

**FREE RADICAL PROMOTED CATIONIC
POLYMERIZATION BY USING
BISACYLPHOSPHINE OXIDE PHOTOINITIATORS:
SUBSTITUENT EFFECT ON THE REACTIVITY OF
PHOSPHONYL RADICALS**

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**BİSAÇILFOSFİN OKSİT SERBEST RADİKAL
FOTOBASLATICILARLA KATYONİK
POLİMERİZASYON: FOSFONİL RADİKALLERİNİN
REAKTİVİTELERİ ÜZERİNE SÜBSTİTÜENTLERİN
ETKİSİ**

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LIST of ABBREVIATIONS

CHO	: Cyclohexene Oxide
UV	: Ultra Violet
TMDPO	: 2,4,6-Trimethylbenzoyldiphenylphosphine oxide
BTBPO	: bis-(2,4,6-trimethyl benzoyl)-phenylphosphine oxide
BDTMPO	: bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide
BTTMPO	: bis-(2,4,6-trimethyl benzoyl)-2,4,4-trimethyl pentylphosphine oxide
Ph₂I⁺PF₆⁻	: Diphenyliodonium Hexafluorophosphate
Ph₃S⁺PF₆⁻	: Triphenylsulfonium Hexafluorophosphate
EMP⁺PF₆⁻	: N-Ethoxy-2-Methylpyridinium Hexafluorophosphate
BVE	: Butyl Vinyl Ether
On⁺	: Onium Salt
THF	: Tetrahydrofuran
CT	: Charge Transfer
NMR	: Nuclear Magnetic Resonance Spectroscopy
GPC	: Gel Permeation Chromatography
M_n	: Number Average Molecular Weight
NVC	: N-vinyl carbazole
<i>p</i>-MSt	: <i>p</i> -Methoxy styrol
DMP	: 2,6-ditertbutyl-4-methyl pyridine

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FREE RADICAL PROMOTED CATIONIC POLYMERIZATION BY USING BISACYLPHOSPHINE OXIDE PHOTOINITIATORS: SUBSTITUENT EFFECT ON THE REACTIVITY OF PHOSPHONYL RADICALS

SUMMARY

In this thesis, the uses of mono- and bisacylphosphine oxides in photoinitiated cationic polymerization were investigated and the effects of the structures of the bisacylphosphine oxides in the polymerization were evaluated. The cationic polymerization of cyclohexene oxide (CHO) was achieved upon UV irradiation ($\lambda=380$ nm) of methylene chloride solutions containing monoacylphosphine oxide, 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TMDPO) or bisacylphosphine oxides, namely bis-(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (BTBPO), bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide (BDTMPO) and bis-(2,4,6-trimethylbenzoyl)-2,4,4-trimethyl pentylphosphine oxide (BTTMPO) and onium salts such diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) or *N*-ethoxy-2-methylpyridinium hexafluorophosphate ($\text{EMP}^+\text{PF}_6^-$). A feasible initiation mechanism involves the photogeneration of phosphinoyl radicals and benzoyl radicals in the first step. Subsequent oxidation of phosphinoyl radicals by onium salts yields phosphonium ions capable of initiating the polymerization of CHO. In agreement with the proposed mechanism, the initiation efficiency was related to redox potential of the onium salts, i.e., $\text{Ph}_2\text{I}^+\text{PF}_6^-$ ($E_{\text{red}}^{1/2}=-0.2$ V) was found to be more efficient salt than $\text{EMP}^+\text{PF}_6^-$ ($E_{\text{red}}^{1/2}=-0.7$ V) in the polymerization. Moreover, bisacylphosphine oxides were more reactive in promoting cationic polymerization than TMDPO. The variations in reactivity of the different phosphorous radicals were correlated with *p*-character on the phosphorous atom as reflected by the ^{31}P hyperfine coupling constant. The applicability of the initiating system to other cationically polymerizable monomers such butyl vinyl ether (BVE) and *N*-vinyl carbazol (NVC) and *p*- methoxy styrol (*p*-MSt) was also demonstrated. The effects of the reaction parameters such as irradiation time, the concentrations of onium salts, and acylphosphine oxides, UV absorber and radical scavenger on the polymerization rate were also investigated.

BİSAÇILFOSFİN OKSİT SERBEST RADİKAL FOTOBAŞLATICILARLA KATYONİK POLİMERİZASYON: FOSFONİL RADİKALLERİNİN REAKTİVİTELERİ ÜZERİNE SÜBSTİTÜENTLERİN ETKİSİ

ÖZET

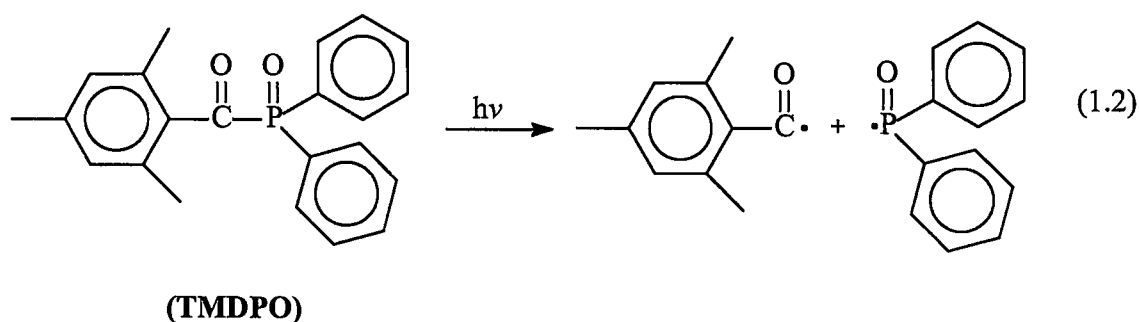
Bu tezde, mono- ve bisaçilfosfin oksitlerin, foto başlatılmış katyonik polimerizasyonda kullanımı araştırılmış ve bisaçilfosfin oksit yapılarının polimerizasyonüzerine etkisi incelenmiştir. Siklohekzen oksitin (CHO) katyonik polimerizasyonu, monoaçilfosfin oksit (2,4,6-trimetilbenzoildifenilfosfine oksit (TMDPO)) veya bisaçilfosfin oksit, (bis-(2,4,6-trimetilbenzoil)-fenilfosfin oksit (BTBPO), bis-(2,6-dimetoksibenzoil)-2,4,4-trimetilpentil fosfin oksit (BDTMPO) ve bis-(2,4,6-trimetilbenzoil)-2,4,4-trimetil pentilfosfin oksit (BTTMPO)) ve onyum tuzları (difeniliyodonyum hekzaflorofosfat ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) veya *N*-etoksi-2-metilpiridinyum hekzaflorofosfat ($\text{EMP}^+\text{PF}_6^-$)) içeren metilen klorür çözeltilerinin UV ışığında ($\lambda=380$ nm) aydınlatılmasıyla gerçekleştirilmiştir. Muhtemel başlama mekanizması, ilk basamakta, ışıkla fosfonil ve benzoil radikallerinin üretilmesini içermektedir. İkinci basamakta ise, fosfonil radikallerinin, onyum tuzları varlığında oksitlenmesiyle CHO'nun katyonik polimerizasyonunu başlatabilecek nitelikte fosfonyum iyonlarının üretilmesini içermektedir. Önerilen mekanizmayla uyumlu olarak, başlama etkinliği, onyum tuzlarının redoks potansiyelleriyle ilgilidir. Örneğin, polimerizasyon reaksiyonlarında, $\text{Ph}_2\text{I}^+\text{PF}_6^-$ tuzunun ($E_{\text{red}}^{1/2}=-0.2$ V) $\text{EMP}^+\text{PF}_6^-$ tuzundan ($E_{\text{red}}^{1/2}=-0.7$ V) daha etkili olduğu bulunmuştur. Ayrıca, bisaçilfosfin oksitler, katyonik polimerizasyonun ilerleme aşamasında, TMDPO'dan daha reaktiftir. Farklı fosfonil radikallerinin ayrı reaktiviteleri de, ^{31}P hyperfine birleşme sabitlerinin de yansıttığı gibi fosfor atomundaki p-karakteriyile alakalıdır. Bu başlatıcı sisteminin, bütül vinil eter (BVE), N-vinil karbazol (NVC) ve *p*-metoksi stiren (*p*-MSt) gibi diğer katyonik yolla polimerleşebilen monomerlere de uygulanabilirliği de gösterilmiştir. Aydınlatma zamanı, onyum tuzu ve bisaçilfosfin oksit konsantrasyonları, UV absorber ve radikal tutucu gibi parametrelerin polimerizasyon üzerine etkileri de incelenmiştir.

1. INTRODUCTION

Photoinitiated cationic polymerization of monomers, such as epoxides and vinyl ethers, plays a crucial role in many commercial applications, such as coatings, inks, adhesives and in the preparation of advanced technical substrates [1-3]. Because of the additives used in different applications, when targeting a specific spectral sensitivity, the wavelength flexibility becomes a fundamental factor in determining the curing performance of specific formulations. Therefore, photoinitiating systems for cationic polymerization sensitive particularly to higher wavelengths are increasingly important for specific applications [4]. Most of the existing photoinitiating systems are based on the use of certain onium salts [5,6], such as diaryliodonium [7], triarylsulfonium [8] and alkoxy pyridinium [9-11] salts. However, these salts do not absorb significantly above 300 nm unless additional chromophores are incorporated into the salt structure. This requires multi-step preparation and purification procedures. For practical reasons, it was, therefore, attempted to extend the photosensitivity of easily available onium salts to wavelengths $\lambda > 350$ nm with the aid of appropriate light sensitive compounds, such as free radical photoinitiators [12-16], charge transfer complexes [17] and photosensitizers [18-20]. In all cases, onium salts act as electron acceptors in redox reactions with free radicals, longliving electronically excited states of sensitizers and electron donor compounds in charge transfer complexes, respectively. Among these approaches, so-called free radical promoted cationic polymerization is an elegant and fairly flexible way to generate cationic species capable of reacting with monomers. The overall mechanism involves oxidation of photochemically formed radicals by onium salts (On^+) with suitable reduction potentials.



There is considerable literature on the use of many photoinitiators in free radical promoted cationic polymerization. Benzoin and derivatives [21], acylphosphine oxides [22], o-phthalaldehyde [23], vinyl halides [24] and polysilanes [25,26] have been successfully used as radical sources in free radical promoted cationic polymerization. More recently, several visible light absorbing systems to generate oxidable radicals were also reported. For instance, radicals formed by the irradiation system containing a xanthen dye and an aromatic amine, were oxidized by a diaryliodonium salt [15]. Similarly, the dimanganese decarbonyl-organic halide combination is an efficient co-initiator for visible light cationic polymerization when used in conjunction with onium salts [27]. In another study, a commercial titanocene type photoinitiator, Irgacure 784, was used as the visible light free radical source. An initiation mechanism involving electron transfer between photoproducts of titanocene and onium salt was proposed [28]. Acylphosphine oxides and acyphosphanates with different structures have been used [29] as photoinitiators for free radical polymerization. Long-wavelength absorption characteristics make these compounds particularly useful for the polymerization of TiO₂ pigmented formulations containing acrylate or styrene type monomers and of glass fiber reinforced polyester laminates with reduced transparency [30]. Extensive investigations [31-33] on the photochemistry of acylphosphine oxides revealed that they undergo α -cleavage with fairly high quantum yields as shown below on the example of trimethylbenzoyl diphenylphosphineoxide (TMDPO).



The capability of acylphosphine oxides to promote the cationic polymerization of appropriate monomers were also examined [22]. Although polymerizations of tetrahydrofuran and butyl vinyl ether were readily initiated upon irradiating them in the presence of TMDPO and diphenyliodonium salt at 379 nm, where only TMDPO absorbs light, it could not be definitely concluded whether and how both radicals

generated can act as free radical promoters according to reaction (1.2). However, polymerization, ESR spin-trapping and laser flash photolysis studies revealed that benzoyl [34,35] and phosphinoyl radicals [22] do not react with Ph_2I^+ ions ($k < 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$) but abstract hydrogen from appropriate donors [36]. The resulting carbon centered radicals are converted to carbocations by reaction with Ph_2I^+ ions.

