İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

**A NEW METHOD FOR PHOTOINITIATED
CATIONIC POLYMERIZATION OF VINYL ETHERS**

M. Sc. Thesis by

Muhammet Ü. KAHVECİ

Department: Chemistry
Programme: Chemistry

Supervisor: Prof. Dr. Yusuf YAĞCI

JUNE 2007

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Supervisor (Chairman) :	**Prof. Dr. Yusuf YAĞCI**
Members of the Examining Committee:	**Prof. Dr. Gürkan HIZAL (I.T.U.)**
	Prof. Dr. Duygu AVCI (B.U.)

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YÜKSEK LİSANS TEZİ
Muhammet Ü. KAHVECİ
509051213

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Tez Danışmanı :   Prof. Dr. Yusuf YAĞCI

Diğer Jüri Üyeleri   Prof.Dr. Gürkan HIZAL (İ.T.Ü.)

                     Prof.Dr. Duygu AVCI (B.Ü)

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May 2007   Muhammet Ü. Kahveci

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LIST of ABBREVIATIONS

IBVE   : Isobutyl vinyl ether
UV   : Ultra Violet
CHO   : Cyclohexene Oxide
EMP$^+$PF$_6^-$: N-Ethoxy-2-Methylpyridinium Hexafluorophosphate
THF   : Tetrahydrofuran
CT   : Charge Transfer
On$^+$: Onium Salt
GPC   : Gel Permeation Chromatography
DPICl   : Diphenyliodonium chloride
DPIBr   : Diphenyliodonium bromide
DPII   : Diphenyliodonium iodide
DVE-DEG   : Divinylether of diethylene glycol
BDVE   : 1,4-butanediol divinyl ether
HDVE   : 1,6-hexanediol divinyl ether
M$_n$: Number Average Molecular Weight

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A NEW METHOD FOR PHOTOINITIATED CATIONIC POLYMERIZATION OF VINYL ETHERS

SUMMARY

The discovery of the living cationic polymerization of vinyl ethers, dienes and styrenes furnished a precious tool in the synthesis of well-defined macromolecules with number of functional groups, molecular weight, and polydispersity. In a classical living cationic polymerization of vinyl ethers, gaseous protonic acids must be used as an initiator with zinc halides. This method has some problems associated with handling of gaseous protonic acid.

Recently, photoinduced living cationic polymerization of IBVE in the presence of various diphenyliodonium and zinc halides was reported. Protonic acid photochemically generated from the diphenyliodonium salt can initiate the polymerization.

The spectral response of simple diphenyliodonium salts is usually below 300 nm. This brings some limitations on the potential uses of cationic polymerization particularly when high wavelength light sources are used. To overcome this problem diphenyliodonium salts may be decomposed using photoinitiators/photosensitizers that absorb light at higher wavelength.

In this thesis a new photoinitiating system for living cationic polymerization of vinyl ethers especially in cold (-5 ^{o}C) has been reported. Furthermore, the possibility of this initiating system to use for UV curing of di-functional vinyl ethers at room temperature has been described. The photoinitiating system comprises free radical photoinitiators such as DMPA, benzophenone or thioxanthone, together with a diphenyliodonium halide and a zinc halide. In the first step, photochemically generated free radicals are oxidized to the corresponding carbocations which subsequently reacts with the monomer to yield an adduct. In the presence of zinc salt, this adduct can initiates living cationic polymerization of IBVE in cold, as well as UV curing of di-functional vinyl monomers at room temperature.

VİNİL ETERLERİN IŞIKLA BAŞLATILAN POLİMERİZASYONU İÇİN YENİ BİR YÖNTEM

ÖZET

Yaşayan katyonik polimerizasyon, çift bağlı monomerlerin polimerleşmesi sonucunda elde edilen ve istenilen özelliklere (belirli molekül ağırlığında, fonksiyonel uçlara sahip, molekül ağırlığı dağılımı düşük, vb.) sahip makromoleküllerin sentezlenmesinde oldukça iyi bir yöntemdir. Vinil eterlerin klasik yaşayan katyonik polimerizasyonunda, çinko halojenür ile birlikte başlatıcı olarak gaz haldeki protonik asitlerin kullanılması gerekmektedir. Ancak, gaz haldeki protonik asidin kullanılması gaz özelliğinden dolayı çok zordur ve çeşitli problemlere neden olmaktadır.

Son yıllarda, çeşitli difeniliyodonyum ve çinko halojenürler varlığında IBVE'nin fotobaşlatıcılarla gerçekleştirilen yaşayan katyonik polimerizasyonu geliştirilmiştir. Bu yöntemde difeniliyodonyum tuzlarının ışıkla uyarılıp bozunması sonucunda reaksiyon ortamında üretilen protonik asit ile reaksiyon başlamaktadır.

Ancak, difeniliyodonyum tuzları yaklaşık olarak 300 nm dalgaboyundaki ışığı absorlamaktadır ki, bu da uzun dalga boyunda ışık kullanıldığında iyodonyum tuzlarının katyonik polimerizasyondaki potansiyel kullanımını kısıtlamaktadır. Bu sorunu aşmak için difeniliyodonyum tuzu indirekt olarak daha yüksek dalgaboylarında absorbsiyon yapan fotobaşlatıcılar veya fotosensitizerler ile parçalanıp katyonik ara yapı oluşturulur.

Bu çalışmada vinil eterlerin özellikle soğukta (-5 ^{o}C) yaşayan katyonik polimerizasyonu için, yeni bir fotobaşlatıcı sistem önerilmiştir. Buna ek olarak bu sistemin oda sıcaklığında çift fonksiyonlu vinil eterlerin UV kürlemesi için kullanılma olanağı da incelenmiştir. Fotobaşlatıcı sistem, bir difeniliyodonyum halojenür ve bir çinko halojenür ile birlikte DMPA, benzofenon veya tioksanton gibi serbest radikal fotobaşlatıcılardan oluşur. İlk aşamada, fotokimyasal olarak üretilen serbest radikaller daha sonra monomerler ile reaksiyona girip "adduct" oluşturacak karbokatyona yükseltgenir. Çinko tuzu varlığında, bu "adduct" soğukta İBVE'nin yaşayan katyonik polimerizasyonunu başlatacabileceği gibi oda sıcaklığında çift fonksiyonlu vinil eterlerin UV kürlemesini de başlatabilir.

1. INTRODUCTION

The discovery of the living cationic polymerization of vinyl ethers, dienes and styrenes furnished a precious tool in the synthesis of well-defined macromolecules with number of functional groups, molecular weight, and polydispersity [1]. A key to the success of the living cationic polymerization is the stabilization of the unstable carbocations via suitable nucleophilic counteranion originating from the initiator and the catalyst. Generally, protonic acids like hydrogen iodide are employed as the initiators, while Lewis acids like zinc iodide are employed as the catalysts [2-5].

Recently, photoinduced living cationic polymerization of IBVE in the presence of various diphenyliodonium salts and zinc halides was reported by Mah and coworkers [6, 7]. Photochemically generated protonic acid reacts with IBVE to form monomer HX-adduct. Terminal carbon-halide bond in this adduct is activated by the coordinating effect of zinc halide. This activation leads to generation of suitable nucleophilic counteranion by stabilizing the growing carbocation. Thus, chain breaking processes are prevented and living cationic polymerization of IBVE proceeds (Figure 1.1).

The spectral response of simple diphenyliodonium salts is usually below 300 nm and for their practical application it is often required to extend it to longer wavelengths. Several attempts have been described to overcome this problem in classical photoinduced cationic polymerization. These include electron transfer reactions either with photoexcited sensitizers **(i)** [8-17], free radicals **(ii)** [18-20], or electron donor compounds in the excited charge transfer complexes **(iii)** [21, 22].

This system may also used in UV curing of vinyl ethers. UV-radiation curing is defined as transformation of liquid multifunctional monomers or oligomers into solid and insoluble crosslinked polymers using UV or laser radiation. In recent decades it has become powerful industrial method widely used in various applications including coatings, inks, adhesives, varnishes, electronics, photolithography, and dyes due to its great advantages [23-25]. It offers high rate of curing at ambient temperatures, lower energy cost, and solvent-free formulation for curing, thus elimination of air

Figure 1.1. Light-induced living cationic polymerization of IBVE in the presence of diphenyliodonium salts and zinc halides

and water pollution [24, 25]. It also devotes temporal and spatial control of the curing when high initiation rate is reached [26].

UV-radiation curing includes cationically UV-initiated photopolymerization, as well as free-radical photopolymerization. Several advantages of the former over the latter have been reported [24, 25, 27] as a means of overcoming volatile emissions, limitations due to molecular oxygen inhibition, toxicity, and problems associated to high viscosity. Furthermore, after the curing of cationically curable monomers, namely the vinyl ethers (VEs) and epoxides, the cationic mechanism of the polymerization allows unreacted monomers undergo dark-curing process in which they slowly polymerize during storage of the sample.

This study describes photochemically initiated free radical promoted living cationic polymerization of IBVE by using free radical photoinitiators, such as DMPA, benzophenone and thioxanthone, or photosensitizers such as anthracene and perylene in the presence of iodonium and zinc halides. Furthermore, this study introduces UV curing possibility of monomers by using the described system. Obviously the system will be based on the generation of cation-monomer adduct by photochemical means.

2. THEORETICAL PART

2.1 Photoinitiated Polymerization

Photoinitiated polymerization is typically a process that transforms a monomer into polymer by a chain reaction initiated by reactive species (free radicals or ions), which are generated by UV irradiation. In recent decades it has become powerful industrial method widely used in various applications including coatings, inks, adhesives, varnishes, electronics, photolithography, and dyes due to its great advantages [23-25]. It offers high rate of curing at ambient temperatures, lower energy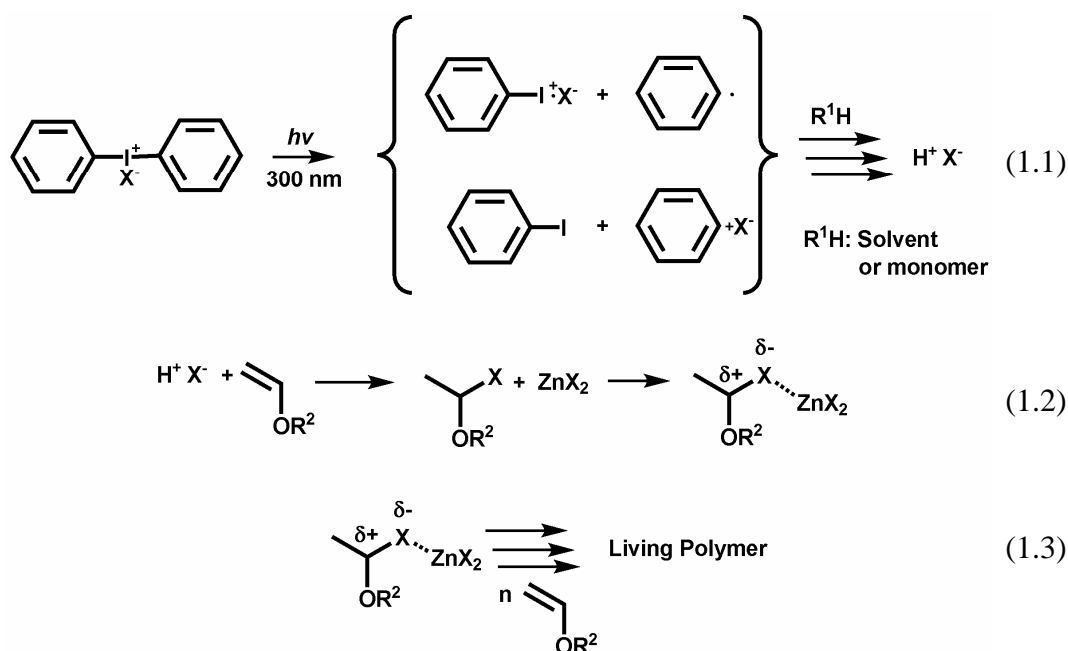 cost, and solvent-free formulation, thus elimination of air and water pollution [24, 25]. It also devotes temporal and spatial control of the polymeriztion when high initiation rate is reached [26].

2.1.1 Overview

Photoinitiated polymerization is considered as a process that is initiated by active species (radicals or ions) generated from light-induced reactions and in which the subsequent reactions of monomers or oligomers to yield polymeric structures. The light-induced initiation includes a photochemical reaction in which a photon is absorbed by an initiator or a sensitizer to commence the reaction. Population of them in the excited state increase and can then undergo some transitions, which can be classified into two processes; photophysical and photochemical. Former do not generate new chemical compounds, but transform excited states to each other or excited states to ground states, or vice versa. On the other hand, photochemical processes produce new chemical species which are different from starting compounds [28].

In photoinitiated polymerization, absorbed light directly or indirectly causes generation of a species which is able to initiate polymerization of the polymerizable constituents, monomers or oligomers. 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 photointiation processes involve a uni- or bimolecular process [28]. This applies to free radical, as well as cationic photoinitiation.

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.

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 [28]. This shift is usually towards longer wavelengths (red-shift or bathochromic shift) to decrease energy cost and increase efficiency of the system. Photoinitiaors 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 [28]. 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 [28]. 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).

2.1.2 Stages of Photoinitiation

In order to initiate a polymerization reaction, photoinitiation process should pass through two successive stages, photophysical and photochemical stages.

2.1.2.1 Photophysical Stage: Absorption

Photochemical reactions can not occur without absorption of energy of a photon; therefore, the first stage in any light-induced polymerization system is the absorption of the energy. Photoinitiators and photosensitizers usually absorb light at UV range.

Not all molecules absorb photons at the wavelength of the incident irradiation and although photons may be absorbed the excited molecule may not yield free radicals or cations, which initiate polymerization reaction. For practical applications, the molecule must have a suitable chromophore to absorb photons [28]. For example, photoinitiators such as iodonium salts; benzophenone; thioxanthone; sulfonium salts, and photosensitizers such as perylene and anthracene contain suitable chromophore groups that absorb light at UV region and initiate polymerization.

Absorption of light by the component of a polymerization system does not usually lead to formation of initiating species. For this reason, a photoinitiator, which absorbs light energy into chemical energy in forms of initiating species, must be added into polymerization system. If absorption of components of the formulation interferes with absorption of the photoinitiation system, efficiency of the initiating process is decreased [28]. Thus, components of the formulation must be selected carefully in order to prevent absorption of light, which should be absorbed by only photoinitiating molecules, by total formulation except photoinitiator or photosensitizer. This enhances efficiency of the initiating process.

2.1.2.2 Photochemical Stage: Production of Chemically New Species

In order to initiate a polymerization reaction, after the absorption process, it is necessary that photoinitiator and the initial excitation produce an initiating species.

