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**KATYONİK BAŞLATICI OLARAK KULLANILAN
YENİ KATILMA BÖLÜŞME REAKTİFLERİ**

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January 1999

Levent Atmaca

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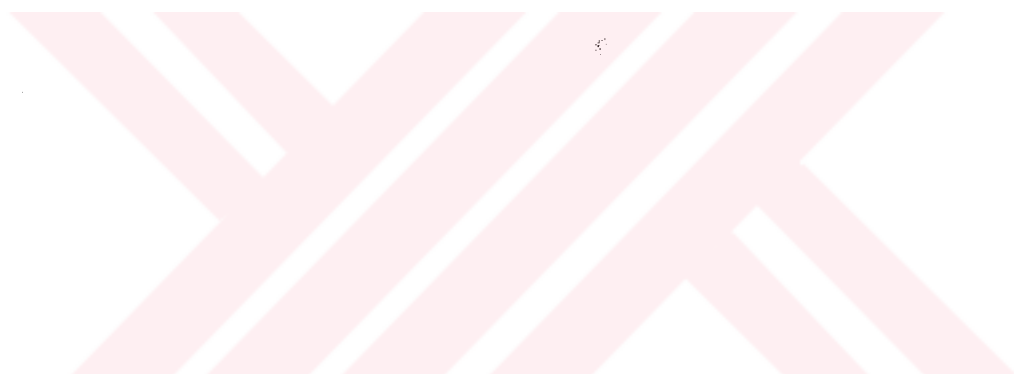
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LIST OF ABBREVIATIONS

AI	: Allyl Isoquinolinium N-Oxide Hexafluoroantimonate
MAI	: Methylallyl Isoquinolinium N-Oxide Hexafluoroantimonate
I	: Initiator
M	: Monomer
R.	: Radical
C ⁺	: Cation
C ^{•+}	: Radical Cation
H-NMR	: Proton Nuclear Magnetic Resonance
EMP	: Etoxy-2-methylpyridinium Salt
CT	: Charge-transfer
AFA	: Addition Fragmentation Agent
S [*]	: Sensitizer
E [*] (S)	: Energy of the Sensitizer
E [*] (I)	: Energy of the Initiator
On ⁺	: Onium Salt
ISC	: Intersystem Crossing
AIBN	: 2,2'-Azobisisobutyronitrile
BPO	: Benzoyl Peroxide
PAT	: Phenyltriphenylazo-methane
CHO	: Cyclohexeneoxide
O.D.	: Optical Density

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NOVEL ADDITION FRAGMENTATION AGENTS AS CATIONIC INITIATORS

SUMMARY

Allyloxy isoquinolinium salts which are allyl isoquinolinium N-oxide hexafluoroantimonate and methyl allyl isoquinolinium N-oxide hexafluoroantimonate were used with radical initiator 2,2'-azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), phenylazotriphenylmethane (PAT) in thermal cationic polymerization and also with photoinitiator benzoin in photo polymerization of cyclohexeneoxide (CHO) and resulted as effective cationic initiators. CHO was chosen as a model monomer since CHO is not polymerizable by a radical mechanism and does not form oxidizable radicals in the course of polymerization. Radicals produced from radical initiators by heating at 70°C add to the double bond of the allyl groups of the salts resulting fragmentation finally produces isoquinolinium radical cation which has an ability to initiate cationic polymerization. The polymerization rates differ as $PAT > BPO > AIBN$ according to the different radical forming capability.

In photopolymerization with allyloxy salts, all photoirradiations was made in the range of 300–400 nm. Additional radical initiators may not only serve in improving the time conversion behavior, but also enable to use light of higher wavelengths for initiating the polymerization.

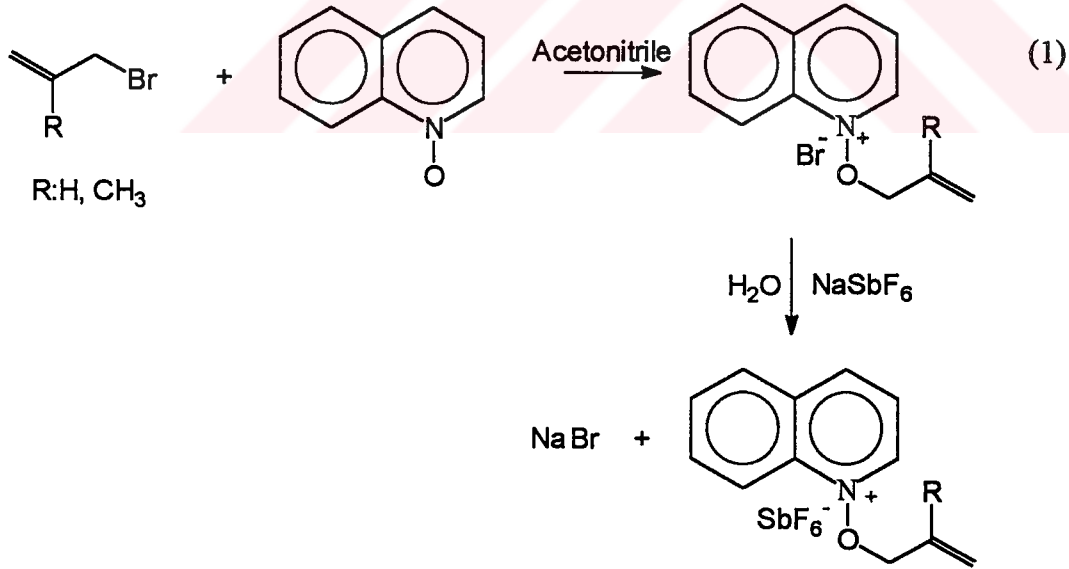
KATYONİK BAŞLATICI OLARAK KULLANILAN YENİ KATILMA BÖLÜŞME REAKTİFLERİ

ÖZET

Bu çalışmada radikalik başlama mekanizması üzerinden gerçekleşen katılma bölüşme tipi katyonik başlatıcı olan alliloksi isokinolinyum tuzları sentezlenmiştir. Bu çalışmada sentezlenen ve katyonik başlatıcı olarak kullanılan allil isokinolinyum N-oksit hekzafloroantimonat (Al^+) ve metilallil isokinolinyum N-oksit hekzafloroantimonat (MAI^+) içerdikleri N-O bağının zayıf olması nedeniyle kolaylıkla homolitik parçalanmaya uğrayarak isokinolinyum radikal katyonlarını verir ki bu da katılma bölüşme reaksiyonları için çok uygun başlatıcılardır. Bu çalışmada bu tuzların termal ve fotokimyasal polimerizasyondaki etkinlikleri incelenmiş ve allilik grup üzerindeki farklı sübstitüentlerin polimerizasyon dönüşümlerindeki etkileri kıyaslanmıştır.

Alliloksi İsookinolinyum Tuzlarının Sentezi

Alliloksi isokinolinyum tuzları oda sıcaklığında aşağıdaki mekanizmaya göre sentezlenmiştir.(1)

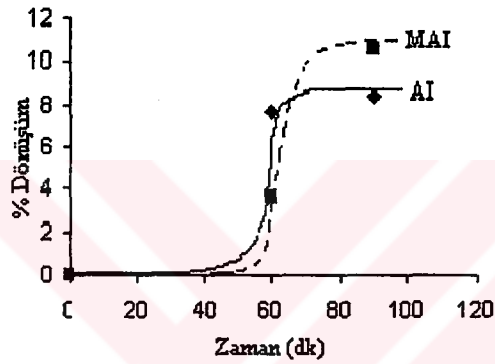


Siklohekzenoksitin Termal Polimerizasyonu

Radikal kaynağı kullanılmadan 70°C'de AI ve MAI kullanılarak yapılan siklohekzenoksitin termal polimerleşmesinde elde edilen verilerden MAI'nın AI'ya kıyasla polimerizasyonu daha hızlandırdığı gözlenmiştir, (Tablo 1, Şekil 1)

Tablo 1 : Radikal kaynağı kullanmadan AI ve MAI varlığında gerçekleşen siklohekzenoksitin termal polimerizasyonu

Tuz türü	Zaman (dk)	% Dönüşüm
AI	90	8.4
MAI	90	10.57



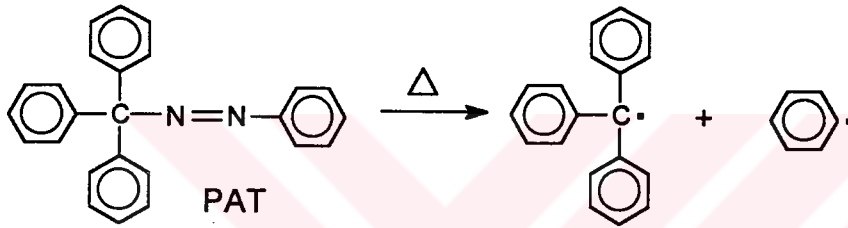
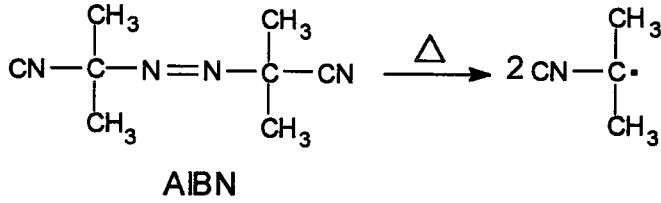
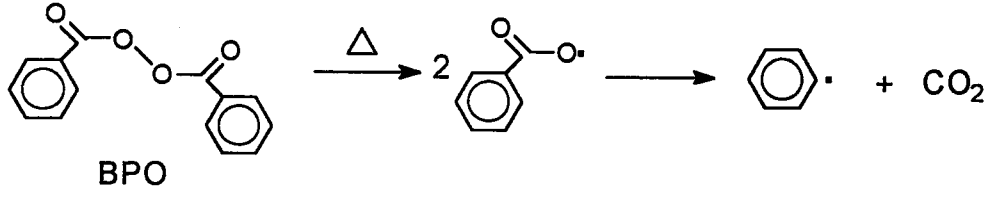
Şekil 1: Radikal kaynağı kullanmadan AI ve MAI varlığında gerçekleşen siklohekzenoksitin termal polimerizasyonu

Eklenen Radikal Başlatıcısının Etkisi

Zaman dönüşüm eğilerinden görüldüğü gibi her iki allilioksi isokinolinyum tuzu radikal kaynağı varlığında 70°C'de gerçekleştirilen siklohekzenoksitin katyonik polimerizasyonunu etkin bir şekilde başlatır.((2),(3))

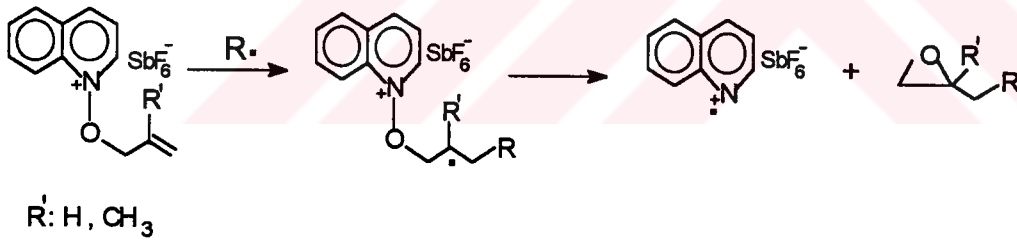
Radikal Üretimi:

(2)

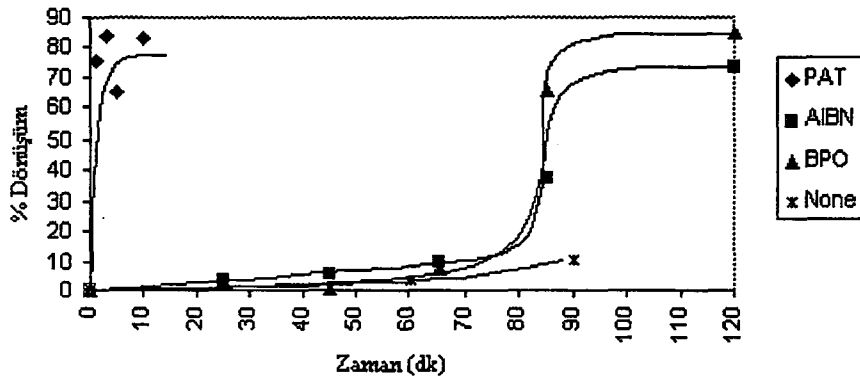


Radikal katılma bölüşme R' = AIBN, BPO, PAT'den üretilen radikaller

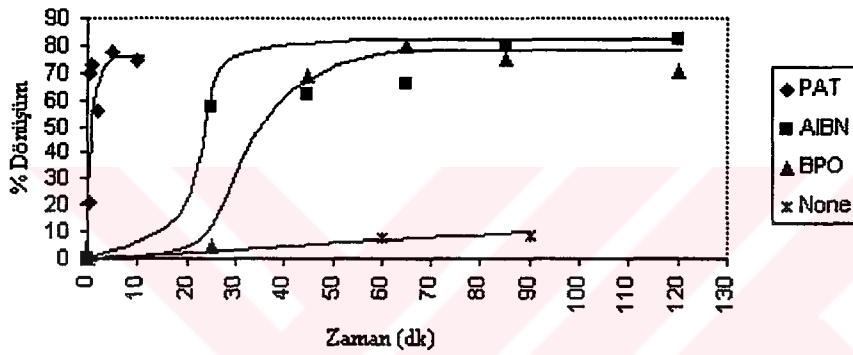
(3)



Seçilen üç farklı radikal başlatıcının, azobisisibutironitril (AIBN), benzoil peroksit (BPO) ve fenilazotriphenilmethan'ın farklı özellikler gösterdiği görülmüştür. Bu radikal başlatıcılarının termal polimerizasyon hızına etkileri $PAT > AIBN \approx BPO$, şeklinde sıralanır. (Şekil 2)

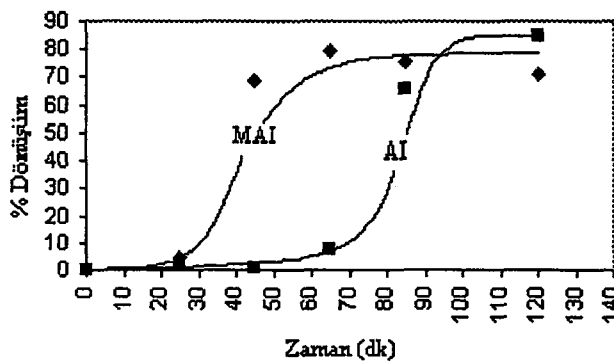


Şekil 2 :AI kullanılarak değişik radikal kaynakları ile sikloheksenoksitin polimerizasyonu



Şekil 3: MAI kullanılarak değişik radikal kaynakları ile sikloheksenoksitin polimerizasyonu

Allilik grup üzerindeki substitüent polimerleşme dönüşümünü etkiler. Bu etki, çift bağ üzerinde elektron verici grupların bulunması halinde N-O bağının kopmasını zorlaştırırken, elektron çekici grupların bulunması halinde bağı zayıf kılarak koparabilmesi şeklinde açıklanır.

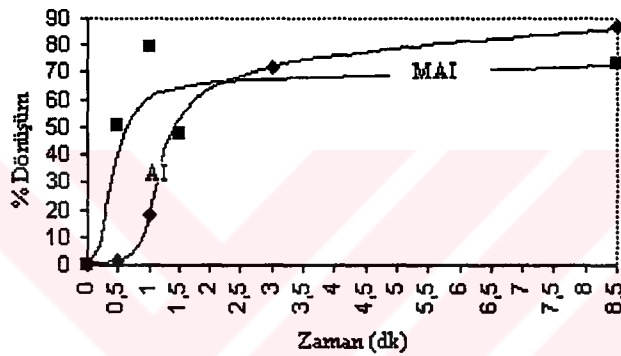


Şekil 4 : Allilik grup üzerindeki substitüentin sikloheksenoksitin PAT varlığında her iki tuz kullanılarak yapılan polimerizasyonundaki etkisi

Fotopolimerizasyon

Radikal Başlatıcı Kullanılmadan Gerçekleştirilen Polimerizasyon

İsokinolinyum N-oksit türevlerinin karakteristik absorpsiyon bandı 337 nm’de gözükmetedir. AI ve MAI’nın UV spektrumları alınmış ve karakteristik olan bu band gözlenmiştir. Bu nedenle bu çalışmada isokinolinyum tuzları 300-400 nm arasında ışık yayan lambalar kullanılarak Merry-Go-Round tipi fotoreaktörde gerçekleştirilmiştir. Tüm deneylerde kullanılan isokinolinyum tuzlarının konsantrasyonları optik yoğunlukları eş olacak şekilde ayarlanmıştır. Şekil 5’de görüldüğü üzere alliloksi isokinolinyum tuzları ile yapılan sikloheksenoksit polimerleşmesinde polimerizasyon hızının oldukça fazla olduğu görülmektedir.