In this thesis, the use of bisacylphosphine oxides as photoinitiators in free radical promoted cationic polymerization is reported and the reactivity on the basis phosphinoyl radical structure is discussed.



2. THEORETICAL PART

2.1 Photoinitiated Polymerization

Photoinitiated polymerization means the initiation of a chain polymerization process by light. In the more general sense, photoinitiated polymerization implies the increase of molecular weight caused by light and includes the photocrosslinking of preexisting macromolecules. Vinyl polymerization can be initiated by ionic species as well as by free radicals, but almost all examples of photoinitiated polymerization are of a free radical character. Photochemical production of primary radicals needs low temperature (10-40 °C), unlike thermal free radical initiators that generally occur above 40 °C. Consequently, photoinitiated polymerization can be carried out at very low temperatures. Hence chain transfer processes leading to branched macromolecules will be absent. Photopolymerization at low temperatures yields the low energy stereospecific polymeric species.

2.1.1 Photoinitiated Free-Radical Polymerization

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 reason for the current developments are the particular attractive features of photoinitiated polymerization process, such as the concept of latency, high speed under mild conditions, reduced energy and space requirements, and last but not least considerable environmental advantages [37].

An essential ingredient of all UV-curable (crosslinkable) compositions is the photoinitiator, or more generally the photoinitiating system. Imperative requirements imposed on the photoinitiating system are:

- i. absorptivity preferably in the 300-400 nm range, with absorption coefficient (ϵ) high or low, depending on the specific application;
- ii. efficient generation of free radicals capable of attacking the olefinic double bond of vinyl monomers;
- iii. adequate solubility in saturated resin systems;
- iv. should not adversely affect the viscosity of the overall system even at elevated temperatures, i.e. high storage stability in the dark;
- v. should not impart yellowing or unpleasant odours to the cured material;
- vi. should be non-toxic itself, as should its irradiation products;
- vii. it should preferably be liquid or low melting for handling and blending convenience.

Over the last years a large number of reviews have appeared on photoinitiators, photocrosslinkable resin systems and their applications [3,4,38,39], illustrating the growing importance of UV curing science and technology.

Regarding initiation by light it has to be pointed out that the absorption of incident light by one or several components of the polymerization mixture is the crucial prerequisite. If the photon energy is absorbed directly by a photosensitive compound, being it monomer itself or an added initiator, this photosensitive substance undergoes a homolytic bond rupture forming radicals, which may initiate the polymerization. In some cases, however, a compound that itself is not prone to radical formation absorbs the photon energy. These so called sensitizers transfer their electronic excitation energy to reactive constituents of the polymerization mixture, which finally generate radicals. The radicals evolved react with intact vinyl monomer starting a chain polymerization. Under favorable conditions, a single free radical can initiate the polymerization of a thousand molecules. The spatial distribution of initiating species may be arranged in any desired manner [40].

Light induced free radical polymerization is of enormous commercial use. Techniques such as curing of coatings on wood, metal and paper, adhesives, printing inks and photoresists are based on photoinitiated radical vinyl polymerization. There are some other interesting applications including production of laser videodiscs and curing of acrylate dental fillings.

Photopolymerization of monofunctional monomers takes place without side reactions such as chain transfer. In thermal polymerization, the probability of chain transfer is high which brings about a high amount of branched macromolecules. Hence, low-energy stereospecific polymeric species, namely of syndiotactic configuration, may be obtained by photopolymerization. Another important use refers to monomers with low ceiling temperature. They can only be polymerized at moderate temperatures, otherwise depolymerization dominates over polymerization. By means of photopolymerization these monomers are often easily polymerizable. Furthermore, biochemical applications, such as immobilization of enzymes by polymerization, do also usually require low temperatures. As far as curing of coatings or surfaces is concerned it has to be noted, that thermal initiation is often not practical, especially if large areas or fine structures are to be cured or if the curing formulation is, like for dental fillings, placed in a surrounding that should rather not be heated.

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 [41] reported on the polymerization of styrene by sunlight more than 150 years ago.

Photocurable formulations are mostly free of additional organic solvents; the monomer, which serves as reactive diluent, is converted to solid, environmentally safe resin without any air pollution. UV curing is often a very fast process, taking place as pointed out above without heating. If the polymerization mixture absorbs solar light and the efficiency of radical formation is high, photocuring can be performed with no light source but sunlight. These features make photopolymerization an ecologically friendly and economical technology, which has high potential for further development.

2.1.1.1 Stages of Photoinitiated Free-Radical Polymerization

The most important stages of photoinitiated stages of photoinitiated free-radical polymerization processes fall into three distinct categories.

a) Photophysical Processes

The very fast act in photoinitiated polymerization processes is the absorption of UV light in the 300-400 nm range by the photoinitiator to populate an excited singlet

manifold which may have $\pi\text{-}\pi^*$ or $n\text{-}\pi^*$ configuration. Through rapid internal conversion the lowest excited singlet state is then reached. In aromatic carbonyl compounds, to which category most photoinitiators belong, singlet triplet energy splitting is usually small, and as a consequence intersystem crossing (i.s.c.) to the lowest excited triplet state ($\pi\text{-}\pi^*$ or $n\text{-}\pi^*$) proceeds rapidly and efficiently (quantum yields between 0.9 and 1.0). Possible competing processes such as fluorescence and non-radiative decay of excited singlets to the ground state usually are of negligible importance [42].

It may be worth noting that in principle it is also possible to populate the lowest excited triplet state of the photoinitiator in a photosensitized process, i.e. absorption of the light by a suitable photosensitizer followed by energy transfer to the photoinitiator molecule [2].

b) Photochemical Processes

Major chemical deactivation pathways open to the excited triplet state of these aromatic carbonyl compounds show an analogy with the major reactions of alkoxy radicals [43-44], i.e. (i) fragmentation, and (ii) hydrogen abstraction from a suitable hydrogen-donor, as is illustrated in Figure 2.1.

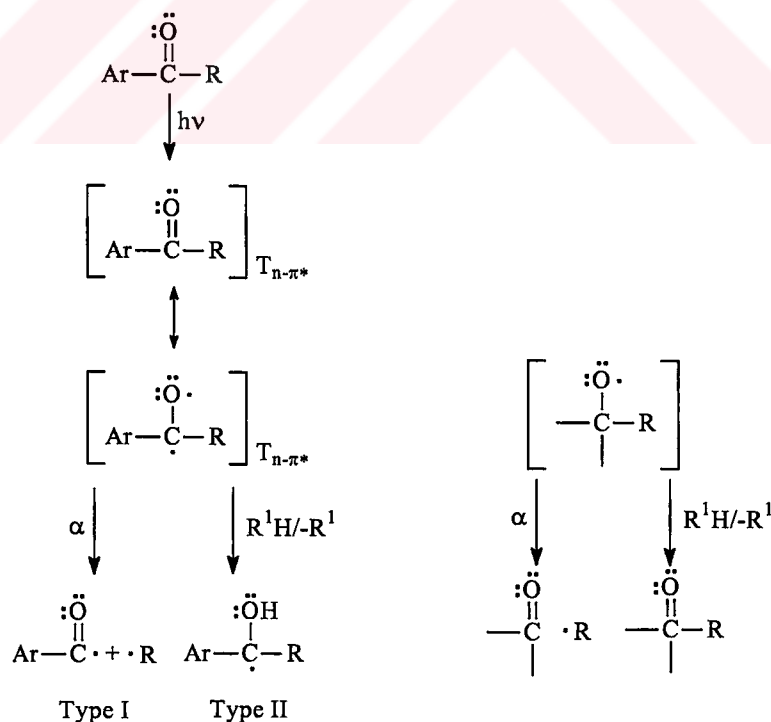


Figure 2.1. ($n\text{-}\pi^*$) Triplet excited carbonyl reactions compared with reactions of an alkoxy radical.

On the basis of these two major reactions photoinitiators have been divided into two major types:

Type I Photoinitiators, being those which undergo unimolecular fragmentation (Norrish type I, α -cleavage) into an aryl and a second radical ($R\cdot$); and

Type II Photoinitiators, being those that only generate radicals through bimolecular hydrogen abstraction from a suitable hydrogen-donor.

Which of these processes prevails depends primarily on the nature of the group R. when R is an alkyl group, preferably carrying substituents capable of stabilizing an adjacent positive charge, α -cleavage is the almost exclusive process [45], whereas when R is an aromatic group α -cleavage does not occur, but hydrogen-abstraction is the favoured process [46].

Moreover, the configuration of the excited state involved also has implications for the rates at which the various processes take place: $n-\pi^*$ triplets are far more reactive than their $\pi-\pi^*$ counterparts in α -cleavage [47,48], as well as in hydrogen-abstraction [46,49] (inter- and intra-molecular) reactions, except when tertiary amines are the hydrogen-donor involved.

Possible competing processes, such as phosphorescence, and non-radiative decay of the excited triplets to the ground state can safely be neglected. However, quenching of the excited triplet states by oxygen, vinyl monomers and other adventitious species does occur in certain Type I cases, and Type II photoinitiators except when tertiary amines are used as the hydrogen-donor.

c) Ground-State Free-Radical Processes

The primary radicals thus generated from the excited triplet state of the various photoinitiators can in principle undergo the usual set of reactions common to free radicals such as:

- i. addition to the double bond of a vinyl monomer present, i.e. the actual initiation step;
- ii. subsequent fragmentation generating a secondary radical that may or may not be reactive towards the double bond of vinyl monomers;

- iii. hydrogen-abstraction, creating another radical center that again may or may not be reactive;
- iv. dimerisation, implying loss of radical activity; and
- v. coupling with other radicals, e.g. growing polymer radicals, implying primary radical termination.

Reaction (i) is of course the desired reaction, but reactions (ii) and (iii) may also contribute to the overall initiation of polymerization.

In reactions (iv) and (v), however, potential initiating radicals are being destroyed and will therefore reduce the overall efficiency of the photoinitiation.

Which of these reactions actually prevails depends largely on the ratio of their rate constants. At the concentration normally used, i. e. low concentration of photo-initiator and relatively high concentration of vinyl functionalities, reactions (iv) and (v) will presumably be of minor importance. More important, however, are reactions of primary, secondary and growing polymer radicals with oxygen from the surrounding air atmosphere [37].

2.1.2 Photoinitiated Cationic Polymerization

In terms of the sheer number and different types of monomers that can be polymerized, cationic polymerizations are by far the most versatile of all addition type polymerizations [50,51]. 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. Virtually every type of known cationically polymerizable monomer can be polymerized with diaryliodonium and triarylsulfonium salt photoinitiators. An attempt to schematically indicate this is shown in Figure 2.2. The versatility of photoinitiated cationic polymerizations has made them very attractive for a wide variety of commercial applications, some of which are detailed later. In addition, there are several reasons why photoinitiation can aid in the academic study of cationic polymerization reactions as well. The use of cationic photoinitiators provides a convenient method of generating powerful Brønsted acid polymerization catalysts in situ and obviates the difficulties of preparing and handling these materials. Furthermore, the cationic polymerizations can be triggered conveniently,

precisely, and homogeneously by irradiation when desired to allow the determination of the kinetic parameters of even the most highly reactive monomers. This degree of control over cationic polymerizations is very difficult to establish with the parent Brønsted acids. The cationic polymerizations of multifunctional monomers are notoriously difficult to follow by conventional techniques because they undergo gel formation during reaction. The kinetics of these systems readily can be studied by photoinitiated polymerizations by using such techniques as real-time infrared spectroscopy [52,53] and differential scanning photocalorimetry [54].