This occurs by a chemical reaction from the excited state (the photoreaction), which is possibly followed by thermal reaction steps [28].

The reaction occurring from the excited state produces new species and is known as the primary photochemical reaction. The primary reactions may involve fragmentation reactions yielding a new chemical constitution, or electron transfer processes. The following thermal reactions, which can not be experimentally distinguishable from the primary reactions, are known as secondary or dark reactions.

Although photochemical reactions yield new species quenching processes through triplet energy transfer may happen [28]. For example, the excited state energy can be transferred to a quenching molecule, such as oxygen [28]. This event is known as quenching process and it is one of two reasons for oxygen inhibition in photoinitiated polymerization (The second reason for oxygen inhibition is that oxygen scavenges carbon-centered primary radicals and terminates polymerization process.). In quenching processes, the acceptor molecule is incapable of generating initiating species from its excited state; therefore these processes are considered as energy wasting.

Photochemical reaction mechanisms include unimolecular reactions (Type I) (i), bimolecular reactions (Type II) (ii), and energy transfers, which occur before unimolecular or bimolecular reactions (iii) [28].

2.1.2.3 Unimolecular Reactions

When the photoinitiator contains a bond with dissociation energy lower than that of the excited state, the covalent bond can be broken leading to formation of a reactive species. This process is termed homolytic cleavage or direct fragmentation. These type photoinitiators are known as Type I photoinitiators [28]. There are many cationic, free radical and photobase generating photoinitiators which are classified as Type I photoinitiators, and some examples of them are given in the Figure 2.1.

Most photoinitiators which initiate polymerization via free radical mechanisms contain carbonyl group [28]. Carbonyl containing organic molecules may undergo various photochemical reactions, after their excitation. However, only Norrish Type I fragmentation generates radical which are capable to initiates polymerization

reactions. Another photoreaction, the Norrish Type II reaction, also produces radicals, but they are not useful for initiation of polymerization [28].

Norrish Type I Reaction: In the primary photochemical process, homolytic cleavage of a bond between the carbonyl group and α-carbon is known as Norrish I cleavage.

Norrish Type II Reaction: The abstraction of a hydrogen atom from the γ position by the carbonyl group leading to a 1,4-biradical is considered as the Norrish Type II reaction.

The structure of the carbonyl compound determines which mechanism will be preferred. As mentioned before, only the products of the Norrish Type I reation are capable to initiates; therefore, it is crucial to select true structures which undergo α-cleavage process with high efficiency in the development of new Type I photoinitiators.

2.1.2.4 Bimolecular Reactions

When certain molecules absorb light leading to excited state molecules, they will not undergo a fragmentation reaction. These molecules may react with other molecules to produce initiating species in a bimolecular reaction. These initiating systems are termed bimolecular or Type II photoinitiators. The radiation absorbing molecule is termed photosensitizer, and the second compound is regarded as the coinitiator. Either the sensitizer or the coinitiator (or both) may, finally, form the initiating active species. In such a system, the presences of both of them (the conitiator and the sensitizer) are indispensable for the initiation system.
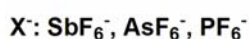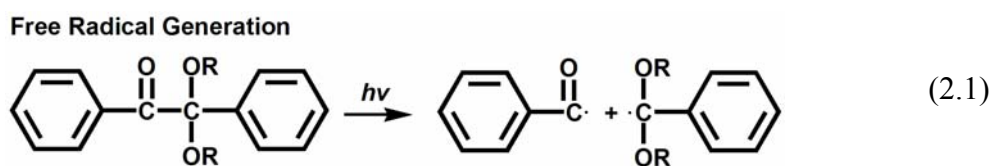

Figure 2.1. Direct fragmentation of Type I photoinitiators

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In some cases, direct excitation of photoinitiators might be difficult under certain conditions due to competitive light absorption of other components of the polymerizable formulation at the wavelength which is necessary for excitation of the photoinitiator [28].

Under this circumstance, it can be helpful to activate the photoinitiator (or the photoinitiator system) via energy or electron transfer from a sensitizer molecule possessing different light absorption characteristics. In the case, the sensitizer absorbs light, in turn, becomes excited, and it transfers its energy to the photoinitiator, which subsequently generates the initiating active species.

The important point is that kinetic studies have shown a Type I photoinitiator is inherently more effective than a bimolecular Type II initiator in a sensitizer/photoinitiation system [28].

A photosensitizer may interact with photoinitiator in the presence of irradiation and forms an excited state complex which is called as "exciplex" [28]. The excess energy of an exciplex can be lost via radiative or non-radiative processes. Also exciplex can form an initiating active species by either an electron transfer or by bond cleavage. Another kind of complex works through electron acceptance and donation between the members of the complex.

In addition to complex formation, hydrogen abstraction is known as bimolecular reaction.

a. Complex Formation:

Complex formation can occur between two molecules when they are either in their ground or excited states. There are various complex formation mechanisms for ground state complexes, such as electron electron donor-acceptor interactions; aggregation; and intramolecular interaction, as well as for excited state complexes including dipole-dipole interactions and charge transfer interactions [28].

In the case of an excited state complex from a ground state complex, firstly, the ground state complex is formed, and then one component of the complex absorbs a photon leading to formation of the excited state complex (Figure 2.2). In contrast, in the other case, before complex formation, one component of the complex absorbs a photon and become an excited state molecule which then interacts with other

component, which is at its ground state to form excited state complex (Figure 2.3) [28].

Many of the reactions occurring within the two types of excited complexes are similar and this can lead to confusion concerning their mechanisms of reaction. Both complexes need the absorption of a photon to form the excited state, the only difference is in the nature of the absorbing species.

b. Hydrogen Abstraction:

When carbonyl compounds are excited by radiation, not all excited state carbonyl compounds will undergo a unimolecular fragmentation reaction, some of them, i.e. diaryl ketones, have another reaction pathway which generates radicals that are capable of initiation of polymerization in a bimolecular process. In the case, diaryl ketones in their excited state are considered as hydrogen abstractors. In many cases, the hydrogen is transferred from an amine employed as a coinitiator to excited state a diaryl ketone employed as a hydrogen abstractor (Figure 2.4). Alcohols and thiols may also provide hydrogen for this type of reactions. In Figure 2.4, a benzophenone is excited by an absorption of a photon, and forms an exciplex with tertiary amine, which is present in its ground state. The α-amino radical produced after hydrogen abstraction can be used in an initiating system.
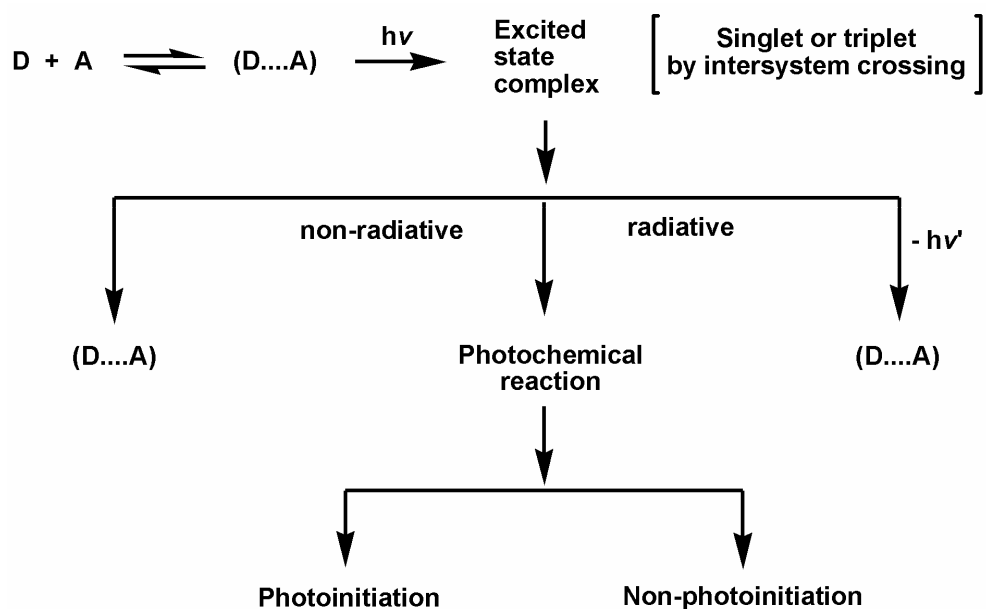
Figure 2.2. Potential reactions of excited charge transfer complex species
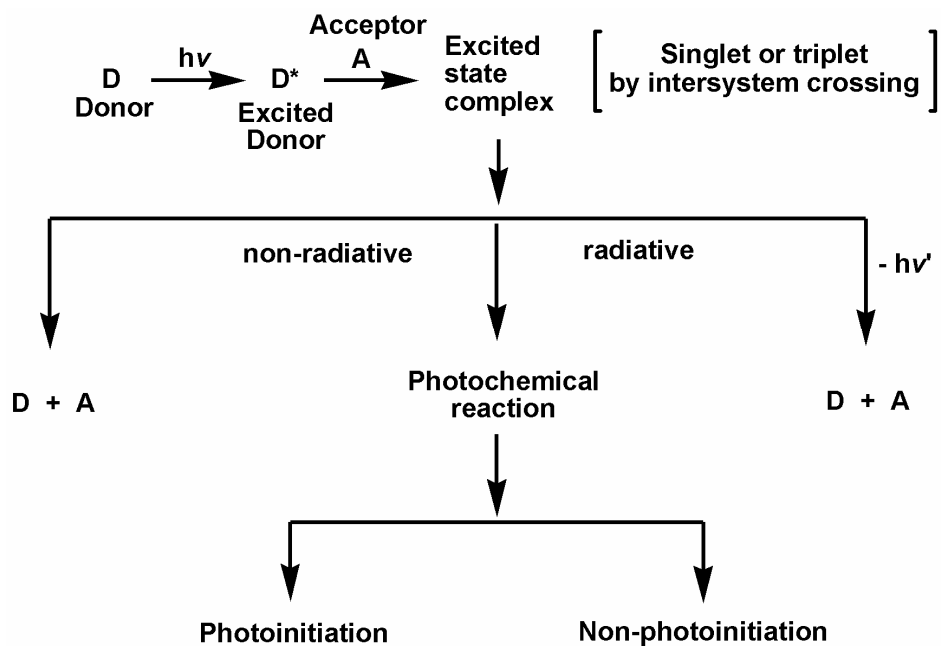
Figure 2. 3. Potential reactions of excited charge transfer complex species

$$(2.4)$$

$$(2.5)$$

$$(2.6)$$
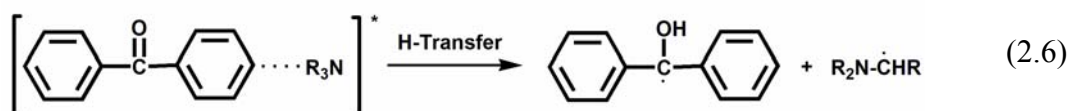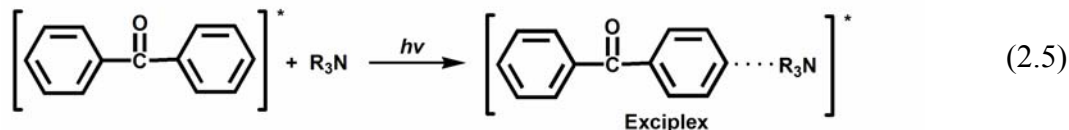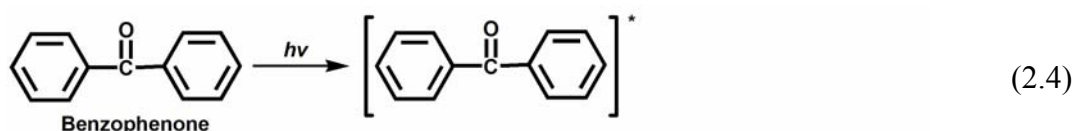
Figure 2.4. Hydrogen abstraction through an exciplex mechanism

There have been very rare examples of photoinitiated anionic polymerization so far, thus photoinitiated polymerization can be mainly classified as free-radical and cationic photoinitiated polymerization.

2.2 Photoinitiated 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 [29] 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 [28].

   i. 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.

   ii. The adoption of radiation curing by new technologies requires new types of photoinitiators to fulfill specific demands.

2.2.1 Stages of Free-Radical Polymerization

A typical free-radical polymerization comprises four elementary steps [30, 31]:

1. initiation
2. propagation
3. chain transfer
4. termination

The first step, *initiation* is decomposition of the initiator molecule into primary radicals $R^{\cdot}$. 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 (reactions 2.7, 2.8 in Figure 2.5) [28]. The actual initiation occurs when free radical react with a monomer (reaction 2.9). 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 (reactions 2.10, 2.11