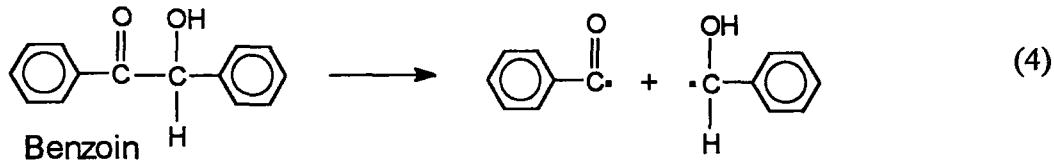


Şekil 5 : Sikloheksenoksit'in Alliloksi İsokinolinyum Tuzları kullanılarak Gerçekleştirilen Fotopolimerizasyonu

Radikal Başlatıcı Kullanılarak Gerçekleştirilen Fotopolimerizasyon

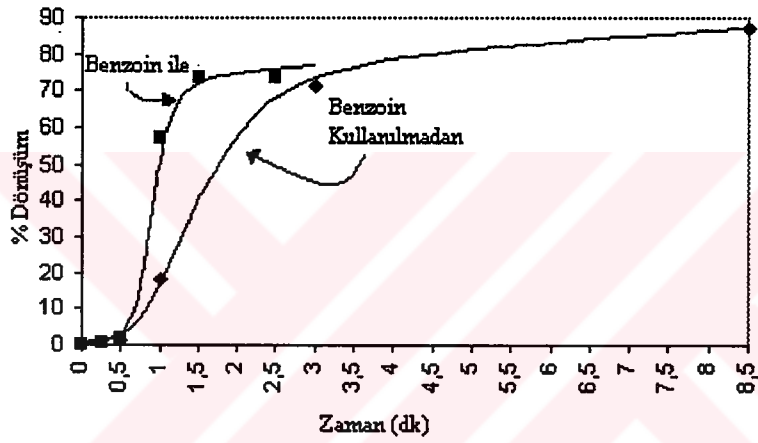
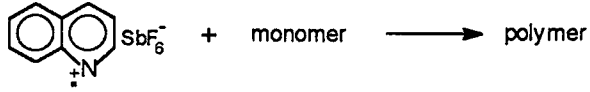
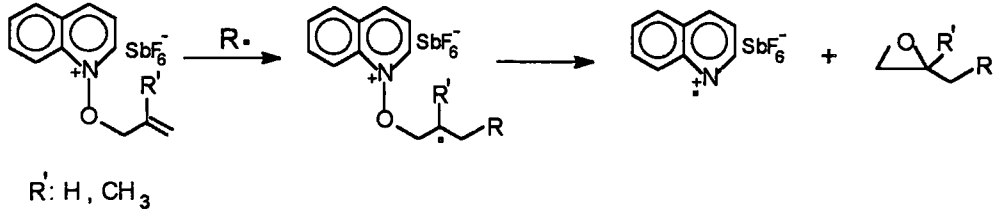
Alliloksi isokinolinyum tuzları kullanılarak radikal kaynağı varlığında gerçekleştirilen sikloheksenoksitin polimerizasyonunda dönüşümün arttığı gözlemlendiği gibi eklenen radikal başlatıcı sayesinde daha yüksek dalga boyunda çalışma olanağı sağlanır. Şekil 6 İsokinolinyum N-oksit tuzunun benzoin varlığında siklohekzenoksiti çok hızlı polimerleştirdiği gözlenir. Reaksiyon yürüyüşünü aşağıdaki gibidir((4),(5)) .

Radikal Oluşumu:



Radikal katılma bölüşme $R^{\cdot}$ = Benzoin'den üretilen radikal

(5)



Şekil 6: Radikal Başlatıcının Etkisi

INTRODUCTION

Cationic polymerizations induced by external stimulations [1], such as heating or photo irradiation are of great practical interest due to their applicability for curing of coatings and printing inks and for resist technology. In previous studies, we introduced systems consisting of specially designed allyloxy-onium salts (addition-fragmentation agent) and a radical initiator for radical promoted cationic polymerization. The initiation follows in most of the cases under investigation the radical addition-fragmentation polymerization scheme. Upon choosing appropriate radical initiators, one can easily tune polymerization conditions to a desired wavelength or temperature range for cationic photo- and thermal polymerization, respectively. The allyloxy-onium salts used in this study which are allyl isoquinolinium N-oxide (AI^+) and methylallyl isoquinolinium N-oxide (MAI^+) are suitable for addition fragmentation reactions, since N-O bond is very weak and may easily be ruptured in the course of fragmentation giving rise to initiating isoquinolinium radical cations. This study concerns about synthesis of novel addition-fragmentation reagents and determining the efficiency as cationic initiators.

THEORY

2.1. General Definition of Polymers

Polymers is a large molecule constructed from many smaller repeating units which are called monomers. Monomers are covalently bonded together in any conceivable pattern. The properties of polymers are directly related with the type of monomer.

When only one species of monomer is used to build up a molecule, the product is called as a homopolymer. If the chains are composed of two types of monomer unit, polymer is called copolymer. When three or more different monomers are incorporated in one chain, a terpolymer results.

2.2. Polymerization Reactions

2.2.1. Classification of Polymerization Reactions

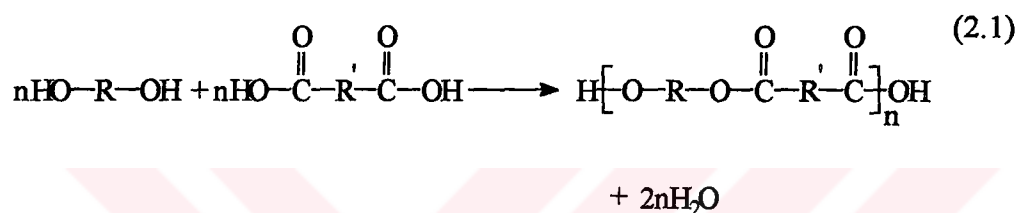
Various methods are used to classify polymerization reactions in encyclopedia and text books. For example classification based on stoichiometry, polymerization mechanisms, the nature of propagating species, product structure, the nature of monomers[2-4]. The classical subdivision of polymers into two main group was made around 1929 by Carothers as addition and condensation types and the processes as addition and condensation polymerization [5].

Although detailed information on the free radical and condensation polymerization exists in the most of the polymer text books, we would like to give introductory knowledge on these processes since they related to the scope of this work.

2.2.2. Condensation Polymerization

Condensation reaction produces a polymer or a small molecule. Products depend on the functionality of reactants. Functionality is the average number of reacting groups per reacting molecule. Functional groups can be -OH, -COCl, -COOH etc. If the functionality is less than two it produces low molecular weight condensation product.

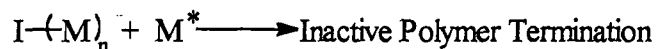
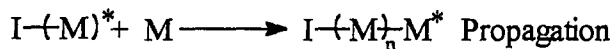
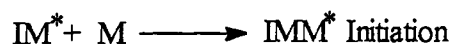
The typical examples being the condensation of an acid with an alcohol to yield low molecular weight ester. However, two or more functional groups containing acid and alcohol gives polyester.



A condensation polymerization begins with producing dimer when the concentration of dimers increase, tetramers and oligomers combine each other and form high molecular weight product. Last step rather slower than the others because the concentration of reactive groups decreases as the length of chain increases. For this reason long reaction times are required to achieve high conversion.

2.2.3. Addition Polymerization

Addition polymerization invariably proceeds by a chain reaction mechanism, chain initiation being achieved by addition of an active centre. Addition of further monomers to the resulting active centers proceeds in a series of rapid propagation step, until termination occurs, either by a chemical reaction of the centre or by exhaustion of the monomer supply,



Addition polymerization is classified into two free radical and ionic polymerization according to the structure of active growing species which may be either a radical or an ion. The types of unsaturated molecule readily undergoing addition polymerization include olefins, conjugated dienes, acetylenes and carbonyl compound with the first two types being of most importance.

2.2.3.1. Free Radical Polymerization

The complete, polymerization proceeds in three main stages: Initiation, propagation, termination. The initiation step is considered to involve following reactions.

Decomposition of initiator :



Photoinduced monomer reaction:



Reaction of initiator with monomer:



Thermally induced monomer reaction:



Where (I) represents initiator molecule, (M) represents monomer and (R.) represents the free radical. The second part of the initiation involves the addition of this radical to the first monomer molecule to produce the chain initiating species M_1 .



k_d and k_i are the rate constants of decomposition and initiation steps. Propagation contains the growth of M_1 . By the successive of large numbers of monomers. In general terms



where k_p is the rate constant of propagation. Propagation takes place very rapidly. The value of k_p for most monomers are in the range of 10^2 - 10^4 liter/mole.sec. The propagating polymer chain stops growing and terminates. Two radicals react other by combination,



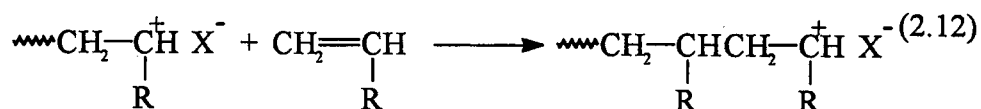
or, more rarely, by disproportionation in which hydrogen abstraction from one end to give two dead polymer chains, one is being an unsaturated and the other is saturated.



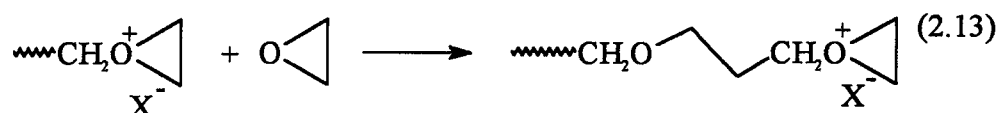
where k_{tc} and k_{td} are the rate constants of termination by coupling and disproportionation, respectively. Typical termination rate constants are in the range of 10^6 - 10^8 liter/mole.sec.

2.2.3.2. General Features of Cationic Polymerization

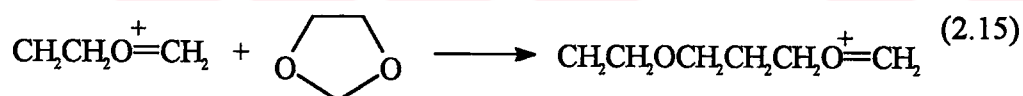
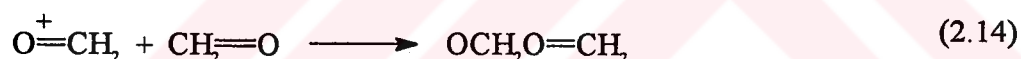
Polymerizations are generally considered as being cationic when they involve a positively charged active species acting as an electrophile towards the monomer. These species may be identified ionic or may appear only in a transition state. Generally, they are located at the end of a growing polymer molecule and react with the monomer acting as nucleophile, but in some cases the situation may be reserved (if the monomer is activated by an acid). Two main categories of monomers have been found to be polymerized by cationic polymerization. The first is that of ethylenic monomers, for which the reactive intermediate has been assumed to be carbocation (also called carbenium ion), the propagation being written schematically as in equation (2.12).



The secondary category is that of heterocyclic monomers containing at least one heteroatom (O,S or P) in the ring, for which propagation has been shown various cases to involve onium ions, for example oxonium ions in the case of cyclic ethers equation (2.13).



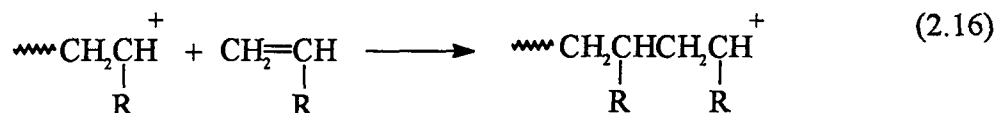
For a third category of monomers including aldehydes and acetals, propagating resembles that of carbocationic polymerization, but strongly delocalized carbocations may be involved equations (2.14, 15)



In carbocationic polymerization, the most important reactions competitive with propagation are transfer reactions, particularly those involving the monomer and termination reactions. Both have been found to decrease in non-reactive solvents of sufficiently high dielectric constants, particularly at low temperatures, the most used being chlorinated hydrocarbons (MeCl, CH₂Cl₂, EtCl). Another particular feature of cationic polymerization is the influence of impurities particularly on the initiation step. Small quantities of polar compounds, have been found to modify strongly the reactivity of Friedel Craft acids, which are generally the most efficient initiators for carbocationic polymerization, also giving polymers of high molecular weight.

Cationic Polymerization of Vinyl Monomers

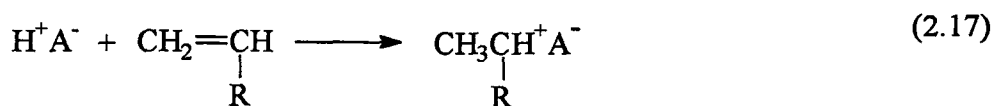
The monomers fitted for cationic polymerization include all those with electron donating substituents, in which the polarization of the double bond makes them sensitive to electrophilic attack by carbenium site.



Solvents used in cationic polymerizations should be stable towards acids and unable to react with electrophiles. Preferred are halogenated solvents such as methylene chloride, methyl chloride, ethylene chloride, carbon tetrachloride, nitro compounds such as nitro methane or nitro benzene and also dioxane. The initiators able to include cationic polymerization of vinylic monomer can be classified in three categories;

a) Protonic Acids

Sulphuric acid (H_2SO_4), perchloric acid (HClO_4), fluorosulphonic acid (FSO_3H), trifluoromethyl-sulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$) and even some cases trifluoroacetic acid (CF_3COOH) have been employed. The initiation reaction proceeds by protonation;



b) Lewis Acids

Such as SnCl_4 , AlCl_3 , BF_3 , when reacted some nucleophilic compound, can also initiate the polymerization of vinylic monomers. These so called “initiator-coinitiator” systems give complexes that are the real cationic initiators.

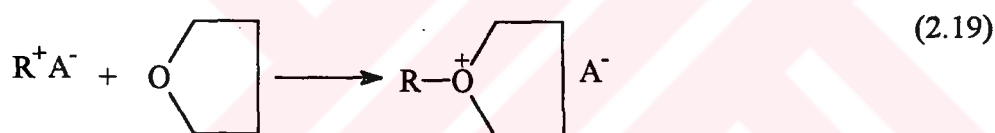


c) Carbenium Salts

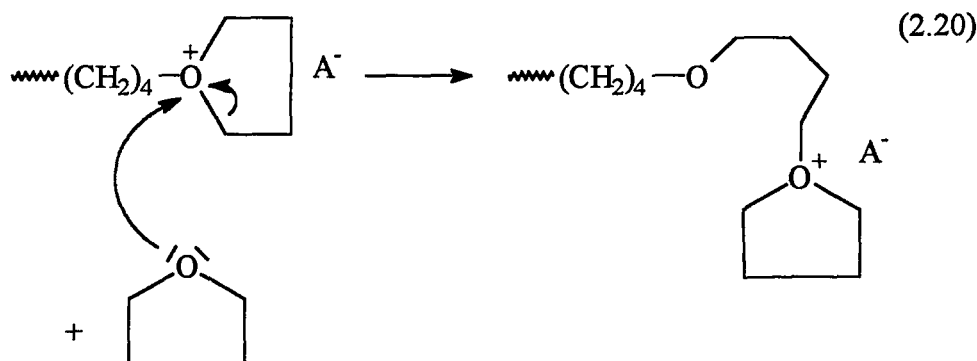
Cationic polymerization can also be initiated by means of existing carbenium salts. The electrophilicity of these species is lower because substituent allowing delocalization of these charge.

Cationic Polymerization of Heterocycles

The ring opening polymerization of several heterocycles proceeds by cationic initiation via oxonium sites that are formed upon alkylation (or protonation) of the monomer:



The mechanism of chain growth involves nucleophilic attack of the oxygen of an incoming monomer onto carbon atom in α -position with respect to the oxonium site, whereby the cycle opens and the active site is reformed on the attacking unit:



All the five-, six, and seven -membered rings are quite stable , and the change in free energy involved in ring opening polymerization is small: As a consequence the depropagation reaction cannot be neglected and conversion is limited to values lower than unity.

The initiators are the same as in cationic polymerization of vinylic monomers.

2.3. Photolatent Systems in Cationic Polymerization

Several vinyl and cyclic monomers, like alkyl vinyl ethers or the industrially important epoxides, may not be polymerized by a radical mechanism. The initiation has to be performed using an ionic initiator. Classical initiators dissociate in the reaction mixture into one initiating cation and a counter anion. The cation is therefore present almost immediately after adding the initiator. Externally stimulated initiators, on the other hand, liberate reacting cations only after stimulations, such as heat or light. Thus, the time between adding the initiator and the actual initiation can be chosen from seconds up to several weeks. This circumstance enables externally stimulated initiators to be applied for curing formulations, where the curing (polymerization or crosslinking) of a coating may be initiated at exactly the time desired and with the curing rate intended. Notably, as indicated in , the counter anion does play a role in polymerization, too. The anion has to be nonnucleophilic in order to prevent the termination of a growing chain by anion-cation combination. In general, for photoinitiated cationic polymerizations with both onium[6-8] and metal salts[9] , molecular weights and percentage conversions increase in the order $\text{BF}_4^- \ll \text{PF}_6^- < \text{AsF}_6^- < \text{SbF}_6^-$.