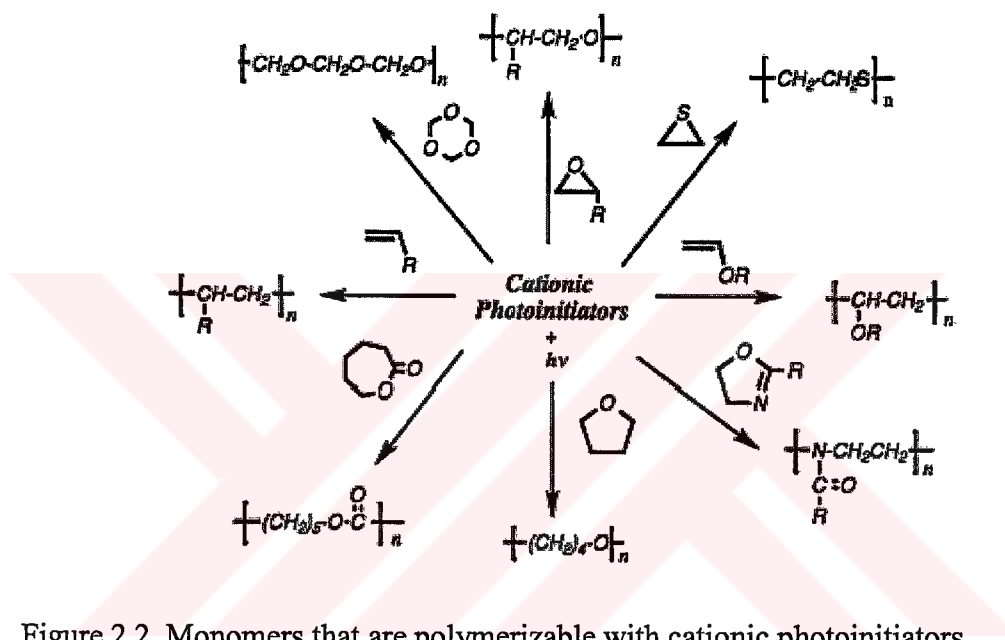
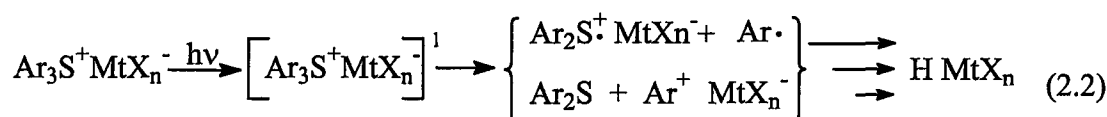
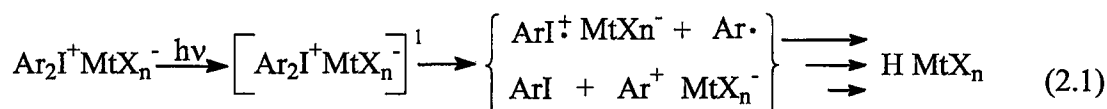


Figure 2.2. Monomers that are polymerizable with cationic photoinitiators.

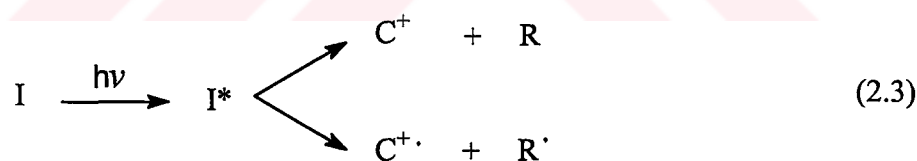
The only portion of a photoinitiated cationic polymerization that is dependent on light is the photolysis of the photoinitiator (2.1 and 2.2). Once the active species are formed, the polymerization itself proceeds by a normal cationic process that is subject to the usual experimental reaction parameters and kinetic considerations. There are, however, some marked differences between cationic and free radical photopolymerizations. For example, there is nearly a first-order dependency of the polymerization rate on the light intensity rather than the half-order relationship that is observed in free-radical photopolymerizations. The rates of cationic photopolymerizations are also highly temperature dependent, whereas the rates of free-radical photopolymerizations display little temperature dependence. The most striking difference between the two techniques is the ability of cationic photopolymerizations, once initiated, to proceed further in the absence of light. Most

free-radical photopolymerizations cease within a millisecond or so after the irradiation is extinguished because of rapid termination. The classical living cationic photopolymerization of tetrahydrofuran can be carried out readily with diaryliodonium salt photoinitiators [55]; however, the corresponding vinyl ether and epoxide polymerizations carried out at room temperature were not living and, not surprisingly, displayed considerable chain transfer. The photopolymerizations of these monomers do exhibit considerable “dark” reaction and can be classified as nonterminating.



2.1.2.1 Direct Photolysis

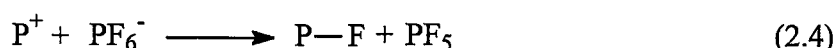
If onium salt initiators I absorb light, electronically excited initiator I* species are produced. The latter undergo a heterolytical or homolytical bond rupture leading to cations C⁺ or radical cations C^{+·}, respectively.



In some cases, these entities are able to react directly with monomer molecules starting a cationic polymerization. Frequently, C⁺ or C^{+·} is inert towards the cationically polymerizable monomer in the manner necessary for initiating the polymerization. This often observed lack in reactivity is mostly explainable in terms of bulkiness of the species C⁺ and C^{+·} produced in the primary reaction. However, both C⁺ and C^{+·} are often able to react with the monomer or solvent molecules thus releasing the Brønsted acid H⁺. Being highly reactive to all sorts of cationically polymerizable monomers, protons will act as initiating species in these circumstances [4].

An important factor which retarded the development of photoinitiated cationic polymerization is the tendency of cationic polymerization to be dominated by termination and chain transfer processes at ambient temperatures. However, this tendency may be retarded by utilizing cationic initiators with highly non-nucleophilic anions, such as PF_6^- , AsF_6^- and SbF_6^- .

The low nucleophilicity of these anions reduces termination processes and allows cationic polymerization to produce under ambient conditions. Furthermore, reaction of growing polymer cations (P^+) with such complex metal halide anions is expected to yield the corresponding Lewis acid, (2.4). To the extent that the Lewis acid becomes involved in initiation of a new chain, (2.4) represents a chain transfer reaction.



Low termination rates in these systems also contribute to continued polymerization following light exposure, a catalytic activity which is not observed in photocrosslinking by radical polymerization. The important absence of air-inhibition further distinguishes cationic from radical polymerization.

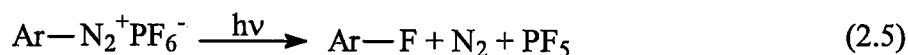
Commercially important photoinitiators for crosslinking by cationic polymerization are onium salts and mixed-ligand arene cyclopentadienyl metal salts with complex metal halide anions. In general for photoinitiated cationic polymerization of epoxides with both onium and metal salts, rates, molecular weights and percentage conversions increase in the order $\text{BF}_4^- \ll \text{PF}_6^- < \text{AsF}_6^- < \text{SbF}_6^-$. These results may be attributed, at least in part, to

- i. increasing stability of the anions in the same order, which is expected to result in decreasing participation;
- ii. increasing initiating ability of the corresponding Lewis acids in the same order, i.e. $\text{BF}_3 < \text{PF}_5 < \text{AsF}_5 < \text{SbF}_5$; and
- iii. increasing acidity of the corresponding Brønsted acids in the same order [56].

a) Onium Salts

Aryldiazonium Salts

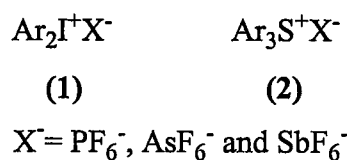
The first commercial system for photoinitiated cationic polymerization in UV curing and imaging applications utilized aryl diazonium salts of complex metal halide anions together with epoxy-functional monomers and oligomers [57]. Photolysis of these salts yields Lewis acids (2.5), which may initiate 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 (2.6).



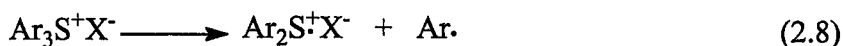
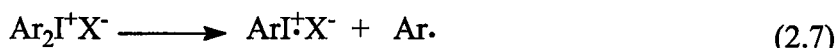
The spectral response of diazonium salts may be varied throughout the near UV-visible range by appropriate substituents on the aryl ring [58]. Furthermore, both the absorptivity and thermal stability of the diazonium salts are enhanced by electron-donating groups (one of the few exceptions to Murphy's 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.

Diaryliodonium and Triarylsulphonium Salts

These deficiencies prompted investigations on alternative photoinitiators for cationic polymerization, which led to the development of diaryliodonium (1) and triarylsulphonium (2) salts with complex metal halide anions [59-60]. In contrast to aryl diazonium salts, the iodonium and sulphonium salts exhibit high thermal stability, as well as hydrolytic stability, and may be considered second-generation photoinitiators for crosslinking by cationic polymerization.



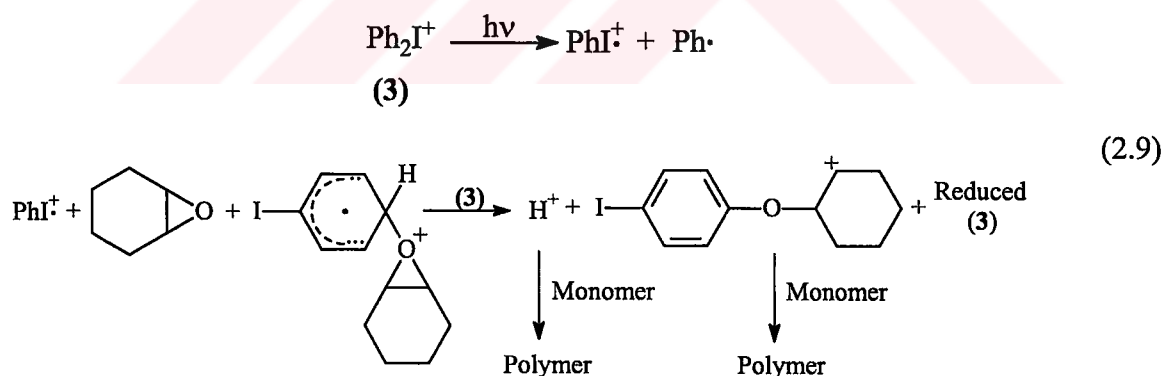
Irradiation of these salts results in homolytic cleavage of Ar-I (or Ar-S) bonds to yield reactive radical cations, as shown in (2.7) and (2.8), respectively.



Direct evidence for this homolytic bond cleavage has been obtained from laser flash photolysis studies [61]. Furthermore, the radical cations have been found to be highly reactive with nucleophiles, including cyclohexene oxide (CHO) and vinyl ethers [61-63].

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

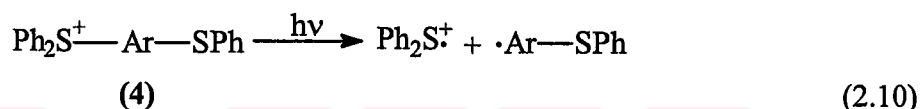
A possible reaction mechanism for photoinitiated polymerization of epoxides utilizing a diphenyliodonium salt (3) as photoinitiator, which is consistent with the laser flash photolysis studies as well as with polymer end-group analysis studies, is provided in (2.9).



Key features of this scheme are (a) direct reaction of $\text{PhI}^{\cdot+}$ 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.

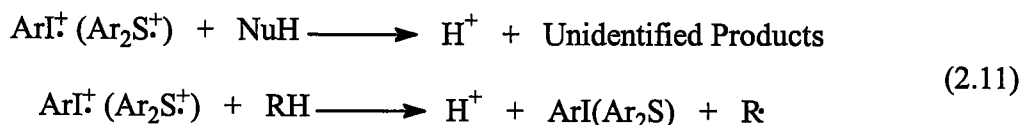
Support for photoinitiator fragment incorporation comes from studies with the triarylsulfonium salt (4) [64]. Utilizing (4) as photoinitiator for cationic polymerization of CHO, spectroscopic evidence (absorption and emission) has been obtained for the incorporation of 4-alkoxydiphenyl sulfide end groups in poly(cyclohexene oxide). These results are readily explicable in terms of initiation by the diphenylsulfinium radical cation ($\text{Ph}_2\text{S}^{\cdot+}$) in accordance with (2.9).

Furthermore, direct evidence for formation of $\text{Ph}_2\text{S}^{\cdot+}$ has been obtained from laser flash photolysis studies (see 2.11) [61]. 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 (2.9).



