

**A NOVEL BIFUNCTIONAL ADDITION
FRAGMENTATION AGENT FOR PHOTOINITIATED
CATIONIC POLYMERIZATION**

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**FOTOBASLATICILI KATYONİK
POLİMERLEŞMEDE BİFONKSİYONEL KATILMA
BÖLÜŞME MEKANİZMALARI**

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ABBREVIATION

AFA	: Addition Fragmentation Agent
BDMP	: 2-Benzyl-2-Dimethylamino-1- (4-Morpholinophenyl)-Butane-1-one
I	: Initiator
M	: Monomer
R.	: Radical
C ⁺	: Cation
C ⁻	: Anion
C ⁺ .	: Radical Cation
¹ H-NMR	: Proton Nuclear Magnetic Resonance
CT	: Charge Transfer
NVC	: N-Vinyl carbazole
CHO	: Cyclohexene oxide
BVE	: n-Butyl vinyl ether
O.D	: Optical Density
AIBN	: 2,2'-Azobisisobutyronitrile
BPO	: Benzoyl Peroxide
PAT	: Phenyltriphenylazo-Methane
On ⁺	: Onium Salt
S [*]	: Sensitiser
E (S [*])	: Energy of Sensitiser
E (I [*])	: Energy of Initiator
MMA	: Methyl Methacrylate
λ	: Wavelength
h ν	: Light
Δ	: Heat
UV	: Ultra-Violet
THF	: Tetrahydrofuran
M _n	: Number of average molecular weight

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A NOVEL BIFUNCTIONAL ADDITION-FRAGMENTATION AGENT FOR PHOTOINITIATED CATIONIC POLYMERIZATION

SUMMARY

In this study addition-fragmentation (AFA) agent, namely 2-benzyl-2-(N,N-dimethyl-2-ethoxycarbonyl-1-propenyl) ammonium hexafluoroantimonate-1-(4-morpholinophenyl)-butane-1-one, for photoinitiated cationic polymerization was synthesized and characterized. With this compound, it is possible to initiate the cationic polymerization of cyclohexene oxide (CHO), n-butyl vinyl ether (BVE), and N-vinyl carbazole (NVC) photochemically. In previous studies addition-fragmentation agents were used with an additional free radical source e.g. Phenylisotriphenylmethane (PAT), 2,2 azobisisobutyronitrile (AIBN) for the cationic polymerization of CHO, BVE, NVC. In contrast to previous AFA agents this α -amino alkyl phenone salt (AFA) does not need any additional free radical source. On the basis of addition-fragmentation mechanism, this compound was expected to be appropriate for generation of both radical and subsequent radical cations since it structurally contains both photochromophoric and allylic groups. The mechanism involves the formation of radicals from alkylphenone moiety and addition of these radicals to the allylic site and fragmentation of the AFA. Cationic polymerisation of CHO was studied via addition-fragmentation mechanism by using this salt. The relationship between time with conversion and concentration with conversion were analysed. In order to understand free radical capacity of this AFA reagent, it was used for methyl methacrylate (MMA) polymerization. Free radical capacity was decreased when AFA agent was used as an initiator. The reason is that AFA salt act as both radical source and addition-fragmentation mechanism. The addition-fragmentation reactivity of this AFA salt was compared with different allyl-onium salt and higher efficiency was observed.

FOTOBASLATICILI KATYONİK POLİMERLEŞMEDE BİFONKSİYONEL KATILMA BÖLÜŞME MEKANİZMALARI

ÖZET

Bu çalışmada fotokimyasal katyonik polimerleşmede kullanılan katılma-bölüşme reaktifi (KBR), 2-benzil-2-(N,N-dimetil-2-etoksikarbonil-1-propinil) amonyum hekzafloroantimonat-1-(4-morfolinofenil)-butan-1-on, sentezlenmiş ve siklohekzin oksit (CHO), n-butil vinil eter (BVE) ve N-vinil karbazol (NVC) monomerlerinin katyonik polimerlerizasyonunda fotobaslatıcı olarak kullanılmıştır. Elde edilen bu tuzun, aydınlatıldığında katılma-bölüşme reaktiflerinin bölünme mekanizmalarına benzer bir şekilde parçalanarak radikal ve radikal katyon oluşturduğu gözlenmiştir. Oluşan radikalin, tuzun allilik kısmına katılmasını takiben bölüşme reaksiyonu gerçekleşir. Gurubumuz tarafından daha önce sentezlenmiş olan katılma-bölüşme reaktifleri, Fenilazotriphenilmetan (FAT), 2,2-azobisisobutironitril (AIBN), gibi ikinci bir radikal başlatıcı varlığında CHO, BVE, NVC gibi monomerlerin katyonik polymerizasyonunda başlatıcı olarak kullanılmıştır. Bu çalışmada ise α - amino yapıda sentezlenen (KBR) tuzun hiçbir ekstra başlatıcıya gerek duyulmadan katılma bölüşme mekanizmaya göre katyonik olarak polimerleşebilen monomerlerin fotokimyasal polimerizasyonunu başlattığı gözlenmiştir. Bunun sebebi bu reaktifin hem fotokimyasal olarak bölünebilen hemde allilik gurup bağlarını aynı yapıda içermesine bağlıdır. Sentezlenen reaktifin CHO monomerinin polimerizasyonunda zaman-dönüşüm eğrileri oluşturulmuş ve ayrıca tuz konsantrasyonunun polimer üzerindeki etkisi incelenip konsantrasyon-dönüşüm eğrileri çıkarılmıştır. Sentezlenen tuzun fotokimyasal radikalik polimerleşme üzerindeki etkisi metil metakrilat (MMA) monomeri üzerinde denenmiş ve fotokimyasal radikalik polimerleşmede azalma olduğu görülmüştür. Tuzun katılma-bölünşe reaktivitesi başka allil onyum tuzları ile karşılaştırılmış ve daha iyi verim verdiği gözlenmiştir.

1. INTRODUCTION

During the past several decades photoinitiated polymerization has received considerable attention and practically applied in variety of areas including printing inks, adhesives, surface coating, microelectronics and printing plates [1]. Photoinitiated polymerization can be performed via radical and cationic mechanism. Much effort have been devoted to free radical systems mainly due to the availability of wide range of photoinitiators and the great reactivity of acrylate- based monomers. Among the many photoinitiators, recently developed α -aminoalkylphenone [2]. derivatives are particularly useful in application where irradiation at long wavelengths is crucial. On the other hand many technologically important monomers such as vinyl ethers and oxiranes polymerizes only by a cationic mode which has been the main reason for the development of cationic photoinitiators [3]. Among these, recently developed allyl-onium salts initiate via addition-fragmentation mechanism [4].

In order to make allyl-onium salts able to initiate cationic polymerization, they have to be reacted with free radicals such as AIBN, PAT, and BPO [3]. In this study an addition- fragmentation reagent, 2-benzyl-2-(N,N-dimethyl-2-ethoxycarbonyl-1-propenyl) ammonium hexafluoroantimonate-1-(4-morpholinophenyl)-butane-1-one, for photoinitiated cationic polymerization was synthesized and used as AFA reagent for polymerization of cationically polymerizable monomers, for example cyclohexene oxide (CHO), n-butyl vinyl ether (BVE), N-vinyl carbazole (NVC).

In contrast to monofunctional AFA salts, this α -amino alkylphenone type AFA reagent does not need any additional radical source. The reason may attribute to its structure since it has contained both photochromophoric and allylic site together.

2. POLYMER AND POLYMERIZATION

2.1. General Definition of Polymer

Polymers are macromolecules built up by the linking together of large numbers of much smaller molecules. The smaller molecules that combine with each other to form polymer molecules are termed monomers, and the reactions by which they combine are termed polymerization. There may be hundreds, thousands, tens of thousands, or more monomer molecules linked together in a polymer molecule [5].

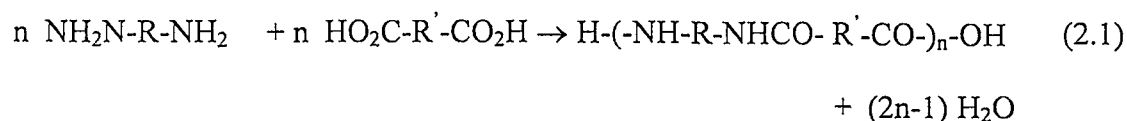
2. 2. Types of Polymers and Polymerization

During the development of polymer science, two types of classifications of polymers have come into use. One classification divides polymers into condensation and addition polymers, and the other divides them into step and chain polymers. The terms condensation and step are used synonymously as are the terms addition and chain.

2. 2. 1. Condensation Polymerization

Condensation polymers are those polymers that were formed from polyfunctional monomers by the various condensation reactions of organic chemistry with the elimination of some small molecule such as water [6]. Another property of condensation polymer is that, polymers whose repeating units are joined together by functional units such as ester, amide, urethane, sulfide, and ether linkages.

An example of such a condensation polymer is the polyamides formed from diamines and diacids with the elimination of water according to



Where R and R' are aliphatic or aromatic groupings. The composition of the repeating unit differs from that of the two monomers by the elements of water. Many of the condensation polymers there are different combinations of reactants that can be employed for their synthesis. All condensation polymerization fall into two groups depending on the type of monomer(s) employed.

The first involves two different bifunctional and / or polyfunctional group. This reaction can be represented by the equation:



The second involves a single monomer containing both types of functional groups. This reaction can be represented by the equation:



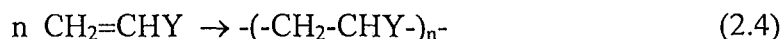
The characteristics of these two polymerization reactions are very similar.

2.2.2. Addition Polymerization

In contrast to condensation polymerization, addition polymerization are formed from monomers without the loss of a small molecule and the repeating unit of an addition polymer has the same composition as the monomer. Addition polymers do not contain functional groups as a part of the polymer chain. Unlike condensation polymerization, in chain polymerization where full-sized polymer molecules are produced almost immediately after the start of the reaction.