Though easy to handle and highly developed, classical cationic initiators lack the following two disadvantages:

(a) Since usually all the initiator is added in the solid form or in a concentrated solution at the beginning of the polymerization and it initiates immediately, the concentration of initiator at the beginning of the polymerization is not constant throughout the reaction mixture.

(b) Due to the instantaneous initiation, upon adding the initiator an extensive evolution of heat is often observed. Therefore, one has to work at relatively low temperatures, what finally leads to relatively low polymerization rates.

Externally stimulated initiator systems do overcome these problems. By stimulations such as irradiation or heating, a *controllable* amount of initiating cations is formed. The concentration of initiating cations and finally of growing polymer chains may conveniently be adjusted by choosing appropriate light intensities and temperatures for photo and thermolatent systems, respectively.

The polymers formed upon initiation by classical or externally stimulated initiators do often differ in molecular weight distribution. Since in externally stimulated polymerizations initiating cations are generated continuously, growing polymer chains with large differences in chain lengths are present at the same time. Therefore, polymers usually have a relatively broad molecular weight distribution. In the case of classical initiators, all chains start to grow directly with adding the initiator. At the moment of termination they are of almost the same lengths giving rise to polydispersities of nearly 1, provided chain-breaking side reactions are of minor importance in the polymerization of the monomer involved.

What type of stimulation is applicable to generate cations depends on the chemical constitution of the system used. In some cases, such as benzylsulphonium or phosphonium salts, initiating cations may be formed by both heat and light. In many *photolatent* cationically polymerizing systems, moderate warming can be applied simultaneously with irradiation in order to enhance the polymerization rate.

Regarding onium salts, which are the most prominent latent cationic initiators, direct and indirect acting systems will be differentiated. This strict differentiation is reasonable, because the initiating species produced by either of both systems are often not the same. In direct acting systems, the energy is absorbed by the onium salt and leads to its decomposition. In contrast to this, in indirect acting systems the energy is absorbed by an additional component. After absorbing the energy, the additives can either react with the onium salt thus producing initiating species, or transfer their energy to the onium salt molecules. With changing the additives, one can often easily

adjust to various temperature ranges or wavelengths for thermo- and photolabile systems, respectively.

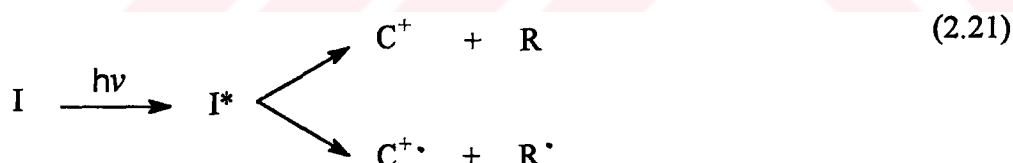
2.3.1. Onium Salts

Onium salts are the most widely used cationic photoinitiators. These salts are compounds containing heteroatoms, with a cationic center on the heteroatom. As counterions, mostly inorganic metal complex anions are used.

The polymerization by onium salts does generally start only after an external stimulation such as irradiation or heating. However, in a few cases dark polymerizations at room temperature have been observed [10].

2.3.1.1 Direct Photolysis

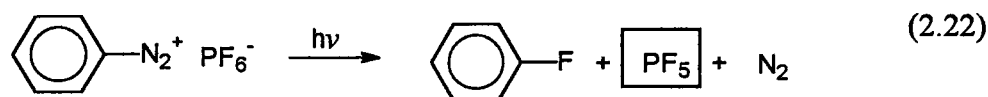
If onium salt initiators I absorb light, electronically excited initiator I^* species are produced. The latter undergo a heterolytical or homolytical bond rupture leading to cations C^+ or radical cations $C^{+\cdot}$, respectively.



In some cases, these entities are able to react directly with monomer molecules starting a cationic polymerization. Frequently, C^+ or $C^{+\cdot}$ 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 $C^{+\cdot}$ produced in the primary reaction. However, both C^+ and $C^{+\cdot}$ 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.

Aryldiazonium Salts

Aryldiazonium salts are prepared by a treatment of aniline derivatives with sodium nitrite and a Brønsted acid, the latter one giving the counter anion. Upon irradiation, these salts with complex metal anions undergo a fragmentation generating a Lewis acid, which can initiate cationic polymerizations directly or react with a hydrogen donating constituent of the polymerization mixture yielding protons.



Simple benzyldiazonium salts absorb light only below 300 nm. By substituting the benzene ring, salts absorbing near UV and even visible light could be obtained. The decomposition quantum yields of aryldiazonium salts are relatively high, being usually between 0.3 and 0.6 [11]. However, these salts were, due to their thermal instability, scarcely used for practical applications. The salt's instability prevents long term storage; the initiation of the polymerization has to be started shortly after preparing the formulation. Another disadvantage derives from the evolution of nitrogen. The evolved gas leads to gas bubbles in the hardening coatings thus making the material porous.

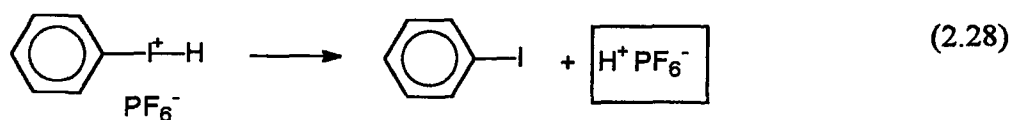
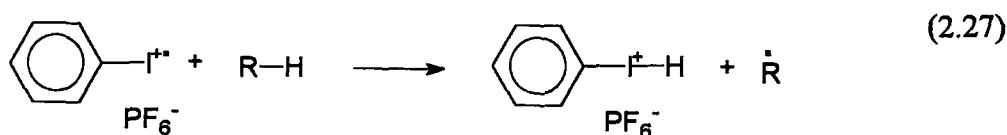
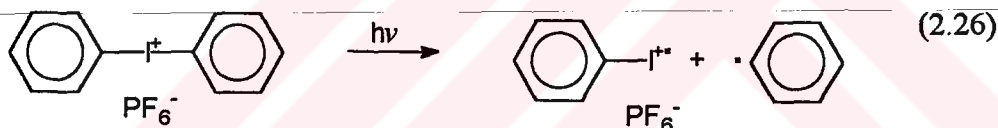
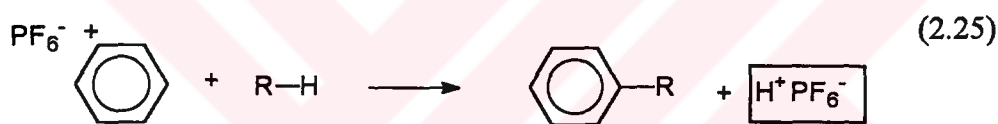
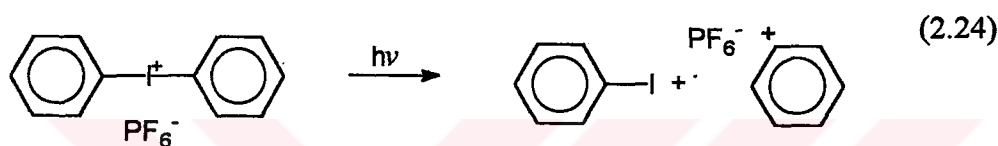
Diaryliodonium Salts

Among halonium salts, diaryl iodonium compounds are most prominent due to the fact that they are easy to prepare and very reactive. Symmetrical diarylsulphonium salts are obtained by a reaction of aromatic compounds with potassium iodate in the presence of sulfuric acid and acetic anhydride [12-13]. Since the products possess nucleophilic counter anions, the anion has to be changed for a less nucleophilic one.

The spectral sensitivity of diaryliodonium salts is relatively poor. For example, the simplest salt, diphenyl iodonium, possesses an absorption maximum at 227 nm. Diphenyl iodonium salts substituted with electron donating groups show absorption

maxima at lower energies. However, in most applications various additives are applied in order to exploit the emission wavelengths of common light sources .

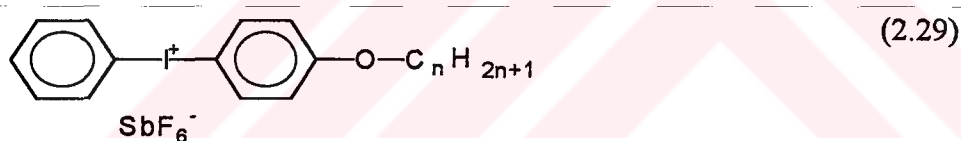
Upon UV irradiation of diphenyl iodonium salts, the Ar-I bonds are ruptured both hetero- and homolytically. Whilst the heterolytic pathway generates a phenyl cation and an iodobenzene molecule (2.24), a phenyl radical and an iodobenzene radical cation are formed by homolytic cleavage (2.26). Both mechanisms involve the interaction with a hydrogen donating solvent or monomer yielding Brønsted acid which initiates the polymerization. An alternative pathway, the reaction of escaping phenyl cations or phenyl radicals with neighboring iodobenzenes also produces protons and additionally various phenyliodobenzene derivatives.



The photolytical formation of phenyliodonium radical cations has been evidenced by its transient absorption spectrum with maxima at 660 and 310 nm [14-15]. The bimolecular rate constant for the reaction of these radical cations with nucleophilic monomer, such as cyclohexene oxide or tetrahydrofuran is in the order $10^5 \text{ l mol}^{-1}\text{s}^{-1}$ [15]. As derived from detailed product analysis, the heterolytic bond cleavage is the dominating reaction pathway for the direct irradiation of diaryliodonium salts [16-17]. The solvent has an appreciable effect on the course of the photolytic decomposition of onium salts [18]. In aqueous solutions, the salt exists

as solvent separated ion pairs. The heterolytic bond rupture is more favored in water containing solutions than in relatively apolar organic solvents, where tight ion pairs are formed. The various substituents of diaryl iodonium salts do not only lead to changes in the UV absorption spectrum, they exert a strong influence onto the initiation efficiency, too [19]. For example, in the presence of diphenyl iodonium salts with electron donating methyl substituents, cationically polymerizable monomers are polymerized with higher rates.

Brønsted acid, formed upon the direct irradiation of diphenyliodonium salts has been used for the polymerization of many monomers. Recent relevant studies were devoted to highly reactive, often crosslinkable monomers with either epoxide [20-24] or vinyl groups [25-28]. Furthermore, monomers derived from renewable resources [29-31] and cationically readily curing silicon based monomers [32-35] have been polymerized with diphenyliodonium salts. In many of these investigations, (4-alkoxyphenyl)phenyliodonium salts were chosen as cationic photoinitiator, for both their excellent photosensitivity ($\Phi \approx 0.7$) and good solubility in many monomers [36].

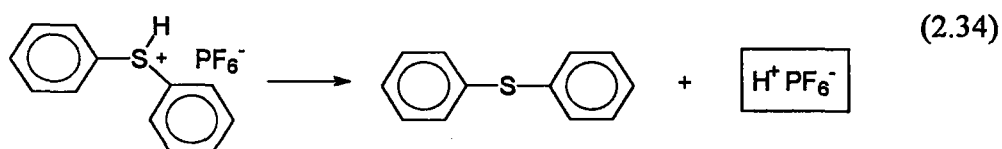
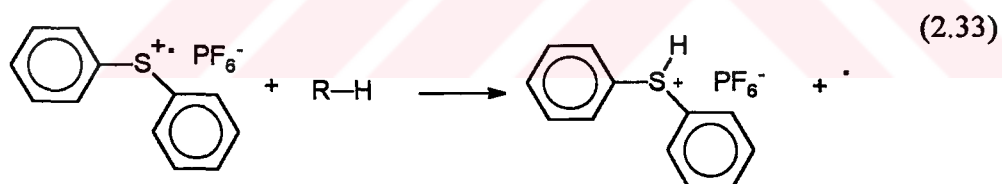
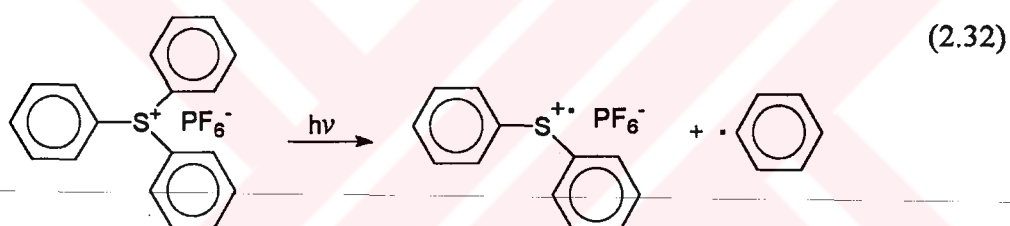
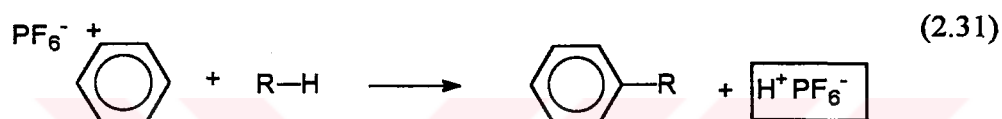
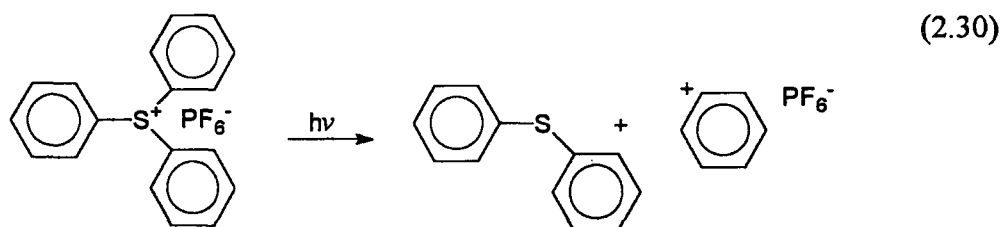


Besides iodonium salts, diaryl chloronium and bromonium salts have also been found to be highly efficient cationic photoinitiators [37,38]. Their spectral response resembles that of analogous diaryl iodonium salts. However, due to the relatively low product yields in the synthesis of these salts and their thermal sensitivity (resulting in dark polymerization) they did not find practical application.

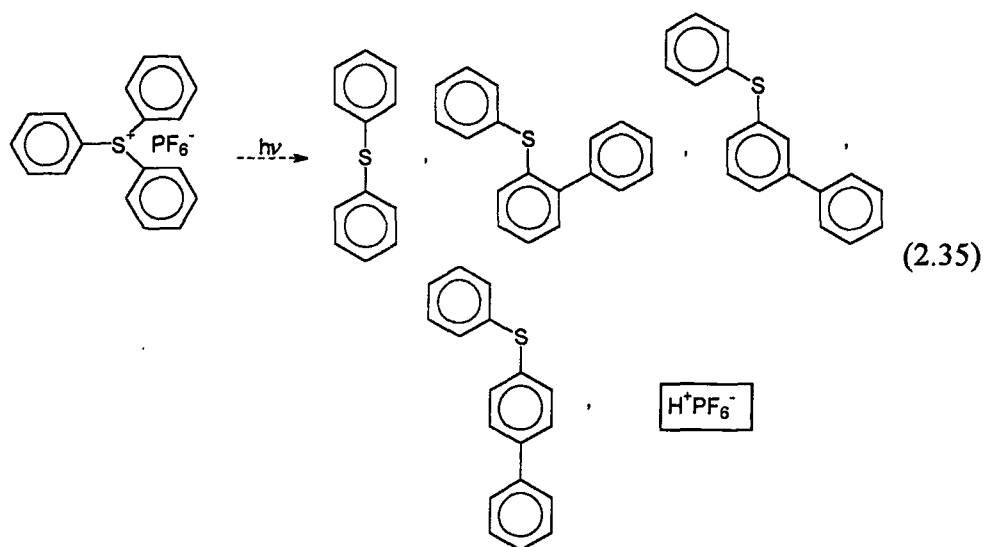
Sulphonium Salts

Regarding cationic photo polymerization, triaryl and alkylaryl sulphonium salts play the predominant role among all sulphonium salts [39]. Trialkyl sulphonium salts are thermally less stable and initiate the polymerization of reactive monomers spontaneously [40].

Regarding the photolysis mechanism of triarylsulphonium salts, both heterolytic (2.30-2.31) and homolytic (2.32-2.34) bond rupture of one sulfur-carbon bond is evidenced. In direct irradiation of triphenylsulphonium salts, the heterolytic bond cleavage starting from the excited singlet state is the preferred reaction pathway [41]. As in the case of diaryliodonium salts, in secondary reactions strong electrophilic Brønsted acid is produced. This acid initiates the cationic polymerization.



The formation of diphenylsulphonium radical cations (homolytic bond dissociation) has been followed by transient absorption measurements [15]. Mechanistic studies based on product analyses [42,43] have shown that both phenyl cations and phenyl radicals formed by either homolysis or heterolysis may add to neighboring sulfur bond aromatic rings thus generating various biphenylthiophenyl isomers (2.35). The selectivity *ortho* > *meta* > *para* observed for these solvent cage products shows that the phenyl cations or phenyl radicals tend to react with the closest available site. In this addition reaction, protons are released.