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photoreactions

$$PI \xrightarrow{h\nu} PI^* \qquad (2.7)$$

$$PI^* \longrightarrow R_1^{\cdot} + R_2^{\cdot} \qquad \text{photoinitiation} \quad (2.8)$$

thermal reactions

$$R_1^{\cdot} + M \longrightarrow R_1\text{-}M\cdot \qquad (2.9)$$

$$R_1\text{-}M\cdot + M \longrightarrow R_1\text{-}MM\cdot \qquad (2.10)$$

$$R_1\text{-}MM\cdot + (n\text{-}1)M \longrightarrow R_1\text{-}M_n^{\cdot} \qquad \text{propagation} \quad (2.11)$$

$$R_1\text{-}M_n^{\cdot} + R_3\text{-}H \longrightarrow R_1\text{-}M_n\text{-}H + R_3^{\cdot} \qquad (2.12)$$

$$R_3^{\cdot} + M \longrightarrow R_3\text{-}M\cdot \qquad \text{chain transfer} \quad (2.13)$$

$$R_1\text{-}M_n^{\cdot} + R_1\text{-}M_i^{\cdot} \longrightarrow R_1\text{-}M_{n+i}\text{-}R_1 \qquad (2.14)$$

$$R_1\text{-}M_n^{\cdot} + R_2^{\cdot} \longrightarrow R_1\text{-}M_n\text{-}R_2 \qquad \text{termination} \quad (2.15)$$

$$R_1\text{-}M_n^{\cdot} + R_1\text{-}M_i^{\cdot} \longrightarrow R_1\text{-}M'_n + R_1\text{-}M'_i \qquad (2.16)$$
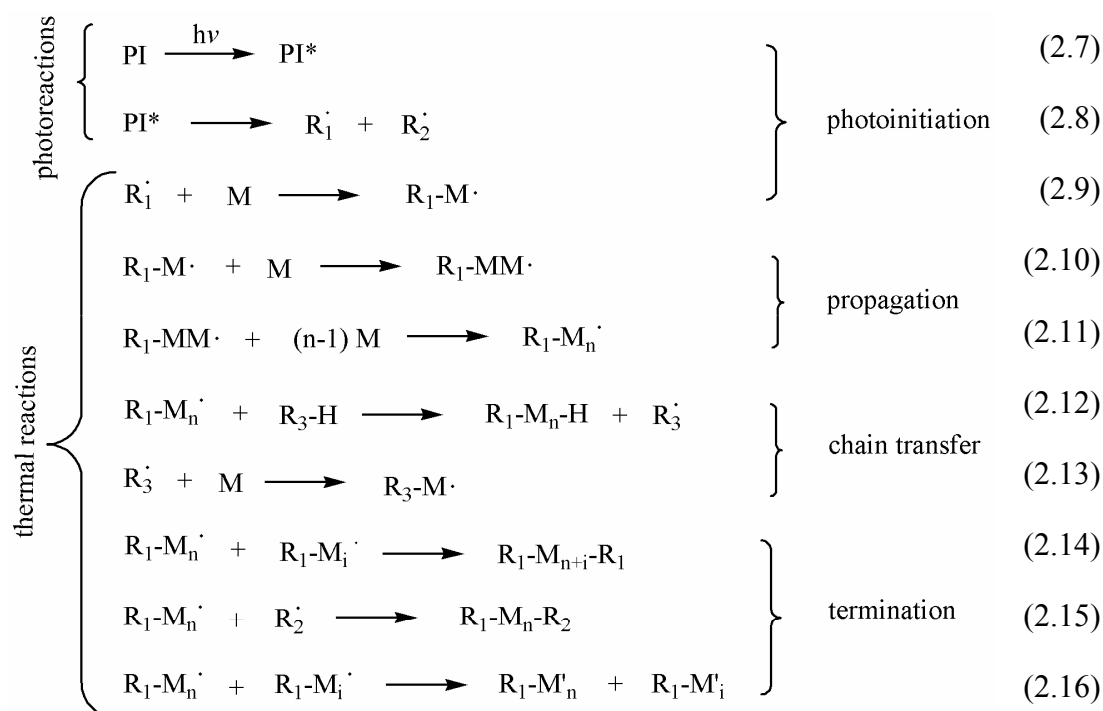
PI = photoinitiator
PI* = excited photoinitiator
$R_1^{\cdot}$, $R_2^{\cdot}$ = radical fragments of the photoinitiator
R_3-H = hydrogen donor
M = monomer

Figure 2.5. Various steps in a photoinitiated free-radical polymerization

in Figure 2.5). 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 destruction of propagating radicals. Normally, in the absence of retarding species that destroy growing radicals, chain termination occurs by bimolecular interaction of radicals (reactions 2.14-2.16 in Figure 2.5).

2.3 Photoinitiated Cationic Polymerization

Much effort has been devoted to free radical systems [32, 33] mainly due to the availability of a wide range of photoinitiators and the great reactivity of acrylate-based monomers. Although the most popular industrial applications are based on the photoinitiated free radical photopolymerization there are some drawbacks associated with this type polymerization such as the inhibition effect of oxygen and post-cure limitations, which may affect the properties of the final product. Several advantages

of the photoinitiated cationic polymerization over the photoinitiated free-radical polymerization have been also reported [24, 25, 27]. This advantages were explained in section 1.

Photoinitiated cationic polymerization differs from photoinduced radical polymerization in the following ways [28]:

i.) The initiating species, which is either a Brønsted or Lewis acid, is usually a chemically stable compound, which in the absence of bases or nucleophiles has an unlimited lifetime, unlike free radicals which unless trapped have a very short lifetime.

ii.) Thermal activation is needed in addition to photochemical activation of the initiator to allow curing of all except the most reactive types of monomers. Free radicals, once generated, do not necessarily require thermal energy to achieve full cure.

iii.) The polymerization once initiated, continues for a long time in the absence of light. Generally, photoinduced free-radical polymerization ceases shortly after exposure ceases.

iv.) Since no radicals are involved in the polymerization reaction, cationic processes are not inhibited by oxygen, unlike free-radical polymerizations which can be severely affected.

v.) Substrate basicity may inhibit cure. Free radical curing is generally independent of the substrate, once free radicals have been formed.

vi.) Residual acid may be present in cationic cured films; whilst free radical cured films may contain trapped free radicals.

2.3.1 Stages of Cationic Polymerization

Cationic vinyl polymerization is given as an example for cationic polymerization in Figure 2.6. It is defined as an addition polymerization reaction mediated by propagating carbocation ($-CH_2-CH(R)^+B^-$) that is derived from a vinyl monomer ($CH_2=CH-R$) and initiator (A^+B^-).

The initiation reaction is known as the formation of the cationic active species (also referred to as "cationation of the monomer") (reaction 2.17) and the propagation reaction is described as a nucleophilic attack of the monomer on the active species
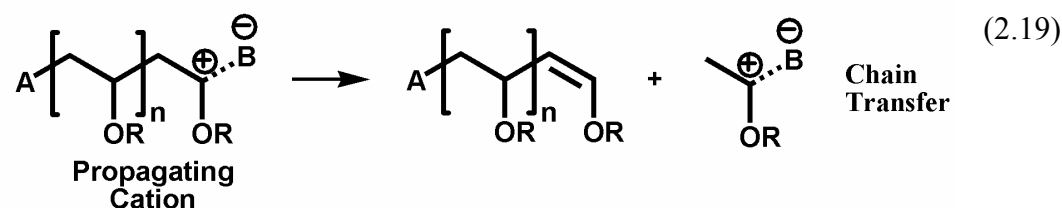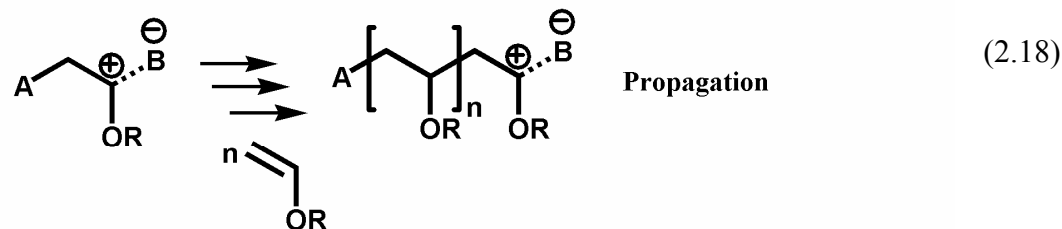
$$(2.17)$$
$$(2.18)$$
$$(2.19)$$

Figure 2.6. Conventional cationic polymerization of vinyl ethers

(reaction 2.18). The polymerization is usually initiated by electrophilic compounds such as Brønsted or Lewis acids, carbocations and trialkyloxonium salts [34]. Indeed, the polymerization begins when a suitable cation reacts with the first monomer molecule.

This reaction scheme is true for all types of cationic initiators. Classical initiators instantaneously dissociate in the reaction mixture into one initiating cation and a counter anion. In externally stimulated initiating systems, thermal initiators or photoinitiators produce reactive species that are capable of cationic initiation upon exposure to heat or radiation, respectively. In all initiating systems, the counter anion has to be sufficiently non-nucleophilic to prevent the termination of a growing chain by anion-cation combination. In recent decades, externally stimulated initiating systems, especially photoinitiators have become more preferable due to their advantages over classical initiators. In general, classical cationic initiators have the following disadvantages:

1. Since usually all of the initiator is added in solid form or in a concentrated solution at the beginning of the polymerization and initiates immediately, theconcentration of initiator at the beginning of the polymerization is not constant throughout the reaction mixture [34].
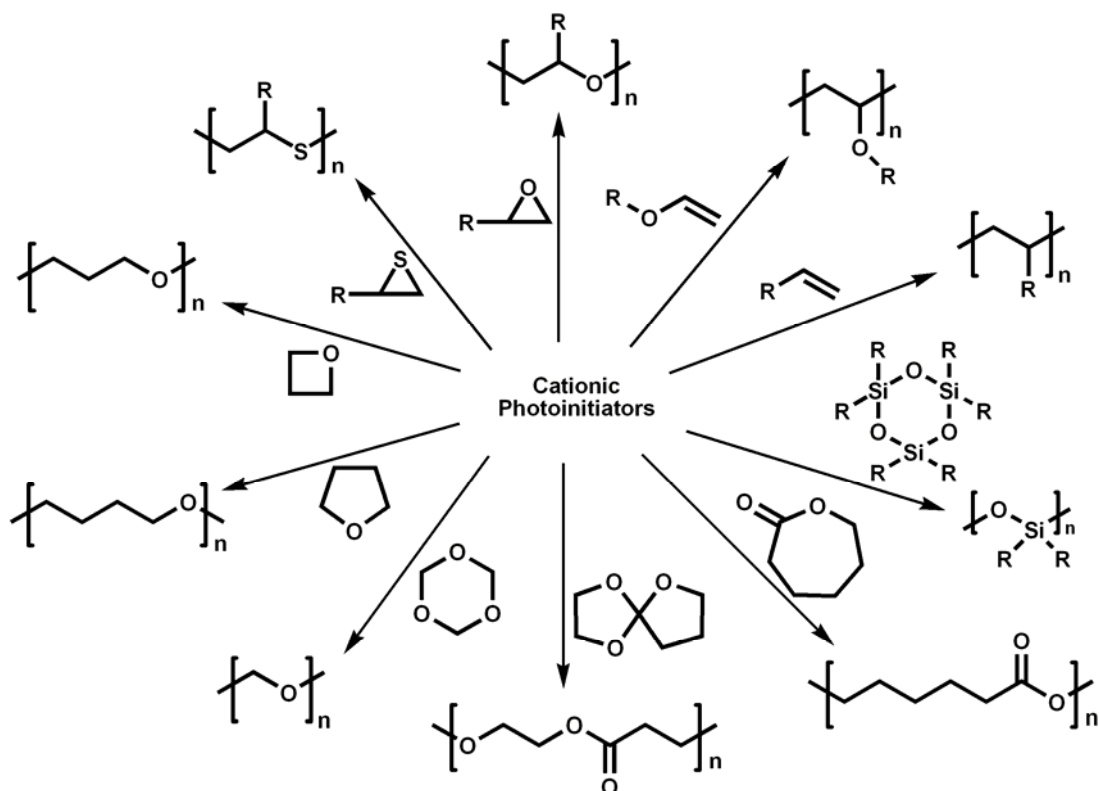
14

Figure 2.7. Monomers that are polymerizable with cationic photoinitiators

2. Due to instantaneous initiation, on adding the initiator, a significant evolution of heat is often observed. Therefore, one has to work at relatively low temperatures which lead to relatively low polymerization rates [34].

3. In many cases, gaseous protonic acids are used for initiation of cationic polymerization. Handling of such protonic acids arises problems due to their gaseous characteristics.

Therefore, externally stimulated initiating systems can overcome these problems. For example, by stimulations with irradiation, a controllable amount of initiating cations is produced. The concentration of initiating species can be regulated by choosing suitable light intensities [34].

2.3.2 Monomers

The range of monomers polymerizable by a cationic mechanism encompasses both vinyl and ring-opening polymerizations, and this permits the synthesis of a wide range of polymers with heteroatoms in the backbone. Monomers that are polymerizable with cationic photoinitiators are represented in Figure 2.7 [28].
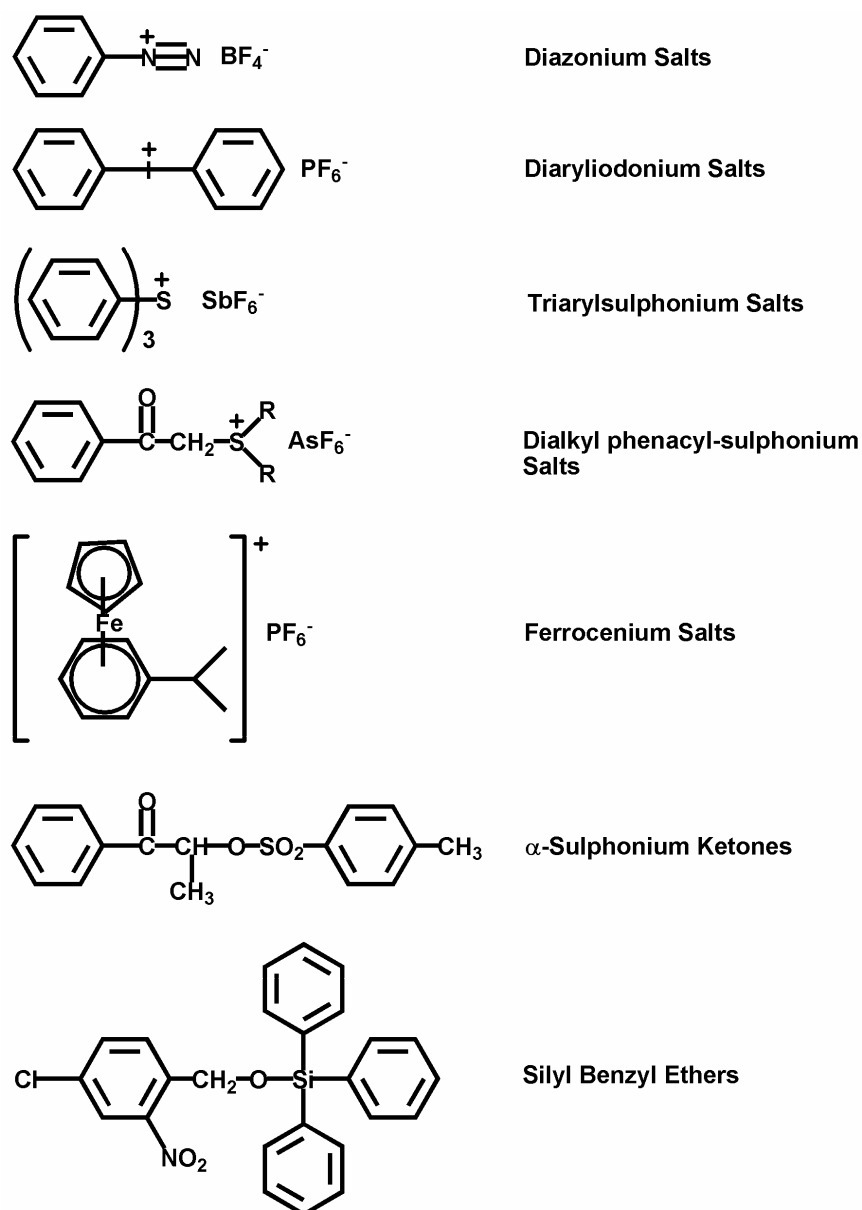
Figure 2.8. Major classes of cationic photoinitiators

2.3.3 Photoinitiators

In recent decades, much effort has been devoted to development of photoinitiators mainly due to extensive application fields of photoinitiated cationic polymerization such as UV curing, inks, adhesives, microelectronic, and photolithography. Therefore, there are many types of photoinitiators for cationic polymerizable monomers. The main types are illustrated in Figure 2.8. Cationic photoinitiators can be structurally classified into [28]:

i. Ionic cationic photoinitiators

    a. Onium salts

      b. Organometallic salts

   ii. Non-ionic cationic photoinitiators

      a. Organosilanes

      b. Latent sulphonic acids

      c. Miscellaneous non-ionic compounds

2.3.3.1 Onium Salts

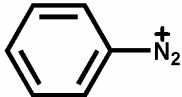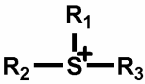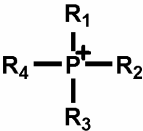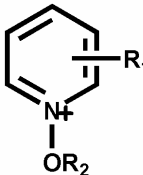Onium salts are the most used cationic photoinitiators. These salts consist of a cationic part containing heteroatom, and an inorganic metal complex anion as a counterion. Table 2.1 summarizes main onium salts used for light-induced cationic polymerization.