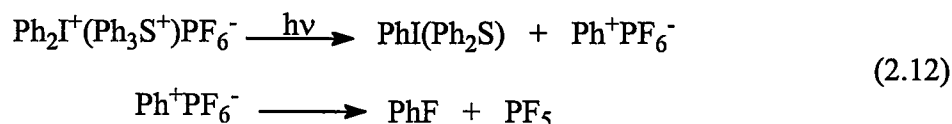
Ar = 1,4-disubstituted benzer

In the absence of reactive monomer, photogenerated ArI^+ and Ar_2S^+ are expected to react with nucleophiles (NuH) and possibly H-donors (RH) to produce protons (see 2.11). The reactions in (2.11) account for polymerization of monomer introduced after irradiation [59], as well as for photoinduced acid catalyzed reactions utilized in photoimaging applications [66,67]. The electrophilicity of diarylsulfonium ions (Ar_2S^+) is well documented [68].



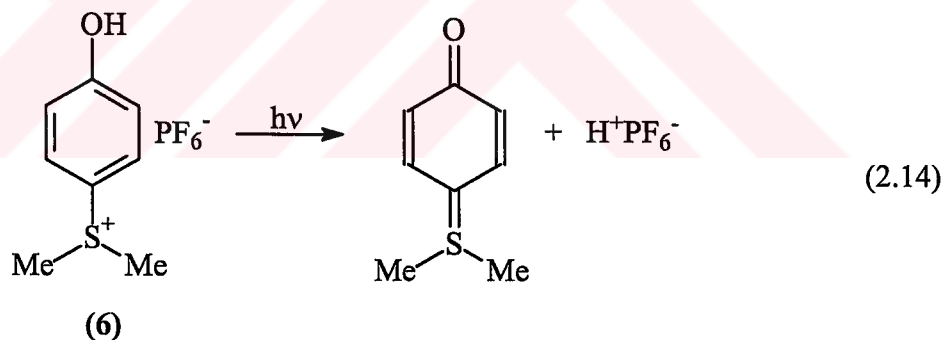
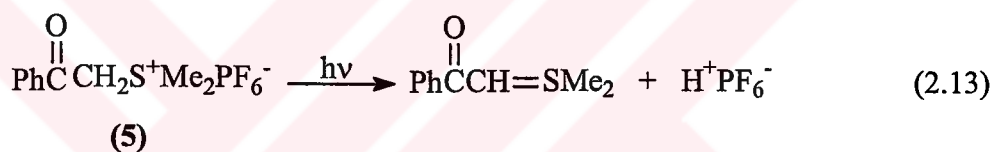
In addition to the proposals for photogeneration of cationic initiators in (2.9) and (2.11), both of which originate with homolytic bond cleavage, evidence for photoinduced heterolytic bond cleavage of diaryliodonium and triarylsulfonium salts in methanol has been reported [69], as shown in (2.12). However, the reported substantial yields of fluorobenzene appear to be inconsistent with earlier studies on the photochemistry of diaryliodonium [70] and triarylsulfonium salts [71], carried

out under similar conditions. Possibly, fluorobenzene arises from secondary photochemical reactions.



Phenylacetylsulfonium and 4-hydroxyphenylsulfonium Salts

Dialkyl phenylacetylsulfonium and 4-hydroxyphenylsulfonium salts, such as (5) and (6), respectively, also function as photoinitiators for cationic polymerization. However, in contrast to triarylsulfonium salts, polymerization is reported to cease following light exposure [55]. Furthermore, polymerization does not occur when (5) and (6) 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 (2.13) and (2.14).



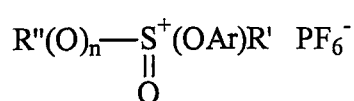
In the case of phenylacetylsulfonium salts, such as (5), ylide ($\text{R}_2\text{C}=\text{SR}_2$) formation proceeds by intramolecular H abstraction by the ketone from the γ carbon [72]. In both cases, monomer can apparently compete for protons with the highly basic ylide products. However, the lifetime of the protons is reduced in the presence of the basic ylides.

Sulfoxonium Salts

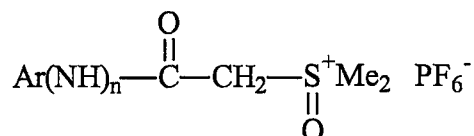
Aryloxysulfoxonium salts of general structure (7) are reported to be efficient photoinitiators for cationic polymerization with activities comparable with or greater

than diaryliodonium and triarylsulfonium salts [73]. They apparently undergo irreversible photolysis and acid generation.

Sulfoxonium salts of general structure (8) are also reported to be efficient photoinitiators for cationic polymerization [73]. With these photoinitiators, cationic polymerization is reported to cease following light exposure, as observed with phenylacetyl- and 4-hydroxyphenyl-sulfonium salts.



(7) $n = 0$ or 1

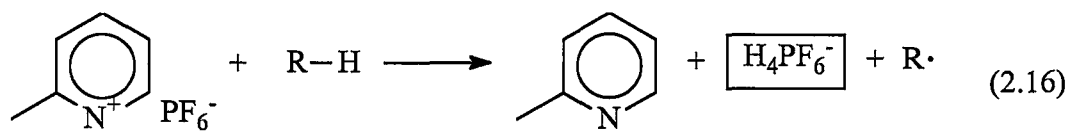
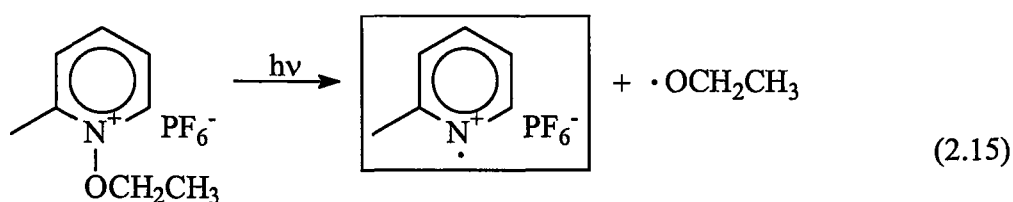


(8) $n = 0$ or 1

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 [9]. Quinolinium salts can also be prepared from the corresponding *N*-oxides [74]. In both cases, an anion exchange is not necessary since the triethyl oxonium salt is available with non-nucleophilic counter anions.

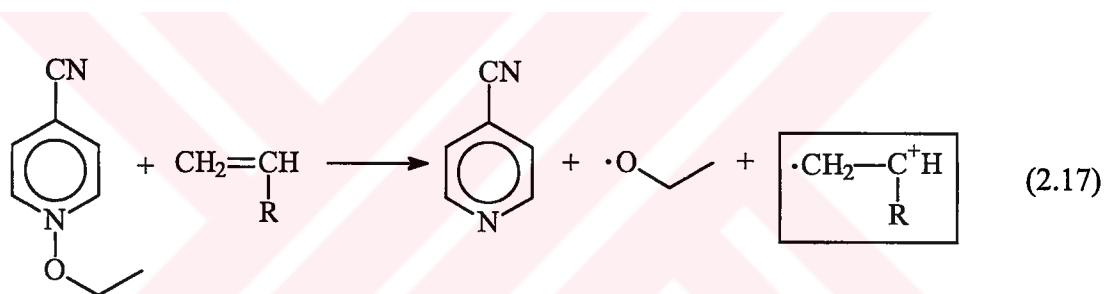
When absorbing UV light in the presence of a cationically polymerizable monomer, pyridinium type salts do readily initiate the polymerization [9,75]. The two initiation mechanisms described are depicted in (2.15) and (2.16) on the example of *N*-ethoxy-2-methylpyridinium hexafluorophosphate ($\text{EMP}^+\text{PF}_6^-$).



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

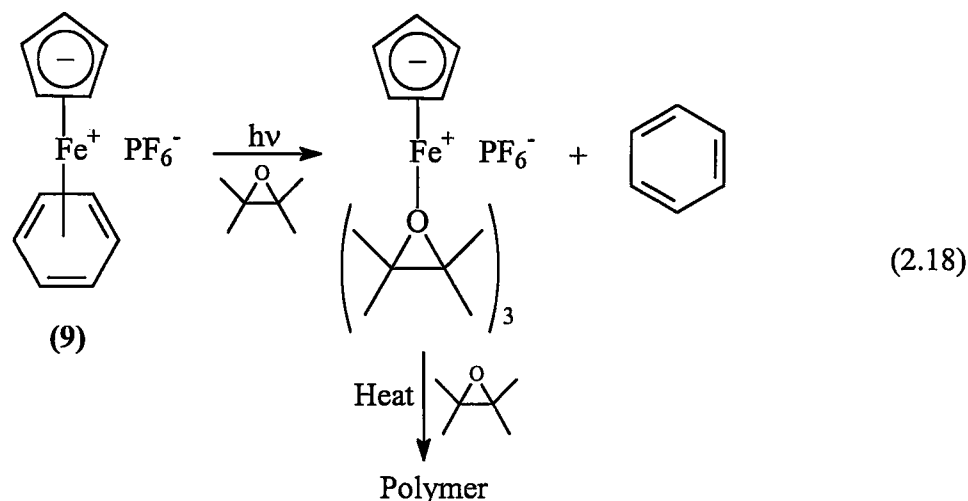
radicals cation with cyclohexene oxide and butylvinyl ether are $k = 10^6$ - 10^7 and $5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, respectively [75a]. In addition to the radical cation, Brønsted acid formed in the presence of hydrogen donors (monomer, solvent) may initiate the polymerization, as illustrated in (2.16).

In a recent paper, Zhu and Schnabel [76] have reported on the dark polymerization (carried out at room temperature) with some onium cations including EMP⁺, N-ethoxy-4-cyanopyridinium (EPP⁺) and N-ethoxyisoquinolinium (EIQ⁺) salts. While the first mentioned salt does not polymerize appropriate monomers in the dark, the latter two initiate the polymerization of isobutylvinylether and N-vinylcarbazol readily without any irradiation. On the contrary, in the case of cyclohexene oxide as a monomer no dark polymerization was observed for any of the three salts under investigation. The mechanism proposed for explaining the dark polymerization involves an electron transfer from monomer molecules to the onium salt. The monomer-based cation might initiate the polymerization.



b) Mixed Ligand Arene Cyclopentadienyl Metal Salts

A newer class of photoinitiators for cationic polymerization are mixed ligand arene cyclopentadienyl metal salts of complex metal halide anions [77], such as (η^6 -benzene)(η^5 -cyclopentadienyl)Fe^{II} hexafluorophosphate (**9**). A mechanism for photoinitiated polymerization of epoxides is provided in (2.18) [78].



The proposed photoinduced ligand exchange of the arene by three-epoxide group is based on earlier ligand exchange studies [79]. With bicyclic epoxides, such as cyclohexene oxide, polymerization is spontaneous under ambient conditions. However, moderate heating (50 to 150 °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 [57].

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 [80].

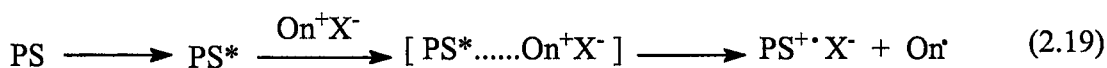
2.1.2.2 Indirect Acting Systems

Several systems were developed to extend the applicability of the onium salt photoinitiators towards longer wavelengths. In these cases additives are present which participate in the reaction sequence to yield reactive species capable of initiating the cationic polymerization.

a) Photosensitization (electron transfer) via Exciplex:

Many aromatic hydrocarbons such as anthracene, phenothiazine, 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. 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. 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. For this type cationic initiation, the following general scheme holds;



The excitation of the sensitizer is followed by the formation of a complex between excited sensitizer molecules and ground state onium salt. In this complex, one electron is transferred from the sensitizer to the onium salt giving rise to the generation of sensitizer radical cations. These can by themselves initiate the polymerization of appropriate polymers or, alternatively, interact with hydrogen containing constituents of the polymerization mixture (solvent, monomer) resulting in the release of Brønsted acid. In the case of alkoxy pyridinium salts, an additional mechanism has to be taken into account. Alkoxy radicals, which are generated by the decomposition of alkoxy pyridinium salts, react with sensitizer radical cations yielding initiating sulfur centered cations [19].

The sensitization of onium salts (Ar_3S^+ and Ar_2I^+) by anthracene has been investigated in detail in a number of papers [14,22,36]. 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 below on the example of diphenyliodonium salt.