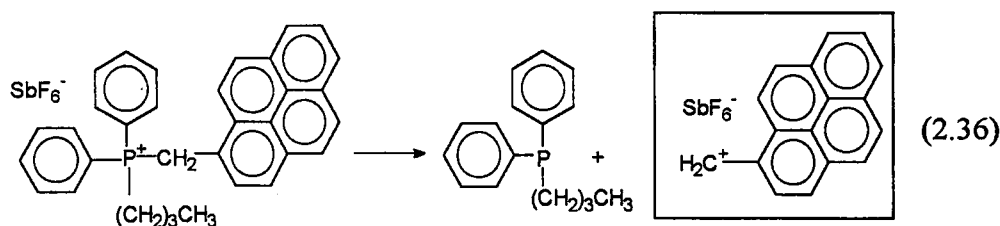


Cationic polymerizations following the direct photolysis of triarylsulphonium salts have been used for the industrially important UV curing of epoxy coatings [44]. Low molecular weight epoxidized natural rubber was found to crosslink within seconds by UV irradiation, if a triarylsulphonium salt is present [45]. Furthermore, triarylsulphonium salts were used in a number of investigations aimed at novel, highly reactive monomers with either epoxide [20, 46-48], or vinyl groups [26]. The acid generating ability of triarylsulfonium salts has also been utilized for resist applications, where the acid catalyzes the deblocking of polystyrene substituted with an ester based dissolution inhibitor [49-51].

Phosphonium Salts

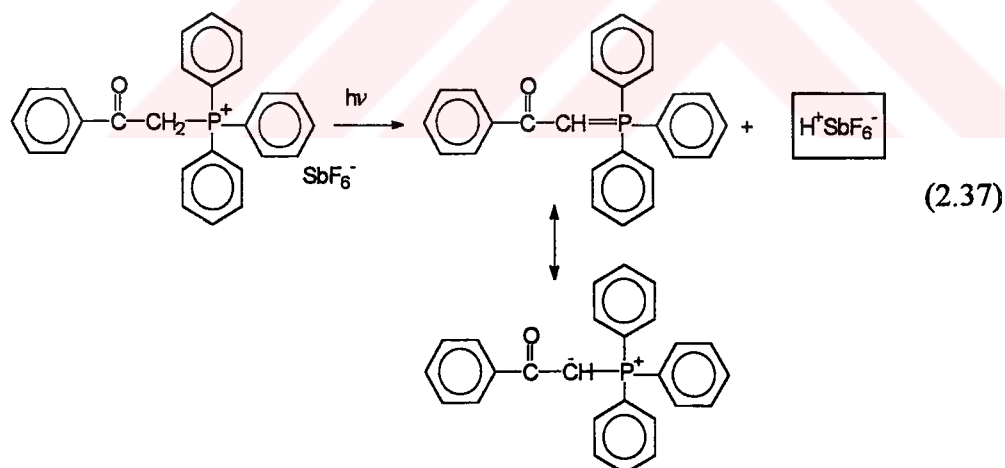
The preparation of phosphonium salts is based on the reaction of chloromethylated or bromomethylated aryl compounds with the corresponding phosphines [52-54]. Phosphonium salts with absorptions acceptable for the direct photolysis have been synthesized.

Benzyl or pyrenylmethyl group containing phosphonium salts produce the respective carbon centered cations after a heterolytic bond rupture according to (2.36) [55-57]. These cations are assumed to be the initiating species in cationic polymerization.



The excellent initiating ability of phosphonium salts containing pyrenylmethyl groups has been demonstrated for epoxides and vinyl monomers [58,59]. In the polymerization of butylvinyl ether, conversions of 100 % were achieved. UV-Vis and $^1\text{H-NMR}$ spectra of the polymers obtained gave clear evidence for the presence of aromatic groups thus proving that indeed carbocations with aromatic substituents start the chain reaction.

In the case of phenacyltriphenyl phosphonium salts, however, Brønsted acid is expected to initiate cationic polymerizations. Upon photolysis of these salts, the resonance stabilized ylide and protons are formed. Phenacyltriphenyl phosphonium salts were used for the cationic polymerization of cyclohexene oxide [54,60], styrene [60] and *p*-methyl styrene [60].



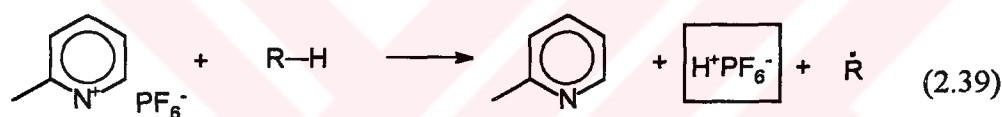
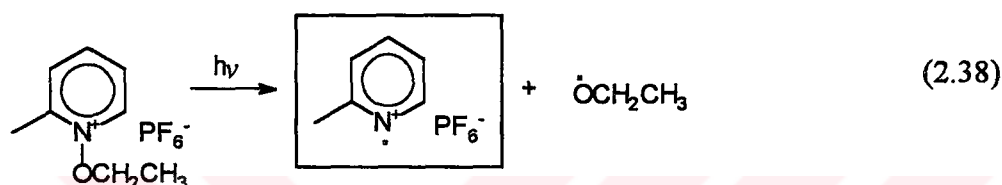
N-Alkoxy Pyridinium Salts

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 [61]. Quinolinium salts can also be prepared from the corresponding *N*-oxides [62]. In

both cases, an anion exchange is not necessary since the triethyl oxonium salt is available with non-nucleophilic counter anions.

The absorption of the pyridinium based photoinitiator lies in the far UV region. Phenyl substituents shift the absorption maximum towards higher wavelengths by c. 40 nm.

When absorbing UV light in the presence of a cationically polymerizable monomer, pyridinium type salts do readily initiate the polymerization [61,63]. The two initiation mechanisms described are depicted in (2.38-2.39) 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. Brønsted acid formed in the presence of hydrogen donors (monomer, solvent) may initiate the polymerization, as illustrated in (2.39).

Polymer Bound Onium Salts

Onium salts may be incorporated into polymers and thus be used for polymerizations. These polymeric initiators often show good miscibility with monomers and polymers obtained in the course of the polymerization. Furthermore, a lower order of toxicity is found owing to the inability of high molecular weight polymers to be absorbed by biological systems.

Styrene based *iodonium salt* containing polymers were shown to be excellent initiators for cationic polymerizations [64].

Triarylsulphonium salts have been incorporated into the backbone of aromatic poly(imides) by either condensation of a sulfur containing dianhydride with an aromatic diamine or the condensation of a sulfur containing aromatic diamine with a dianhydride and subsequent phenylation with diphenyliodonium salts [65]. The macroinitiators obtained undergo extensive chain cleavage upon UV irradiation and can therefore be applied for cationic photopolymerizations and for positive tone, high temperature resistant (up to c. 270°C) photoresists.

Polymers containing *alkoxy pyridinium* functionalities either at the side of the chain or at the chain ends have been investigated recently. These polymers turned out to be useful initiators for the UV light initiation of cationically polymerizable monomers, such as butylvinyl ether and cyclohexene oxide.

2.3.1.2 Indirect Acting Systems

Without absorption of the incident photon energy, photochemical processes cannot occur. Medium and high pressure mercury lamps that are frequently used as light sources, provide essentially emissions at 313 and 366 nm. If day light is to be used for curing a coating formula, light absorption at wavelengths above 400 nm is highly desired.

As shown above, the spectral response of simple onium salts is only rarely acceptable for their practical application. One possible pathway in tackling this dilemma is the chemical attachment of chromophoric groups to the onium salt making it absorb at higher wavelengths.

Besides that, appropriate chemicals may be added to the polymerization mixture. Some aromatic compounds, like 1,2,4-trimethoxybenzene or hexamethylbenzene are able to form *charge-transfer (CT) complexes* with pyridinium salts. Being formed in the electronic ground state, these complexes exhibit higher optical absorptions than the pyridinium salt alone. In these circumstances, the incident light is absorbed by the CT complexes.

Furthermore, strongly light absorbing compounds may be added to the polymerization mixtures. At the wavelength chosen for the polymerization, the onium salt initiator is virtually transparent. Incident light is almost entirely absorbed by the

additive. Provided the systems thus obtained do initiate cationic polymerizations, the initiation can be explained through one of the following mechanisms:

Classical energy transfer. The electronic excitation energy is transferred from the excited additive (sensitizer) to the onium salt initiator producing the excited state of the latter. The route of onium salt decomposition often differs from that observed for direct photolysis of the onium salt.

Oxidation of free radicals. Many photolytically formed radicals can be oxidized by onium salts. The cations thus generated are used as initiating species for cationic polymerizations.

Electron transfer via *exciplexes*. Sensitizers such as anthracene, perylene or phenothiazone form exciplexes with onium salts. Being formed in the consequence of light absorption by the sensitizer, these energy rich complexes consist of non-excited onium salt and electronically excited sensitizer molecules. In the complexation state, electron transfer to the onium salt is observed giving rise to positively charged sensitizer species.

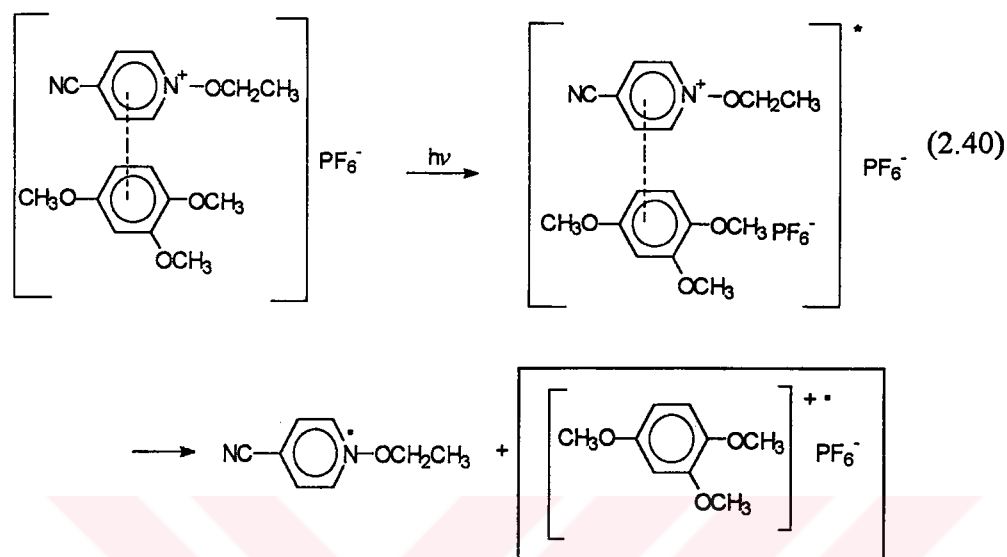
Addition fragmentation reactions. The principle of this class of reactions consists in the reaction of a photolytically formed radical with an allyl-onium salt generating a radical onium intermediate. These reactive species undergo a fragmentation giving rise to the formation of initiating cations.

Notably, the last three reaction types do not involve the electronic excitation of the onium salt. Consequently, the initiation mechanism is entirely different from that found for direct photolysis of onium salts.

Ground state Charge-Transfer Complexes

Pyridinium salts are capable of forming ground state CT complexes with electron-rich donors such as methyl- and methoxy-substituted benzene [66]. 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-trimethoxybenzene possesses an absorption maximum at 420 nm. The absorption maxima of the two constituents are 270 nm and 265 nm for the pyridinium salt and trimethoxybenzene, respectively. It

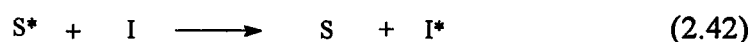
was found that the CT complexes formed between pyridinium salts and methyl- and methoxy-substituted benzene act as photoinitiators for the cationic polymerization of cyclohexene oxide and 4-vinyl cyclohexene oxide. The following mechanism for the initiation of the cationic polymerization has been suggested:



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 containing components can be excluded.

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. However, in all examples discussed in this chapter, triplet energy is transferred.



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 [15,16,67] An obvious explanation for this difference is the spin multiplicity: in the below discussed sensitized excitations triplet states of the onium salts are populated. In contrast to this, through direct irradiation of the onium salt, electrons are excited primary to the singlet state.

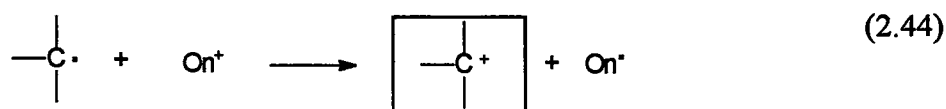
A sufficient energy transfer requires the excitation energy of the sensitizer $E^*(S)$ to be at least as large as the excitation energy of the photoinitiator $E^*(I)$.

$$E^*(S) \geq E^*(I) \quad (2.43)$$

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.

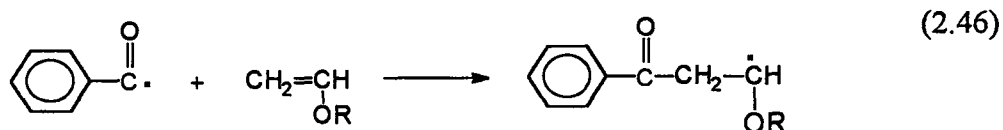
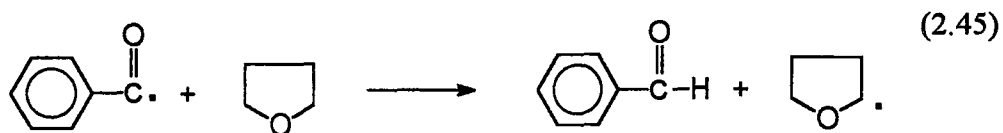
Oxidation of free radicals

As mentioned above, though being cations, onium salts can only rarely initiate a cationic polymerization by themselves. Instead, they may be used to oxidize free radicals according to reaction (2.44) thus generating reactive cations.



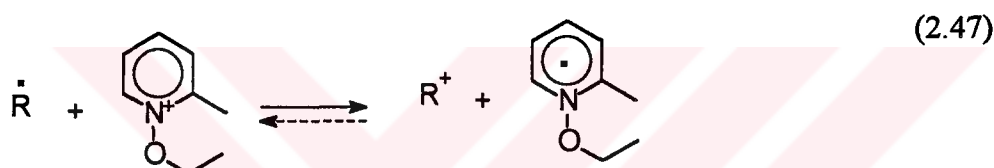
This so-called free radical promoted cationic polymerization is an elegant and fairly flexible type of externally stimulated cationic polymerizations [68,69]. Free radicals may be produced by various modes: photochemically, thermally or by irradiating the system with high energy rays. Suitable radical sources for all modes of stimulation are available.

Being photolized with fairly high quantum yields (0.41 for benzoin [70]), benzoin derivatives are so far the most effective photoinitiators. The photolysis of benzoin salts results in the generation of strong electron donor radicals.

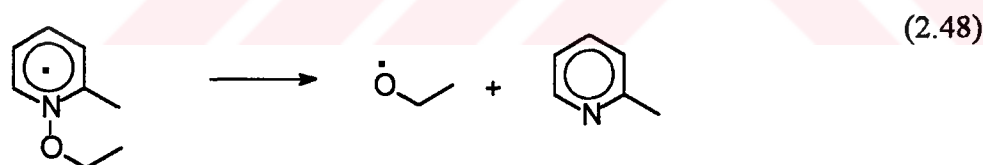


Thus formed, these radicals can easily be oxidized by onium salts yielding initiating species. The efficiency of onium salts as oxidizing agents is related to their electron affinity.

Pyridinium salts may be used for oxidizing carbon centered free radicals. Carbocations formed with the aid of N-ethoxy-2-methyl pyridinium (EMP^+) were used to initiate the polymerization of butylvinyl ether and cyclohexene oxide [71].

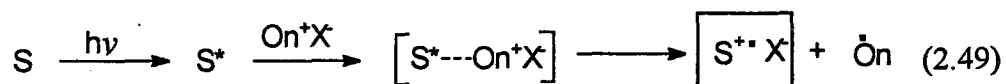


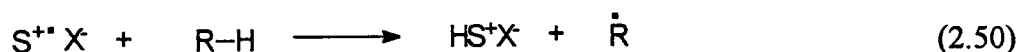
It was found that the pyridinyl radical formed by reaction (2.47) is very short lived decomposing rapidly according to (2.48). The fast decomposition of the pyridinyl radical is the reason why the back reaction of (2.47) can be excluded.



