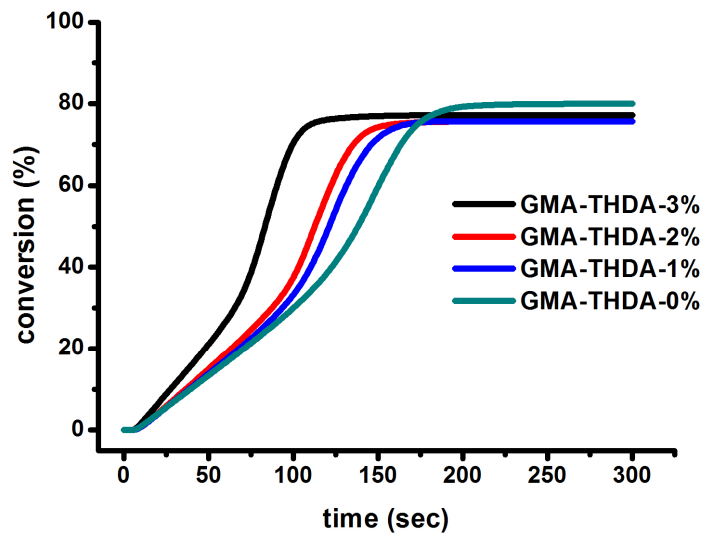


Figure 5.8: Conversion vs. time plots for GMA-THDA formulations

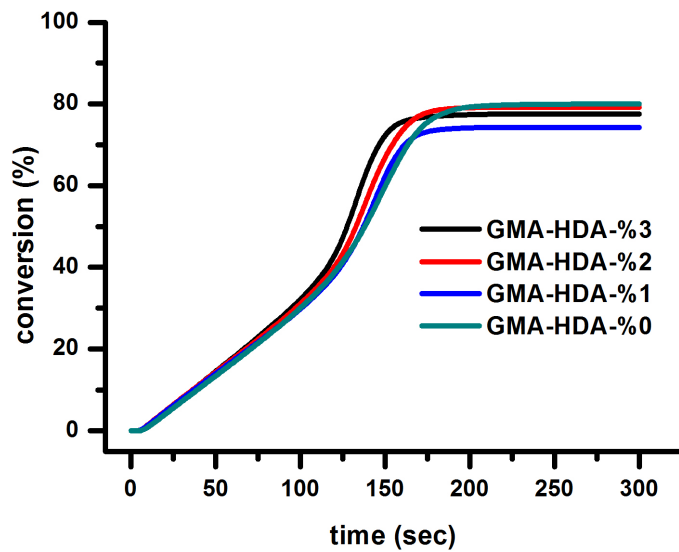


Figure 5.9: Conversion vs. time plots for GMA-HDA formulations

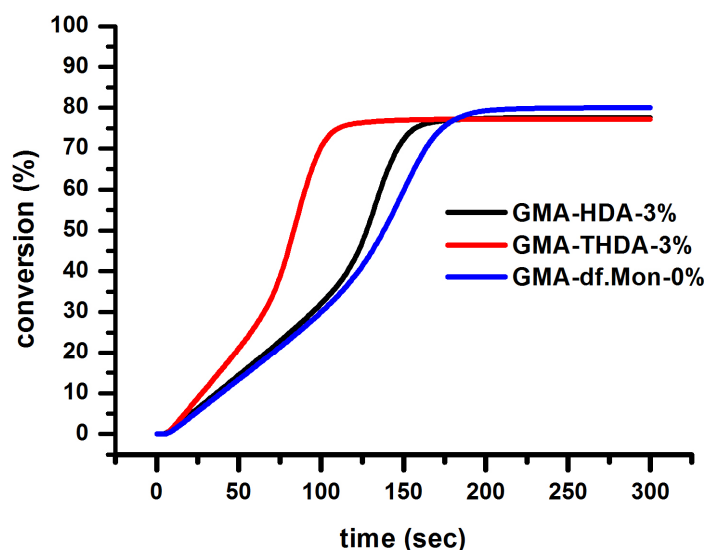


Figure 5.10: Conversion vs. time plots for GMA-3% crosslinker formulations

5.5.2 HEMA and HEA formulations

Similar considerations are acceptable for sample b and sample c series including 2-hydroxyethyl acrylate HEA and 2-hydroxyethyl methacrylate HEMA as monofunctional monomers respectively. Disadvantage of working with these monomers is that the solubility of THDA in HEA and HEMA is lower than in GMA. Therefore, maximal 1% molar crosslinker containing formulations could be prepared. For this reason, distinguish of photopolymerization inequalities among different formulations of HEA and HEMA would get difficult. Furthermore influence of crosslinker type and concentration on (meth)acrylate monofunctional monomers exhibiting relatively rapid photopolymerization rates is restricted since the photopolymerization rate is already fast enough (Figure 5.11 and 5.12).