The major addition polymers are those formed by polymerization of monomers containing the carbon-carbon double bond. The existence of an active site (carbon-carbon double bond) which is capable of attacking a monomer molecule to have it linked to the chain, whereby the active site is restored at chain end. Vinyl

monomers can be made to react with themselves to form polymers by conversions of their double bonds into saturated linkages, for example:

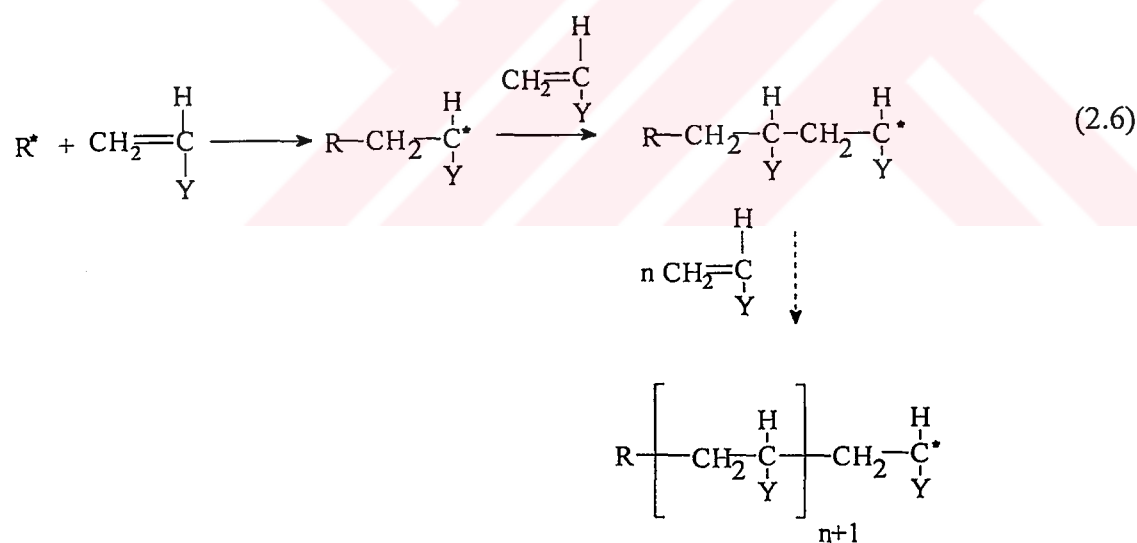


Where Y can be any substituent group such as hydrogen, alkyl, aryl, nitrile, ester, acid, ketone, ether, and halogen.

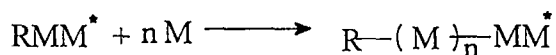
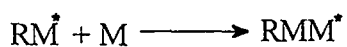
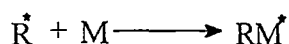
Chain polymerization is initiated by a reactive species R^* produced from some compound I termed an initiator.



The reactive species (R^*), which may be a free radical, cation, or anion, adds to a monomer molecule by opening the π -bond to form a new radical, cation, anion centre, as the case may be. The process is repeated as many more monomer molecules are successively added to continuously propagate the reactive centre.



Polymer growth is terminated at some point by destruction of the reactive centre by an appropriate reaction depending on the type of reactive center and the particular reaction conditions. The addition reactions can be represented by the equations:



I: initiator

$R^{\bullet}$: reactive species (radical, cation, and anion)

M: monomer

The addition polymerization can be divided into three categories according to reactive species $R^{\bullet}$ and monomer supply.

1- Free radical chain polymerization

2- Cationic polymerization

3- Anionic polymerization

2. 2. 2. 1. Free Radical Chain Polymerization

Almost all monomers containing carbon-carbon double bond undergo free radical polymerization. Free radical chain polymerization is initiated by a reactive species $R^{\bullet}$ produced from some compound I termed an initiator.



The reactive free radical species adds to a monomer molecule by opening π -bond to form a new radical. This process is repeated as many more monomer molecules are successively added to continuously propagate the reactive centre.

Free radical chain polymerization is a chain reaction consisting of a sequence of three steps-initiation, propagation, and termination.

Initiation: The initiation step is considered to involve two reactions. The first is the production of free radicals by anyone of a number of reactions. The homolytic dissociation of an initiator or catalyst species I to yield a pair of radicals $R^{\bullet}$.

These radicals are formed either by heating or irradiation.



K_d is the rate constant for catalyst (I) dissociation

The second part of the initiation involves the addition of this radical to the first monomer molecule to produce the chain initiation species M_1 .



M: Monomer

K_i : Rate constant for initiation

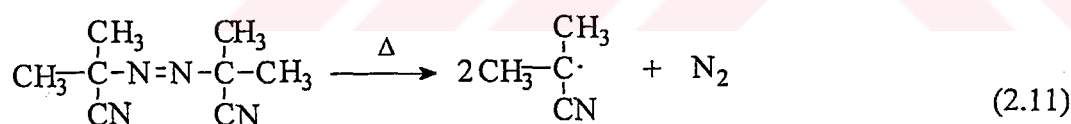
$\dot{R}$: Initiator radical or primary radical

Most commonly used free radical initiators are:

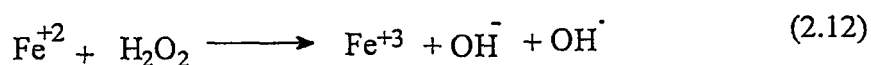
Peroxides: organic or inorganic: dibenzoyl peroxide, potassium peroxodisulfate, hydrogen peroxides.

Peresters: t-butyl perbenzoate

Alifatic azocompounds: azobisisobutyronitrile (AIBN)



Oxidation reduction processes:



Propagation: Propagation consists of the growth of M_1 by successive addition of large numbers (hundreds, thousands) of monomer molecules. Each addition creates a new radical, which has the same identity as the one previously, except that it is larger by one monomer unit.

The propagating can be represented:



In general



K_p is the rate constant for propagation in the range of $10^2 - 10^4$ liters /mol-sec.

Therefore high rate high polymer proportions obtained in this step.

Termination: Propagating polymer chains stops growing and terminated. Termination with the annihilation of the radical centers occurs by bimolecular reaction between radicals. Two kinds of termination occur:

a) Combination (coupling): Two radicals react with each other.



K_{tc} is the rate constant for coupling termination

b) Disproportionation: In which a hydrogen atom is transferred from one chain to the other. The result is the formation of two polymer molecules –one saturated and one unsaturated.



K_{td} is the rate constant for disproportionation termination

Typical termination rate constants are in the range of $10^6 - 10^8$ liter /mol-sec.

In both terminations reaction radical is destroyed. Termination reaction occurs so fast

that these two process can not be distinguished but their results concern the molecular weight and polydispersity of polymer formed are different.

2. 2. 2. 2. Cationic Polymerization

Most cationic polymerizations are chain polymerizations involving positively charged electrophilic active centers at the growing chain end.[7] Polymerization mechanisms are classified as either chain growth or step growth. In addition to cationic chain polymerization, there are also cationic step polymerizations involving coupling and Friedel- Craft reactions. Both alkenes and heterocyclic monomers can be polymerized cationically. The two systems differ in that the active species in the polymerization of alkenes are carbenium-ions, whereas onium-ions are the active species in the polymerization of heterocycles. However, there are more similarities between the two systems than differences.

Cationic polymerizations are used in industry for the synthesis of butyl rubber (a copolymer of isobutane and isoprene), for various ring-opening polymerizations (oxolane, trioxane), and for adhesive materials. Cationic photoinitiator, producing protonic acids upon irradiation, can also be used for imaging systems, containing dyes which change colour, as a function of pH of the environment. Living cationic polymerizations recently have been developed in which polymers with controlled molecular weights and narrow polidispersity can be prepared.

Similarly free radical chain polymerization, cationic chain polymerizations involve four elementary reactions of initiation, propagation, transfer and termination. Unlike the free radical chain polymerization, solvent is required in cationic polymerizations to control the heat that generated. In most cases, an exothermic polymerization ensues immediately a mixing the monomer and initiation. Therefore, it is difficult to obtain good homogeneous mixing of the monomer and the initiator before polymerization commences. In cationic polymerizations, monomer is mixed typically with a solution of the cationic initiator at ambient temperature; initiation is thus first order in monomer and first order in initiator. In contrast, a radical initiator is generated in situ by homolytic cleavage of weak chemical bonds using either heat, light, or high energy irradiation; radical initiation is thus zero order in monomer. Because solvent is the component present in the highest concentration in most

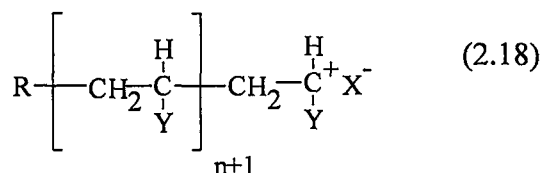
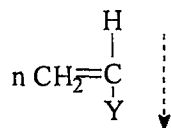
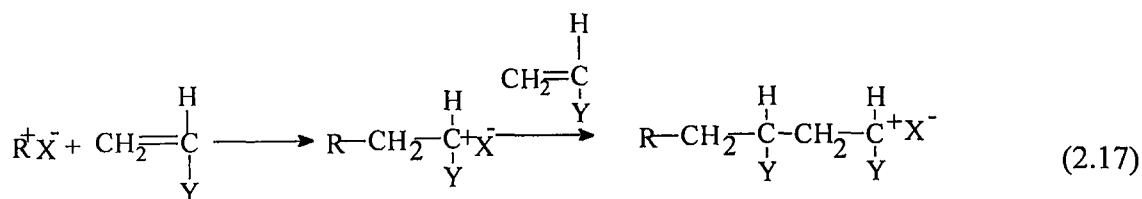
cationic polymerizations, solvent that either terminate the active site or that act as chain transfer agents must be avoided.

Termination is generally occur in cationic polymerizations by unimolecular collapse of the ion pair or by reaction with impurities and / or terminated agents. Termination sometimes occurs by formation of highly delocalized and therefore unreactive carbocations. However termination can be avoided in cationic polymerization under appropriate conditions. If both transfer and termination are absent as in some cationic polymerization, the polymerization is living.