Table 2.1. Onium salts that are used in photoinitiated caionic polymerization

Aryldiazonium salts	Iodonium salts	Sulphonium salts	Phosphonium salts	N-alkoxy pyridinium salts

Aryldiazonium Salts

The first commercial system for photoinitiated cationic polymerization in UV curing and imaging applications utilized aryl diazonium salts of complex metal halide anions together with epoxy-functional monomers and oligomers [35]. Photolysis of these salts yields Lewis acids (reaction 2.20), which may initiate cationic polymerization of epoxides directly and/or produce protic (Brønsted) acids by reaction with adventitious (or purposefully added) hydroxyl substances, such as water or alcohols (reaction 2.21). The spectral response of diazonium salts may be varied throughout the near UV-visible range by appropriate substituents on the aryl ring [36]. Furthermore, both the absorptivity and thermal stability of the diazonium salts are enhanced by electron-donating groups (one of the few exceptions to Murphy's law). Nevertheless, the inherent thermal instability of aryl diazonium salts limits their practical utility as photoinitiators in crosslinking systems. In addition, the

evolution of N_2 limits film thickness to ca. 15 μm or less due to formation of bubbles and pinholes in thicker films.

$$Ar\!-\!N_2^+\ PF_6^- \xrightarrow{\ h\nu\ } Ar\!-\!F\ +\ N_2\ +\ PF_5 \qquad\qquad (2.20)$$

$$PF_5\ +\ ROH \longrightarrow H^+\ PF_5(OR)^- \qquad\qquad\qquad (2.21)$$
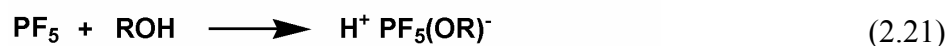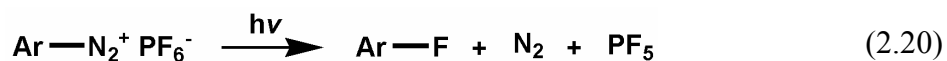
Diaryliodonium and Triarylsulphonium Salts

These deficiencies prompted investigations on alternative photoinitiators for cationic polymerization, which led to the development of diaryliodonium and triarylsulfonium salts with complex metal halide anions [37, 38]. In contrast to aryl diazonium salts, the iodonium and sulfonium salts exhibit high thermal stability, as well as hydrolytic stability, and may be considered second-generation photoinitiators for crosslinking by cationic polymerization.

Irradiation of these salts results in homolytic cleavage of Ar-S (or Ar-I) bonds to yield reactive radical cations, as shown in (reaction 2.2) and (reaction 2.3), respectively. Direct evidence for this homolytic bond cleavage has been obtained from laser flash photolysis studies [39]. Furthermore, the radical cations have been found to be highly reactive with nucleophiles, including CHO and vinyl ethers [39-41].

The phenyliodonium radical cation ($PhI^{+\cdot}$) was found to be >10 times more reactive with CHO relative to other oxygen nucleophiles, including methanol, THF and water. These results provide experimental support for direct initiation of CHO polymerization by $PhI^{+\cdot}$ even in the presence of other oxygen nucleophiles as well as hydrogen-donors (e.g. THF)

A possible reaction mechanism for photoinitiated polymerization of epoxides utilizing a diphenyliodonium salt **(1)** as photoinitiator, which is consistent with the laser flash photolysis studies as well as with polymer end-group analysis studies, is provided in reactions 2.22 and 2.23.

Key features of this scheme are (a) direct reaction of $PhI^{+\cdot}$ with the epoxide, (b) oxidation of the resulting adduct by a second diphenyliodonium salt, and (c) initiation of polymerization by both the resulting proton (H^+) and activated epoxide. This mechanism predicts both hydroxyl and 4-alkoxyphenyl iodide polymer end groups.

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$$Ph_2I^+ \xrightarrow{h\nu} PhI^{+\cdot} + Ph\cdot \qquad (2.22)$$
$$(1)$$

(2.23)
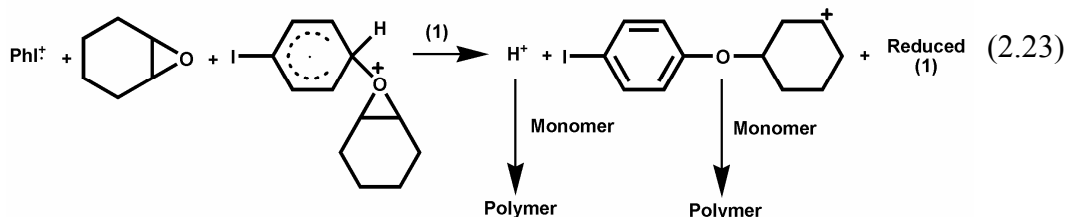
Support for photoinitiator fragment incorporation comes from studies with the triarylsulfonium salt **(2)** [42]. Utilizing **(2)** as photoinitiator for cationic polymerization of CHO, spectroscopic evidence (absorption and emission) has been obtained for the incorporation of 4-alkoxydiphenyl sulfide end groups in poly(cyclohexene oxide). These results are readily explicable in terms of initiation by the diphenylsulfinium radical cation (PhS$^{+\cdot}$) in accordance with reaction 2.22.

Furthermore, direct evidence for formation of PhS$^{+\cdot}$ has been obtained from laser flash photolysis studies (see reactions 2.25 and 2.26) [39]. Thus, the laser flash photolysis and end-group analysis studies are complementary and support direct initiation of cationic polymerization (of CHO) by the reactive phenyliodonium and diphenylsulfinium ions, derived from the corresponding iodonium and sulfonium salt photoinitiators, in accordance with reaction 2.22.
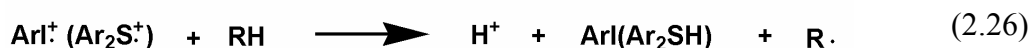

(2.24)
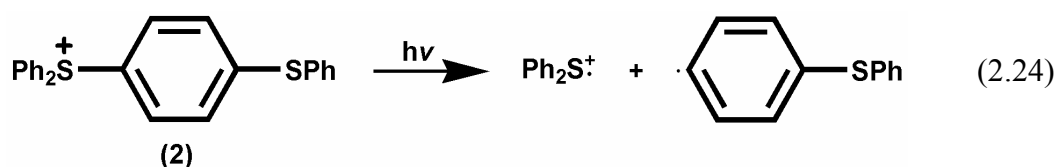
In the absence of reactive monomer photogenerated ArI$^{+\cdot}$ and Ar$_2$S$^{+\cdot}$ are expected to react with nucleophiles (NuH) and possibly H-donors (RH) to produce protons (see reactions 2.25 and 2.26). The reactions 2.25 and 2.26 account for polymerization of monomer introduced after irradiation [37], as well as for photoinduced acid catalyzed reactions utilized in photoimaging applications [43, 44]. The electrophilicity of diarylsulfinium ions (Ar$_2$S$^{+\cdot}$) is well documented [45].

$$ArI^{+\cdot} (Ar_2S^{+\cdot}) + NuH \longrightarrow H^+ + \text{Unidentified Products} \qquad (2.25)$$

$$ArI^{+\cdot} (Ar_2S^{+\cdot}) + RH \longrightarrow H^+ + ArI(Ar_2SH) + R\cdot \qquad (2.26)$$
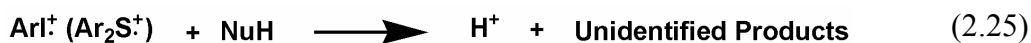
In addition to the proposals for photogeneration of cationic initiators in reactions 2.22, 2.25 and 2.26, both of which originate with homolytic bond cleavage, evidence for photoinduced heterolytic bond cleavage of diaryliodonium and triarylsulfonium salts in methanol has been reported [46], as shown in reactions 2.27 and 2.28. However, the reported substantial yields of fluorobenzene appear to be inconsistent with earlier studies on the photochemistry of diaryliodonium [47] and triarylsulfonium salts [48], carried out under similar conditions. Possibly, fluorobenzene arises from secondary photochemical reactions.

$$Ph_2I^+(Ph_3S^+)PF_6^- \xrightarrow{h\nu} PhI(Ph_2S) + Ph^+PF_6^- \qquad (2.27)$$

$$Ph^+PF_6^- \longrightarrow PhF + PF_5 \qquad (2.28)$$
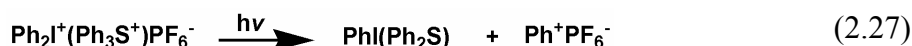
Phenylacylsulfonium and 4-hydroxyphenylsulfonium Salts

Dialkyl phenylacylsulfonium and 4-hydroxyphenylsulfonium salts, such as (3) and (4), respectively, also function as photoinitiators for cationic polymerization. However, in contrast to triarylsulfonium salts, polymerization is reported to cease following light exposure [49]. Furthermore, polymerization does not occur when (3) and (4) are irradiated in the absence of monomer followed by monomer addition. These results, together with additional evidence (including deuterium exchange studies) have been interpreted in terms of reversible photogeneration of acid, as shown in reactions 2.29 and 2.30.
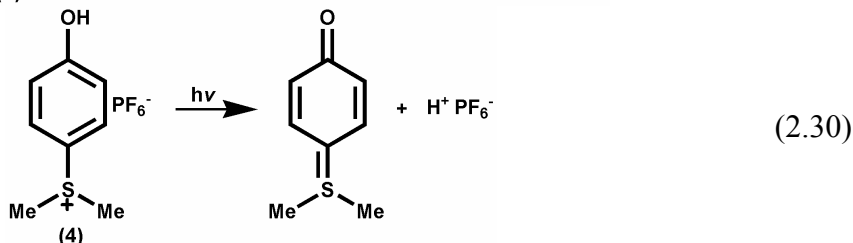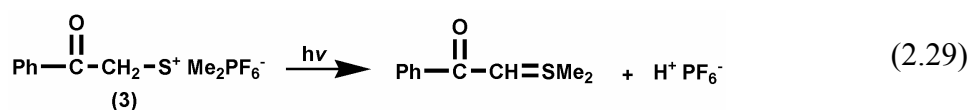
In the case of phenylacylsulfonium salts, such as (3), ylide ($R_2C=SR_2$) formation proceeds by intramolecular H abstraction by the ketone from the γ carbon [50]. In both cases, monomer can apparently compete for protons with the highly basic ylide products. However, the lifetime of the protons is reduced in the presence of the basic ylides.

Sulfoxonium Salts

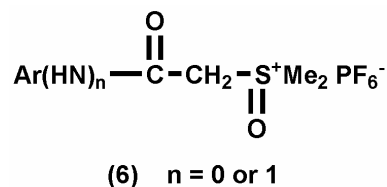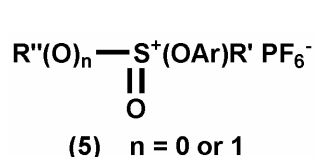Aryloxysulfoxonium salts of general structure (**5**) are reported to be efficient photoinitiators for cationic polymerization with activities comparable with or greater than diaryliodonium and triarylsulfonium salts [51]. They apparently undergo irreversible photolysis and acid generation.

Sulfoxonium salts of general structure (**6**) are also reported to be efficient photoinitiators for cationic polymerization [51]. With these photoinitiators, cationic polymerization is reported to cease following light exposure, as observed with phenylacyl- and 4-hydroxyphenyl-sulfonium salts.

$$R''(O)_n \!-\! \underset{\underset{O}{\|}}{S^+}(OAr)R' \; PF_6^-$$

(**5**)   n = 0 or 1

$$Ar(HN)_n \!-\! \overset{\overset{O}{\|}}{C} \!-\! CH_2 \!-\! \underset{\underset{O}{\|}}{S^+}Me_2 \; PF_6^-$$

(**6**)   n = 0 or 1

N-Alkoxy Pyridinium Salts

N-Alkoxy pyridinium salts are obtained with relatively high yields by a reaction of pyridine N-oxides with a triethyloxonium salt in methylene chloride or chloroform [52]. Quinolinium salts can also be prepared from the corresponding N-oxides [53]. In both cases, an anion exchange is not necessary since the triethyl oxonium salt is available with non-nucleophilic counter anions.

When absorbing UV light in the presence of a cationically polymerizable monomer, pyridinium type salts do readily initiate the polymerization [52, 54]. The two initiation mechanisms described are depicted in reaction 2.31 and 2.32 on the example of $EMP^+PF_6^-$.

Upon photolysis, the initiator's nitrogen-oxygen bond is ruptured forming a pyridinium type radical cation and an alkoxy radical. Detected by laser flash photolysis, the former were found to be highly reactive towards various nucleophilic monomers. The bimolecular rate constants for the reaction of *m*-methyl pyridinium radicals cation with cyclohexene oxide and butylvinyl ether are k = 10^6-10^7 and 5×10^9 l mol^{-1}s^{-1}, respectively [55]. In addition to the radical cation, Brønsted acid formed in the presence of hydrogen donors (monomer, solvent) may initiate the polymerization, as illustrated in reaction 2.32.