HEA is a Class “A” type monomer lacking the first plateau region and displaying very fast polymerization rates. Though HEMA is a class “B” monomer like GMA having plateau region before the onset of auto-acceleration, it displays faster rates than GMA [16].

In Figure 5.11, differentiations among simple HEMA (*sample b*), 1% HDA (*sample b2*) and 1% THDA (*sample b1*) formulations are slightly discernable in spite of mentioned reasons. Thus parallel changes are observed that maximum rate of

polymerization increases and plateau region get narrower with HDA, and little more change in rate and plateau region is observed with THDA.

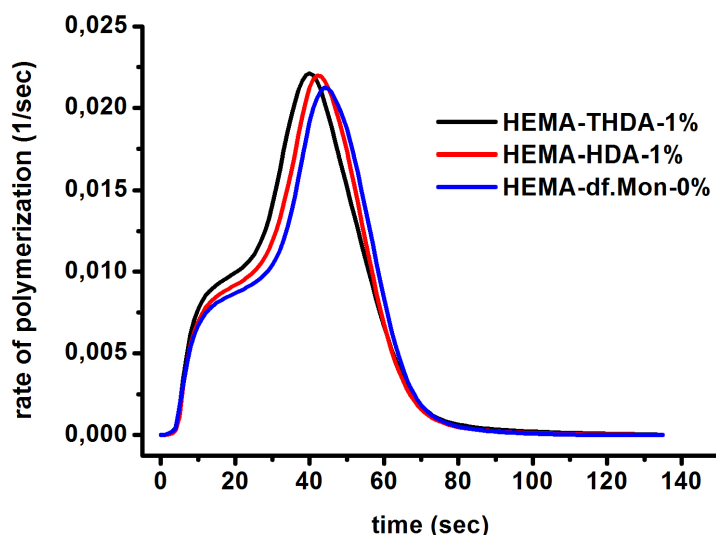


Figure 5.11: Rate vs. time plots for HEMA-1% crosslinker formulations

However in the event of HEA, HDA containing formulation (*sample c2*) exhibits little faster rate than THDA (*sample c1*). Besides, in Figure 5.12 lack of plateau regions and enormously fast rates belonging to HEA (class “A” monomer) is displayed. Therefore, contrary to expectations, the effect of THDA is not distinctive in this case.

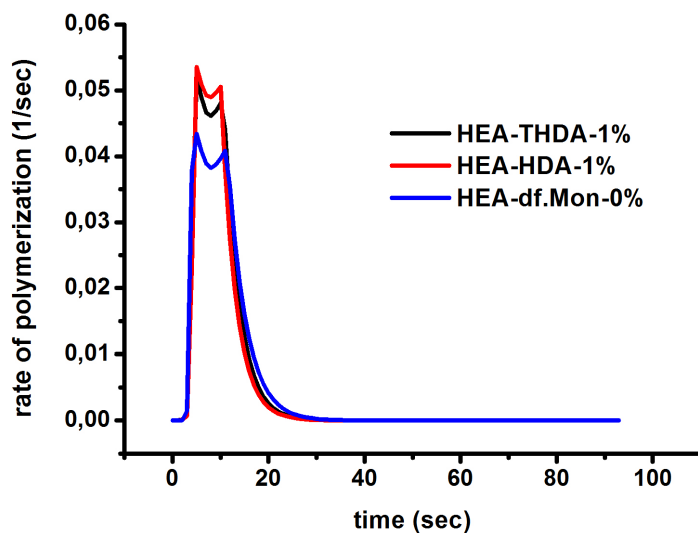


Figure 5.12: Rate vs. time plots for HEA-1% crosslinker formulations

Conversion values of HEA formulations are relatively low because of so fast polymerization rates (Figure 5.14). Final conversions are almost same independently for each HEMA and HEA formulations when HDA or THDA is added (Figure 5.13 and Figure 5.14). Since the molar ratio is too low (1%) for both cases microgelation effect is negligible so final conversions are observed at nearly same level.