An important feature of cationic polymerization is the use of acids possessing anions of very low nucleophilicity, which do not terminate the polymerization process. Therefore, most cationic photoinitiators are based on salt of non-nucleophilic anions such as BF_4^- , PF_6^- , AsF_6^- , and SbF_6^- . In general, for photoinduced cationic polymerizations with both onium and metal salts, molecular weights and percentage conversions increase in the order $\text{BF}_4^- < \text{PF}_6^- < \text{AsF}_6^- < \text{SbF}_6^-$ [8].

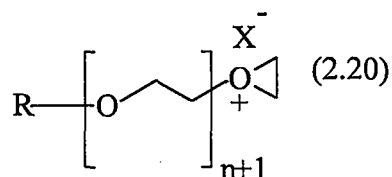
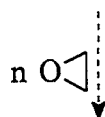
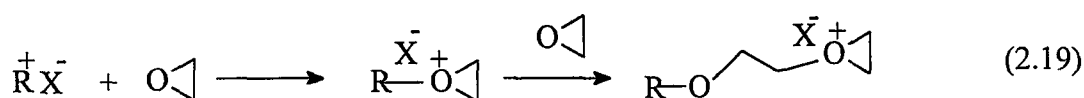
Vinyl polymerization:

For a vinyl monomer to polymerize, it must contain a substituent capable of stabilizing the resulting active species. Therefore, most 1- substituted alkenes undergo facile radical polymerizations (although α -olefins do not), whereas an electron donating substituents is required to motivate the olefins to cationic initiation and propagation. Typical vinyl monomers for cationic polymerization are vinyl ester, N-vinylcarbazole, styrenes and 1,1-disubstituted alkenes such as isobutylene and α -methylstyrene



Heterocyclic monomer polymerization:

Heterocyclic monomers, ie. cyclic compounds containing one or more (identical or different) heteroatom (O, S, N, P) within the ring. Cationic polymerization proceeds by a ring opening reaction. Similarly vinyl polymerization, heterocyclic polymerization process proceeds an electron –deficient active species: cations or species with a partial positive charge. Thus, propagation in both cases involves attack of the nucleophile (double bond or heteroatom) an electrophilic active centers.

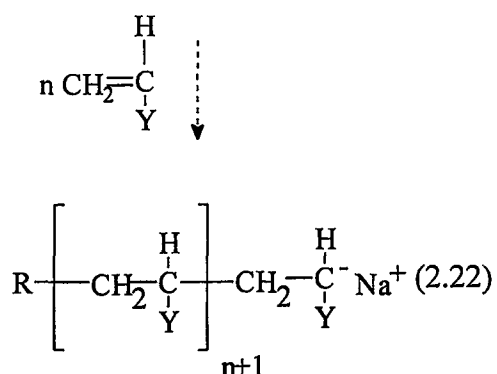
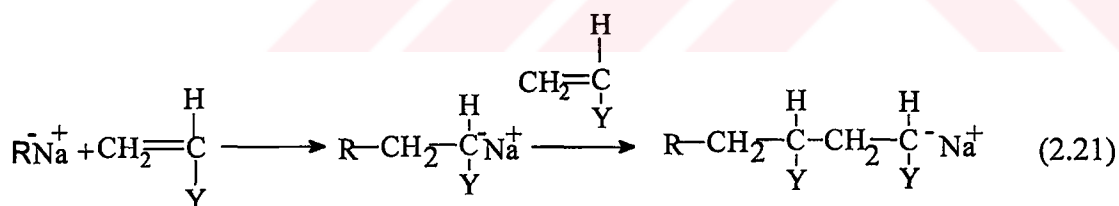


The difference between vinyl and ring opening cationic polymerization is that: polymerization of vinyl monomers leads to polymers having all carbon chains however polymerization of heterocyclic monomers give polymers containing heteroatoms within the main chain. Because there are several possible combinations within the cyclic monomer molecule, ring-opening polymerization allows the

preparation of polymers with various sequences of carbon atoms and heteroatoms within the main chain. Cations of the vinyl monomer give carbenium ions, whereas cationation of heterocyclic monomer results in onium ion. The vinyl polymerization is essentially carried out on carbenium active species whereas ring-opening polymerization is carried out on onium active species. The reactivity of onium is much lower than the reactivity of carbenium ions since various side reactions (leading transfer and termination) are much easier in ring opening polymerization. Another important difference is that the nucleophilic site of vinyl monomer, ie. double bond is consumed in propagation step, whereas the nucleophilic site of the heterocyclic monomer, ie., heteroatom, is still in the formed chain.

2. 2. 2. 3. Anionic Polymerization

Monomers in two broad classifications are amenable to anionic polymerization: vinyl, diene, and carbonyl- type monomers with difunctionality provided by one or more double bonds; and cyclic (eg. heterocyclic) monomers with difunctionality provided by a ring that can open by reaction with nucleophiles. For anionic polymerizability it is generally considered that there must be substituents on the double bond that can stabilize the negative charge that develops in the Transition State for the monomer addition step[9].



These substituents must also be stable to the reactive anionic chain ends; thus, relatively proton donating groups (eg. amino, hydroxyl, acetylene functional groups)

or strongly electrophilic functional groups that react with bases and nucleophiles must be present or must be protected by conversion to a suitable derivative. In general, substituents that stabilise negative charge by anionic charge delocalisation are the substituents that render vinyl monomers polymerizable by an anionic mechanism. Such substituents include aromatic rings, double bonds, carbonyl, ester, cyano, sulfoxide, and sulfonyl and nitro groups. Monomers with polar substituents such as carbonyl, cyano, and nitro groups often undergo side reactions with initiators and propagating anions; therefore, controlled polymerization to provide high-molecular-weight polymer is not always possible.

Cationic and anionic polymerization have many similar characteristics. Both depend on the formation and propagation of ionic species, a positive one in one case, and a negative one in the other. The formation of ions with sufficiently long lifetimes for propagation to yield high molecular-weight products generally requires stabilisation of the propagating centers by solvation. Consequently low or moderate temperatures are also needed to suppress termination, transfer and other chain-breaking reactions which destroy propagating centers.

A variety of basic (nucleophilic) initiators have been used to initiate anionic polymerization. These include covalent or ionic metal amides such as NaNH_2 , $\text{LiN}(\text{C}_2\text{H}_5)_2$, alkoxides, hydroxides, cyanides, phosphines, amines and organometallic compounds such as $n\text{-C}_4\text{H}_9\text{Li}$ and PhMgBr .

2. 3. Principles of Photochemistry

Photochemistry is the study of chemical reactions produced by light. Absorption of a photon of light may raise a molecule to an excited electronic state, where it will be more likely to undergo a chemical reaction than in the ground electronic state. In photochemical reactions, the activation energy is supplied by absorption of light. However in thermal reactions the activation energy is supplied by intermolecular collisions. UV or visible lights initiate photochemical reactions [10].

In a photochemical reactions a photon is absorbed to commence the reaction that the excited state can then undergo a variety of transitions, which can be classified as photophysical and photochemical process. Photophysical process do not produce

new chemical compounds, however photochemical reactions produce new chemical species which are different from the starting materials.

The absorption of light by a molecule and the subsequent evolution of its excited states are usually pictured by well-known Perrin-Jablonski diagram. Photophysical process consist of:

1) Radiative processes:

a) Absorption of a photon by a molecule in its ground electronic state.

b) Emission of a photon form an electronically excited state

1. Fluorescence (F)

2. Phosphorescence (P)

2) Nonradiative Processes:

a) Internal conversions (IC)

b) Intersystem crossing (ISC)

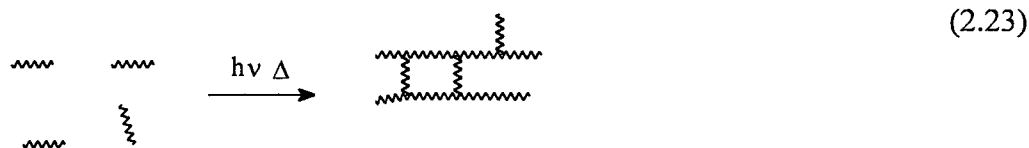
The photochemical processes that result in a transformation of the starting molecule (eg. throughout cleavage processes, electron transfer reactions, hydrogen abstraction reactions, isomerizations, rearrangements, cycloadditions, etc.) often take place in triplet state (T) and to the lesser extend, in singlet state (S). S_0 , S_1 , S_n , or T_1 , T_2 are electronic states where the molecule possesses all paired electrons or two unpaired electrons, respectively.

2. 4. Photo Initiated Polymerization

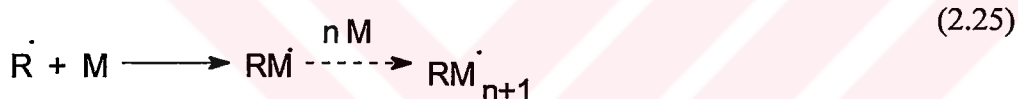
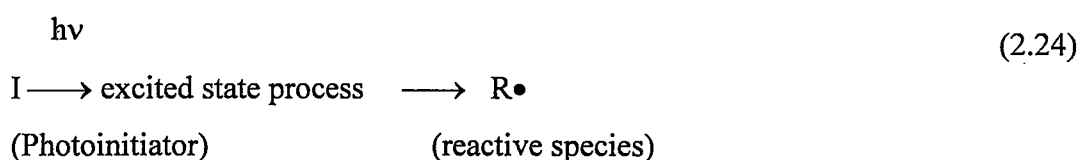
A photoinitiator is a molecule (usually organic) employed alone or in a chemical system (involving two or more molecules) that absorbs light and forms reactive initiating species; radicals, H^+ , or cationic radicals. A coinitiator is a part of the chemical system that does not absorb light but participates in the production of the reactive species. A photosensitiser is defined as a molecule that is able to absorb light and transfer the excitation to another molecule that will be used as a photoinitiator.

The starting materials, will be used for polymerization, are liquid materials that have to be cured usually consist of monomers, oligomers, or prepolymers.