21

$$(2.31)$$

$$(2.32)$$
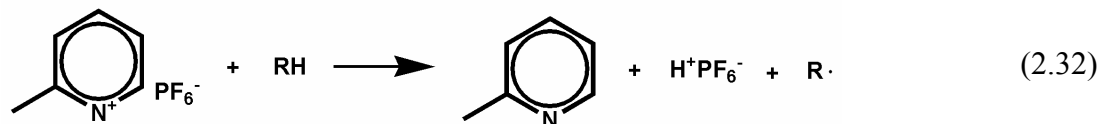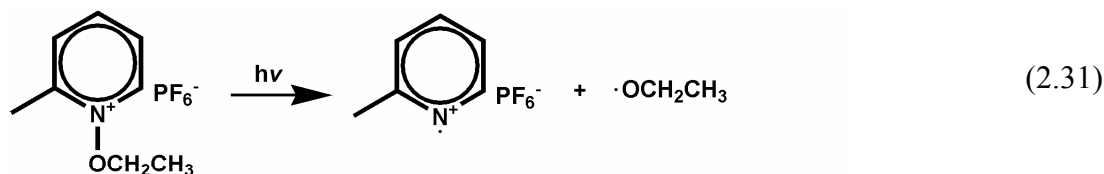
2.3.3.2 Organometallic Salts

A newer class of photoinitiators for cationic polymerization are mixed ligand arene cyclopentadienyl metal salts of complex metal halide anions [56], such as (η^6-benzene)(η^5-cyclopentadienyl)Fe^{II} hexafluorophosphate **(7)**. A mechanism for photoinitiated polymerization of epoxides is provided in reaction 2.33 [57].

$$(2.33)$$
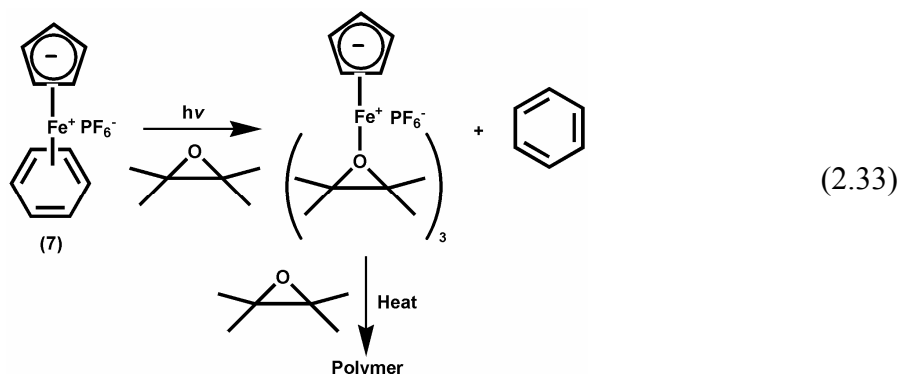
The proposed photoinduced ligand exchange of the arene by three-epoxide group is based on earlier ligand exchange studies [58]. With bicyclic epoxides, such as cyclohexene oxide, polymerization is spontaneous under ambient conditions. However, moderate heating (50 to 150 $^{\circ}$C) is required with less reactive epoxides, such as glycidyl ethers. The thermal requirement may be reduced substantially in the presence of oxidizing agents, such as peroxides, which apparently oxidize Fe^{II} to the more reactive Fe^{III} state. It is noteworthy, in this regard, that photoinitiated polymerization of epoxides, utilizing triarylsulfonium salts, is also enhanced by moderate heating, which also reduces the adverse effects of high humidity [35].

The spectral response of the mixed arene cyclopentadienyl metal salts may be varied throughout the near UV-visible region by proper selection of the arene component and also by photosensitization [59].

$$(2.34)$$

$$(2.35)$$
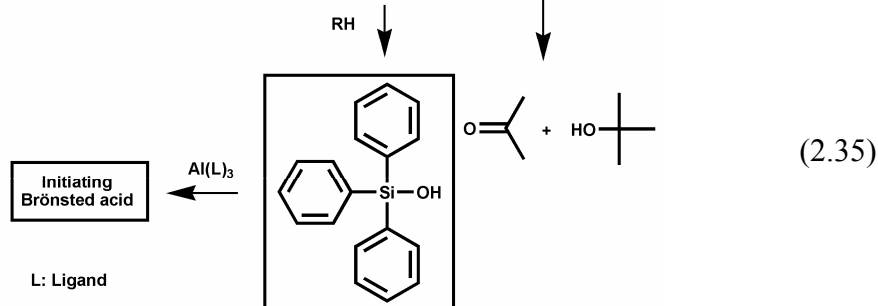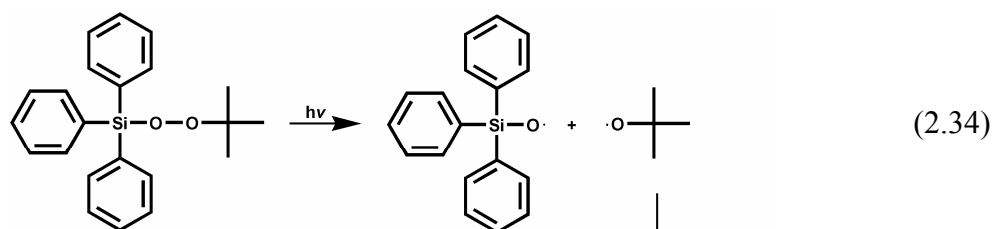
2.3.3.3 Organosilanes

Mixtures of silanol and aluminium(III) complexes of β-keto esters or β-diketones initiate the thermal polymerization of highly rective cycloaliphatic epoxides [60-62]. Triarylsilanols may be generated by the photochemically induced decomposition of triarylperoxides [63]. This reaction generates the silanols more efficiently than the photolysis of o-nitrobenzyl ethers. The arylsilyl tert-butyl peroxides are reported to be stable against heat and impact. The triarylsilyl tert-butyl peroxides undergo photolytic homolysis of the oxygen-oxygen linkage (reaction 2.34). The silanol resulted from hydrogen abstraction yields initiating Brønsted acid in the presence of aluminium(III) complexes (reaction 2.35).

2.3.3.4 Latent Sulphonic Acid

Sulphonic acids are not strong enough as acids and posses anions which are too nucleophilic to initiate the polymerization of epoxides. However, they are versatile catalysts for the curing of coatings based on aminoplast resins. For example α-sulphonyloxy ketones produce sulphonic acid upon irradiation. Whilst various structural types of α-sulphonyloxy ketones are highly reactive initiators, benzoin tosylate (8) has found most interest for practical applications.

(8)
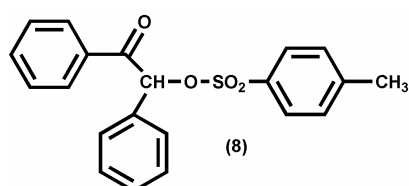
2.3.4 Photoinitiating Systems for Light-Induced Cationic Polymerization

There are two possible classes of initiating systems for photoinitiated cationic polymerization; direct acting system and indirect acting system.

2.3.4.1 Direct Acting System

Even though the cationic polymerization has several advantages it has not as yet achieved the commercial significance of radical polymerization in UV curing applications due to the limited choice of the cationic photoinitiators and monomers that were commercially available until recently. Cationically polymerizable important classes of monomers such as vinyl ethers and epoxides changed this situation changed with two significant improvements. Furthermore, a new class of cationic photoinitiators with non-nucleophilic counter ions such as SbF_6^- and AsF_6^- has been utilized [64].

Since the photoinitiator is one of the most important parts of a UV initiated polymerization, many research efforts have been devoted to understand what type of photoinitiators is applicable to generate cations. Among the various types of photoinitiators that can lead to the formation of cation as a result of UV light induced fragmentation, onium salts have found considerable application in UV curing and photoresist technology. The photochemistry of these novel classes of photoinitiators is well documented [65, 66]. Upon photolysis, these initiators undergo irreversible photolysis to produce directly cation radicals and Brønsted acids. Reactive species thus produced photochemically with onium salts initiate the cationic polymerization of suitable monomers as illustrated below.

$$On^+ \longrightarrow On^{\cdot +}, H^+ \tag{2.36}$$

$$On^{\cdot +} + M \longrightarrow Polymer \tag{2.37}$$

$$H^+ + M \longrightarrow Polymer \tag{2.38}$$

Onium salts used in cationic photopolymerization mainly absorb the wavelengths of light between 225 and 350 nm [64, 65, 67].

2.3.4.2 Indirect Acting System

For practical applications, onium salts should absorb light appreciably at wavelengths longer than 350 nm where the commercially available medium and

high-pressure mercury lamps emit much of their radiation. The indirect actions of these systems, in which an activator play a crucial role, extend their spectral sensitivity to longer wavelengths. Several indirect ways have been developed to expand wavelength range. All of these pathways involve electron transfer reactions with:

(i) photoexcited sensitizers,

(ii) photoexcited free radicals,

(iii) electron donor compounds in the excited charge transfer complexes.

i. Initiation by Photoexcited Sensitizers

Photosensitization is very attractive way to initiate cationic polymerization since the triggering of the initiation may be extended too much longer wavelengths where the photoinitiator is transparent and photosensitizers such as heterocyclic and polynuclear aromatic compounds (see Figure 2.9) absorb the incident light (reaction 2.39). Photosensitization is considered as an energy transfer process, which occurs from the excited photosensitizer molecule (PS*) to the ground state photoinitiator (PI) producing the excited state of the latter (reaction 2.40).

$$PS \xrightarrow{h\nu} (PS^*) \tag{2.39}$$

$$(PS^*) + PI \xrightarrow{\text{Energy Transfer}} PS + (PI^*) \tag{2.40}$$

However, in many cases, photoinduced decomposition of the cationic photoinitiator was observed via electron transfer since most onium salts are capable of oxidizing these sensitizers in exciplex formed between sensitizer and onium salt.

$$(PS^*) + On^+X^- \longrightarrow (PS^{+\cdot})X^- + On^\cdot \tag{2.41}$$
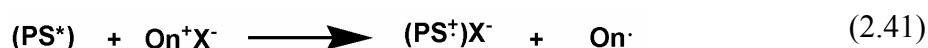
Depending upon the two components involved the photosensitization can occur through energy transfer or electron transfer. The basic requirement for the energy transfer is the excitation energy of the sensitizer E*(PS) should be higher than that of excited onium salt E*(On$^+$). On the other hand the electron transfer is energetically allowed, if ΔG calculated by equation 2.42 (extended Rehm- Weller equation) is negative.

25

$$\Delta G = F\ [\ E_{ox}^{1/2}\ (PS) - E_{red}^{1/2}(On^+)\ ] - E^*(PS) \qquad (2.42)$$

Where $E_{ox}^{1/2}$ and $E_{red}^{1/2}$ are half wave oxidation and reduction potential of photosensitizer and photoinitiator respectively, F= 97 kJ mol^{-1} V^{-1}, is the conversion factor and E*(PS) is the excitation energy of photosensitizer.
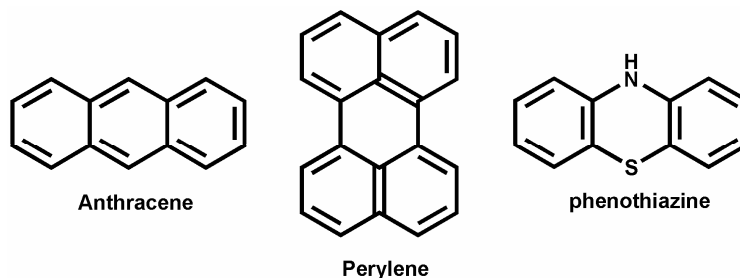
Figure 2.9. Some photosensitizers used in initiation of cationic polymerization

Classical Energy Transfer

Energy may be transferred from excited sensitizer (PS*) to onium salt (PI) by either resonance excitation or exchange energy transfer. Depending on the two components involved, energy transfer may proceed either excited singlet or in triplet state. Diphenyliodonium cations were excited to their first excited triplet state by energy transfer from *m*-trifluoromethyl acetophenone [68]. As can be seen from Tables 2.1 and 2.2, the energy transfer is energetically allowed. Electron transfer in the exciplex can be totally excluded, since the oxidation potential of *m*-trifluoromethylacetophenone is relatively low. In the case of triphenyl sulfonium salt energy transfer may occur from sensitizers with triplet energies above 314 kJ mol^{-1}.
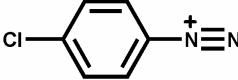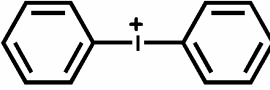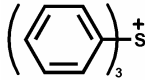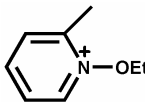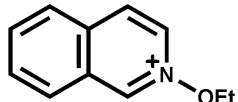
Table 2.2. Half wave oxidation potentials $E^{ox}_{1/2}$ (PS) (vs. SCE) and triplet or singlet energies E*(PS) of commonly used photosensitizers [64]

Photosensitizer	$E^{ox}_{1/2}$ (PS)(V)	E*(PS) (kJ mol^{-1})
Acetophenone	2.9	308 (E_t)
Benzophenone	2.7	290 (E_t)
Thioxanthone	1.7	277 (E_t)
Anthracene	1.1	319 (E_t)
Perylene	0.9	277 (E_t)
Phenothiazine	0.6	239 (E_t)
m-trifluoromethyl acetophenone	- 2.7	305 (E_t)
Xanthone	-	311 (E_t)

It has been shown that photosensitized decomposition of onium salt follows different route from that observed for direct photolysis of the onium salts [69, 70]. This can

be attributed to the different spin multiplicities involved in the corresponding decompositions. It should be pointed out that the energy transfer sensitization is not a technically useful process due to the high-energy requirements.

Table 2.3. Reduction potential and triplet excitation energies of selected oniom ions [64]

Onium Cation	$E^{red}_{1/2}(V)$ (vs SCE)	$E^*_t(kJ\ mol^{-1})$
	0.35	
	- 0.2	268
	- 1.1	314
	- 0.7	-
	- 0.5	-

Electron Trasnfer via Exciplex

Many aromatic hydrocarbons such as anthracene, phenothiazine, and perylene are able to sensitize the decomposition of onium salts via electron transfer. The irradiation of the sensitizer is followed by the formation of a complex between excited sensitizer molecules and ground state onium salt (reaction 2.43). In this complex, one electron is transferred from the sensitizer to the onium salt giving rise to the generation of sensitizer radical cation as a result of homolytic cleavage of the corresponding onium salt (reaction 2.43). The radical cations themselves initiate the polymerization of appropriate monomers or, alternatively, interact with hydrogen donor constituents of the polymerization mixture (such as solvent or monomer) resulting in the release of Brønsted acid (reaction 2.44). For this type cationic initiation, the following general scheme holds; molecules and ground state onium salt.