Sensitization via Exciplexes

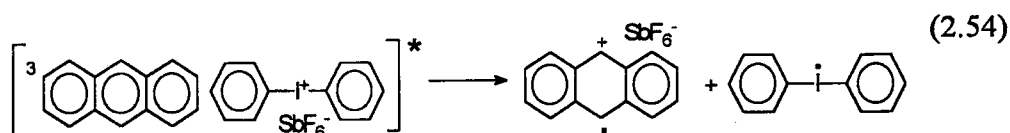
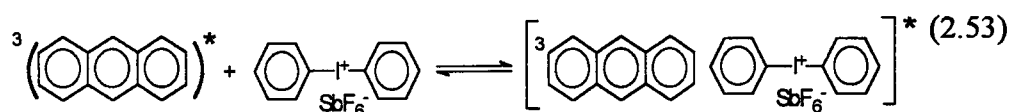
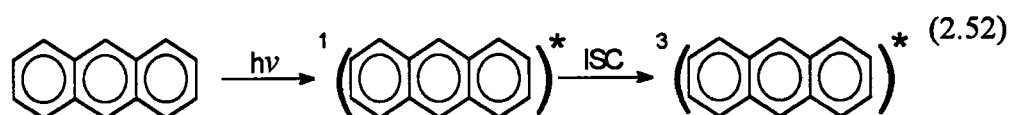
Many aromatic hydrocarbons are able to sensitize the decomposition of onium salts via electron transfer in an excited complex referred to as exciplex. For this type of cationic initiation, the following general scheme holds:

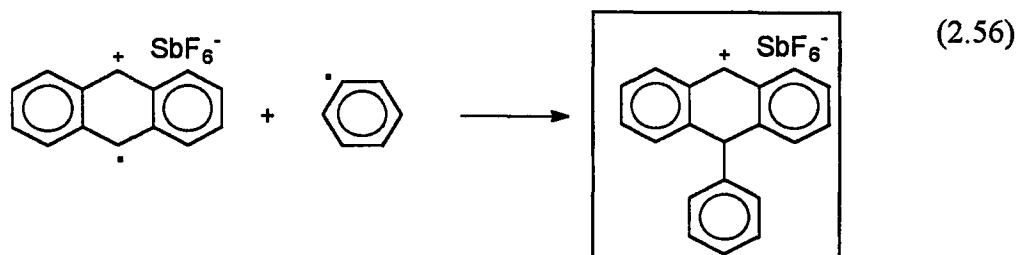
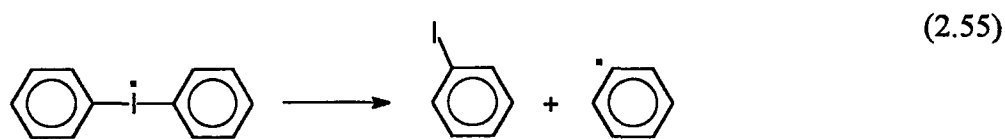




The excitation of the sensitizer is followed by the formation of a complex between excited sensitizer molecules and ground state onium salt. In this complex, one electron is transferred from the sensitizer to the onium salt giving rise to the generation of sensitizer radical cations. These can by themselves 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 centred cations [72].

The sensitization of onium salts (especially diphenyliodonium and triphenylsulphonium salts) by anthracene has been investigated in detail in a number of papers [73-75]. While some authors expected the sensitization to start from anthracene's excited singlet state[73], a recent paper based on triplet quenching has shown that the excited triplet state is the starting point of c. 95 % of all energy transfer events, what leaves the exciting singlet state a minor importance [76]. 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.

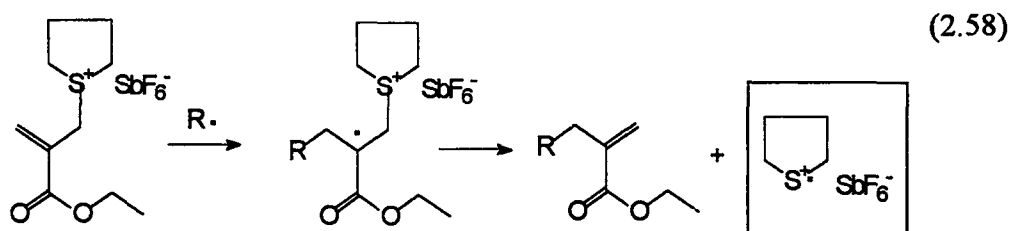
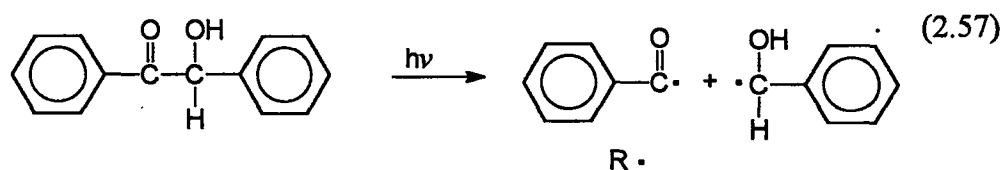




Addition fragmentation reactions

The use of addition fragmentation type reactions for photoinduced cationic polymerizations has been the subject of a few recent investigations [77-79]. Being not based on easily oxidizable cations or molecules that form exciplexes with onium cations, addition fragmentation reactions are indeed a very versatile method to adjust the spectral response of the polymerization mixture. These compounds are synthesized by a reaction of ethyl- α -(bromomethyl)acrylate with the corresponding heteroaromatic compound, or, in the case of $\text{ETM}^+\text{SbF}_6^-$, with picolin N-oxide.

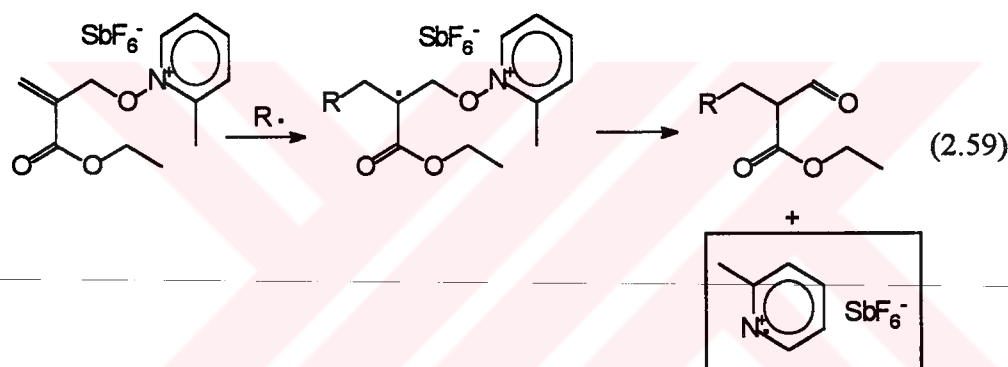
The mechanism of the addition fragmentation type initiation is depicted on the example of $\text{ETM}^+\text{SbF}_6^-$ and benzoin.



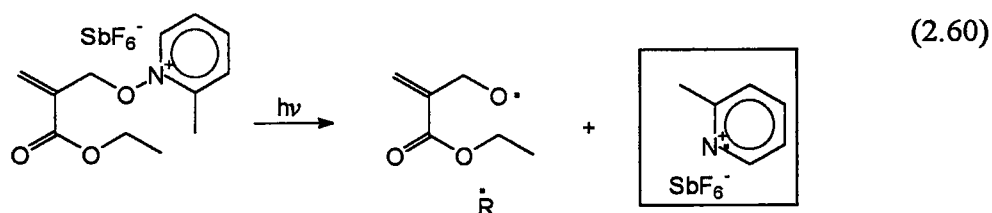
The first step consists in the photogeneration of free radicals. Virtually any photolabile compound undergoing homolytic bond rupture may be used as a radical source. The radicals add to the double bond of the allylonium salt thus producing a

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.

In the case of $\text{ETM}^+\text{SbF}_6^-$, after the addition of the photogenerated radical a radical in γ position with respect to nitrogen is formed. Being relatively weak, the N-O bond is ruptured giving rise to initiating pyridinium radical cations. Besides a direct initiation by these radical cations, the formation of reactive Brønsted acid after an interaction with hydrogen donating constituents of the polymerization mixture has also been proposed.



Notably, upon irradiation of monomer solutions containing $\text{ETM}^+\text{SbF}_6^-$ at 270 nm in the absence of any additional radical source, cationic polymerizations take place[79]. As it is known from alkoxy pyridinium salts, the N-O bond can easily be cleaved by irradiation. The radicals thus generated can add to the allylic double bond starting an addition fragmentation event. Moreover, the picolinium type radical cations formed directly upon photolysis of $\text{ETM}^+\text{SbF}_6^-$ can initiate the cationic polymerization as discussed above.



To sum this up, the advantage of systems based on addition fragmentation reactions is that virtually all types of radical sources may be applied for the initiation.

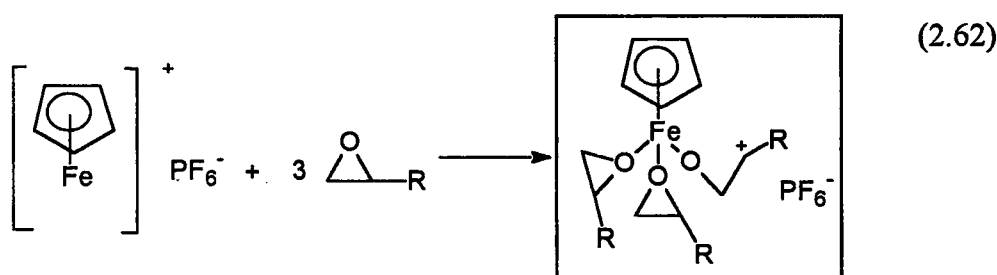
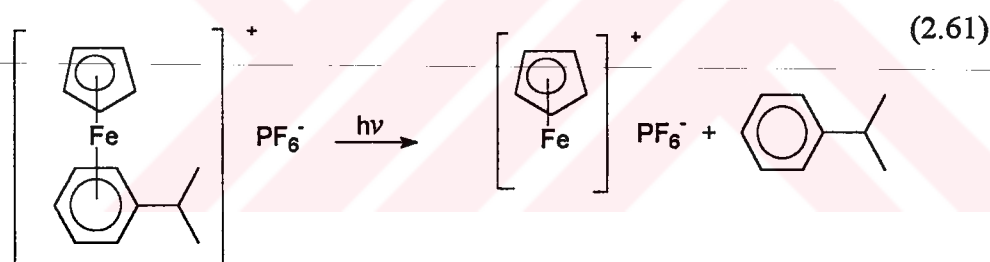
Therefore, by choosing radical sources with suitable spectral response one can adapt the polymerization elegantly to the wavelength of incident light.

2.3.1.3 Iron Arene Complexes

Iron arene complexes have been used for photoinduced cationic polymerizations for more than 10 years [80,81]. The advantages of these compounds include easy synthesis, variability in spectral response by exchanging the arene ligands, high thermal stability and high efficiency in cationic polymerization of epoxides.

Iron arene complexes are usually prepared from ferrocene by exchange of one cyclopentadienyl moiety for a neutral aromatic species, followed by metathesis with a salt possessing an appropriate counter anion [82,83].

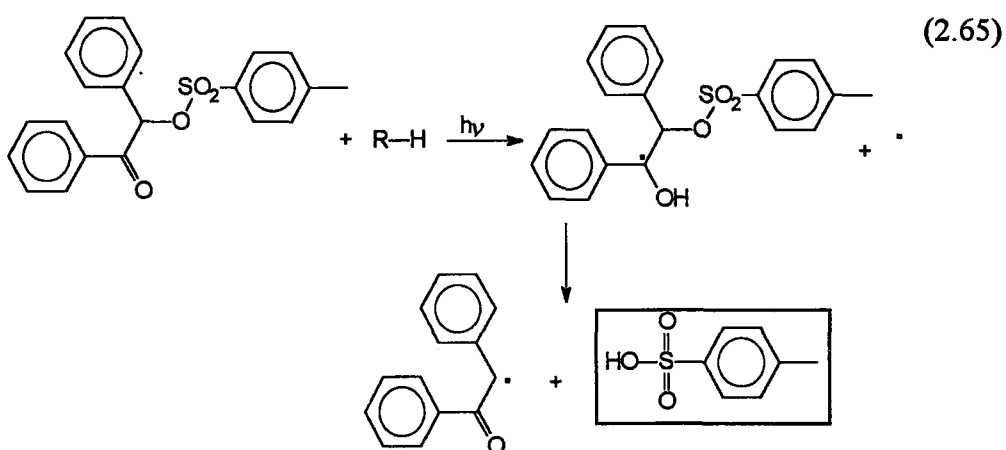
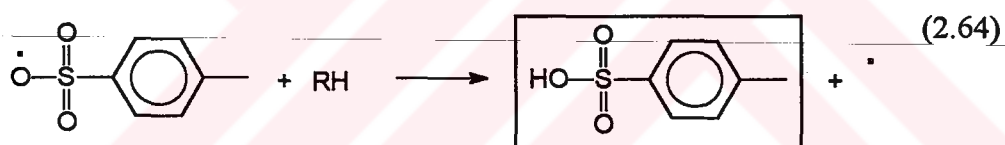
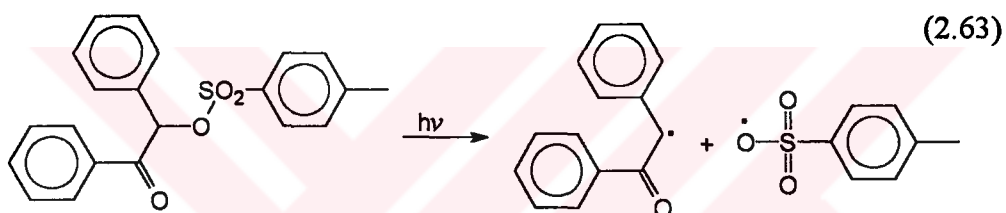
The light induced initiation of cationic polymerizations by iron arene complexes is demonstrated in the following equations.



The initiation is based on a photoinduced ligand exchange reaction followed by ring opening of one epoxy ligand and epoxy resin polymerization [84]. Notably, iron arene complexes may only be used for ring-opening cationic polymerizations. Since the Lewis acid produced upon the irradiation of iron arene complexes is relatively weak, generally a post-irradiation thermal treatment is required.

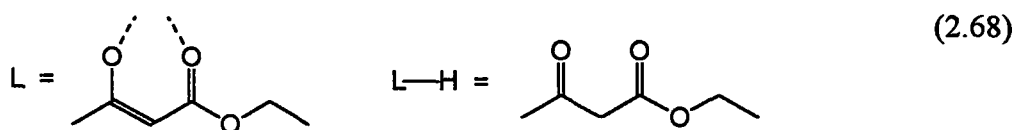
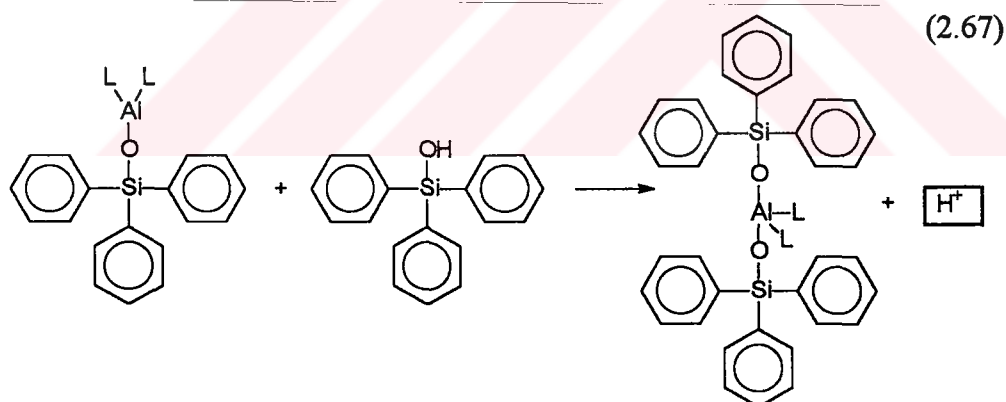
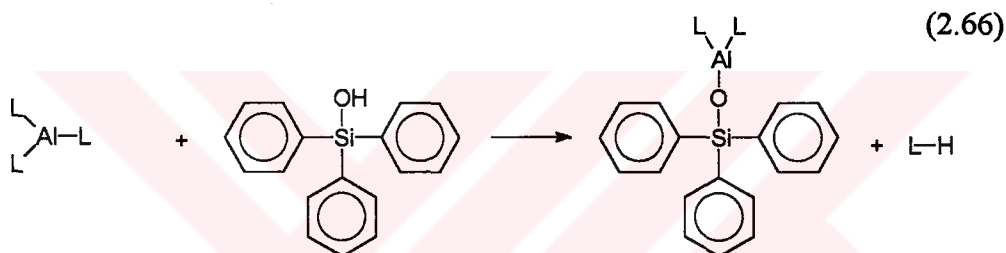
2.3.1.4 Latent sulphonic acids

Sulphonic acid, produced upon irradiation of appropriate sulphonyl compounds, may be utilized for photoinduced cationic polymerizations. The most prominent compound photolytically generating sulfonic acid is benzoin tosylate. Pros of this initiator are the ease of synthesis and the high yield of acid formation. Below, the mechanism of acid release by benzoin tosylate is illustrated. In an environment with relatively little hydrogen containing molecules (aprotic solvent), β -cleavage is the primary photoreaction. On the other hand, if the photolysis is carried out in hydrogen donating solvents, the mechanism starts with the protonation of the carbonyl group (photoreduction), but ends up with the same reaction products.