They polymerise and/ or crosslink upon light exposure. Photocrosslinking relates to the formation of crosslinks between two macromolecular chains.



Since most monomers, oligomers, or prepolymers commonly employed do not produce initiating species, it is necessary to introduce low molecular-weight organic molecule (called “photoinitiators (I)”) that will start the polymerization.



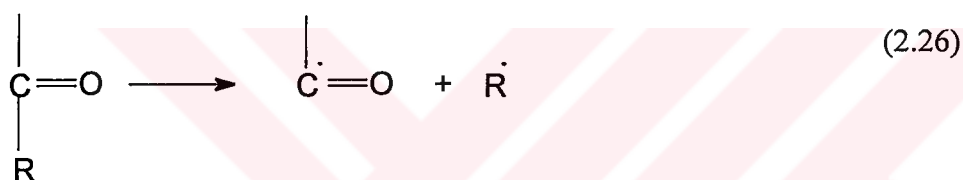
A photoinduced polymerization reaction is usually considered as a chain reaction where the initiation step is produced by photochemical event (ie. a radical chain reaction). The role of photoinitiator is to convert the physical energy of incident light into chemical energy in the forms of reactive intermediates. These intermediates are either radical capable of adding to vinylic or acrylic double bonds, thereby initiating radical polymerization or reactive cationic species, which can initiate cationic polymerization.

Photochemical or photoinitiated polymerizations occur when UV and visible light irradiation of a reaction system produce radicals. In general light absorption results in radical production by either of two ways: First some compound in the system undergoes excitation by energy absorption and subsequent decomposition into radicals. Second some compounds undergoes excitation and the excited species interacts with a second compound (by either energy transfer or redox reaction) to form radicals derived from the latter and/ or former compounds.

The absorbing molecule must have a chromophore, which strongly absorbs at the wavelengths or some of the wavelengths of irradiation. However radiation of certain wavelengths will result in excitation events. Therefore, photoinitiators and/or photosensitizers must be selected so that they are absorbing at wavelengths, which are not absorbed by another components in the formulation.

2. 4. 1. Photoinitiated Radical Polymerization

Excited processes play a key role in the design of efficient photoinitiators [11]. The primary process occurring in the excited states of a UV radical photoinitiator and stresses the fact that the transient state responsible for the generation of radicals is mainly the triplet state. Photoinitiators sensitive to UV radiation are usually built on carbonyl group (benzoyl chromophore) which exhibits a good absorption in this wavelength range and a good photochemical reactivity.



This carbonyl group exhibits two kinds of electronic transitions:

Singlet state:



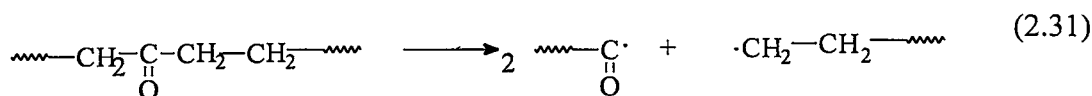
Triplet state:



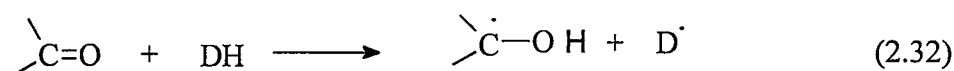
Optical electronic transitions obey the selection rule which state that such $n \rightarrow \Pi^*$ are symmetry forbidden and $\Pi \rightarrow \Pi^*$ transitions symmetry allowed.

The photochemical routes that are productive for radicals include:

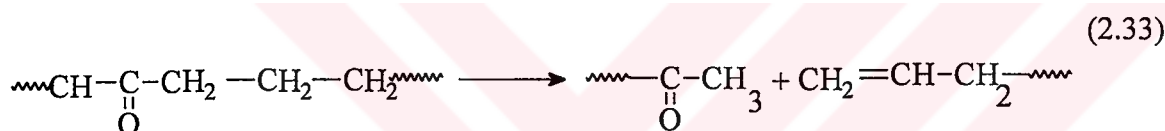
- 1- Photocission (or cleavage) reactions: mostly α -cleavage (Norrish I) or β cleavage.



- 2- Intermolecular Hydrogen abstraction (only for $n \Pi^*$ triplet state):



- 2- Intermolecular γ hydrogen abstraction (Norrish II)



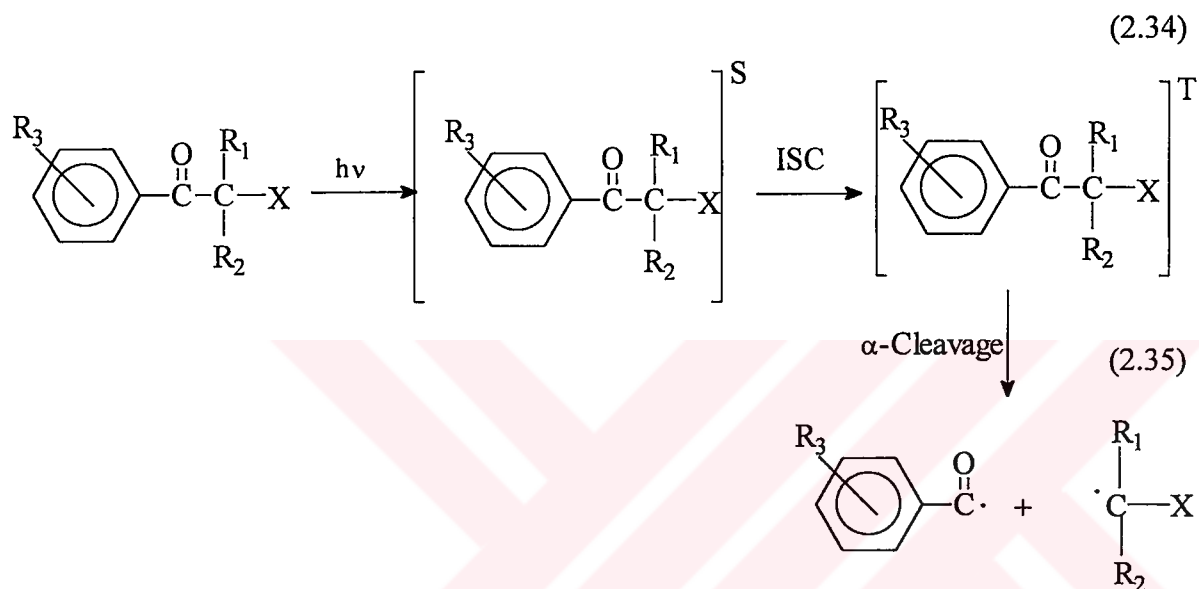
- 4- Electron transfer followed by proton transfer

2. 4. 1. 1. α -Cleavage Type Photoinitiated Radical Polymerization

If a photoinitiator contains a bond with dissociation energy lower than that of the excited state, then the bond dissociate forming a reactive species. This is termed direct fragmentation or homolytic scission. Both cationic and free radical photoinitiators can undergo this mechanistic pathway. However, the bond dissociation energy must not be so low that the bond readily fragments at the temperature to which an initiator is usually exposed. Thus, the photoinitiators must have good thermal stability.

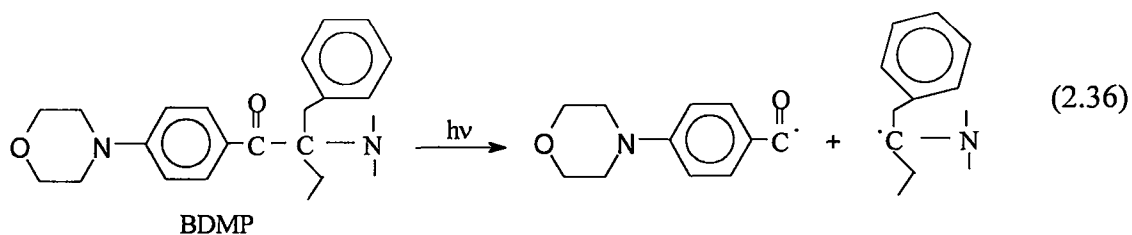
The photoinduced α -cleavage reaction of alkylaryl ketones usually occurs from the lowest $n\pi^*$ triplet state, which is more reactive in the α -cleavage reaction than the singlets state. After absorption of light by initiator, intersystem crossing from the singlets to triplet takes place. Two factors determine the rate of α -cleavage reactions from the lowest Triplet State. First, the configuration of the excited state.

Triplet states possessing an $n\pi^*$ configuration are much more reactive than $\pi\pi^*$ states. Second the type of substituents at the α -position. The higher substituted molecules undergo a faster α -cleavage reactions. In addition, substituents capable of stabilising a positive charge on the α -carbon greatly enhance the rate of cleavage. Therefore most unimolecular photoinitiators are alkylaryl ketones carrying one or more heterosubstituents, such as oxygen, nitrogen, and positively aromatic substituents at α -position.



α -Aminoacetophenone derivatives are the most recent type of α -cleavage photoinitiators commercially available. The most versatile derivatives are substituted at the 4-position on the benzoyl moiety by strong electron donating substituents, such as alkylthio or dialkylamino groups. This feature induces a red shift of the main absorption band into the region above 300nm, with the end absorption reaching for into the near UV or even visible range of spectra. Since their initiating efficiency is very high, they have found widespread use in systems such as printing inks, white lacquers, resist applications and printing plates.

Commercially available α - amino photoinitiator shown below was used in this project.