Not all sensitizers are suitable in conjunction with onium salts. According to equation 2.42, the requirements are low oxidation potentials, $E^{ox}_{1/2}$ (PS), and relatively high excitation energies $E^*(PS)$ of the sensitizer. It should also be noticed that only onium salts with high (low negative) reduction potentials $E^{red}_{1/2}(On^+)$, such as diphenyliodonium or alkoxy pyridinium salts are easily reduced by sensitizers.

$$PS \xrightarrow{\text{hv}} PS^* \xrightarrow{\text{On}^+\text{X}^-} [PS^*.....On^+X^-] \longrightarrow PS^{+\bullet}X^- + On^\bullet \qquad (2.43)$$

$$PS^{+\bullet}X^- + RH \longrightarrow HPS^+X^- + R^\bullet \qquad (2.44)$$

$$HPS^+X^- \longrightarrow H^+X^- + PS \qquad (2.45)$$
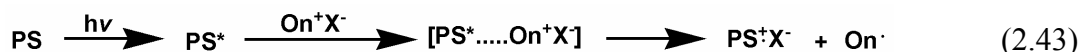
The sensitization of onium salts (Ar_3S^+ and Ar_2I^+) by anthracene has been analyzed in detail in a number studies [16, 71]. Exciplex formation is followed by a partly loss of anthracene's aromatic system as concluded from the decrease in the sensitizer fluorescence. These reactions are illustrated in equations 2.46-2.50 on the example of diphenyliodonium salt. Notably, similar coupling reactions of radical cations with the radicals formed from the salts were also observed with alkoxy pyridinium salts [14].

The sensitization of thioxhanthone follows only partly the general mechanism described for the exciplex formation [14]. To some extent, this sensitization is based upon the oxidation of photolytically formed radicals.

(2.46)

(2.47)

(2.48)

(2.49)

(2.50)

Counter ion is omitted
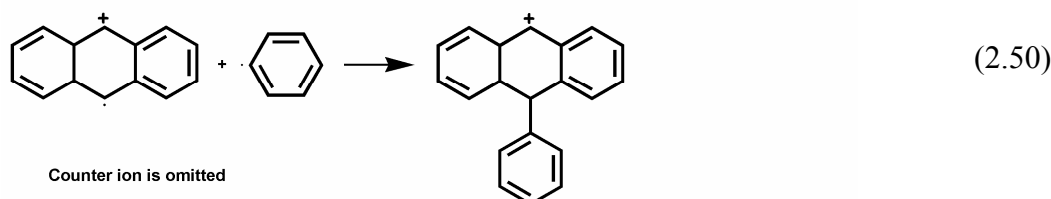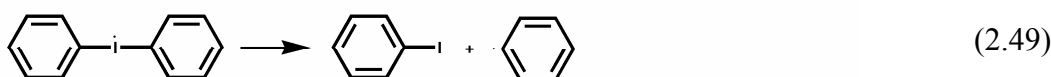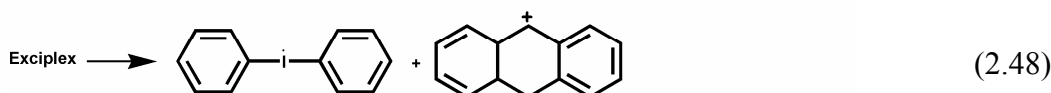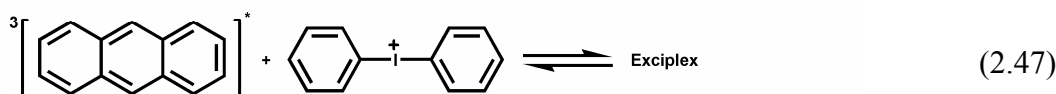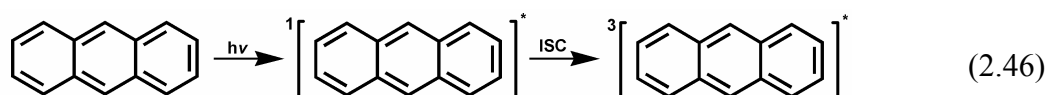
ii. Initiation by Free Radicals

Free radicals can also induce decomposition of onium salts. Two types of free radical induced initiation are currently available: oxidation of radicals and addition fragmentation reactions.

Oxidation of Radicals

Among the indirectly acting initiating systems, free radical promoted cationic polymerization is the most flexible route, since free radical photoinitiators with a

wide range of absorption characteristics are available. Many photochemically formed radicals can be oxidized by onium salts. The cations thus generated are used as initiating species for cationic polymerization according to the following reactions.

$$PI \xrightarrow{h\nu} R\cdot \qquad (2.51)$$

$$R\cdot \xrightarrow{On^+} R^+ + On\cdot \qquad (2.52)$$

$$R^+ \xrightarrow{Monomer} Polymer \qquad (2.53)$$

The cations thus generated are used as initiating species for cationic polymerization. This process is usually termed as the free radical promoted cationic polymerization. This so-called free radical promoted cationic polymerization is an elegant and fairly flexible type of sensitized cationic polymerization. Free radicals may be produced not only by photochemically but also thermally or by irradiating the system with high-energy rays. Table 2.3 shows free radical photoinitiator and onium salt combinations generally used in free radical promoted cationic polymerization.

Table 2.4. Initiating systems for free radical promoted cationic polymerization system [64]

Free radical source	Onium salt
Acylphosphine oxides	Iodonium /pyridinium salts
Vinyl halides	Sulfonium/pyridinium salts
o-Phtaldehyde	Pyridinium salts
Benzoin derivatives	Iodonium /pyridinium salts
Benzophenone	Iodonium /pyridinium salts
Azo compounds	Iodonium /pyridinium salts
Dye-amine	Iodonium salt
Polysilanes	Iodonium /pyridinium salts

Addition Fragmentation Reactions

The use of addition fragmentation reactions for photoinduced cationic polymerization has been subject of recent investigations [21, 72-76]. Being not based on easily oxidizable radicals, addition fragmentation reactions are indeed a very versatile method to adjust the spectral response of the polymerization mixture with the aid of free radical photoinitiators. The allylic salts have so far been applied for addition fragmentation type initiations.

The advantage of allylic salts that can undergo addition fragmentation reactions derives from the fact that virtually all sorts of thermal and light-sensitive radical initiators may be utilized for cationic polymerization, which enables an adaptation to most initiation conditions. In contrast to radical promoted cationic polymerization based on the oxidation of radicals, one is not limited to oxidizable radicals.

The mechanism of the addition fragmentation type initiation is depicted on the example of ETM$^+$SbF$_6^-$ and benzoin [77].

$$(2.54)$$

$$(2.55)$$
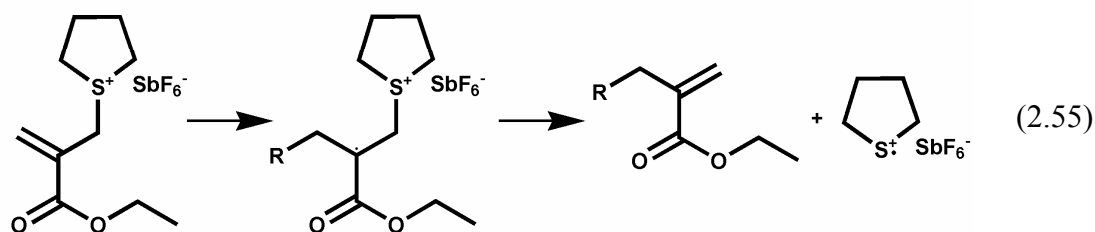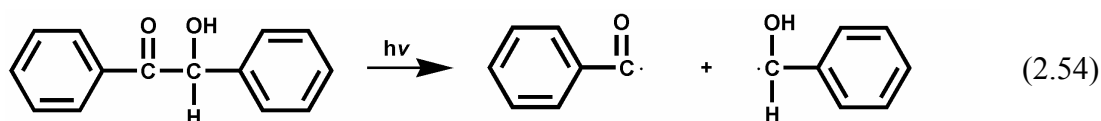
The first step consists in the photogeneration of free radicals (reaction 2.54). Virtually any photolabile compound undergoing homolytic bond rupture may be used as a radical source. The radicals add to the double bond of the allylonium salt thus producing a radical in β position to the heteroatom of the onium salt cation. Consequently, the molecule undergoes fragmentation yielding initiating cations (reaction 2.55). The proposed mechanism was evidenced by analysis of the photolysis products. The initiating efficiency has been demonstrated on a number of cationically polymerizable monomers, such as cyclohexene oxide, butylvinyl ether and N-vinylcarbazol.

iii. Initiation by Excited Charge Transfer Complexes

Pyridinium salts are capable of forming CT complexes with electron rich donors such as methyl- and methoxy-substituted benzene [21]. Notably, these complexes absorb at relatively long wavelengths, where the components are virtually transparent. For example, the complex formed between *N*-ethoxy-4-cyano pyridinium hexafluorophosphate and 1, 2, 4-trimethoxy benzene possesses an absorption maximum at 420 nm. The absorption maxima of the two constituents are at 270 and 265 nm for the pyridinium salt and trimethoxybenzene, respectively.

It was found that the CT complexes formed between pyridinium salts and aromatic electron donors act as photoinitiators for the cationic polymerization of cyclohexene oxide and 4-vinyl cyclohexene oxide. The mechanism illustrated in reactions 2.56 and 2.57 for the initiation of the cationic polymerization has been suggested [21].

The CT complexes are applicable for the photoinitiation of epoxide monomers but not for the photoinitiation of vinyl ethers and *N*-vinyl carbazol. The latter monomers are already polymerized in a dark reaction upon addition of these complexes.

$$(2.56)$$

$$(2.57)$$
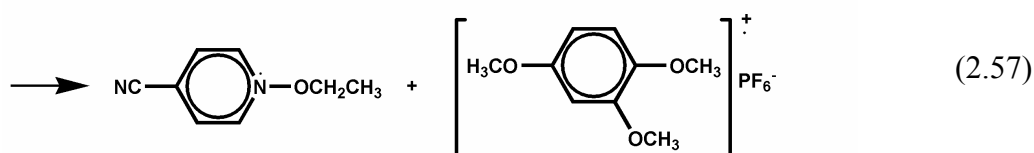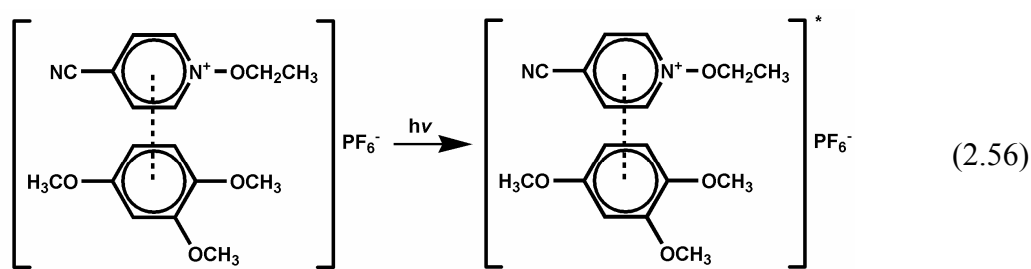
2.4 Living Cationic Polymerization of Vinyl Ethers

Living polymerizations are polymerizations in which propagating centers do not undergo either termination or transfer. In this system, after 100 % conversion is reached, additional polymerization takes place by adding more monomer to the reaction system. Living systems make significant contributions on well-defined polymer structure. Following features [78] of the polymer obtained can be manipulated easily:

i.   Molecular weight

ii.   Molecular weight distribution

iii. Pendant functional group

iv.   End functional group

v.   Stereoregularity of backbone

vi.   Spatial shape (topology)

vii. Sequence of repeat units

Considering conventional cationic polymerization of vinyl ethers, it is almost impossible to prepare polymers of controlled of structures. Because of the positive charge, the *β*-proton of "propagating carbocation" (see Figure 2.6) is inherently acidic; cationically polymerizable monomers are, by definition, nucleophilic or basic; and therefore the proton abstraction from "propagating carbocation" by the monomer is a kind of built-in side-reaction (reaction 2.19) that is very difficult to suppress. As a result, chain transfer to monomer which do not allow to control the polymeric structure occurs. Living cationic polymerization was first reported in 1984 by Higashimura and Sawamoto for alkyl vinyl ethers and around at the same time by Faust and Kennedy for isobutylene.

Higashumura *et al.* proposed that living cationic polymerization might be achieved by stabilizing the propagating carbocation by nucleaophilic interactions including:

    (i)   interaction with suitably nucleophilic counteranion **(9)**

    (ii)   addition of Lewis base (X) leading to interaction with a weakly nucleophilic counteranion **(10)**

          (9)   (10)
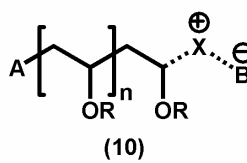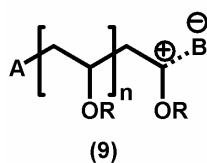
A typical example for method (i) is the hydrogen iodide/iodine (HI/I_2) initiating system [3], where the nuleophilic counteranion B^- is the iodide anion (I^-…I_2) that is activated by molecular iodine and is considered to stabilize the carvbocationic site into the living site. Cationogen/ethylaluminım dichloride (EtAlCl$_2$) system [79, 80] can be given as an example for method (ii). In this system cationogen/EtAlCl$_2$ generates weakly nucleophilic counteranion, B^- The Lewis bases include esters, ethers, and some pyridine derivatives [80]. In addition to these methods, in recent years, Mah and coworkers have developed photo-induced living cationic polymerization of isobutyl vinyl ether in the presence of diphenyliodonium and zinc halides (Figure 1.1) [6, 7].

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Initiators and Other Chemicals

Diphenyliodonium halides

DPICl (Fluka), DPIBr (Alfa Aesar) and DPII (Alfa Aesar) were used as received.

Benzophenone (Merck)

Benzophenone was recrystallized from heptane.

Thioxanthone (Fluka)

Thioxanthone was recrystallized from hexane.

DMPA (Ciba Specialty Chemicals)

DMPA was used as received.

Anthracene (Acros Organics)

Anthracene was used as received.

Perylene (Aldrich)

Perylene was used as received.

Zinc halides

Zinc chloride ($ZnCl_2$, Aldrich), zinc bromide ($ZnBr_2$, Aldrich), and zinc iodide (ZnI_2, Merck) were used as received.

3.1.2 Monomers

IBVE, BDVE, HDVE and DVE-DEG were used as received. Solvents were purified by conventional drying and distillation procedures.

3.1.3 Solvents

Dichloromethane (CH$_2$Cl$_2$) (Lab-scan)

Methylene chloride was used as solvent for dissolving polymers. It was first washed with conc. H$_2$SO$_4$ until the acid layer remained colorless, then washed with water, aq. %5 NaOH and then water again. It was pre-dried with CaCl$_2$ and distilled from CaH$_2$.

Methanol (Technical)

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

3.2 Equipments

3.2.1 GPC

Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) consisting of a Waters 410 Differential Refractometer detector, a Waters 515 HPLC pump, and Waters styragel columns (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0.3 mL/min.

3.2.2 Photoreactors

Photoreactor (Rayonet) equipped with 16 lamps emitting light nominally at 350 nm was used for photopolymerization of formulations which were polymerizable around 350 nm.