2.3.1.5. Photosensitive organosilanes

It has been found that, mixtures of silanol and aluminum(III) complexes of β -diketones, β -ketoesters or orthocarbonylphenolate are able to polymerize cyclohexene oxide upon UV irradiation or moderate heating (40°C) [85,86]. The initiation mechanism is demonstrated on the example of the triphenylsilanol/tris(ethyl acetoacetate) aluminum system in (2.66-2.67). The release of protons is a thermal reaction. If the ligands are 1,3-diketones (2.68), the release of Brønsted acid is strongly accelerated by UV light due to the formation of light sensitive intermediates [87].



The disadvantage of the system described is its instability - it may be stored for only short time.

2.4. THERMOLATENT SYSTEMS

In many curing applications, the hardening of monomer containing curing formulas by heat is desired. Regarding radical polymerization, a large number of initiating thermolabile compounds is known, which contain mostly either azo or peroxide groups. One can cure coatings at virtually any temperature desired by choosing the appropriate initiator compound.

As far as cationic polymerization is concerned, it has to be said that some of the onium salts described in the previous section 2.3 may be activated thermolytically, too. However, mostly onium salts with slight differences in the pattern of substitution are used. For example, for photoinitiation N-alkoxy pyridinium salts serve as initiators whereas for thermal polymerization, N-benzyl pyridinium salts are utilized. Besides the direct thermolysis of the initiator, also indirect methods which are similar to that described in section 2.3, have been reported. Thermally generated radicals can be used in radical oxidation and addition fragmentation schemes for producing appropriate initiating cations.

Concerning energy absorption, thermal and photolytical initiations differ for the following: in the case of thermal initiation, all chemical bonds absorb energy, whereas for photoinitiation, the photon energy is absorbed only by suitable chromophoric groups. For cationic photoinitiators, much effort has been made to introduce chromophoric groups absorbing at high wavelengths into the molecule or to use additives containing appropriate chromophores. In contrast to this, for thermal cationic initiators, research has been devoted to chemical groups that undergo the bond rupture desired to a sufficient extent at relatively low temperature. The initiating compounds have however to be stable at room temperature; otherwise their thermal latency would be lost.

As described in this section, initiators suitable for an application at various temperature ranges are available. Approaches to overcome the solubility problem often observed with onium salts are also described.

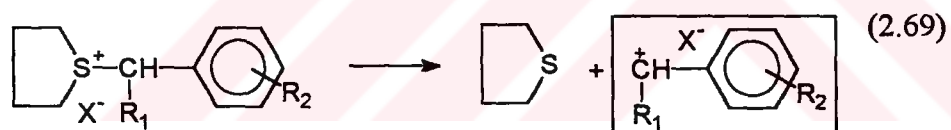
2.4.1. Direct Thermolysis

2.4.1.1. Sulphonium Salts

Sulphonium salts have a considerable potential as cationic *photo*initiators. This refers, however, only to triarylsulphonium salts. Alkyl substituted sulphonium salts are thermally unstable, decomposing sometimes already at room temperature. The reason, why alkylsulphonium salts are more thermally reactive than arylsulphonium salts is that the former are stabilized only by hyperconjugation, whereas the latter by resonance.

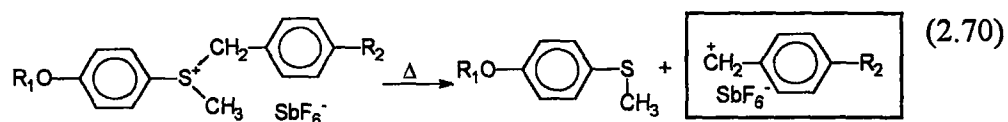
Due to the stabilization of the leaving *benzyl cation* by resonance, alkyl*benzyl*sulphonium and alkylaryl*benzyl*sulphonium salts possess a high thermal sensitivity.

The synthesis of *benzylthiophenium salts* is achieved through a reaction of respectively substituted benzylhalides with tetrahydrothiophene and a subsequent anion exchange. As confirmed by NMR analyses of polymer formed [88], the initiating species are thermolytically generated benzyl cations.



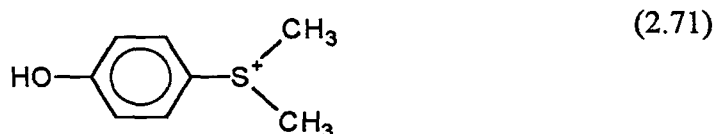
Regarding the effect of the substituent in the aromatic ring, R_2 , it turned out clearly that electron donating substituents enhance the initiation activity by stabilizing the benzyl cation evolved.

Other highly thermosensitive benzylsulphonium salts are *benzyl phenylalkyl sulphonium salts* [8,89,90]. In this case, benzyl cations have been shown to initiate the polymerization.



As far as the substituents in the benzyl group, R_2 , are concerned, electron donating substituents were found to enhance the thermal sensitivity by stabilizing the

benzyl cation. The reactivity diminishes in the order $\text{CH}_3 > \text{H} \approx \text{Cl} > \text{NO}_2$ [90]. Regarding phenyl ring substituents, R_1 , electron withdrawing groups were found to increase the thermal sensitivity due to the destabilization of the sulfur centered cation. In the case of the $p\text{-CH}_3\text{OC(O)O}$ derivative (strong - I effect), polymerizations were initiated even at room temperature. Notably, no difference in activity between OH and OCH_3 derivatives was found, thus confirming that the possible formation of protons by the cleavage of the O-H bond is of no importance regarding the initiation. Instead, the initiation is also in this case due to benzyl radicals. The comparison with the phenyldimethylsulphonium salt [90].



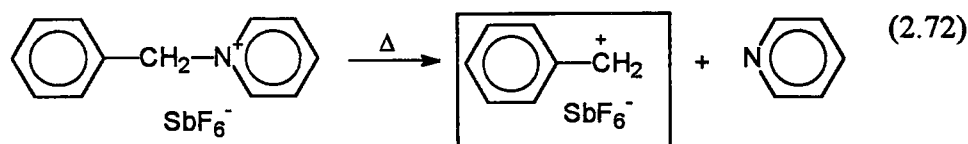
Revealed clearly the importance of the benzyl group for thermal sensitivity. In the case of the benzyl free sulphonium salt, bulk polymerizations of phenyl glycidyl ether were observed only at temperatures above 150°C , whereas for the benzyl containing derivative (unsubstituted benzyl group), 90°C were fully sufficient.

2.4.1.2 N-Containing Onium Salts

Benzyl Pyridinium Salts

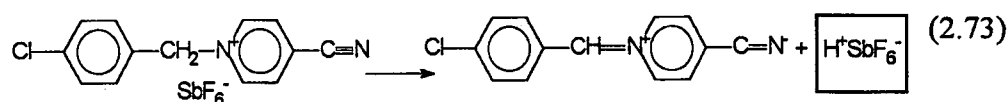
N-Benzyl pyridinium salts, the N-containing onium salts most frequently used for thermal cationic polymerization [91], are facile to prepare by reacting benzyl chlorides with corresponding pyridines [92]. That reaction yields pyridinium salts possessing nucleophilic chloride anions. Therefore, the counter anion has to be exchanged for a less nucleophilic one.

N-benzyl pyridinium salts were successfully applied for the polymerization of cyclic and vinyl monomers. It was found that they possess a much better thermal initiation ability than aliphatic ammonium salts. This is, undoubtedly due to the low bond energy of benzylic C-N bond giving rise to bond ruptures at moderate temperatures. The reaction mechanism that has been evidenced by the chemical analysis of obtained polymer [93] is depicted in (2.72).

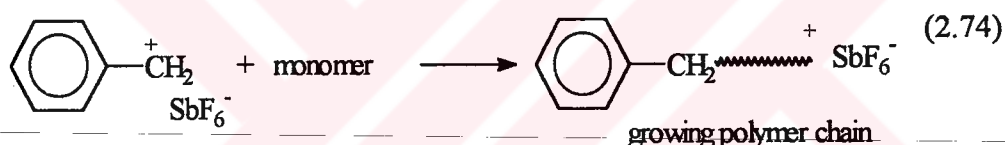


The *substituents in the pyridinium ring* exert a strong effect on the activity of these salts. The *p*-CN substituted benzyl pyridinium salt has often been used for cationic polymerizations. It is more reactive than unsubstituted N-benzyl pyridinium, but suffers from the disadvantage of still requiring high temperatures for a successful polymerization (>100°C) [92,94]. Other analogs with *p*-substituents in the pyridinium moiety show a worse performance in cationic polymerization. The activity for pyridinium ring *p*-substituents was found to decrease in the order *p*-CN > H > *p*-CH₃ > *p*-N(CH₃)₂. This order indicates that electron accepting groups stabilize the cation on the pyridinium N-atom thereby diminishing the leaving ability of the pyridinium moiety ^[94]. If the pyridinium ring is substituted by *o*-CN instead of *p*-CN, the thermal sensitivity is drastically improved, increasing the activity by a factor of 20 to 30 [95,96] The effect of the *o*-CN substituent was attributed to both steric and electronic factors.

The *substitution of the benzene ring* by electron donating groups stabilizes the benzyl cation formed thermolytically thus further enhancing the thermal activity. The activity of pyridinium salts with various *p*-substituents at the benzene ring falls in the order CH₃O > Cl > *t*-C₄H₉ > CH₃ > H [97]. Notably, if the benzene ring is substituted by CH₃O, the thermal latency may be lost: with *p*-methoxybenzyl *o*-cyanopyridinium, polymerizations are observed already at room temperature [98]. The relatively high activity of N-benzyl pyridinium salts substituted with electron withdrawing *p*-Cl groups at the benzene ring has been attributed to the occurrence of side reactions like the formation of ylide and Brønsted acid. The latter acts as an additional cationically initiating species. In the case of *p*-Cl substituted N-benzyl pyridinium salts, IR and ¹H-NMR measurements of the polymers obtained gave no evidence for the presence of benzyl moieties in the polymer. Thus it has been confirmed that the initiating species are protons rather than benzyl cations. For other N-benzyl pyridinium salt, the incorporation of benzyl groups into the polymer has been proven by chemical analysis [97].

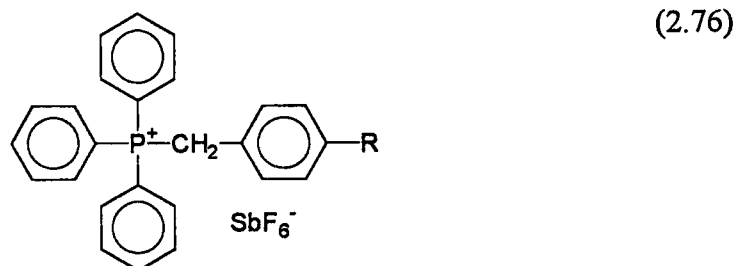


It has to be pointed out that the substituted or unsubstituted pyridine liberated in the course of decomposition of N-benzyl pyridinium salts (see (2.72)) plays a significant role in the propagation step. Pyridine is a relatively strong base, which is potentially able to react with the cationic chain ends. The basicity of pyridine's N-atom is enhanced by electron withdrawing groups, such as CN. Thus, after adding additional *o*-cyanopyridine or *p*-cyanopyridine to the polymerization mixtures, the bulk and solution polymerization of glycidyl phenylether was strongly suppressed, indicating the interaction of pyridine moiety with propagating chain ends [94]. NMR studies of the polymerization mixture in which propylene oxide was used as a monomer, revealed that this interaction is weaker for *o*-cyanopyridine than for *p*-cyanopyridine. The role of pyridine in the propagation is illustrated as follows.



Phosphonium Salts

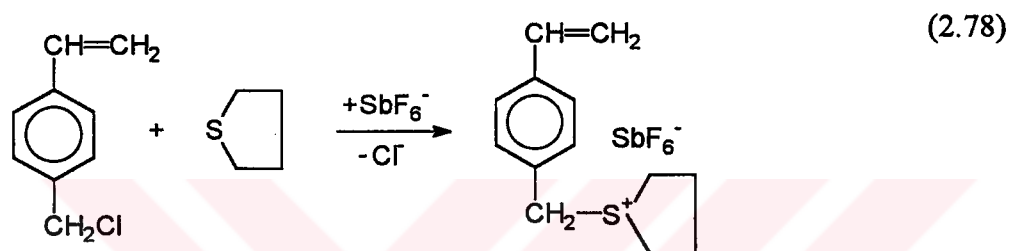
Substituted benzylphosphonium salts of the general structure



Polymer Bound Onium Salts

As far as applications are concerned, polymer bound onium salts are of great interest. Mostly, using these polymeric initiators one is not faced with the solubility problems often occurring with low molecular weight onium salts. Moreover, polymeric initiators open gates for the synthesis of specially designed copolymers.

Polymer bound sulphonium salts have been used for the preparation of graft copolymers [92,102]. In the first step, a sulphonium containing styrene based monomer was prepared.



This monomer was polymerized or copolymerized with styrene in the presence of AIBN at 60°C, thus yielding sulphonium modified poly(styrene) with variations in the concentration of sulphonium containing units. Heating the macroinitiator in the presence of cationically polymerizable monomer makes the latter grafted onto polystyrene backbones. This scheme was followed using a bicyclo ortho ester as cationically polymerizable monomer

Regarding *pyridinium salts*, a similar polymeric initiator [93] has been synthesized. The monomer was obtained by a treatment of *p*-chloromethyl styrene with pyridine. The polymer bound pyridinium salt was heated in the presence of a bicyclo ortho ester at 120°C to yield grafted polymers. For the sake of comparison, copolymers, obtained by a copolymerization of styrene with the pyridine containing monomer and homopolymer with all units containing the pyridine moiety have been used as thermolatent initiators. It was found that the activation efficiency of the initiator copolymer is higher than that of the homopolymer. However, the thermal sensitivity of both macroinitiators turned out to be lower than that of low molecular weight analogs.

Though not being typical thermolatent initiators, *iodonium salts* bound to macromolecules have been successfully applied in the thermal initiation of cationic

polymerizations, as was demonstrated on the example of epichlorohydrin polymerization [103]. The styrene based macroinitiator was in this case found to be more reactive than low molecular weight iodonium salts.

Salt Free Initiators

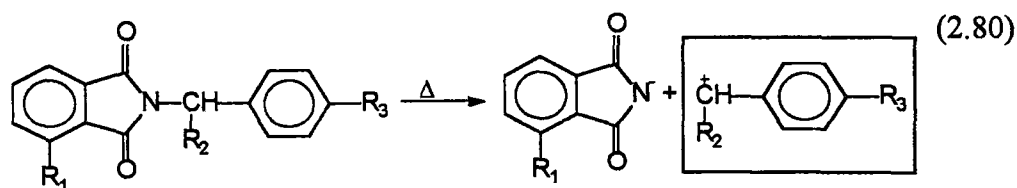
Since onium salt initiators are often not particularly soluble in common monomers and, furthermore, introduce inorganic impurities (stemming from the counterion) into the polymer, effort has been made to create salt free thermolatent systems.

Recently, carboxylic acid esters have shown great potential in thermal cationic initiation [104]. The esters (with $R_1 = \text{CH}_3, \text{CHCl}_2, \text{CF}_3, \text{CCl}_3$ and $R_2 = \text{OCH}_2\text{CH}(\text{CH}_3)_2, \text{Ph}$) have been found to produce a resonance stabilized carbocation upon heating. The compound was used for the thermal bulk polymerization of isobutylvinyl ether. By product analysis, the formation of Brønsted acid as a possible initiating species was excluded.



The substituents R_1 and R_2 exert a strong influence on the polymerization activity. For different derivatives, polymerization temperatures between 25°C (no thermal latency) and 100°C were chosen. In the case of R_1 , the thermal sensitivity falls in the following order: $\text{CF}_3 > \text{CCl}_3 > \text{CHCl}_2 > \text{CH}_3$. The increased activity for the derivatives with electron withdrawing groups has to be explained by the stabilization of carboxylanions formed. Regarding R_2 , the $\text{OCH}_2\text{CH}(\text{CH}_3)_2$ containing derivative was much more active than the phenyl substituted one. This is surely due to the higher stability of the oxonium ion compared with the benzyl cation.

Another type of salt free initiators successfully applied for ring opening polymerizations are N-benzyl phthalimide derivatives [105]. These compounds undergo ion pair formation by heating - initiating benzyl cations along with the low nucleophile phthalimide anions are produced. The initiating efficiency has been demonstrated on the polymerization of aziridines.