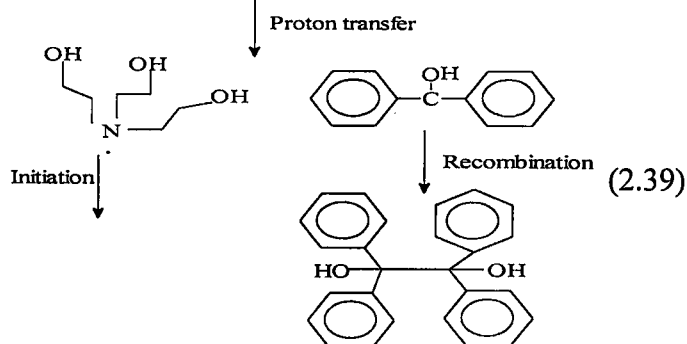
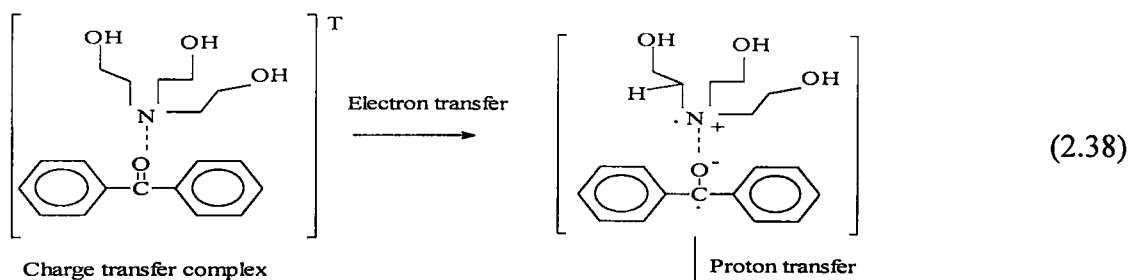
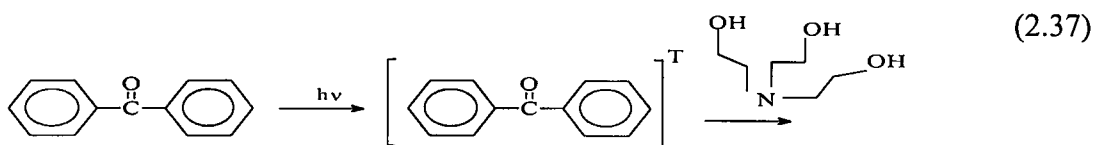


2. 4. 1. 2. Hydrogen Abstraction Type Photoinitiated Radical Polymerization

Not all excited carbonyl compounds will undergo a unimolecular fragmentation reaction. (Norrish I, or α -cleavage). Diaryl ketones, as example, do not have a α -bond suitable for homolytic cleavage. However, diaryl ketones have another reaction pathway, which produces radicals useful for the initiation of polymerization in a bimolecular process.

It is possible for some aromatic ketones to form free radicals by abstracting a hydrogen atom from another type of molecule present in the system and they are frequently called hydrogen abstracters. These initiators react with many types of hydrogen donor (coinitiators) to give products in which the carbonyl group is reduced to alcohol. Two different reaction pathways are known to lead to reduction products, either hydrogen abstraction from hydrogen donating compound by the excited state ketone or electron transfer from a suitable electron donor to the excited ketone, followed by a proton transfer.

Various types of compounds (alcohols, ethers, thiols, and amines) can react with excited ketone in photoreduction.



2. 4. 2. Photoinitiated Cationic Polymerization

Most cationic polymerizations are chain polymerizations involving positively charged or electrophilic active centers at growing chain end. Both alkenes and heterocyclic monomers can be polymerized cationically [12]. The two systems differ in that the active species in the polymerization of the alkenes are carbenium-ions, whereas onium are the active species in the polymerization of heterocycles. Cationic photoinitiator, producing proton acids upon irradiation, can also be used for imaging systems, containing dyes with charge colour, as a function of the pH of the environment. Many technologically important monomers such as vinyl ethers and oxiranes polymerizes only by a cationic mode which has been the main reason for development of the cationic photoinitiators.

Some properties of cationic photoinitiators are:

- 1- The compound must process chromophores, which permit the absorption of UV or visible light.
- 2- Upon excitation, the compound must undergo some photochemical transformation.

- 3- The photoreaction should occur with high quantum efficiency.
- 4- The photoinitiator should be easy to handle and sufficiently soluble in ink.
- 5- The photoinitiator should be odourless and nontoxic.

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

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

2-Due to the instantaneous initiation, on adding the initiator, a significant evolution of heat is often observed. Therefore, one has to work at relatively low temperature, which leads to relatively low polymerization rates.

2. 4. 2. 1. Onium Salts

Onium salts are the most widely used cationic photoinitiators. These salts are compounds containing heteroatoms, with cationic centers on the heteroatoms. As counter ions, 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. The onium salts can be classified as direct or indirect photolysis [3].

2. 4. 2. 1. 1. Direct Photolysis

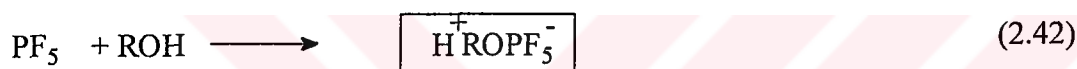
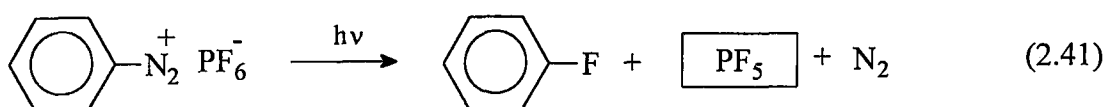
If onium salt initiators, I , absorb light, electronically excited initiator, I^* , species are produced. The latter undergo a heterolytic or homolytic bond rupture leading to cations C^+ or radical cations $C^{\cdot+}$, respectively.



Both C^+ and C^{+} are often react with the monomer or solvent molecules thus releasing the Brönsted acid H^+ . Being highly reactive to all sorts of cationically polymerizable monomer, proton will act as initiating species in these circumstances.

Aryldiazonium salts:

Aryldiazonium salts can be prepared by treatment of aniline derivatives with sodium nitrate and Brönsted acid, the latter 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 polymerization mixture yielding protons[13].



Simple benzyldiazonium salts absorb light only below 300nm. By substituting the benzene ring, salts absorbing near ultra-violet (UV) and even visible light could be obtained. The thermal instability of the salt prevents long term storage and therefore limits practical applications. Another disadvantage derives from the evolution of nitrogen forming bubbles in the hardening coatings, thus making the material porous.

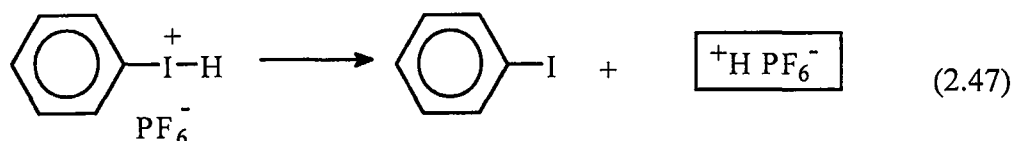
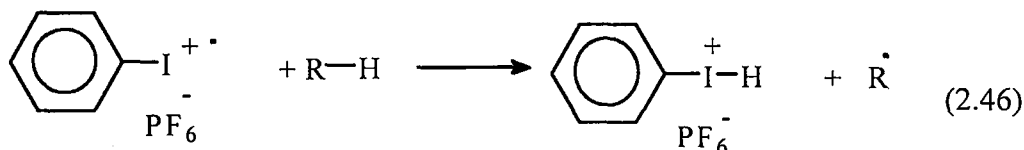
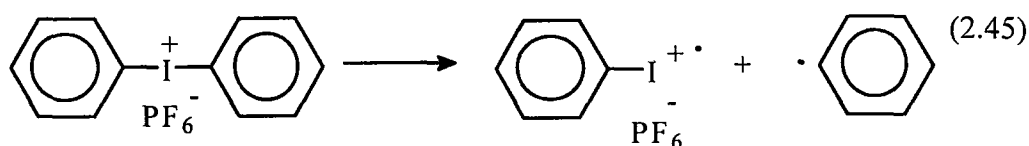
Diaryliodonium salts

Diaryliodonium salts are the most prominent cationic initiators since they are easy to prepare and very reactive [14-15]. Symmetrical diarylsulphonium salts can be synthesised by reaction of aromatic compounds with potassium iodate in the presence of sulphuric acid and acetic anhydride. Because of the possessing nucleophilic counter anions, the anion must be exchanged with non-nucleophilic one. The cation of the diaryliodonium salt is the photosensitive moiety of the initiator; similar to aryldiazonium salts ie. relatively poor. Substituents on the aryl residue have little influence on the position of the main absorbing band in the UV spectra. For example all alkoxy substituted iodonium salts have absorption maxima between 245 and 247nm. Although the longer wavelength absorbing (above 300nm) of these derivatives is advantageous compared to the non-substituted diphenyl iodonium salts

(227nm), the limit to absorption is, nevertheless, situated around 320nm and photosensitivity of these iodonium salts lies in the short wavelength region of the UV spectrum. Long chain group of substituents on the aryl moieties greatly increases the solubility of iodonium salt [16].

Upon irradiation, diaryliodonium salts undergo both homolytic and heterolytic cleavages of the carbon halogen bond [17-18]. The primary product of both cleavage reactions can undergo either fast subsequent reaction within the same solvent cage, or then undergo further reactions. Heterolytic cleavage reaction pathway is the direct irradiation of iodonium salts. Heterolytic cleavage is even more predominant with diphenylbromonium and diphenylchloronium salts. Either homolytic or heterolytic cleavage involves the interaction with hydrogen donating solvent or monomer yielding Brönsted acid, which initiates the polymerization. An alternative pathway, the reaction of escaping phenyl cations or phenyl radicals with neighbouring iodobenzenes also produces protons and additionally phenyliodobenzene derivatives.