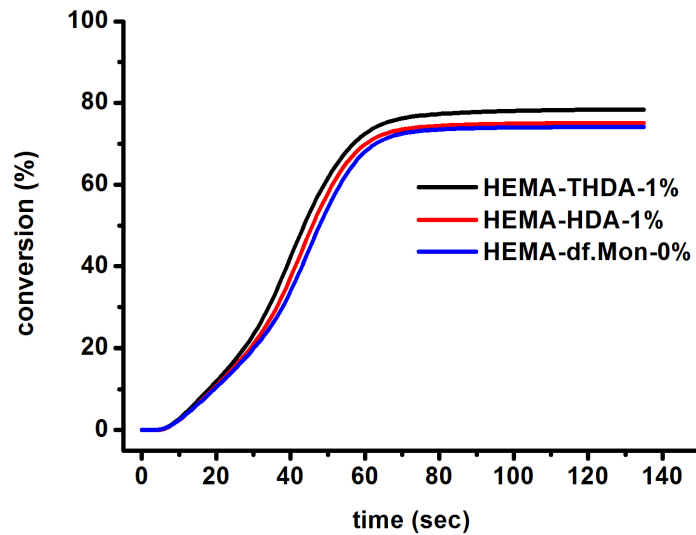


Figure 5.13: Conversion vs. time plots for HEMA-1% crosslinker formulations

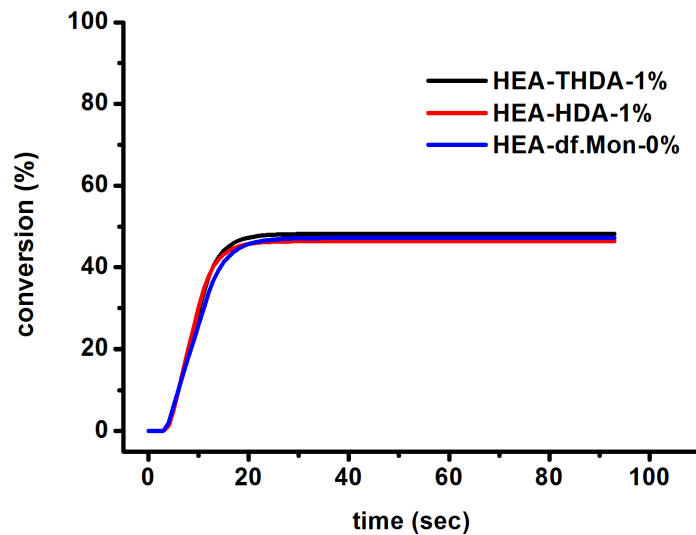


Figure 5.14: Conversion vs. time plots for HEA-1% crosslinker formulations

6. CONCLUSIONS AND FURTHER WORK

Photoinduced polymerization is very rapid, useful and durable technique for generating crosslinked polymer networks. These UV curable systems have wide range of applications including many type of coatings, paintings, printings and graphic arts and also they used in manufacturing optical fibers and electronics. The vast majority of free-radical photopolymerization studies concentrate on (meth)acrylate crosslinking systems. In this work, a novel triptycene type crosslinker triptycene hydroquinone diacrylate was synthesized and its influences on photopolymerization kinetics of (meth)acrylate curable systems were investigated. Since triptycene structure has rigid benzene rings and bulky geometry, it increases maximum rate of photopolymerization and narrows plateau region prior to onset of auto-acceleration when it is compared with analog crosslinker and non-crosslinker including formulations. Hereby, the influences of the new crosslinker on photopolymerization kinetics could be derived from additionally increase in glass transition temperature and stiffness of the produced crosslinked polymer. Besides possibility of interlocking between triptycene units could bring improvement in mechanical strength, particularly simultaneous enhancement in ductility and stiffness of formed crosslinked polymer. Thus, further studies would be preparing of thin films of curing formulations consisting each of crosslinkers THDA and HDA under UV radiation. Later on mechanical properties of those films should be investigated by using dynamic mechanical analyzer (DMA) in order to demonstrate whether triptycene units develop mechanical and thermal behaviors of cured polymer.

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