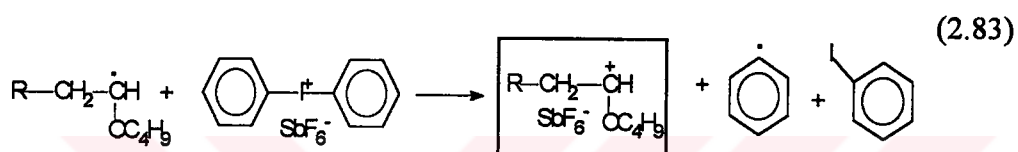
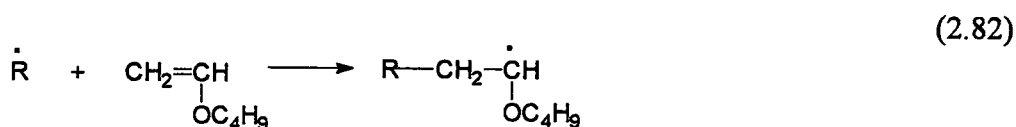
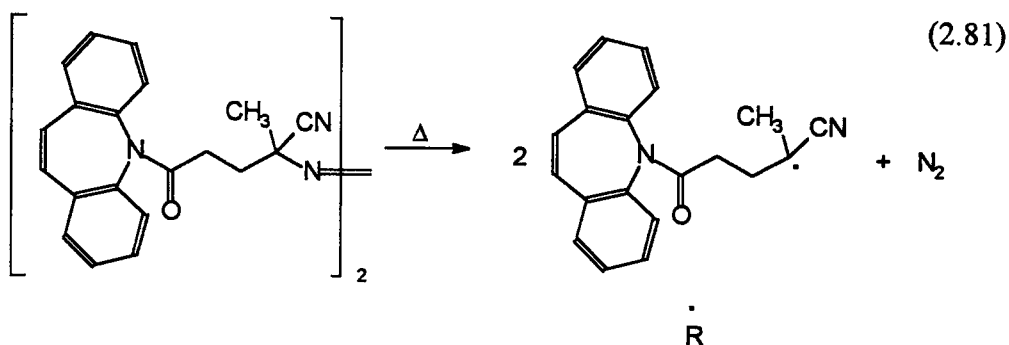
2.4.2. Indirect acting Thermolatent Systems

2.4.2.1. Thermally induced Radical Promoted Polymerization

As was explained above, free radicals produced upon external stimulation can be oxidized by onium salts. The mode of stimulation by which the radical is produced, being it heating or irradiation, has no effect on the oxidation or initiation mechanism

Due to their high reduction potential, *diaryl iodonium salts* are highly suitable oxidation agents for free radicals. They have been used for oxidizing radicals, generated by various radical sources [106-110]. In the case of tetrahydrofuran polymerization, the molecular weight was found to depend strongly upon the thermal radical initiator used [106]. For example, for AIBN, $M_n \approx 9 \times 10^5$ was obtained, whereas for phenylazotriphenylmethane, the molecular weight was in the order $M_n \approx 5 \times 10^4$. These differences have been explained in terms of different initiating species. In the case of PAT, triphenylmethyl carbocations initiate the polymerization. If AIBN is used, oxygen centered tetrahydrofuranyl cations act as initiating species. The latter are assumed to initiate much longer growing chains.

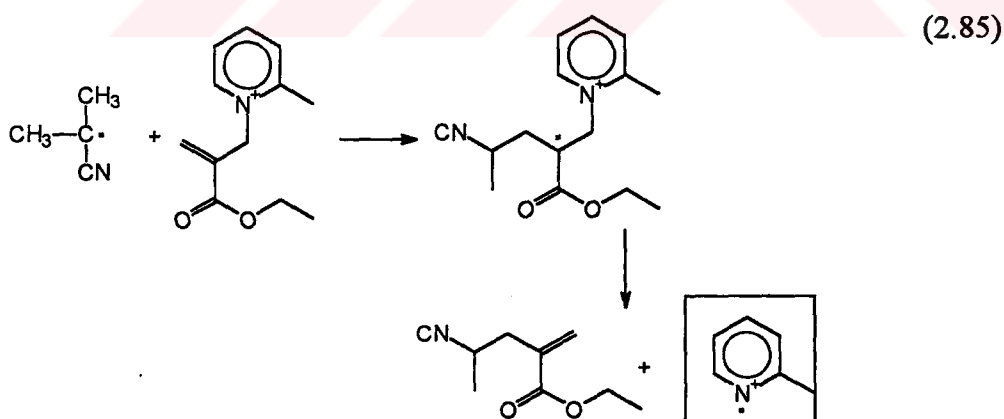
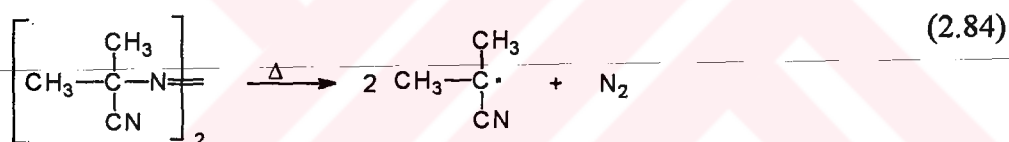
In order to obtain poly(n-butylvinylether) with N-acyl dibenz(b,f)azepine terminal units, an azoinitiator containing the respective functional groups was heated in the presence of n-butylvinylether and diaryliodonium salt [110]. The functionalized polymer contained a large number of dibenzazepine units. Upon irradiation of this polymer with UV light, chain extension via dimerization occurred, a phenomenon characteristic for substances containing dibenzazepine groups.



The oxidation of thermally generated free radicals by *ethoxy pyridinium salts* has been applied for the polymerization of cyclohexene oxide and n-butylvinylether. Cyclohexene oxide could only be polymerized by the system benzoyl peroxide or AIBN/1-ethoxy-2-methylpyridinium hexafluorophosphate, if catalytic quantities of tetrahydrofuran were added to the polymerization mixture. This is surely due to the fact that the radicals stemming from either benzoyl peroxide or AIBN may not be oxidized themselves and do not form oxidizable radicals after a reaction with cyclohexene oxide.

2.4.2.2. Thermally induced Addition Fragmentation Reactions

There are several allyl compounds that may be used in conjunction with free radicals in a reaction scheme referred to as addition fragmentation. For the addition fragmentation mechanism, the mode, by which the radical was generated is of minor importance. For thermal initiation, AIBN, benzoyl peroxide and phenylazotriphenylmethane were applied. The addition of the thermolytically formed radical to the unsaturated C=C bond is followed by the cleavage of a neighboring bond, giving rise to the formation of appropriate initiating species. In (2.84) and (2.85), this reaction principle is illustrated on the example of AIBN and 2-ethoxycarbonyl-2-propenylpyridinium hexafluoroantimonate. Following the addition fragmentation scheme, various oxiranes and vinyl ether monomers have been polymerized. Besides the pyridine derivative, an allyloxy pyridine and an allyl tetrahydrothiophenium derivative have been used in conjunction with thermosensitive radical donors.



If phenylazotriphenylmethane was used together with the latter two initiators, the oxidation of the triphenylmethyl radicals to the respective cations has been inferred from the characteristic triphenylmethyl cation absorption spectrum. These cations account for the remarkably high initiator efficiency of the system phenylazotriphenylmethane/allyl compound.

EXPERIMENTAL WORK

3.1. Materials and Chemicals

Isoquinoline N-Oxide was a product of Fluka, no further purification is applied.

Allyl Bromide was a product of Aldrich, no further purification is applied.

3-Bromo-2-Methyl Propene was a product of Aldrich and used directly.

Sodium hexafluoroantimonate used as anion exchanger in synthesis of AFA , was a product of Aldrich, used directly.

Cyclohexeneoxide used as monomer, was a product of Aldrich and distilled with fractionation under calciumhydride.

Azobisisobutyronitrile (AIBN) was a product of Fluka and recrystallized from ethanol.

Phenylazotriphenyl-methane (PAT) was a product of Fluka and used directly.

Benzoylperoxide (BPO) was a product of Fluka and recrystallized from diethylether.

Benzoin was a product of Fluka and recrystallized from ethanol.

Acetonitrile, used as solvent in synthesis of addition-fragmentation agents (AFA), was a product Carlo-Erba.

Methanol (technical grade) used in precipitation processes of cyclohexeneoxide polymers

Methylenechloride is used as solvent for dissolving bulky polymer formations and in UV measurements, is cleaned by sulphuric acid then water then 5% sodium hydroxide solution again water, dried with sodium sulfate distilled from fractionation column.

Diethylether used as solvent in synthesis of AFA, was a product of Carlo-Erba.

3.2. Equipments

3.2.1. Photo reactor

A merry-go-round type photoreactor with 16 Philips 8W/06 lamps, emitting overwhelmingly light at c. 370 nm, was used.

3.2.2. UV Spectrophotometer

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

3.2.3. Elemental Analysis

Elemental Analysis were recorded on a CHNS-932 (LECO) instrument.

3.2.4. Nuclear Magnetic Resonance Spectrospin

¹H-NMR analysis were recorded on a Bruker 250 MHz NMR Spectrospin.

3.3. Synthesis of Cationic Initiator Salts

Allyl Isoquinoline N-Oxide Hexafluoroantimonate:

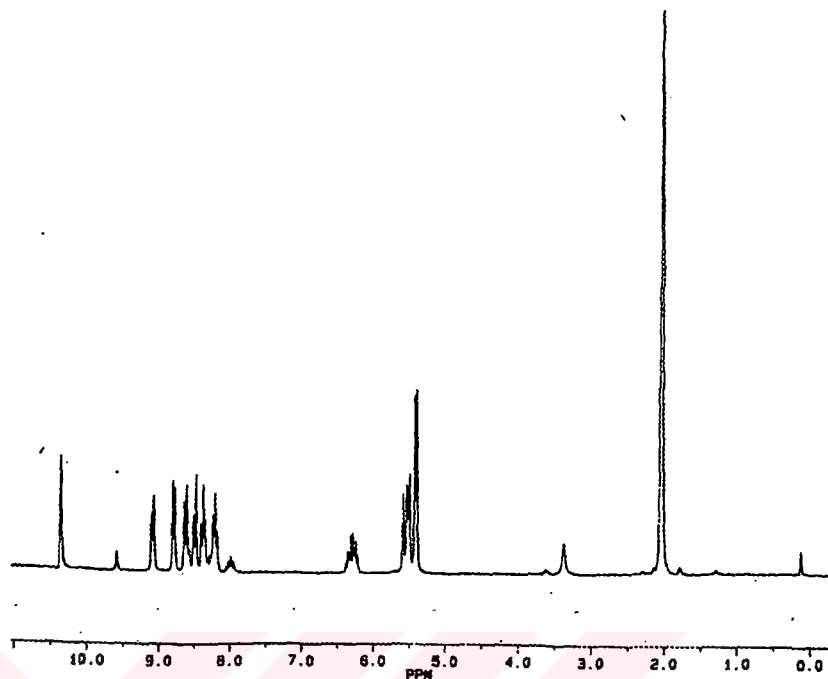
Isoquinoline N-oxide (0.3123g, 2.15mmol) is dissolved in acetonitrile in room temperature. Allyl bromide (0.26g, 2.15mmol) is added and the mixture is agitated for 3 days. Solvent is evaporated and enough water is added. The mixture is extracted with diethylether. Sodium hexafluoroantimonate (0.556g, 2.15mmol) is added to the

water phase. Precipitated allyl isoquinoline N-oxide hexafluoroantimonate salt (0.3g, Melting Point : 46 ° C) is collected and dried in vacuum oven.

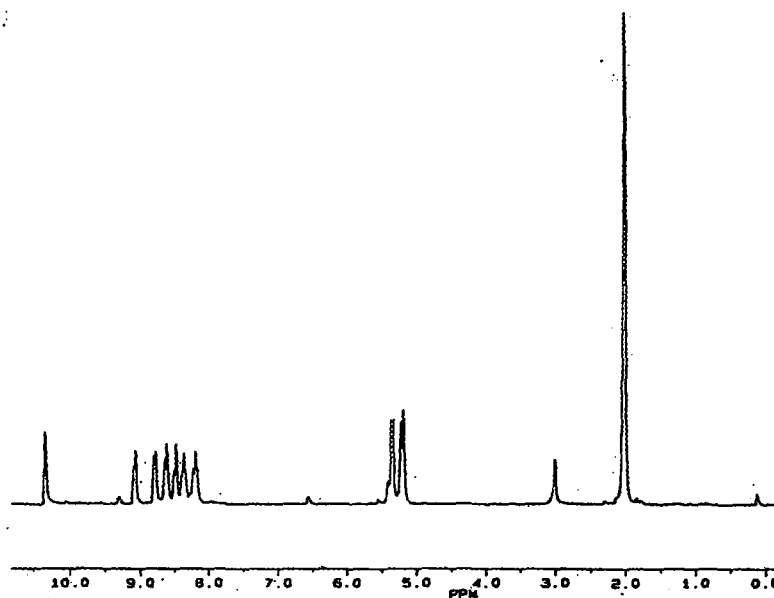
Methylallyl Isoquinoline N-Oxide Hexafluoroantimonate:

Isoquinoline N-oxide (0.3123g, 2.15mmol) is dissolved in acetonitrile in room temperature. 3-Bromo 2-Methyl Propene (0.29g, 2.15mmol) is added and the mixture is agitated for 3 days. Solvent is evaporated and enough water is added. The mixture is extracted with diethyether. Sodium hexafluoroantimonate (0.556g, 2.15mmol) is added to the water phase. Precipitated methy allyl isoquinoline N-oxide hexafluoroantimonate salt (0.1433g, Melting Point : 78 ° C) is collected and dried in vacuum oven.

	$Al^+SbF_6^-$			$MAI^+SbF_6^-$		
	% C	% H	% N	% C	% H	% N
Calculated	34.14	2.845	3.32	35.8	3.71	3.21
Found	34.80	2.99	3.30	35.71	3.19	2.6



Scheme 1: NMR Spectrum of $\text{Al}^+ \text{SbF}_6^-$



Scheme 2 : NMR spectrum of $\text{MAI}^+ \text{SbF}_6^-$

3.4. Polymerization Techniques

3.4.1. Thermal Polymerizations

Coinitiator (radical initiator), AFA and monomer were mixed in a pyrex tubes that were closed with a teflon stopcock after bubbling through with nitrogen gas which was passed through firstly from molecular sieve, secondly from P_2O_5 and lastly from silica-gel and H_2SO_4 . These tubes were immersed for a given time in a water-bath kept at constant temperature. Tubes were taken from the water-bath according to the adjusted time durations and the resulting polymers were precipitated from methanol, filtered off and were dried in vacuum oven and tared from an analytical balance. From the tared polymers conversion percents were calculated according to the following equation:

$$\% \text{ Conversion} = \frac{W}{M} * 100$$

W : amount of the polymer obtained

M : amount of the monomer used

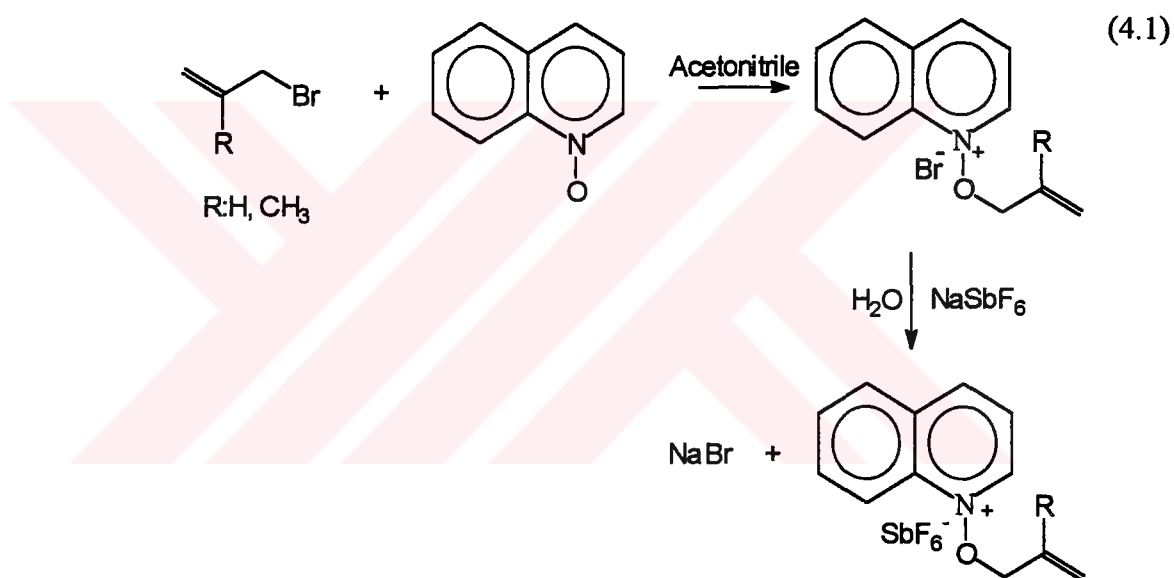
3.4.2. Photo Polymerization

Coinitiator (radical initiator), AFA and monomer were mixed in a pyrex tubes that were closed with a teflon stopcock after bubbling through with nitrogen gas which was passed through firstly from molecular sieve, secondly from P_2O_5 and lastly from silica-gel and H_2SO_4 . Photo polymerizations were performed with a merry-go-round type photo reactor. Tubes were taken from the photo-reactor according to the adjusted time durations and the resulting polymers were precipitated from methanol, and were filtered off and were dried in vacuum oven and tared from an analytical balance. From the tared polymers conversion percents were calculated by using the equation above.