Photoreactor (Kerman) equipped with 12 lamps emitting light nominally at 300 nm was used for photopolymerization of formulations which were polymerizable around 300 nm.

3.2.3 UV Spectrophotometer

UV-Vis spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer.

3.3 Preparation Methods

3.3.1. Photopolymerization of IBVE

Monomer (IBVE, 3.84 mol L^{-1}) solution in CH$_2$Cl$_2$ (2 mL), initiator (DPICl, 2.45 x 10^{-3} mol L^{-1}), photosensitizer (DMPA, 2.45 x 10^{-3} mol L^{-1}), and catalyst (ZnBr$_2$, 3.15 x 10^{-3} mol L^{-1}) were put into a Pyrex tube that was heated *in vacuo* with a heat gun

and flushed with dry nitrogen. Almost homogenous mixture was irradiated at -5 ^{o}C in a photoreactor (Rayonet). The light intensity was 1.04×10^{-3} mW cm^{-2} as measured by Delta Ohm model HD-9021 radiometer. After one hour, the mixture was allowed to stand in the dark at -5 ^{o}C for a given time. The resulted polymers were precipitated in the ammonical methanol. After precipitation, the polymer was washed with 10 % aqueous sodium thiosulfate solution and distilled water, and then dried under reduced pressure. Conversion of monomer was determined gravimetrically. Molecular weights and polydispersities of the polymers were determined by GPC.

3.3.2. Photo-induced Curing of Di-functional Monomers

For investigation of gel content and gelation time, following procedure was performed in each curing.

A quartz ampoule was flushed with dry nitrogen. Then components (2.45×10^{-3} mol L^{-1}) of the photoinitiating system were dissolved in solvent (methylene chloride). Finally, monomer (3.84 mol L^{-1}) was added into the ampoule. The formulations containing only iodonium salt to absorb light were cured in a photoreactor equipped with lamps emitting light nominally at 300 nm.

4. RESULTS and DISCUSSION

4.1 Living Cationic Polymerization of IBVE

The discovery of the living cationic polymerization of vinyl ethers provided a valuable new tool in the synthesis of materials with novel architectures [81]. However, the corresponding photoinitiated polymerization has only been scarcely investigated [6, 7]. As stated in the introduction section, the only report that concerns the photochemical generation of the protonic acids from onium salts with nucleophilic counter anions. This way, the problems associated with handling of gaseous protonic acid required in the classical living cationic polymerization procedure for the preparation of monomer acid adduct are avoided. The decomposition of onium salts was achieved around 300 nm as related to their absorption characteristics. This brings some limitations on the potential uses of cationic polymerization particularly when long wavelength light sources are used [82, 83]. Moreover, weak absorbance of the components of the initiating system may
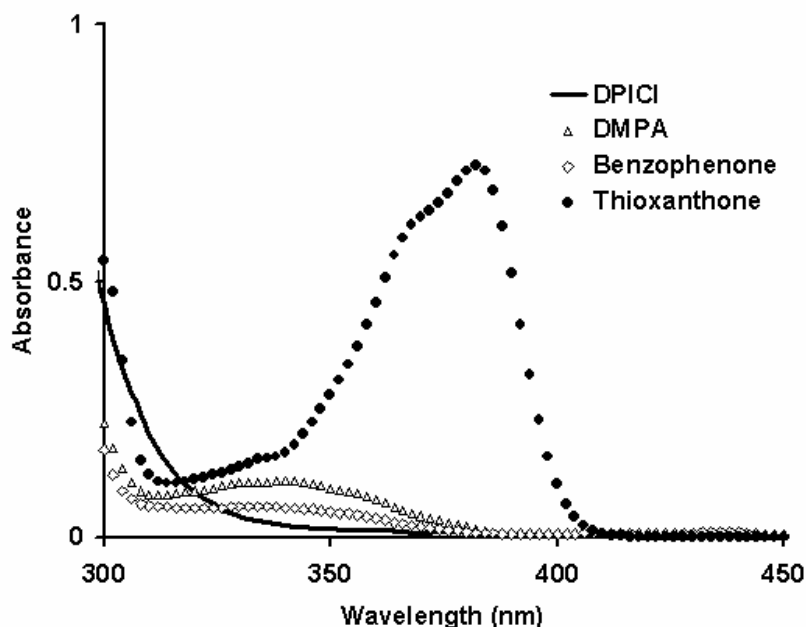

Figure 4.1. UV spectra of the solutions of the photoinitiators and diphenyliodonium chloride in CH_2Cl_2. The concentration of solutions was 3.5 x 10^{-4} mol L^{-1} in all cases

interfere with that of the iodonium salt. Therefore, it seemed appropriate to employ indirect photoinitiating systems to overcome such limitations. Among the indirectly acting initiating systems described for photoinitiated curing applications, free radical promoted cationic polymerization is the most flexible route, since free radical photoinitiators with a wide range of absorption characteristics are available. Many photochemically formed radicals [84-93] can be oxidized by onium salts. In free radical promoted living cationic polymerization, DMPA was used as a radical source. When irradiated in the presence of onium salts such as diphenyl iodonium chloride at 350 nm where the onium salt is transparent, the light is absorbed only by DMPA (Figure 4.1).

The photolysis of DMPA results in α-cleavage, and alkoxybenzyl and benzoyl radicals were formed. The strong electron donor alkoxy benzyl radicals thus formed were oxidized by iodonium salt to yield corresponding carbocations which form adducts with the monomer. Subsequent polarization of C-halide terminal of the adduct by the coordination action of zinc bromide facilitates insertion of weakly basic monomer. It should be pointed out that the iodonium salt with nucleophilic chloride counter anion was deliberately chosen to allow the formation of the monomer adduct in the initial step. Non-nucleophlic counter anions such as PF_6^-, SbF_6^- *etc*. would have caused fast but uncontrolled chain growth as observed in conventional photoinitiated cationic polymerization of vinyl ethers. The overall process is presented in Figure 4.2.

In principle, it should not matter whether the initiating free radicals are obtained via α-cleavage or hydrogen abstraction mechanisms. Both types of radical sources have been utilized in order to support mechanistic ideas. Representative results are given in Table 4.1. It is interesting to note the higher activity of the hydrogen abstraction type photoinitiators, namely benzophenone and thioxanthone which absorb the light between 350 and 450 nm in their ground states (see Figure 4.1). In these cases, the electron donor ketyl radicals, formed from the hydrogen abstraction of photoexcited initator, are oxidized by the iodonium salt. As illustrated on the example of benzophenone in Figure 4.3, the resulting carbocations release acids (reaction 4.8) which may react more favorably with the monomer compared to the sterically hindered carbocations formed from α-cleavage photoinitiators (see reaction 4.3 in Figure 4.2).

Notably, the polydispersities are relatively broader in all indirect systems studied indicating the importance of the reaction steps. Although at longer wavelengths (lower energies), indirect systems involve several reaction sequences i.e. photoinduced radical generation, oxidation and adduct formation. Therefore, growing polymer chains with some differences in chain lengths are formed.

$$(4.1)$$

$$(4.2, 4.3)$$

$$(4.4)$$

$$(4.5)$$
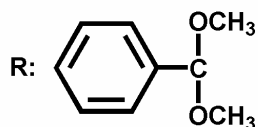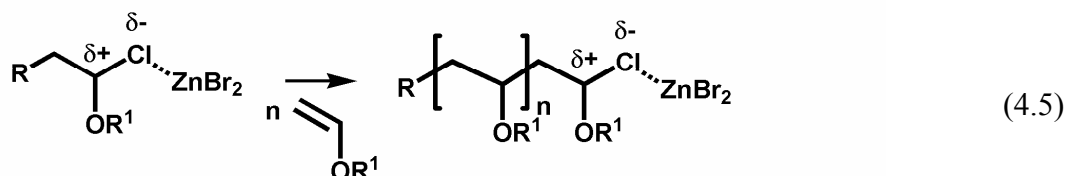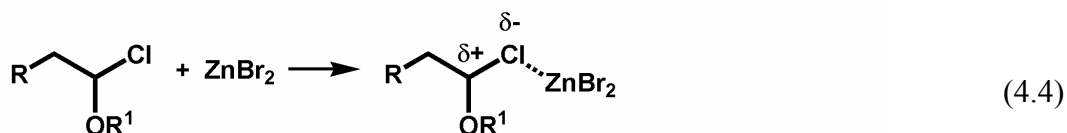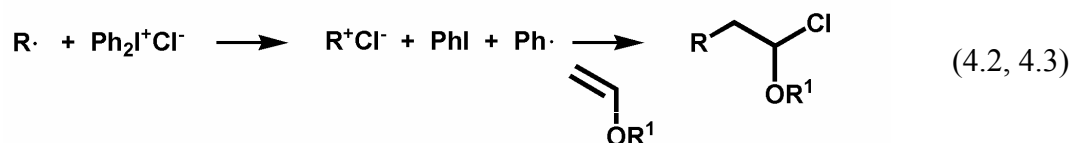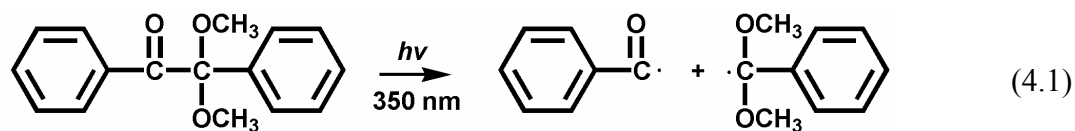
Figure 4.2. Living cationic polymerization of IBVE with DMPA in the presence of DPICl and ZnBr$_2$

$$(4.6)$$

$$(4.7)$$

$$(4.8)$$
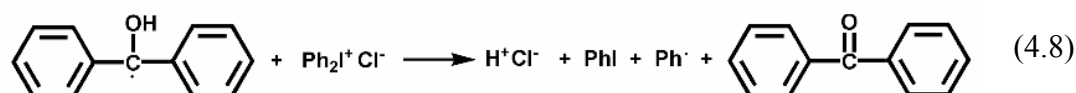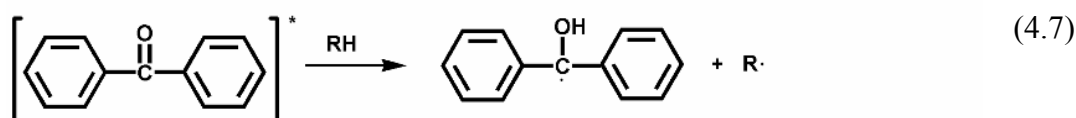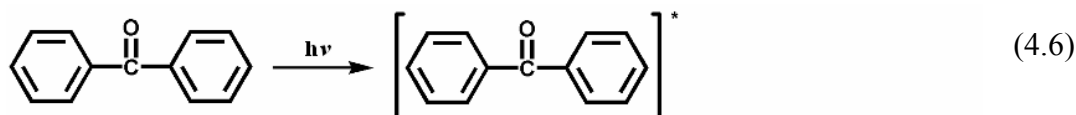
Figure 4.3. Protonic acid generation upon irradiation of benzophenone
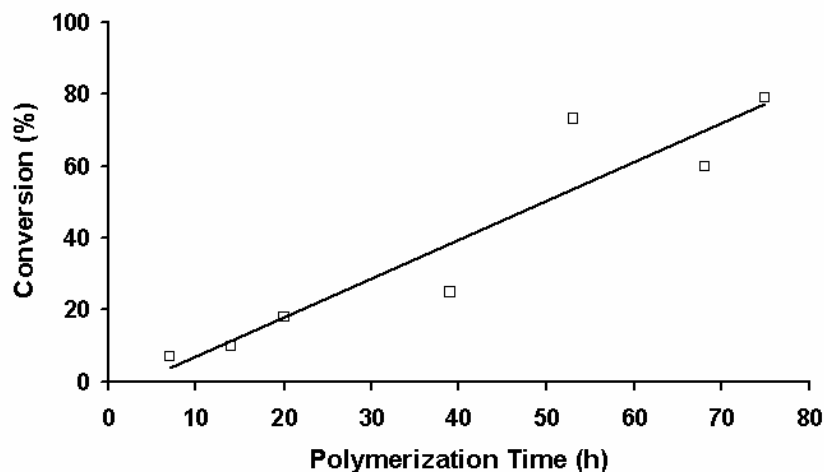
Figure 4.4. Time–conversion curve of living cationic polymerization of IBVE carried out in the dark after 1 h photolysis in the presence of DPICl and zinc bromide at -5 °C. Concentrations: [IBVE] = 3.84 mol L^{-1}, [DPICl] = 2.45 x 10^{-3} mol L^{-1}, [DMPA] = 2.45 x 10^{-3} mol L^{-1}, and [ZnBr$_2$] = 3.15 x 10^{-3} mol L^{-1}
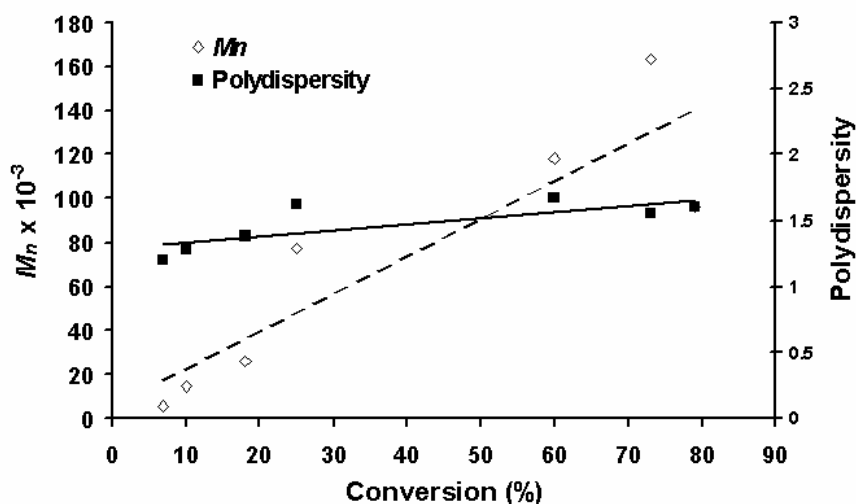
Figure 4.5. The dependence of the number-average molecular weight (M_n) and polydispersity index (M_w/M_n) on the percentage of conversion in photoinduced living cationic polymerization of IBVE (See Figure 4.4 for the experimental details)

In order to examine the living nature of photoinitiated free radical promoted cationic polymerization of IBVE, time-conversion and conversion-polydispersity index (PDI)-molecular weight (M_n) studies were carried out. Conversion of monomer increased almost linearly with increasing polymerization time (Figure 4.4). Conversion-M_n studies indicated that there was also a linear relationship between conversion and M_n (Figure 4.5).