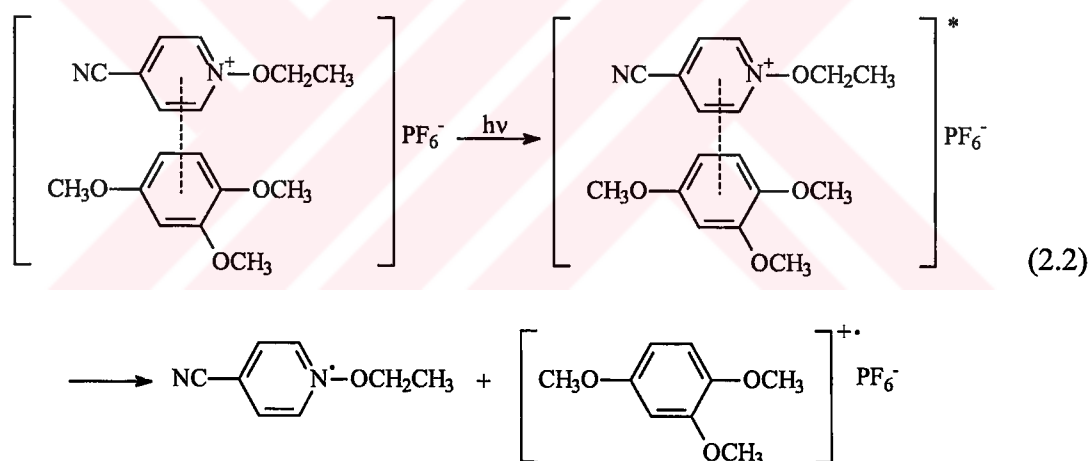
Notably, similar coupling reactions of radical cations with the radicals formed from the salts were also observed with alkoxy pyridinium salts.

The sensitization of thioxanthone follows only partly the general mechanism described for the exciplex formation [15]. To some extent, this sensitization is based upon the oxidation of photolytically formed radicals.

Recent studies show that metal complexes and dyes such as acridine, flavin exhibit appreciable sensitization activity in the photosensitized cationic polymerization [24,81].

b) Charge Transfer Complex:

Pyridinium salts are capable of forming charge transfer (CT) complexes with electron rich donors such as methyl- and methoxy- substituted benzene [23]. Notably, these complexes absorb at relatively high 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 following mechanism for the initiation of the cationic polymerization has been suggested [23].



Since the proton scavenger 2,6-di-*tert*-butylpyridine did not noticeably influence the polymerization, the initiation by Brønsted acid that could be formed after an interaction with hydrogen donor components can be excluded. Notably, the CT complexes described above 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.

c) Sensitization by Classical Energy Transfer:

This mechanism involves the electronic excitation of the sensitizer, a molecule possessing a suitable absorption spectrum, to its excited state. Energy may be transferred from the sensitizer (S*) to the onium salt (I) by either resonance excitation or exchange energy transfer. Depending upon the two components involved the energy transfer may proceed either in the excited singlet or in the triplet state.



In consequence of the transfer process, the sensitizer returns to its ground state and excited onium salt species (I*) are formed. The further reactions may also differ from those, taking place when the onium salt is excited by direct absorption of light. This conclusion has been drawn on the bases of product analyses [82,83,84]. An obvious explanation for this difference is the spin multiplicity. In contrast to this, through direct irradiation of the onium salt, electrons are excited primarily to the singlet state.

A sufficient energy transfer requires the excitation energy of the sensitizer $E^*(S)$ to be at least as large as the excitation energy of the photoinitiator $E^*(I)$.

$$E^*(S) \geq E^*(I) \quad (2.25)$$

The photopolymerization with most onium salts can be sensitized by commonly used photosensitizers, such as acetophenone or naphthalene. However, in many cases this reaction does not proceed via energy transfer, since most onium salts are capable of oxidizing these sensitizers in an exciplex formed between sensitizer and onium salt.

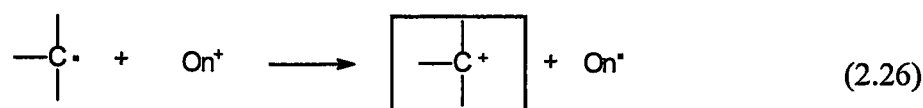
d) Free Radical Induced Cationic Polymerization:

Sensitization by free radical photoinitiators

Free radicals can also induce decomposition of onium salts. Two types of free radical induced initiation are currently available.

i) Radical Oxidation

Many photochemically formed radicals can be oxidized by onium salts according to the following reaction:



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 [20,85]. Free radicals may be produced by various modes: photochemically, thermally or by irradiating the system with high-energy rays.

The efficiency of onium salts as oxidizing agents is related to their electron affinity. The higher the oxidation power of the onium salt, the higher (more positive) is the reduction potential $E_{\text{red}}^{1/2}(\text{On}^+)$.

The efficiency of onium salts in this mode of polymerization rises in the order of trialkyl sulfonium salts < alkoxy pyridinium salts < diaryliodonium salts < aryldiazonium salts. Aryldiazonium salts are most suitable for the oxidation of radicals. However, their practical application is hampered by the lack of thermal stability. Diphenyliodonium salts have also a relatively high reduction potential. Being very suitable for the oxidation of free radicals, these salts have been most frequently used for the oxidation of photogenerated free radicals. On the other hand, triphenylsulphonium salts have only limited potential for radical induced cationic polymerizations due to their low reduction potential. However, some highly nucleophilic radicals could be oxidized with sulfonium salts.

Provided the oxidation and reduction potentials of the free radical and the onium ion, respectively, are known, it can be estimated on the bases of the Rehm-Weller equation whether a radical can be oxidized by a given onium salt or not.

$$\Delta G = F [E_{\text{ox}}^{1/2}(\text{R}\cdot) - E_{\text{red}}^{1/2}(\text{On}^+)] \quad (2.27)$$

F: Faraday constant

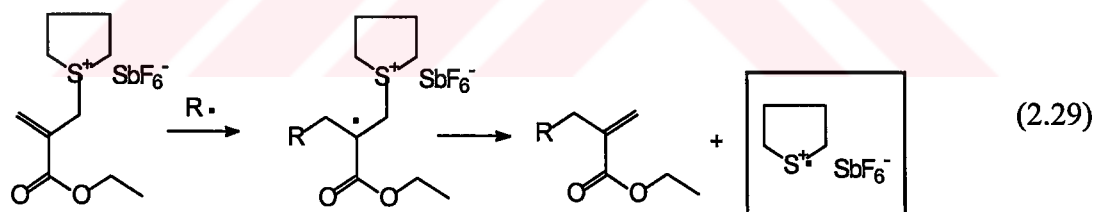
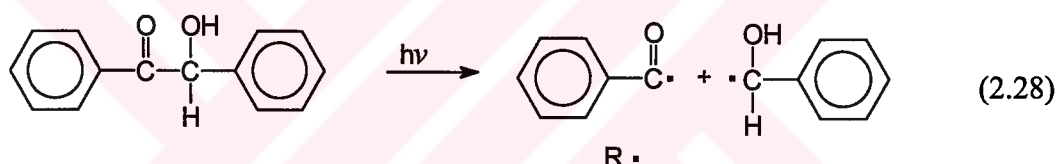
However, the calculation of ΔG is usually not feasible since the exact oxidation potentials $E_{\text{ox}}^{1/2}(\text{R}\cdot)$ of most radicals involved in radical promoted polymerizations are unknown.

ii) Addition – Fragmentation Reactions

The use of addition fragmentation reactions for photoinduced cationic polymerization has been subject of recent investigations [17,86-90]. 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 $\text{ETM}^+\text{SbF}_6^-$ and benzoin.



The first step consists in the photogeneration of free radicals. 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. 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.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Cyclohexene oxide (CHO) (Aldrich)

Cyclohexene oxide (CHO) was a product of Aldrich and washed with aqueous NaOH solution, dried over CaH₂ and distilled under reduced pressure.

***N*-Vinyl carbazol (NVC) (Fluka)**

N-Vinyl carbazol (NVC) was a product of Fluka and recrystallized from ethanol.

Butylvinyl ether (BVE) (Aldrich)

Butylvinyl ether (BVE) was a product of Aldrich and washed with aqueous NaOH solution, dried over CaH₂ and distilled under reduced pressure.

***p*-Methoxy styrol (*p*-MSt) (Aldrich)**

p-Methoxy styrol (*p*-MSt) used as monomer, was a product of Aldrich, purified by usual methods and distilled in reduced pressure (41-42 °C / 0.5 mm Hg) from calcium hydride.

3.1.2 Solvents

Dichloromethane (CH₂Cl₂) (Lab-scan)

Dichloromethane (CH₂Cl₂) was used as solvent in polymerization, dilution of polymer solutions and in UV measurements. It was first extracted with sulphuric acid, washed with water, then extracted with 5 % NaOH solution, and again washed with water. It was dried over calcium chloride and distilled by fractionation column.

Methanol (Technical)

Methanol (technical grade) was used in precipitation processes of polymers.

Chloroform (J.T. Baker.)

Chloroform was a product of J.T. Baker. It was shaken with several portions of conc. H_2SO_4 washed throughly with water and dried with CaCl_2 before filtering and distilling (61 °C / 760 mm Hg).

3.1.3 Initiators

Acylphosphine Oxides

2,4,6-Trimethylbenzoyldiphenylphosphine oxide (TMDPO), bis-(2,4,6-trimethyl benzoyl)-phenylphosphine oxide (BTBPO), bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide (BDTMPO) and bis-(2,4,6-trimethyl benzoyl)-2,4,4-trimethyl pentylphosphine oxide (BTTMPO) were products of Ciba, no further purification was applied.

3.1.4 Onium Salts

Diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) (Fluka)

Diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) was a product of Fluka and used directly.

***N*-ethoxy-2-methylpyridinium hexafluorophosphate ($\text{EMP}^+\text{PF}_6^-$)**

N-ethoxy-2-methylpyridinium hexafluorophosphate ($\text{EMP}^+\text{PF}_6^-$) was prepared as described previously [74].

Triphenylsulfonium hexafluoroarsenate ($\text{Ph}_3\text{S}^+\text{AsF}_6^-$) (Johnson Matthey Alfa)

Triphenylsulfonium hexafluoroarsenate ($\text{Ph}_3\text{S}^+\text{AsF}_6^-$) was a product of Johnson Matthey Alfa Products and used directly.

3.1.5 Other Chemicals

Tinuvin 292 (Ciba)

Tinuvin 292 used as radical scavenger was a product of Ciba and used as received.

Tinuvin 400 (Ciba)

Tinuvin 400 used as UV absorber was a product of Ciba. No further purification was applied.

2,6-ditertbutyl-4-methyl pyridine (DMP)

2,6-ditertbutyl-4-methyl pyridine used as proton scavenger was a product of Fluka and used as received.

2-picolin-N-oxide (Aldrich)

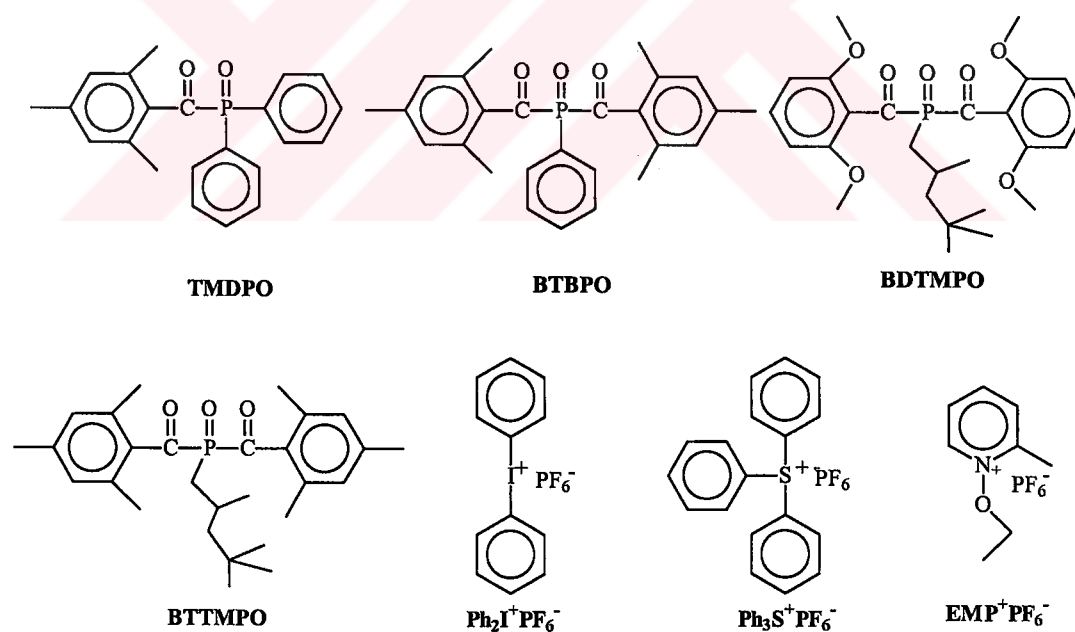
2-picolin-N-oxide was a product of Aldrich and used as received.