RESULTS AND DISCUSSION

4.1. Synthesis of Allyloxy Isoquinolinium Salts

Synthesis was performed at room temperature according to the procedure given in Chapter 3. Resulting salts were analysed by elemental analysis and by H-NMR. (4.1) indicates applied general synthetic strategy.



4.2. Thermal Polymerization of Cyclohexeneoxide (CHO)

4.2.1. Polymerization in the Absence of Additional Radical Initiators

As seen in Figure 1 and Table 1, in the absence of additional radical initiators the polymerization of CHO takes place only at relatively high temperatures with

satisfactory yield. The efficiency in this mode of cationic polymerization is higher with MAI .

Table 1: Polymerization of CHO in the absence of Radical Initiators

Type of Salt	Time (min)	% Conversion
AI	90	8.4
MAI	90	10.57

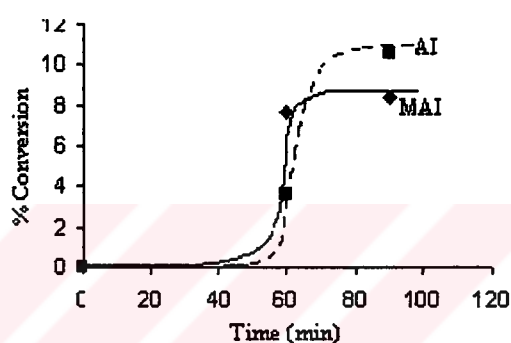


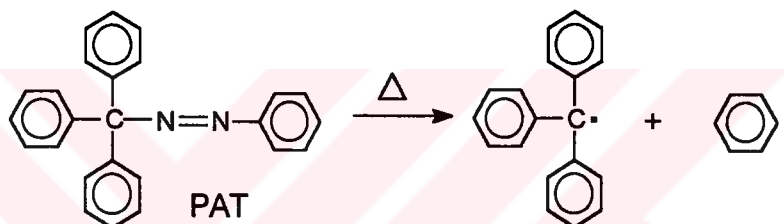
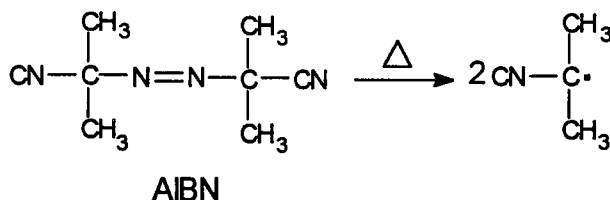
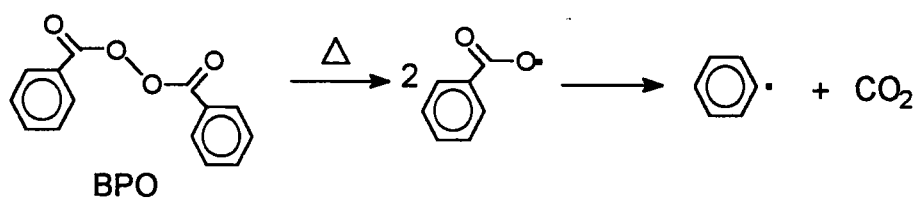
Figure 1 : Polymerization of CHO in the Absence of Radical Initiators

4.2.1.Effect of Added Radical Initiator

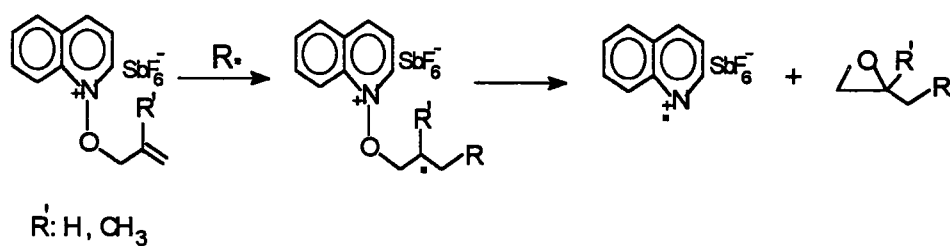
The time conversion curves for CHO polymerization at 70°C presented in Figure 2 and 3 clearly suggest that for all allyloxy isoquinolinium salts the addition of free radical initiator promotes the cationic polymerization. ((4.2),(4.3))

Radical Formation:

(4.2)



Radical addition-fragmentation $R^\bullet$ = Radicals produced from AIBN, (4.3)
BPO, PAT



The three radical initiators chosen, azobisisobutyronitrile (AIBN), benzoylperoxide and phenylazotriphenylmethane (PAT), show a slightly different

behavior. The polymerization rates differ as $\text{PAT} > \text{AIBN} \approx \text{BPO}$ according to the different radical forming capability. Notably, PAT shows the highest initiation efficiency in the combined system. For example decomposition rate constants being $1.1 \times 10^{-5} \text{ s}^{-1}$ (70°C), $3.12 \times 10^{-3} \text{ s}^{-1}$ (80°C), $1.62 \times 10^{-4} \text{ s}^{-1}$ (80°C) for BPO, PAT, AIBN respectively.

Table 2 : Thermal polymerization of CHO with allyloxy isoquinolinium salt using various radical initiators. $[\text{Radical Source}] = 5.10^{-3} \text{ mol l}^{-1}$, $[\text{salt}] = 5.10^{-3}$, $(\text{CHO}) = 1\text{ml}$

RadicalSource	Time (min)	% Conversion
none	90	10.57
AIBN	85	37.05
BPO	85	66
PAT	3	83.65

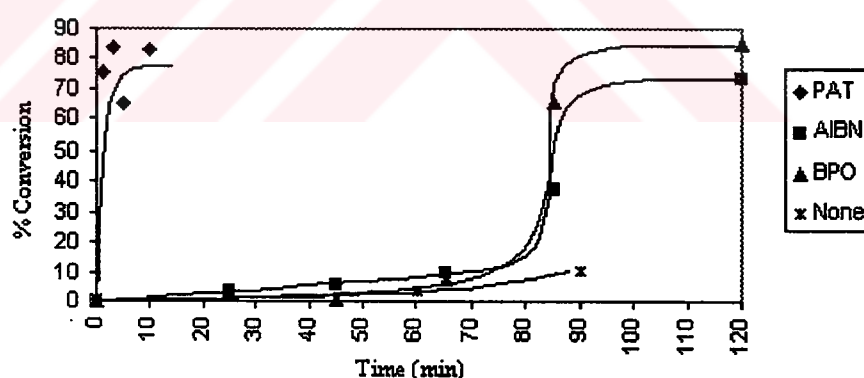


Figure 2 : Thermal Polymerization of CHO with various radical initiators using AI

Table 3 : Thermal polymerization of CHO with methylallyloxy isoquinolinium salt using various radical initiators. $[\text{Radical Source}] = 5.10^{-3} \text{ mol l}^{-1}$, $[\text{salt}] = 5.10^{-3}$, $(\text{CHO}) = 1\text{ml}$

Radical Source	Time (min)	% Conversion
none	90	8.4
AIBN	85	79.68
BPO	85	75.64
PAT	2	56.13

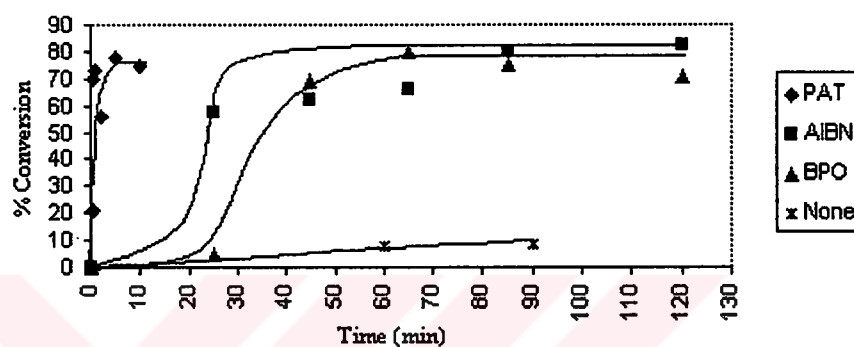


Figure 3: Thermal polymerization of CHO with various radical initiator using MAI

The effect of substituent on allylic moiety differs in polymerization rates. As seen in Figure 4, methyl substituent on allylic moiety reduces the induction periods in thermal polymerization of CHO. This effect was seen with all types of radical radical initiators. Also conversions differs with this substituent effect. As seen again in Figure 4, the conversion reaches above 80 % with allyl salt whereas about 70 % with methylallyl salt . This effect can be explained by the electron donating ability of $-CH_3$ group on allylic moiety makes N-O bond ruptures more difficult.

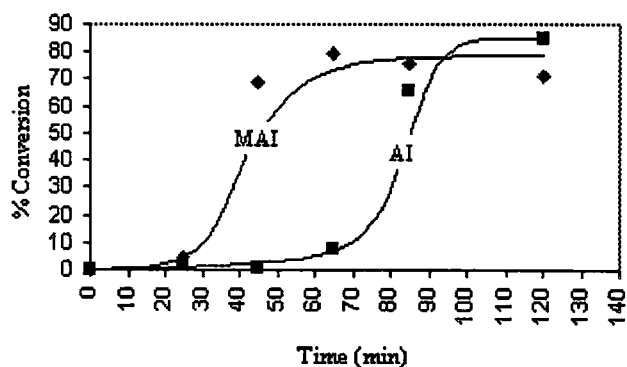


Figure 4 : Effect of Substituent on Allylic Moiety in Thermal Polymerization of CHO with PAT using both allyl and methyl allyl isoquinolinium salts.

4.3. Photo Polymerization of CHO

4.3.1. Excitation of the Isoquinolinium N-Oxide Moiety

The absorption spectra of allyloxy isoquinolinium salts show a $\pi-\pi^*$ absorption band with a maximum at c. 337 nm characteristic of isoquinolinium N-Oxide derivatives. The wavelength of incident light chosen in this study for directly exciting the isoquinolinium N-oxide moiety lies in that range (300-400 nm). The salt concentrations were adjusted to obtain identical optical density (O.D.) values in all experiments (O.D._{337nm} = 0.90). As Figure 5 shows fast polymerizations were found for all allyloxy isoquinolinium salts.

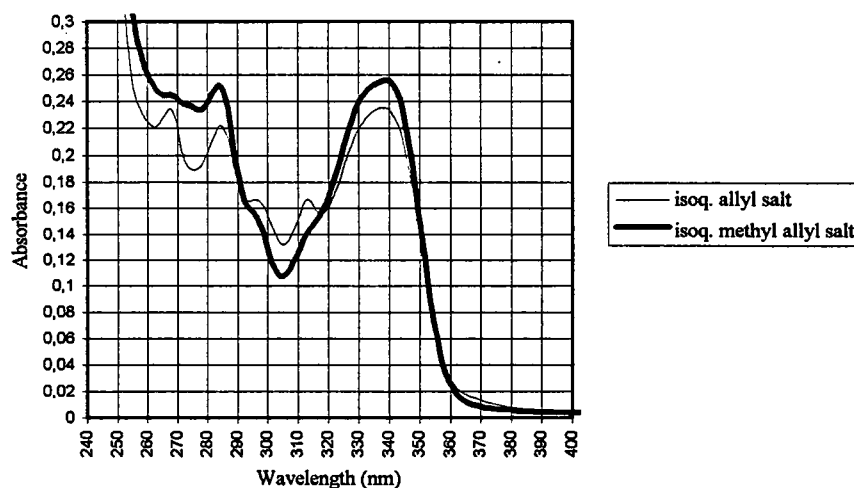


Figure 5 : Absorbance Spectrum of Allyloxy Isoquinolinium Salts

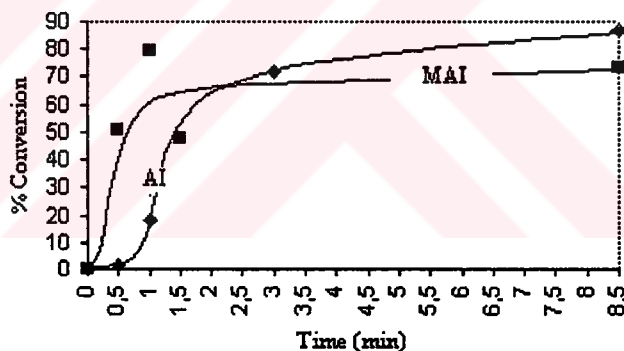


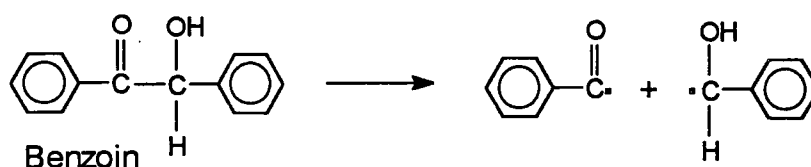
Figure 6 : Photo Polymerization of CHO using allyloxy Isoquinolinium Salts

4.3.2. Use of Additional Radical Type Photo Initiators

In photopolymerization with allyloxy salts, additional radical initiators may not only serve in improving the time conversion behavior, but also enable to use light of higher wavelengths for initiating the polymerization. As stated in the previous paragraph, if allyloxy isoquinolinium salts are to be excited directly, light of wavelength 337 nm has to be employed. With, benzoin as a radical initiator, light of

up to 400 nm can also be used. Figure 7 shows that with benzoin in conjunction with allyl isoquinolinium N-oxide salt CHO polymerizes very quickly. (4.4), (4.5) indicates the mode of action.

Radical Formation: (4.4)



Radical addition-fragmentation $\text{R}' = \text{Radicals produced from Benzoin}$ (4.5)

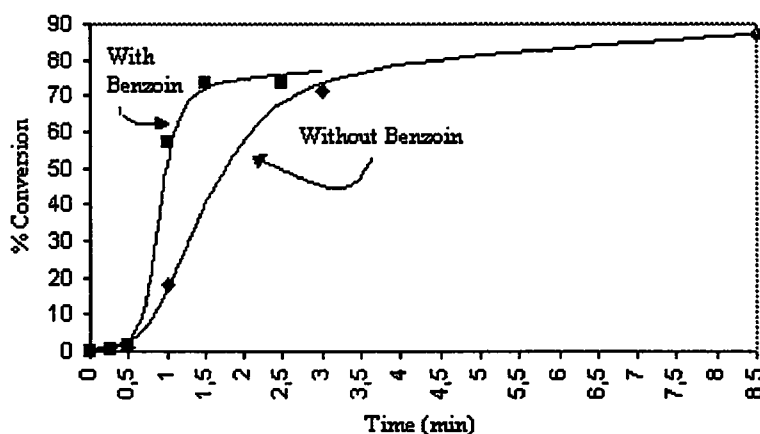
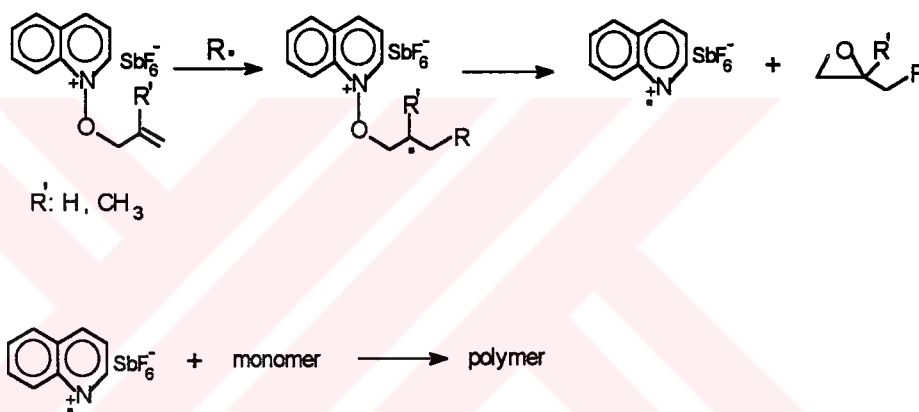


Figure 7 : Effect of Additional Radical Initiator

CONCLUSIONS AND SUGGESTIONS

In this study, allyloxy isoquinolinium salts were synthesized from the reaction allylbromide and 3-Bromo-2-methyl propene with isoquinolinium N-oxide effectively. These salts (AI^+ and MAI^+) were used in radical promoted cationic polymerization of CHO. High conversions were observed through this process.

Polymerization action was proceed through addition fragmentation principle in both radical promoted thermal and photo induced processes.

The three radical initiators chosen, azobisisobutyronitrile (AIBN), benzoylperoxide and phenylazotriphenylmethane (PAT), show a slightly different behavior. The polymerization rates differ as $PAT > BPO \approx AIBN$ according to the different radical forming capability.

In the absence of additional radical initiators the polymerization of CHO takes place only at relatively high temperatures with satisfactory yield. The efficiency in this mode of cationic polymerization rises in order $MAI^+ > AI^+$. Methyl substituent on allylic moiety reduces the induction periods in thermal polymerization of CHO. This effect was seen with all types of radical initiators. Also conversions differs with this substituent effect.

In photopolymerization with allyloxy salts, additional radical initiators may not only serve in improving the time conversion behavior, but also enable to use light of higher wavelengths for initiating the polymerization. The spectral shift thus achieved may particularly be useful in pigmented formulations where titanium dioxi pigments absorb the light around 300 nm region.

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