Table 4.1. Photoinitiated free radical promoted living cationic polymerization[a] of IBVE in the presence of DPICl with zinc bromide by using various free radical photoinitiators at -5 ^{o}C in CH$_2$Cl$_2$ at λ = 350 nm

System	Photosensitizer	Conversion (%)	Polydispersity[b]	M_n[b]
Direct[c]	-	21	1.20	8500
Indirect	DMPA	18	1.58	17,200
Indirect	Thioxanthone	56	1.57	127,700
Indirect	Benzophenone	63	1.65	141,800

[a][IBVE] = 3.84 mol L^{-1}, [DPICl] = 2.45 x 10^{-3} mol L^{-1}, [Sensitizer] = 2.45 x 10^{-3} mol L^{-1}, and [ZnBr$_2$] = 3.15 x 10^{-3} mol L^{-1}; Irradiation time = 1 h, Total polymerization time = 20 h.
[b]Estimated by GPC based on polystyrene standards.
[c]Photopolymerization carried out at 300 nm.

In conclusion, preliminary experimental results fully support the idea that suitable photochemical free radical sources in combination with iodonium salts and zinc halides may be used to promote living cationic polymerization of alkyl vinyl ethers. Mechanistic details remain to be evaluated but for all systems studied, an important feature is the generation of carbocations or acids from free radical sources leading to the formation of monomer adducts which in the presence of zinc salt initiate living polymerization in a manner similar to that described for HX-ZnX$_2$ systems.

4.2 UV Curing of Di-functional Vinyl Ethers

The possible use of the polymerization system described in section 4.2 at room temperature for UV curing of di-functional vinyl ethers including BDVE, HDVE and DVE-DEG was examined. UV induced crosslinked polymerization of curing of BDVE via photosensitization in the presence of iodonium salt and zinc halide is represented in Figure 4.6.

Efficiencies of direct and direct acting mechanisms for various photoinitiating systems were investigated. In Table 4.2, effect of type of photosensitizer/photoinitiator used for generation of initiating species on gelation time and gel content was illustrated. The photosensitzers/photoinitiators which produce free radical leading to generation of cationic species by oxidation of the iodonium salt more effective than those which produce cation through exciplex, namely anthracene and perylene.

$$PS \xrightarrow{h\nu} \left[PS\right]^* \tag{4.9}$$

$$\left[PS\right]^* + Ph_2I^+X^- \longrightarrow R_1^+X^- + PhI + Ph + R_2^+ + \ldots \tag{4.10}$$
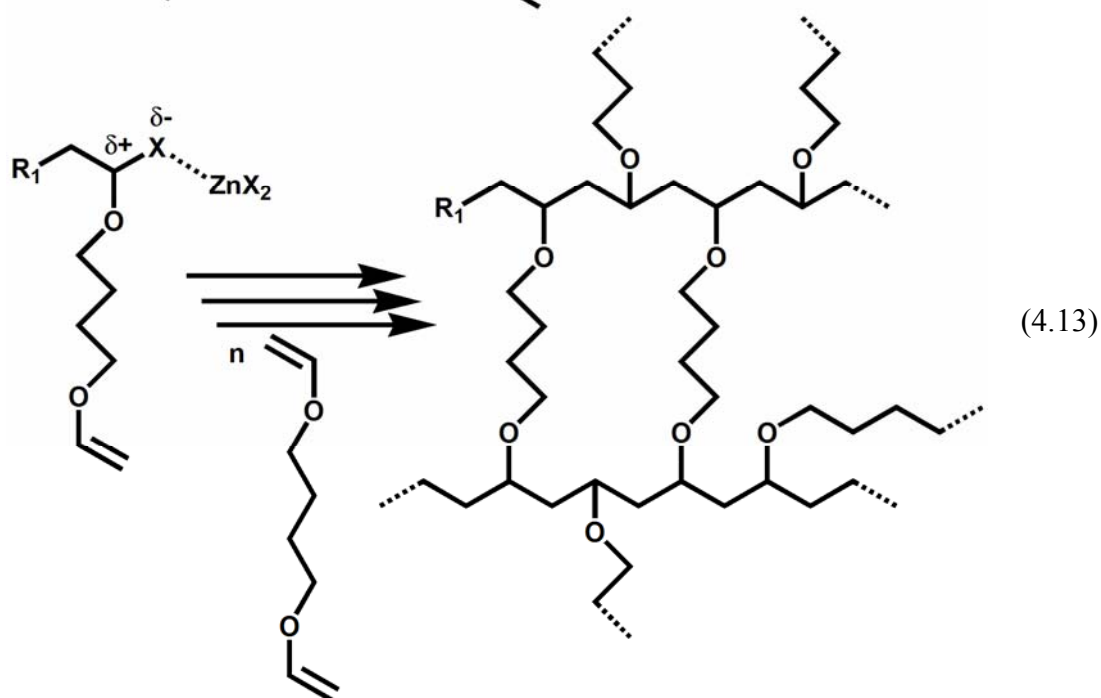

(4.11)

(4.12)

(4.13)
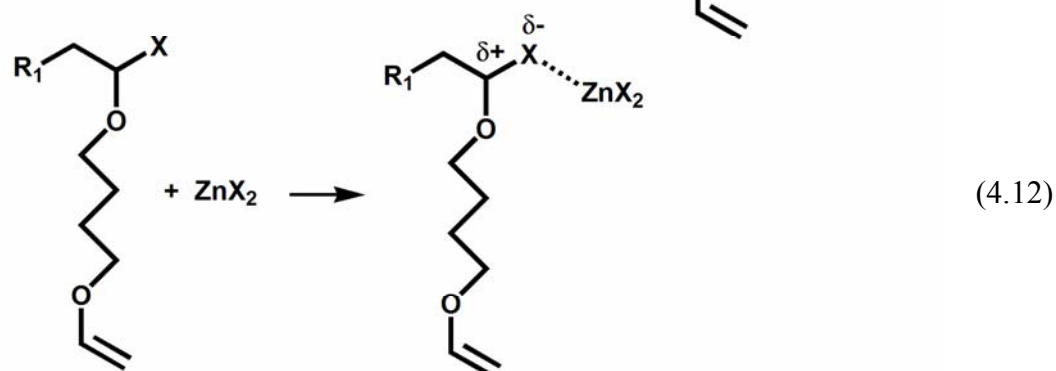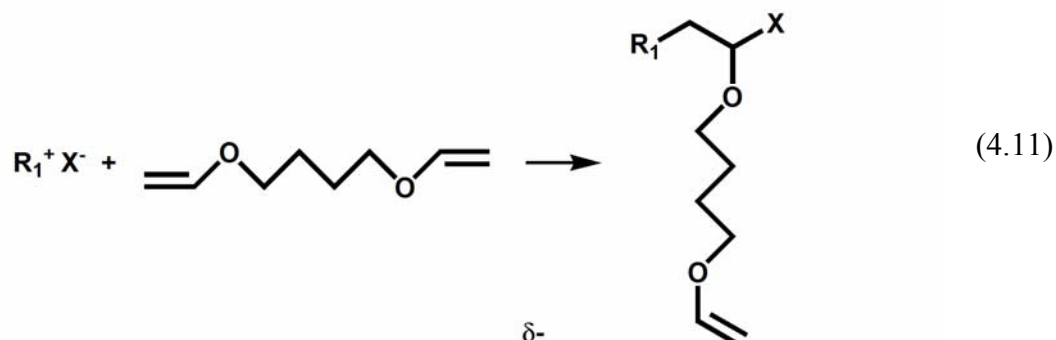
Figure 4.6. Photosensitized UV curing of BDVE in the presence of diphenyliodonium and zinc halides

Table 4.2. The dependence of the gelation time and the gel content on type of the photosensitizer/photoinitiator used for activation of DPICl which was employed as a co-initiator in the photoinduced curing of BDVE in the presence of zinc bromide at room temperature in CH_2Cl_2 at 350 nm

Photosensitizer/ Photoinitiator	Gelation Time (s)[a]	Gel Content[b] (%)
Anthracene	305	91
Perylene	1220	78
DMPA	45	92
Thioxanthone	65	97
Benzophenone	125	94

Concentrations; [BDVE] = 3.84 mol L^{-1}, [DPICl] = 2.45 x 10^{-3} mol L^{-1}, [Photosensitizer or Photoinitiator] = 2.45 x 10^{-3} mol L^{-1}, and [ZnBr$_2$] = 2.45 x 10^{-3} mol L^{-1}
[a] The irradiation time of the curing was equal to corresponding gelation time.
[b] Gel contents were estimated gravimetrically

Table 4.3. The dependence of the gelation time and the gel content on type of the diphenyliodonium salt which was employed as a photoinitiator and the zinc halide which was employed as a catalyst in the photoinduced curing of BDVE via two-component initiating system at room temperature in CH_2Cl_2 at 300 nm

Photoinitiator	X of ZnX$_2$	Gelation Time (s)[a]	Gel Content[b] (%)
DPICl	Br	325	89
DPIBr	Br	140	95
DPII	Br	120	96
DPICl	Cl	No gelation	No gel
DPIBr	Cl	165	98
DPII	Cl	158	88
DPICl	I	53	97
DPIBr	I	52	100
DPII	I	48	98

Concentrations; [BDVE] = 3.84 mol L^{-1}, [DPIX] = 2.45 x 10^{-3} mol L^{-1}, and [ZnX$_2$] = 2.45 x 10^{-3} mol L^{-1}
[a] The irradiation time of the curing was equal to corresponding gelation time.
[b] Gel contents were estimated gravimetrically.

Dependence of gelation time and gel content on counter anion of iodonium and zinc halides was, also, investigated (Table 4.3). Terminal C-X bond of the X$^-$-monomer adduct (see reaction 4.12 in Figure 4.6) have to be polarized enough for successive insertion of new monomer [7]. The polarization of C-X bond resulted from coordination effect of ZnX$_2$, thus X determines the rate of polymerization. According to Table 4.3, rate of polymerization increases in the order of chloride << bromide < iodide.

1,4-butanediol divinyl ether
(BDVE)

1,6-hexanediol divinyl ether
(HDVE)

Di(ethylene glycol) divinyl ether
(DVE-DEG)
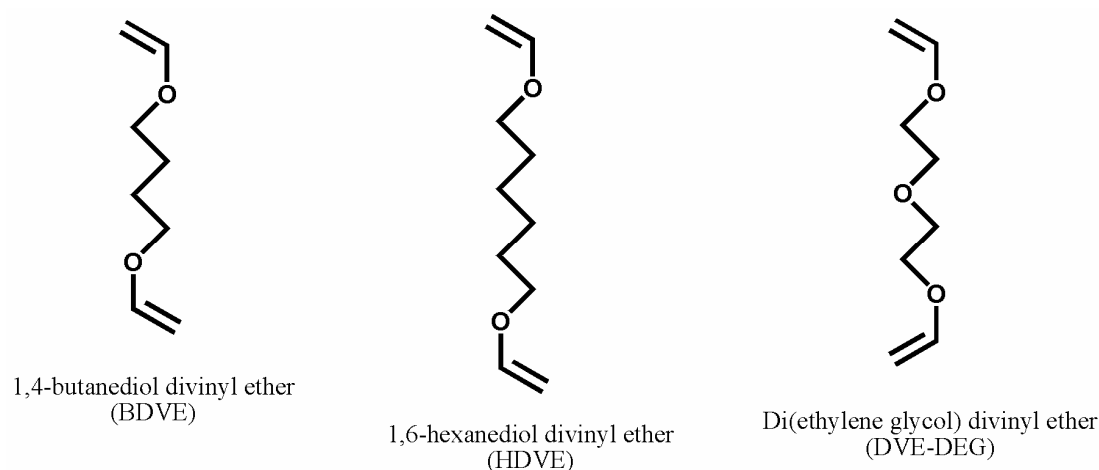
Figure 4.7. UV curable di-functional vinyl ethers

The efficiency of direct and indirect acting systems was compared in the curing of BDVE. Also, in direct systems, curing features of various di-functional vinyl ethers such as BDVE, HDVE and DVE-DEG were analyzed. Polymerization via indirect system is faster than via direct system probably because in indirect system, more initiating species are produced (see reactions 4.1 - 4.3 in Figure 4.2) than those produced in direct system (see reaction 1.1 in Figure 1.1). The fast polymerization observed when BDVE was used as monomer compared to HDVE and DVE-DEG (Table 4.4). This is probably due to high diffusion rate of BDVE compared to HDVE and DVE-DEG since the molecular size of BDVE is smaller than those of others (Figure 4.7).

Table 4.4. Comparison of the gelation time and the gel content of the crosslinked polymer of various divinyl ether monomers cured in direct curing system consisting of a photoinitiator (DPII) and a catalyst (zinc iodide), and in indirect curing system consisting of photoinitiator (DMPA), co-initiator (DPII) and a catalyst (zinc iodide)

System	Initiating component	Monomer	Wavelength (nm)	Gelation Time (s)[a]	Gel Content[b] (%)
Indirect	DMPA and DPII	BDVE	350	21	94
Direct	DPII	BDVE	300	48	98
Direct	DPII	HDVE	300	237	97
Direct	DPII	DVE-DEG	300	142	85

Concentrations; [Monomer] = 3.84 mol L^{-1}, [Photoinitiator or co-initiator] = 2.45 x 10^{-3} mol L^{-1} and [ZnI$_2$] = 2.45 x 10^{-3} mol L^{-1}
[a] The irradiation time of the curing was equal to corresponding gelation time.
[b] Gel contents were estimated gravimetrically.

In conclusion, the results suggest, regardless of direct or indirect action, the cationically curable formulations bearing cation-monomer adduct with high

nucleophilic counter anion can be used in curing. In curing systems, indirect systems are more effective than direct systems due to fast polymerization. Fast curing has several advantages, thus the indirect curing formulations described in this study may find many possible applications in curing.

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AUTOBIOGRAPHY

Muhammet Ü. KAHVECİ was born in Bayburt in 1981. He was graduated from Bayburt Medicinal High School in 2000. He was admitted to Aegean University, Department of Chemistry in 2000, and transferred to Istanbul Technical University (ITU) in 2002. In 2003, he was also admitted to Molecular Biology and Genetics as a Double Major Program student. He was graduated as a chemist in 2005.

He was registered as M.Sc. student to the Chemistry Program of of the Institute of Science and Technology of Istanbul Technical University in 2005.

He is co-author of the following scientific paper published in an international journal:

Photochemically initiated free radical promoted living cationic polymerization of isobutyl vinyl ether.
Polymer, *Volume 48, Issue 8, 5 April 2007, Pages 2199-2202*
Muhammet U. Kahveci, M. Atilla Tasdelen and Yusuf Yagci