Ethyl iodide (C₂H₅I) (Aldrich)

Ethyl iodide (C₂H₅I) was a product of Aldrich and used directly.

Potassium hexafluorophosphate (KPF₆) (Aldrich)

Potassium hexafluorophosphate (KPF₆) was a product of Aldrich. No further purification was applied.



3.2 Equipment

3.2.1 Photoreactor

For photo irradiations at monochromatic wavelength, AMKO Ltd. photoreactor equipped with a HBO 100 W xenon lamp and monochromator.

3.2.2 UV Spectrophotometer

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

3.2.3 Nuclear Magnetic Resonance Spectrospin (NMR)

H-NMR analysis were recorded on a Bruker 250 MHz NMR Spectrospin.

3.2.4 Gel Permeation Chromatography (GPC)

GPC analyses were performed with a setup consisting of a Waters pump and 3 Waters styragel HR3, HR4, and HR4E columns with THF at a flow rate of 1mL/min, and the detection was carried out with a differential refractometer. Molecular weights were calculated with the aid of polystyrene standards.

3.3 Preparation of *N*-ethoxy-2-methylpyridinium hexafluorophosphate, (EMP⁺PF₆⁻)

The mixture of 3.87 mL (48 mmol) of ethyl iodide (C₂H₅I) and 2.1826 g (20 mmol) 2-picolin-N-oxide was mixed in an erlenmeyer flask and waited for 24 hours at room temperature. After 24 hours, hexane was added to the mixture to crystallize. Some white precipitation occurred. Precipitated material was filtered and dried. Saturated solution of potassium hexafluorophosphate (KPF₆) was prepared by using 4.5 g of KPF₆, and it was added to previous dry precipitate. This mixture was stirred for one hour, and then the newly formed precipitation was filtered and dried. Dry precipitate was washed with chloroform, recrystallized in methanol and dried at vacuum.

3.4 Photopolymerization

Photopolymerizations were carried out under nitrogen atmosphere. Prior to irradiation, the appropriate solutions of monomers containing given amounts of acylphosphine oxides, onium salts, and dichloromethane (solvent) were placed in pyrex tubes previously heated with a heat gun and flushed with dry nitrogen and irradiated at $\lambda=380$ nm in an AMKO Ltd. photoreactor equipped with a HBO 100 W xenon lamp and a monochromator. The viscous polymer solutions formed during the irradiation were poured into methanol. The precipitated polymers were then filtered off and dried in vacuo.

Photopolymerizations with additives were also done as same as previous procedure. The appropriate amounts of additives were added to the mixture.

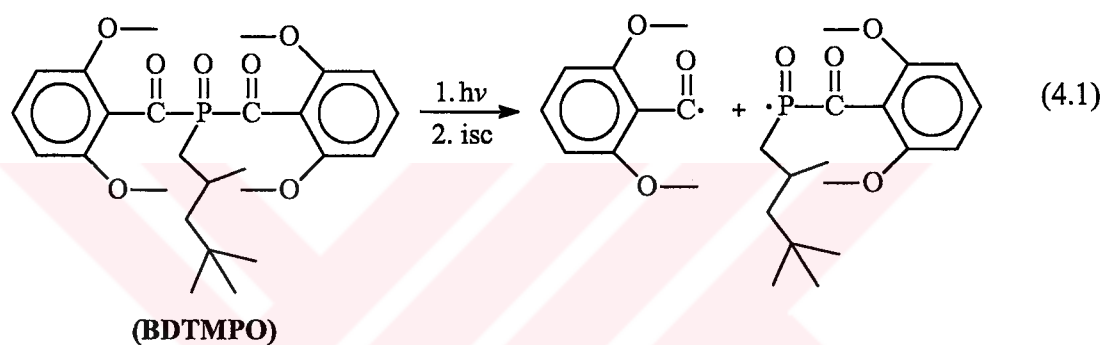
3.5. Analysis

Number average molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters instrument equipped with R410 differential refractometer and 600E pump using monodisperse polystyrene standards. THF was used as the eluent at a flow rate of 1.0-mL/min. $^1\text{H-NMR}$ measurements were performed in CDCl_3 solution using a Bruker 250 MHz instrument. UV spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer.

4. RESULTS and DISCUSSION

4.1 Synthesis

Bisacylphosphine oxides, a related class of initiators, undergo initial α -cleavage from the triplet-excited state to afford radicals [91] as shown in reaction (4.1) for the example of bis(2, 6-dimethoxy)-2,4,4-trimethylpentylphosphine oxide (BDTMPO).



Cyclohexene oxide (CHO) was polymerized with combination of acylphosphine oxides and an onium salts. Polymerizations were performed at $\lambda=380$ nm where all onium salts are transparent and all the light emitted is absorbed by the acylphosphine oxide photoinitiators (Figure 4.1).

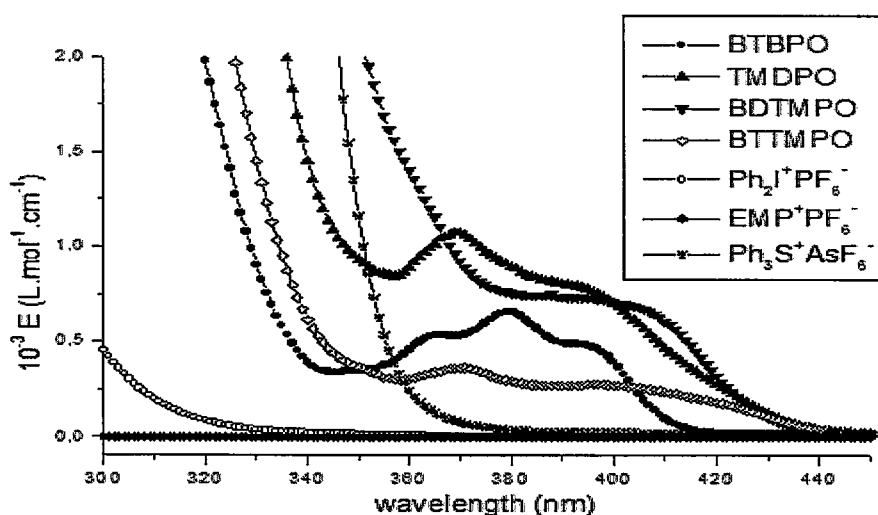


Figure 4.1. Molar absorbance of acylphosphine oxides and onium salts.

4.2 Photopolymerization

CHO was deliberately chosen as cationically polymerizable model monomer since it is not prone to undergo hydrogen abstraction nor can be polymerized by a radical mechanism. As shown in Table 4.1, CHO was polymerized quite effectively with all the acylphosphine oxide photoinitiators as promoters in the presence of diphenyl iodonium salt. In the case of pyridinium salt, however, only bisacylphosphine oxides are effective in inducing cationic polymerization with a lower rate. The structure of polymer was confirmed by ¹H-NMR spectrum (Figure 4.2). The weak bands at 6.5-7.05 ppm corresponding to aromatic protons confirm the attachment of phosphonyl groups to polymer chains. However, it is not easy to evaluate the extend of functionalization consequently number of initiating species.

Table 4.1. Free radical promoted cationic polymerization of CHO by using acylphosphine oxides^a in the presence of onium salts^b in CH₂Cl₂ at λ=380 nm for 100 min.

Acylphosphine Oxide	Onium salt	Conversion (%)	M_n^c (g.mol ⁻¹)
TMDPO	Ph ₂ I ⁺	5.58	3400
	EMP ⁺	-	-
	Ph ₃ S ⁺	-	-
BDTMPO	Ph ₂ I ⁺	8.82	3000
	EMP ⁺	1.87	2800
	Ph ₃ S ⁺	-	-
BTTMPO	Ph ₂ I ⁺	30.92	4500
	EMP ⁺	9.58	4300
	Ph ₃ S ⁺	-	-
BTBPO	Ph ₂ I ⁺	34.87	3500
	EMP ⁺	13.72	3400
	Ph ₃ S ⁺	-	-

^a [Acylphosphine Oxide] = 5x10⁻³ M

^b [Onium Salt] = 5x10⁻³ M

^c Determined by GPC

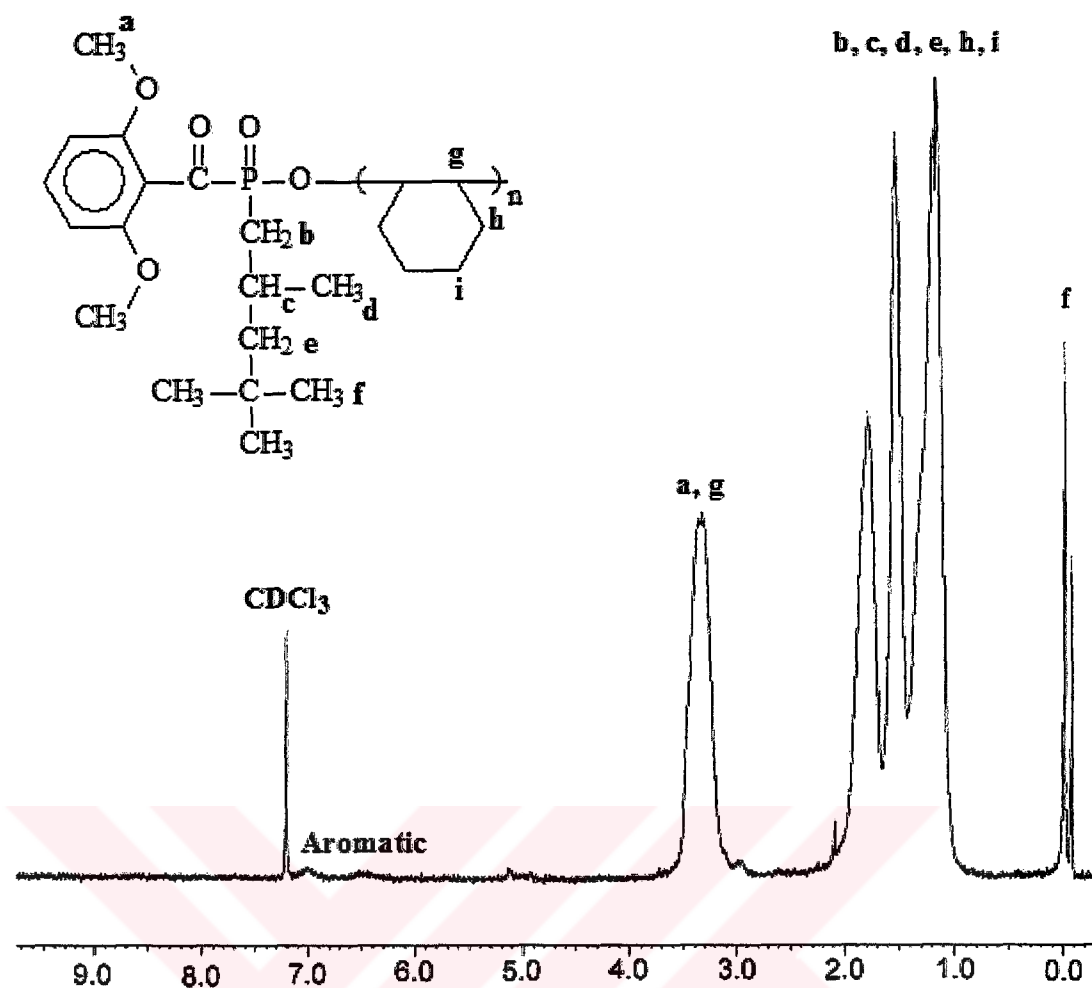


Figure 4.2. $^1\text{H-NMR}$ spectrum of resulting polymer in CDCl_3 .