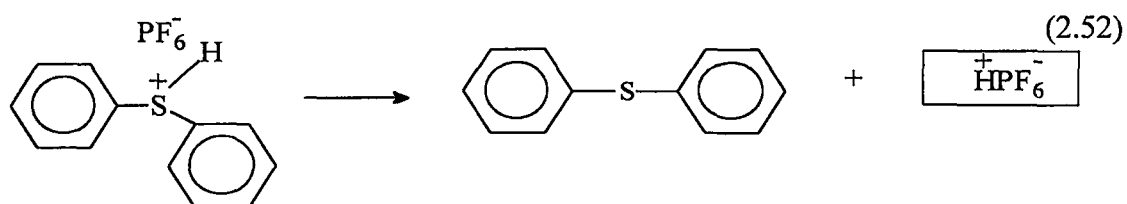
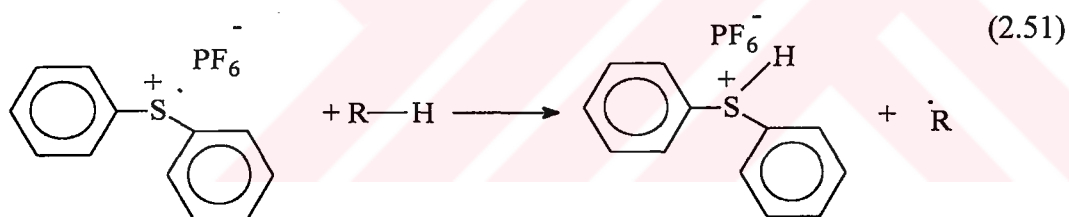
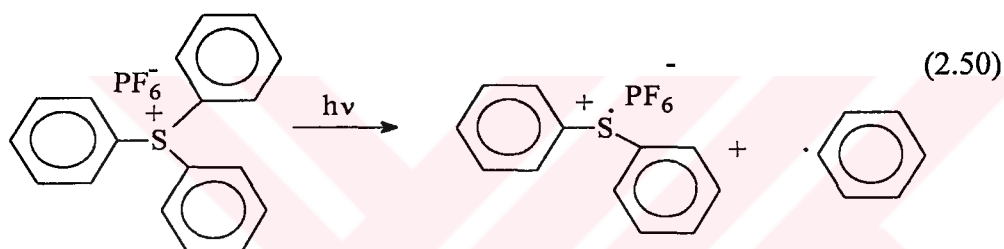
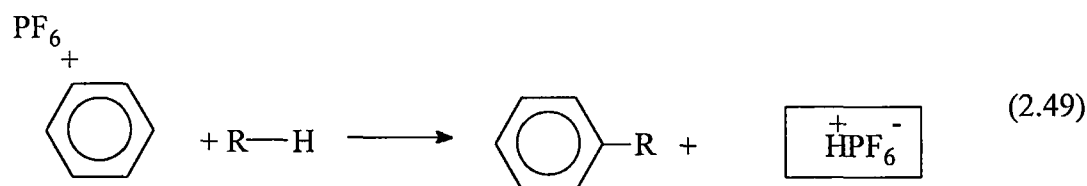
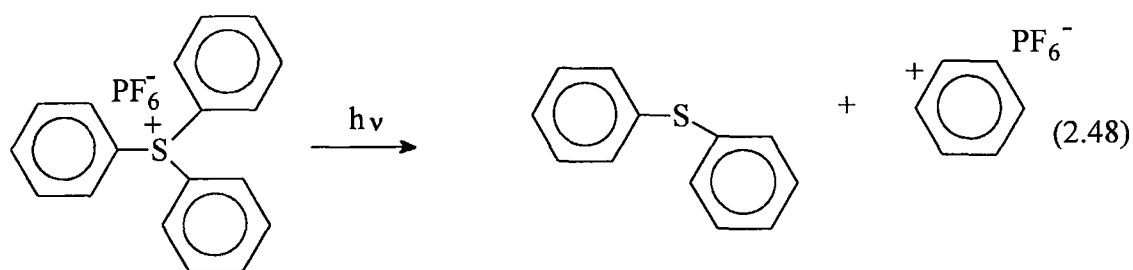




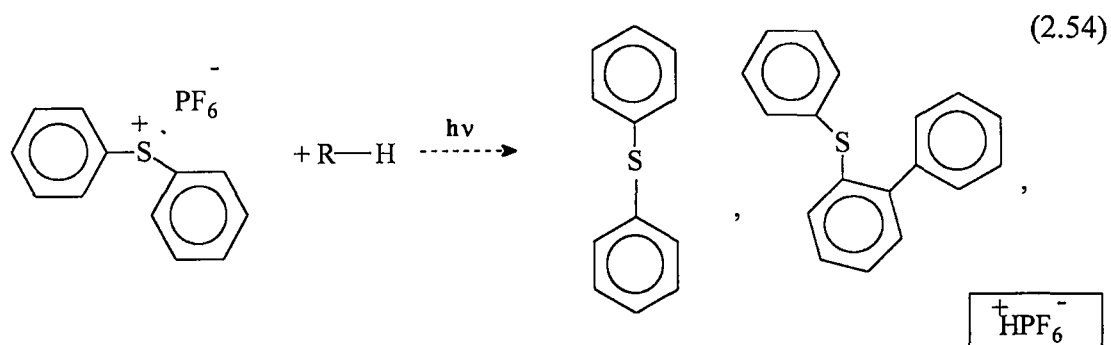
Brönsted acid, forming upon direct irradiation of diphenyliodonium salts has been used for the polymerization of many monomers. Recent studies were devoted to highly reactive, often crosslinkable monomers with either epoxide or vinyl groups [19-22].

Sulphonium salts

Sulphonium salts containing non-nucleophilic anions have found considerable usage as cationic photoinitiators. Trialkylsulphonium [23] salts spontaneously initiate the cationic polymerisation of reactive monomers, like trioxane[24]. However, these salts show little tendency to thermally initiate polymerisation. Since they can be heated to 300 °C without decomposition and do not initiate polymerisation of highly reactive monomers, even upon prolonged heating at 120 °C in the dark. When the same solutions are irradiated at wavelengths of 190 to 400nm, immediate exothermic polymerization ensues. Regarding the photolysis mechanism of triarylsulphonium salts both heterolytic and homolytic bond rupture of one sulphur- carbon bond is evidenced. Indirect irradiation of triphenylsulphonium salts, the heterolytic cleavage starting from the excited singlets state is the preferred reaction pathway [25]. Similar to diaryliodonium salts, in secondary reactions strong electrophilic Brönsted acid is produced. This acid initiates the cationic polymerisation. Within the series of non-nucleophilic anions, the order of reactivity $\text{SbF}_6^- > \text{AsF}_6^- > \text{PF}_6^- > \text{BF}_4^-$.

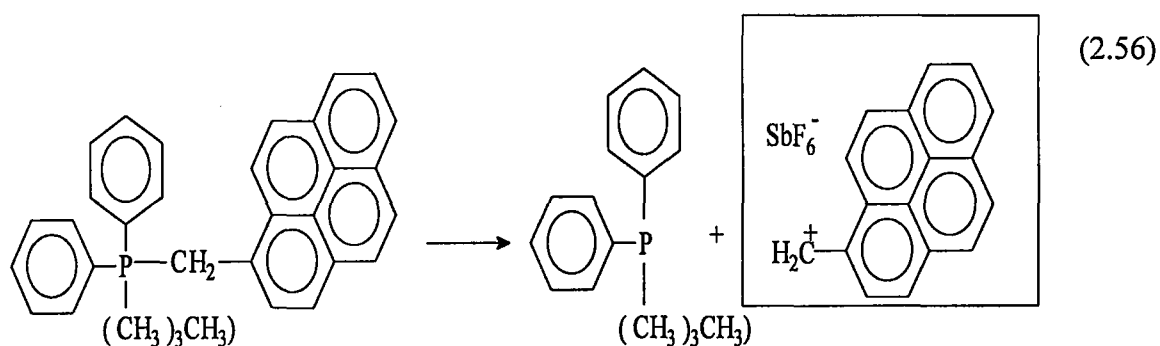


Mechanistic studies based on product analyses have shown that both phenyl cations and phenyl radicals formed by either homolysis or heterolysis may add to neighbouring sulphur bond rings thus generating various biphenylthiophenyl isomers [26-28]. The selectivity *ortho* > *meta* > *para* observed for these solvent cage products shows that the phenyl cations or radicals tend to react with the closest available site. Thus proton released.



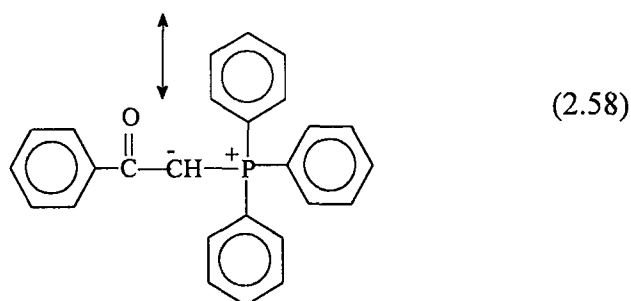
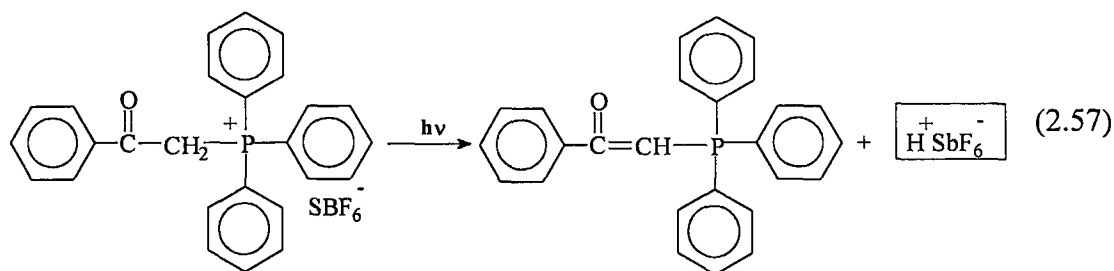
Phosphonium salts

Phosphonium salts can be prepared by the reaction of chloromethylated or bromomethylated aryl compounds with the corresponding phosphine [29-31]. Direct photolysis of phosphonium salts has been synthesized. After the heterolytic bond rupture benzyl or pyrenylmethyl groups containing phosphonium salts produce the respective carbon centred cations. These cations can initiate polymerization.



Pyrenylmethyl containing phosphonium salts show ability toward epoxides and vinyl monomer [32-33]. For the polymerization butylvinyl ether %100 polymerisation obtained. Phosphonium salts that contain aromatic groups start the chain reaction by carbocations with aromatic substituents. However, upon photolysis phenacyltriphenyl

phosphonium salts initiate the polymerisation by Brönsted acid because of resonance stabilization of forming ylide and protons [34].