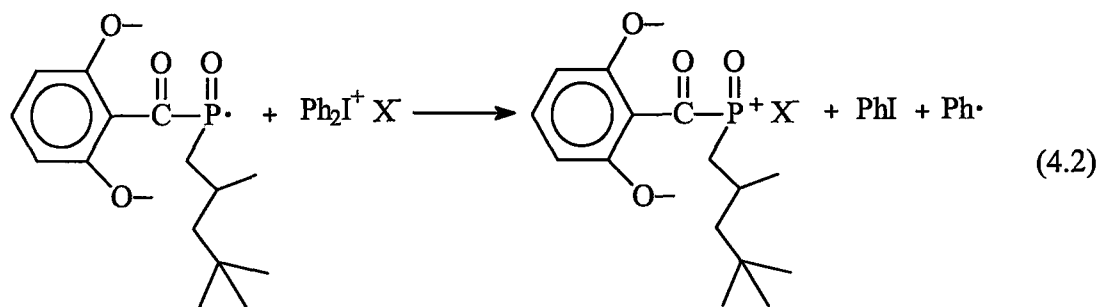
Notably, triphenyl sulfonium salt is not capable of initiating free radical promoted cationic polymerization. The difference in the reactivity of the salts is related to their redox potentials (Table 4.2).

Table 4.2. Redox potentials of the cationic salts.

Cationic salt	$E_{\text{red}}^{1/2}$ V(SCE)	Reference
Ph_2I^+	-0.2	92
MV^{2+}	-0.46	93
EMP^+	-0.7	14
Ph_3S^+	-1.2	94

Since benzoyl radicals, produced from all the acylphosphine oxides, do not undergo redox reactions with even strong oxidants such as iodonium salts, phosphoryl radicals formed concomitantly must be responsible for the formation of reactive cationic species. This process involves a redox reaction in which the onium salt is

reduced while phosphonyl radical is oxidized as shown in reaction for the BDTMPO and iodonium salt couple.



It can also be seen from Table 4.1 that bisacylphosphine oxides are more reactive than the monoacylphosphine oxide, TMDPO. The only difference in both cases is the structure of the phosphonyl radicals formed upon photolysis. Phosphonyl radicals formed from TMDPO possess two phenyl groups while those from bisacylphosphine oxide are attached to benzoyl and long alkyl chain or phenyl group. Provided the oxidation and reduction potentials of the free radical and the onium salt, respectively are known, it can be estimated on the basis of the Rehm-Weller equation [95] whether a radical can be oxidized by a given salt or not

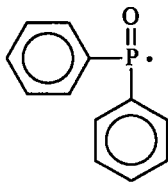
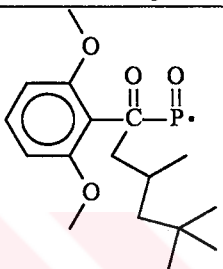
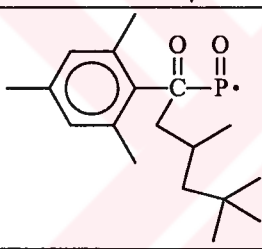
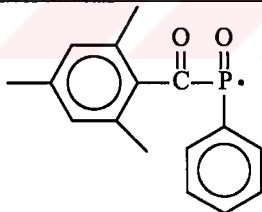
$$\Delta G = F [E_{1/2}^{\text{ox}}(\text{R}\cdot) - E_{1/2}^{\text{red}}(\text{On}^+)]$$
(4.3)

where F = Faraday constant

However, the calculation of ΔG is usually not feasible since the exact oxidation potentials of the phosphonyl radicals are not known. It is expected that electron donating/withdrawing effect of the substituents plays an important role in the reactivity of the radicals in the oxidation process. Radicals with electron donating groups undergo oxidation more favorably. It should be pointed out that phosphonyl radicals formed from bisacylphosphine oxides possess electron withdrawing benzoyl substituents and their reactivity should be lower than those formed from TMDPO. Contradictorily, the bisacylphosphine oxides perform significantly better than with monoacylphosphine oxide. This better performance could be caused by the other possible factors. Radical reactivity towards olefins is often correlated [96,97] with radical stability, which is related to localization of the radical or s-character of a localized orbital. On the other hand, electron delocalization and enhanced p-character should improve reactivity of the radicals in the oxidation process. ^{31}P hyperfine

coupling, an experimental parameter for the s-character of in localized orbitals, is tabulated in Table 4.3 together with the relative efficiencies in promoted cationic polymerization and the rate constants for electron transfer reactions.

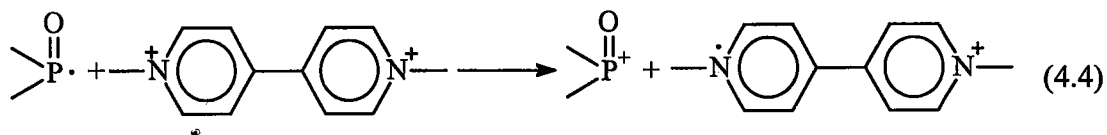
Table 4.3. ^{31}P Hyperfine coupling and rate constants for oxidation of phosphonyl radicals and relative initiation efficiencies of the precursor acylphosphine oxides.

Radical	Onium salt	Relative efficiency ^a	$k_{\text{R}\cdot \rightarrow \text{R}^+}$ ($\text{M}^{-1}\cdot\text{s}^{-1}$)	^{31}P hyperfine coupling ^b
	Ph_2I^+ EMP^+	1 0	$<10^6$	369G
	Ph_2I^+ EMP^+	1,58 0,34	1.5×10^9	286G
	Ph_2I^+ EMP^+	5,54 1,72	2.6×10^9	255G
	Ph_2I^+ EMP^+	6,25 2,46	2.8×10^9	270G

^aEstimated on the basis of conversion for $\text{TMDPO}/\text{Ph}_2\text{I}^+\text{PF}_6^-$ initiating system under the same experimental conditions.

^bData taken from Ref. 97

For the latter we have deliberately selected methyl viologen as a standard electron acceptor since it is expected to exhibit intermediate behaviour on the basis of its reduction potential (see Table 4.2). Moreover, the reduced form of methyl viologen, the paraquat radical cation possesses a strong optical absorption with a maximum at 608 nm for an accurate determination of the rate constants.



As can be seen from Figure 4.3, the relative efficiencies correlate well with the rate constants of the oxidation reactions of the phosphonyl radicals.

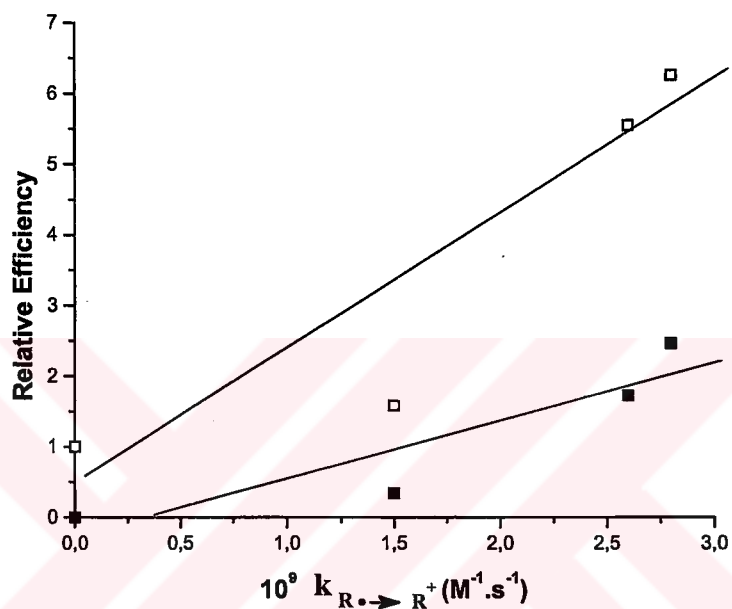


Figure 4.3. Relative efficiency of onium salts in the polymerization of CHO to bimolecular rate constants for quenching of phosphonyl radicals by methyl viologen (Ph_2I^+ , ; EMP^+ ,).

Interestingly, relative efficiencies of acylphosphine oxides in promoted cationic polymerization correlates inversely with the ^{31}P hyperfine coupling (see Table 4.3 and Figure 4.4).

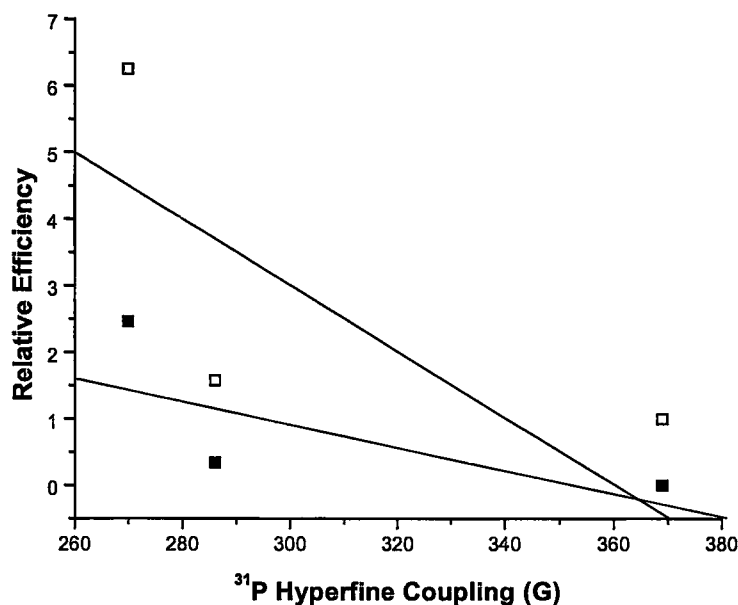
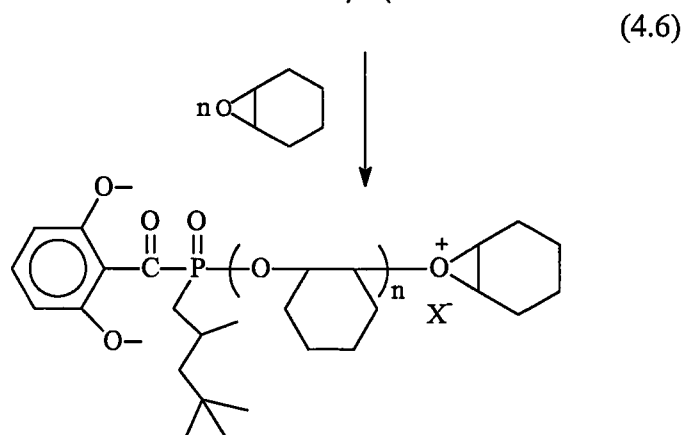
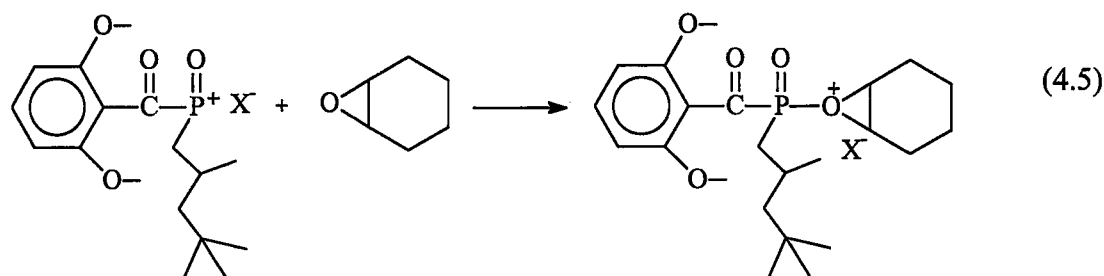


Figure 4.4. Relative efficiency of onium salts in the polymerization of CHO to ^{31}P hyperfine coupling (Ph_2I^+ , ; EMP^+ ,).