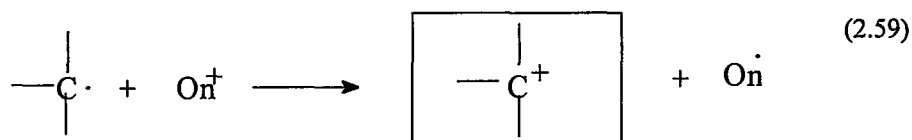


2. 4. 2. 1. 2. Indirect Photolysis:

The absorption of a photoinitiator in the spectral range available for excitation may be insufficient to initiate complete polymerization. Without absorption of the incident photon energy, photochemical processes can not occur. Several systems were developed to extend the applicability of the onium salt photoinitiator towards longer wavelengths. In these cases additives are present which participate in the reaction sequences to yield reactive species capable of initiating the cationic polymerization. There are four types of indirect initiation process are known depending on the role played by the additives.

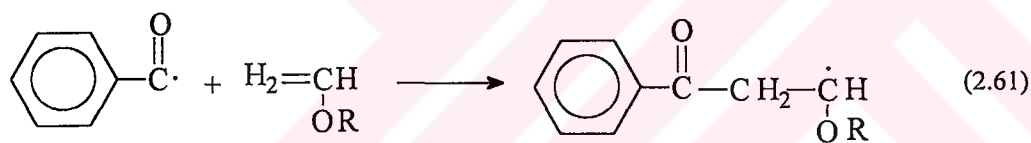
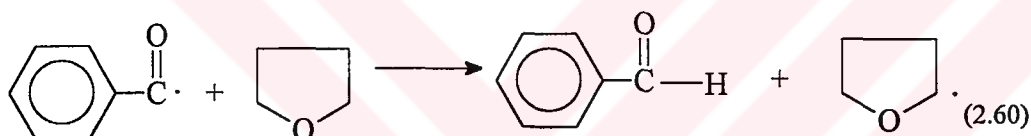
Free radical promoted cationic polymerization

Onium salts according to the following mechanism can oxidize many photochemical formed radicals:

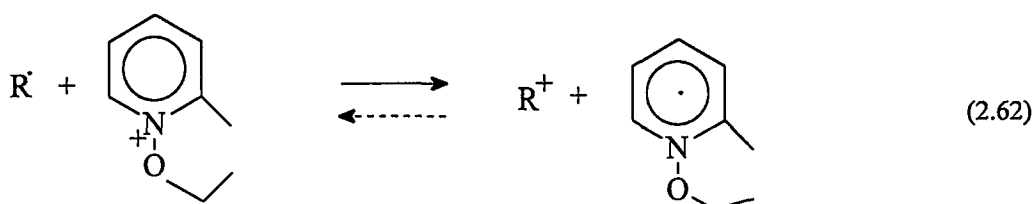


The cations thus generated are used as initiating species for cationic polymerization [35-36]. The process is usually termed as the free radical promoted cationic polymerization. This type of polymerization is a fairly flexible type of externally stimulated cationic polymerization. Free radicals may be produced by via photochemically, thermally or irradiating the system with highly energy rays. The photochemical generation of radicals can be applied even at low temperatures.

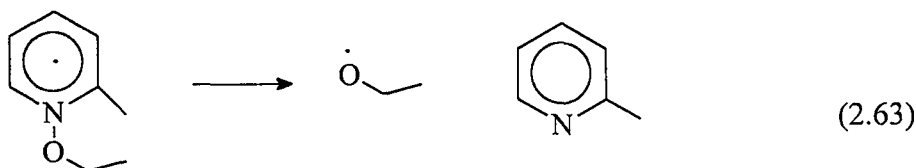
Benzoin derivatives are the most effective photoinitiator for giving high quantum yield [37]. By photolysis of these salts, generation of strong electron donor radicals formed. Light intensity, onium salt concentration or the type of radical source influences the rate of radical induced cationic polymerization with benzoin derivatives/ onium salts. In addition to direct generation of electron donating radicals, non-nucleophilic radicals, like $\text{PhCO}^\bullet$, $\text{Ph}^\bullet$ formed upon photolysis of the photolabile compound may react with monomer producing electron-donating radical.



Onium salts producing initiating species can easily oxidize these radicals. The efficiency of onium salts as oxidizing agents is related to their electron affinity. Aryldiazonium salts are the most suitable for the oxidation of radicals with the aid of N-ethoxy-2-methyl-pyridinium (EMP^+) carbocation can be obtained and this initiate the polymerization of butylvinylether (BVE) and cyclohexene oxide (CHO) [38].



Fast decomposition of pyridiniyl radical causes the back reaction so it has very short life.



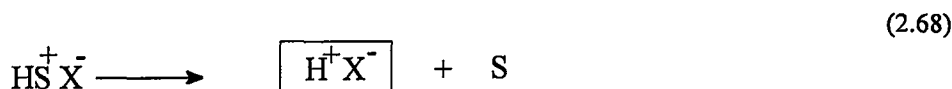
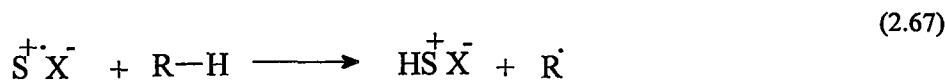
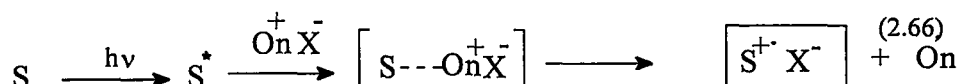
Sensitization

The decomposition of onium salts via electron transfer in an excited complex can be sensitized by aromatic hydrocarbons. The mechanism involves the electronic excitation of the sensitizer, a molecule possessing a suitable absorption spectrum, to its excited state. Energy is transferred from sensitizer to the onium salt via resonance excitation or energy exchange [39]. Energy transfer occurs either in the excited triplet state or in the singlets state.



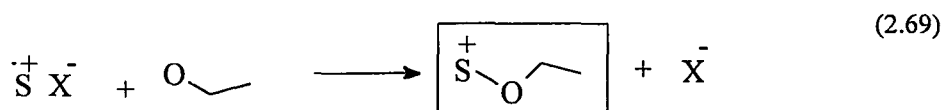
As a result of transfer process, the sensitizer returns to its ground state and excited onium salts are obtained. The energy requirement of excitation of the sensitizer should be bigger than the excitation energy of photoinitiators.

$$E^*(\text{S}) \geq E^*(\text{I}) \quad (2.65)$$

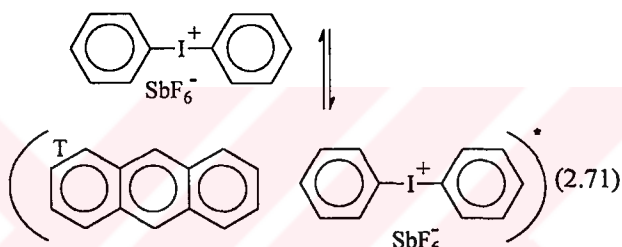
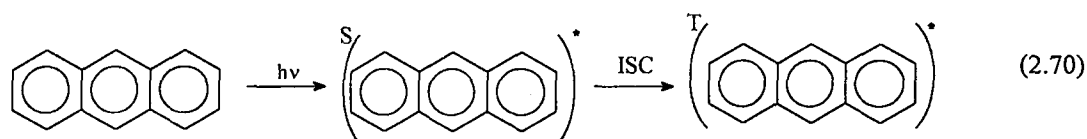


After the excitation of the sensitizer, a complex is formed between excited sensitizer and ground state onium salts. Because of the one electron transfer from the sensitizer to the onium salt, radical cations of sensitizer formed. This radical cation

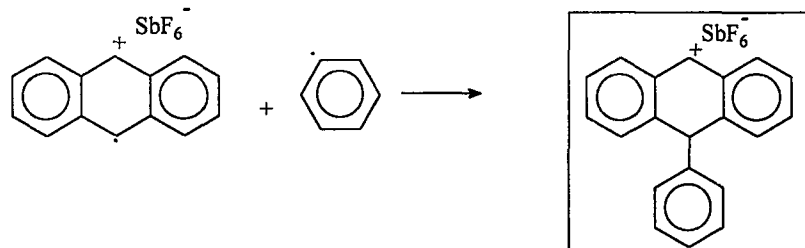
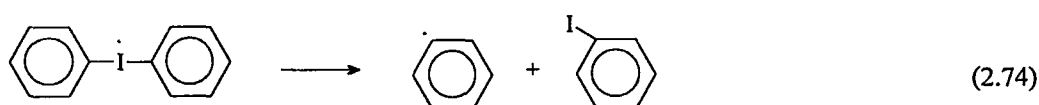
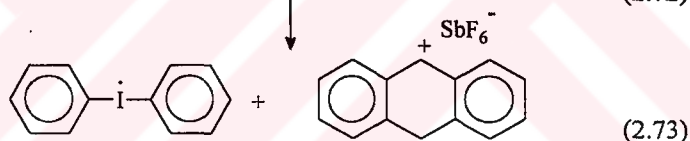
either initiates the polymerization of polymers or interacts with hydrogen containing constituents of polymerization mixture (solvent, monomer) causing Brönsted acid. However, decomposition of alkoxy pyridinium salts generates alkoxy radicals, which react with sensitizer radical cations producing initiating sulphur centred cations [40].



The sensitization of onium salt and anthracene aromatic system is shown below [41].