High efficiencies were observed for acylphosphine oxides yielding radicals with low ^{31}P hyperfine coupling (higher degree of spin delocalization, more p-character). Under our experimental conditions, no polymerization with TMDPO/ EMP^+ system was observed, suggesting that the carbonyl α to the phosphorous in radicals produced from BAPO, BDTMPO and BTTMPO, essential for the successful polymerization. Phosphonyl radicals, which do not possess carbonyl groups, promote the polymerization only with strong oxidants such as diphenyl iodonium salt at a lower rate. It is notable that neither diphenyl iodonium nor pyridinium salts initiates the polymerization in the absence of bisacylphosphine oxides upon irradiation at this wavelength. It follows that posphonium ions are formed according to the reaction (4.2) must be capable of initiating the cationic polymerization of CHO as described in the reactions (4.5) and (4.6):



Poly(cyclohexene oxide) chains with attached benzoylphosphonyl groups should be formed. Indeed, $^1\text{H-NMR}$ measurements revealed, apart from aliphatic protons also existence of aromatic protons in the polymer.

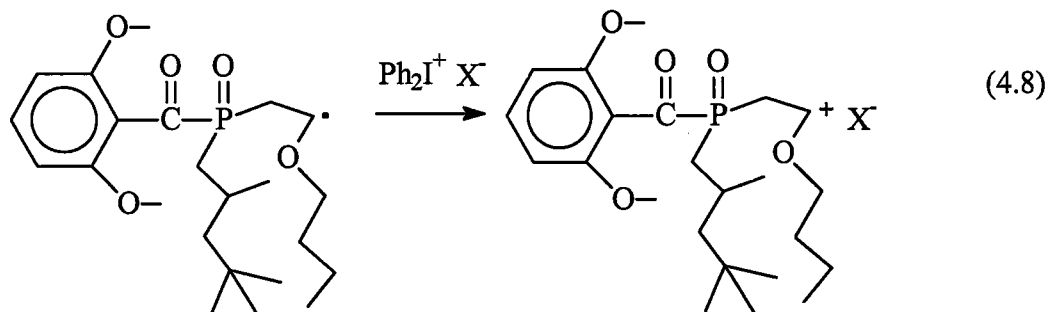
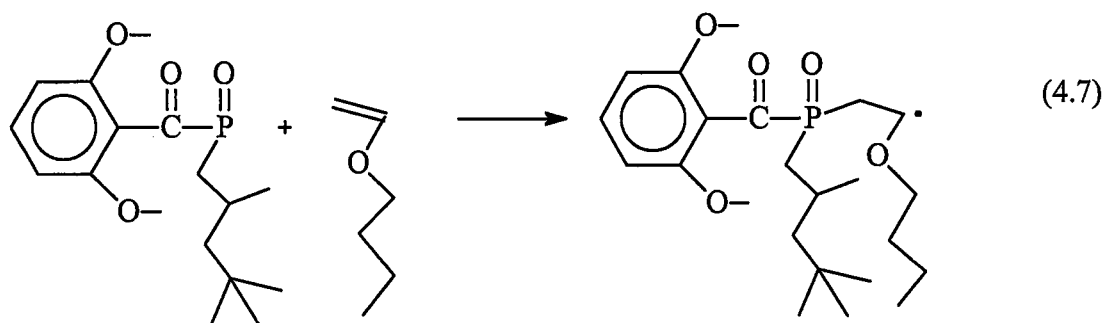
In addition to CHO, butyl vinyl ether (BVE), N-vinyl carbazol and *p*-methoxy styrol were also examined (Table 4.4). These monomers also polymerized readily in methylene chloride solutions containing BAPO and diphenyl iodonium salt.

Table 4.4. Polymerization of some monomers in the presence of BAPO, $\text{Ph}_2\text{I}^+\text{PF}_6^-$ and CH_2Cl_2 at 380-nm for 60 min.

Run	Monomer	Conversion (%)	Mn ($\text{g}\cdot\text{mol}^{-1}$)
1	CHO	34,87	3500
2	BVE	78,20	8500
3	NVC	86,50	10750
4*	NVC	20,90	16600
5	<i>p</i> -MSt	55,76	51000

* $\text{Ph}_2\text{I}^+\text{PF}_6^-$ was not added to the polymerization mixture.

In the case of the BVE monomer, in addition to direct oxidation phosphonyl radicals react with the monomer molecules producing electron donor radicals. Thus formed, these radicals can easily be oxidized by onium salt to the corresponding initiating species.



In the case of NCV, a more powerful monomer, very efficient polymerization occurred. It should be pointed out that NVC is also polymerizable via a free radical mechanism. For comparison, free radical polymerization of NVC with BAPO, in the absence of diphenyl iodonium salt, was also included. The initiation efficiency of the cationic system under the same absorptivity and experimental conditions was much higher.

4.3 Effects of Additives

We have also studied the effect of radical scavenger and UV absorber in order to see whether formulations, containing such additives, can also be polymerized. As can be seen from Table 4.5, the polymerization was completely inhibited when the radical scavenger (Tinuvin 292) was added indicating radicalic nature of the polymerization mechanism. In the presence of Tinuvin 400, UV absorber, polymerization rate was reduced. This behaviour may be due to the some screening effect of the additive at the irradiation wavelength.

Table 4.5. The effect of UV absorber (Tinuvin 400) and radical scavenger (Tinuvin 292) in the polymerization of CHO in the presence of BAPO, $\text{Ph}_2\text{I}^+\text{PF}_6^-$ and CH_2Cl_2 at 380-nm for 60 min.

<i>Run</i>	Additive	Conversion (%)	Mn ($\text{g}\cdot\text{mol}^{-1}$)
1	-	34,87	3500
2	Tinuvin 400	12,73	2700
3	Tinuvin 292	0	-

We have also investigated the effect of proton scavenger in order to elucidate the nature of initiating species. As seen from Table 4.6, the conversion is reduced in the presence of 2,6-ditertbutyl-4-methyl pyridine. These results indicate that not only the phosphonium cations formed from the oxidation of phosphonyl radicals, as may confirmed by $^1\text{H-NMR}$ spectrum (see Figure 4.2), but also protons are responsible for the initiation. However, it is not known that how these protons can form.

Table 4.6. The effect of Proton Scavenger (2,6-ditertbutyl-4-methyl pyridine, DMP, (1×10^{-2} M) in the polymerization of CHO (0,5-mL) in the presence of BAPO (5×10^{-3} M), $\text{Ph}_2\text{I}^+\text{PF}_6^-$ (5×10^{-3} M) in CH_2Cl_2 at 380-nm for 60 min.

<i>Run</i>	Additive	Conversion (%)	Mn ($\text{g}\cdot\text{mol}^{-1}$)
1	-	34,87	3500
2	DMP	12,69	2800

4.4 Effects of Various Parameters

From Figures 4.5 and 4.6, it is seen that the rate of polymerization of CHO increases and approaches a limiting value upon increasing the time or the iodonium salt concentration. This behaviour may be attributed to the formation of iodobenzene, which is produced during the oxidation of phosphonyl radicals (4.9).

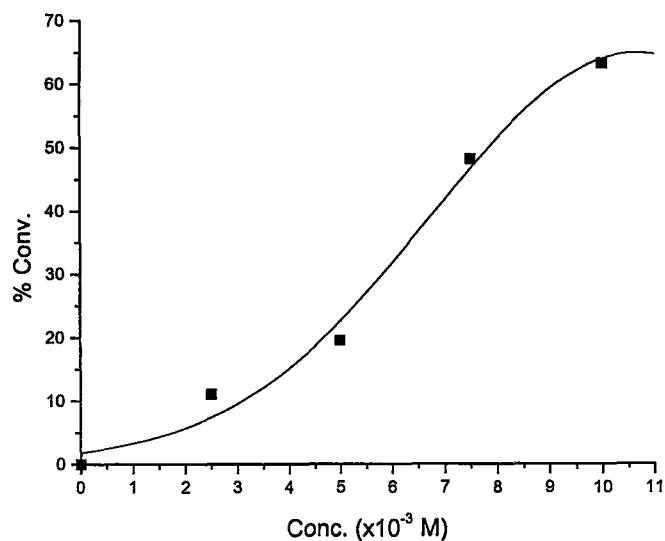


Figure 4.5. Dependence of rate of polymerization of CHO on the iodonium salt concentration at $\lambda=380$ nm.

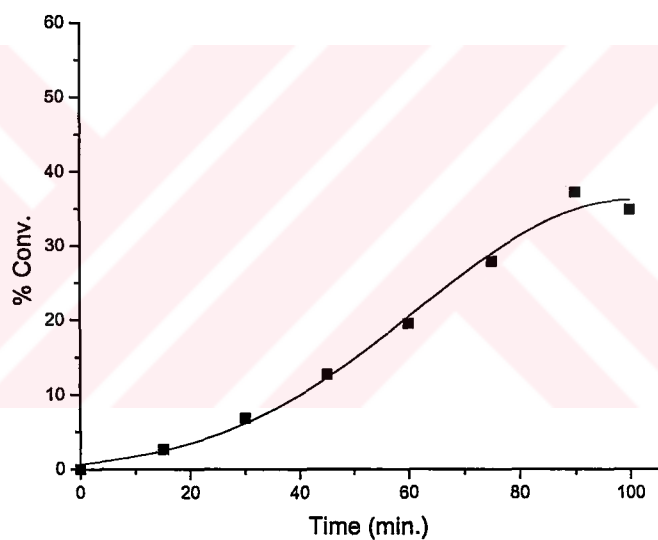


Figure 4.6. Dependence of rate of polymerization of CHO on time at $\lambda=380$ nm.

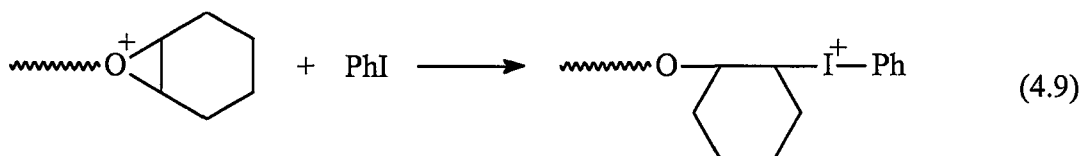


Figure 4.7 represents the influence of the radical source on the polymerization. The unsteady behaviour is probably due to the primary coupling reactions of non-oxidizable benzoyl radicals with the cation generating phosphonyl radicals.

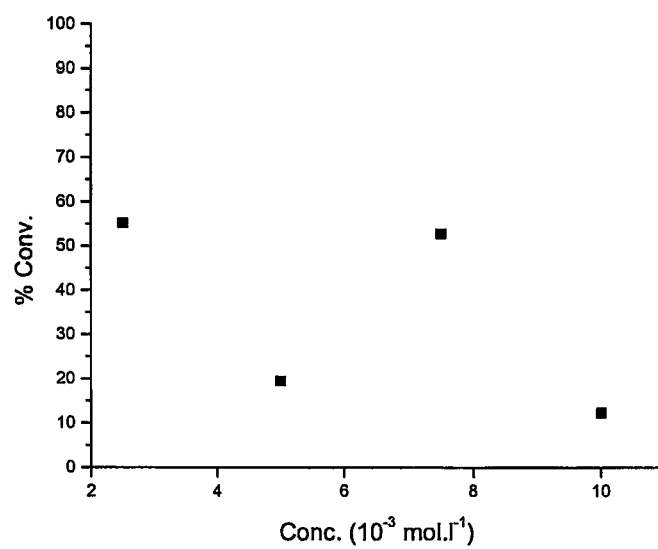


Figure 4.7. Dependence of rate of polymerization of CHO on the BTBPO concentration at $\lambda=380 \text{ nm}$.

5. CONCLUSIONS

In conclusion, substituent effect on the reactivity of phosphonyl radicals have been demonstrated.

Mono- and bis-acylphosphine oxides are recently developed radical photoinitiators and find application in UV curing of formulation containing pigments as they absorb the light at relatively long wavelenghts. They are efficient co-initiators for long UV range cationic polymerization when used in conjunction with suitable onium salts such as iodonium and pyridinium salts. The mechanism follows free radical generation by photolysis and subsequent oxidation of phosphonyl radicals to yield reactive cations. The efficiency of the latter step is controlled by the redox potential of the onium salt and electron delocalization, and p-character of the phosphonyl radical.

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Canan Dursun, Mustafa Degirmenci, Yusuf Yagci, Sateffen Jockusch, Nicolas J. Turro.

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Scientific Activities

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