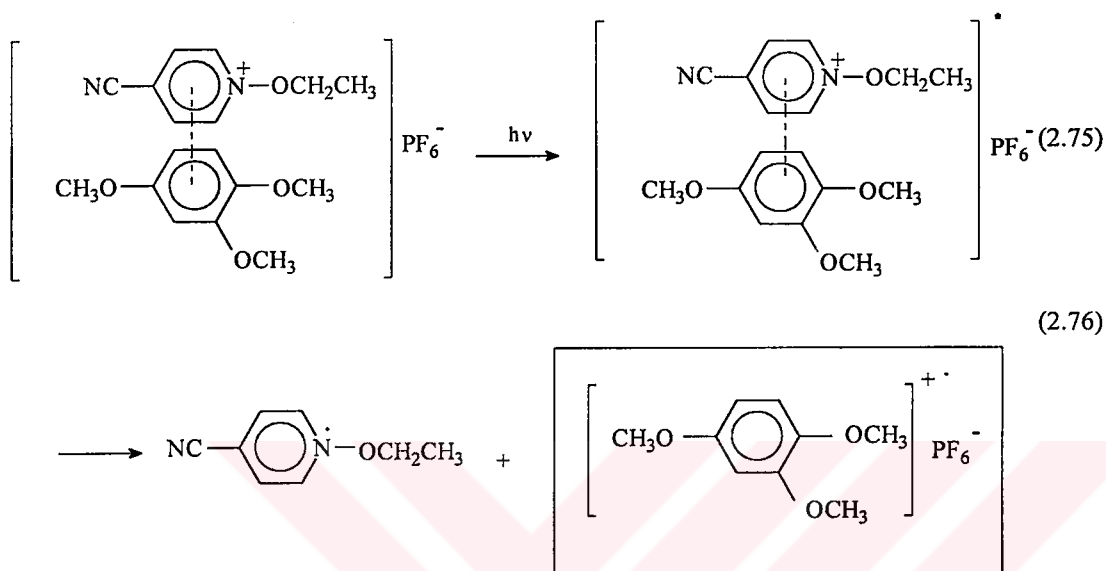
(2.72)



Charge transfer complexes

Electron rich- donors such as methyl- and methoxy substituted benzene form ground state CT complexes with pyridinium salts.[42] Because of transparency of components, these complexes absorb at relatively high wavelengths such as the

complex formed between N-ethoxy-4-cyano pyridinium hexafluorophosphate and 1,2,4-trimethoxybenzene cause absorption maxima at 420 nm. For pyridinium salt the absorption maxima is 270 nm. However, it is 265nm for trimethoxybenzene. This CT complexes act as photoinitiator for cationic polymerization of cyclohexene oxide and 4-vinyl cyclohexene oxide. Its mechanism is:



Addition -Fragmentation reactions

Polymerizations which are induced by external stimulation, such as heating or photoirradiation are of great interest due to their utilisation for curing of coatings and printing inks and resist technology . Many technological monomers (vinyl ethers, oxiranes) are only polymerizable in a cationic mode. However, onium salts (pyridinium, sulfonium, thiophenium salts, etc.) contain organic cations which themselves (without external stimulation like, eg. heat or light) because of steric reason only scarcely initiate polymerizations [43]. In order to make the presented allyl- onium salts able to initiate cationic polymerizations; they have to be reacted with free radicals. In other words, although the polymerization is eventually of a cationic mode, free radicals have to be produced in the first instance [44].

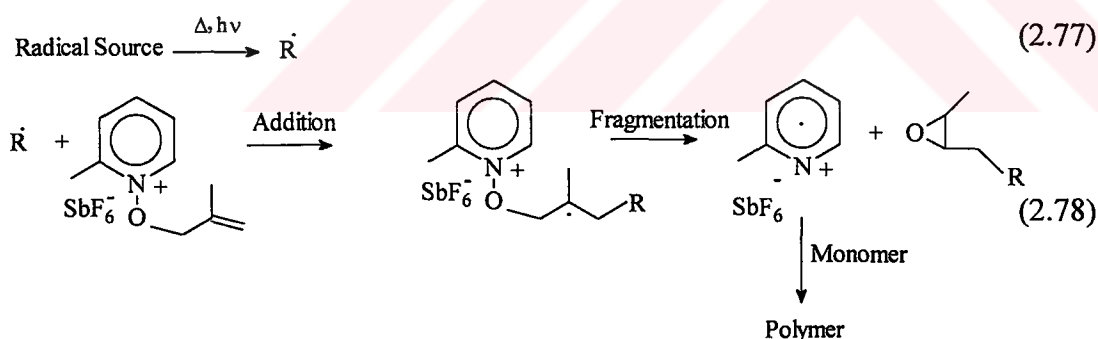
Addition- Fragmentation reactions are a versatile and exceptionally interesting tool in preparative chemistry. With the aid of specially designed ally-onium salts (addition- fragmentation agent, AFA) in conjunction with conventual radical initiators

it is possible to very efficiently initiate cationic polymerization. The mechanism involves:

- The formation of radicals by heating or irradiating the radical initiator.
- The addition of these radicals to an AFA molecule.
- The fragmentation of the AFA.
- Radical cations produced, which with high rates initiate the polymerization of cationically polymerizable monomers (eg., cyclohexene oxide, CHO)

In order to show good performance in initiation reactions, AFAs have to be equipped with functional groups or substituents, which either promote radical addition or facilitate the fragmentation of reaction intermediates.

Cationic polymerizations were succeeded using thermal radical initiators, like 2,2-azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), or radical photo-initiators, such as benzoin or acylphosphine oxides, as free radical source. The radicals generated by either heat or light added to the double bond of the allyl onium salt and subsequently an onium radical cation is released, which initiates the polymerization [45]. The reaction mechanism is illustrated on the example of a methyl-allyl pyridinium salt.

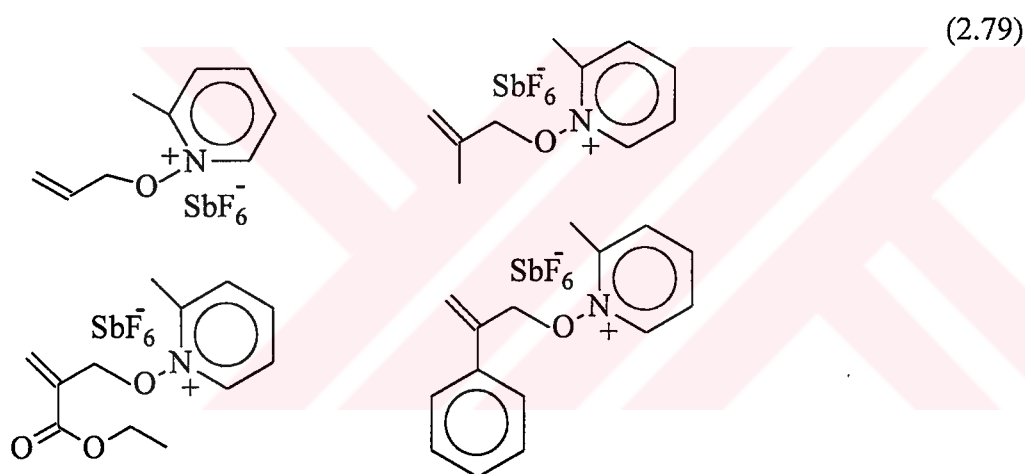


Fragmentation brings about the elimination of substituents that prevented the cationic centre from reacting with monomer, ie. the onium salt becomes unblocked. The allylic moiety represents the reactive site for the addition step whereas the charged onium cation is a latent initiating species, which is released only by fragmentation. Naturally, the bond to be ruptured should be one of the weakest bonds in the molecule.

The obvious advantage of using AFAs for cationic polymerization is that, depending on the nature of radical source used, initiation can be triggered by either heat (eg. with AIBM or BPO) or light (with, eg. benzoin). Moreover, as far as photo polymerization is concerned, it is extremely easy to a desired wavelengths' range (the emission maximum of the irradiation source used) by choosing appropriate radical initiators. Notable, the development of radical polymerization led to numerous radical initiators with excellent radical yields and good storage stability.

Allyloxy-Pyridinium based AFAs

Allyloxy-pyridinium salts with various substituents at the allylic moiety were shown to be very efficient coinitiators in radical promoted cationic polymerization of monomers such as cyclohexene oxide (CHO) [44]. Some common Allyloxy-pyridinium salts of AFAs are shown below:



Their synthesis involves the reaction of the respective bromoallylic compound with picolinium N-oxide. In this reaction the target cation is directly obtained. The counter anion, bromide, however is too nucleophilic. It would make a cationic polymerization rather difficult since bromide easily recombines with growing cationic chain ends thus terminating polymerisations at a very early stage. Therefore, bromide has to be exchanged for an anion with a lower nucleophilicity, such as hexafluoroantimonate, SbF_6^- . The anion exchange can often be carried out in aqueous solution by directly adding NaSbF_6 .



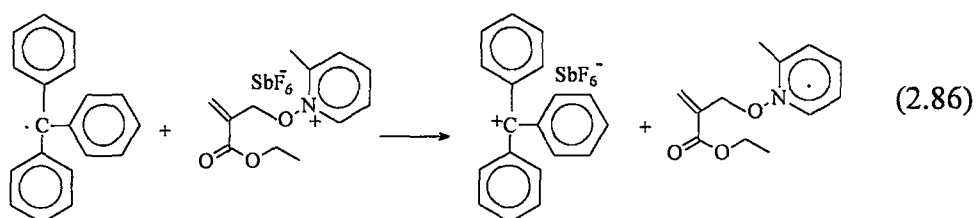
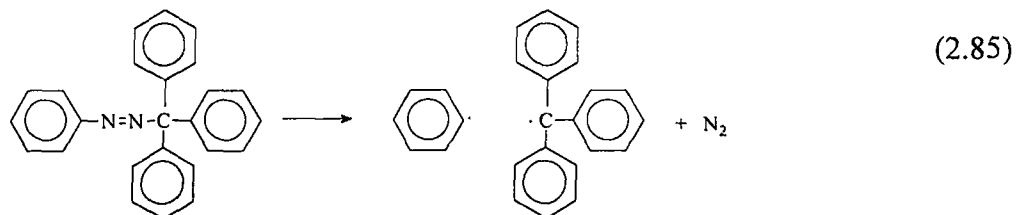
type initiators and has been utilized for numerous cationic polymerizations.



of one photon up to two initiating species could be produced, providing the quantum

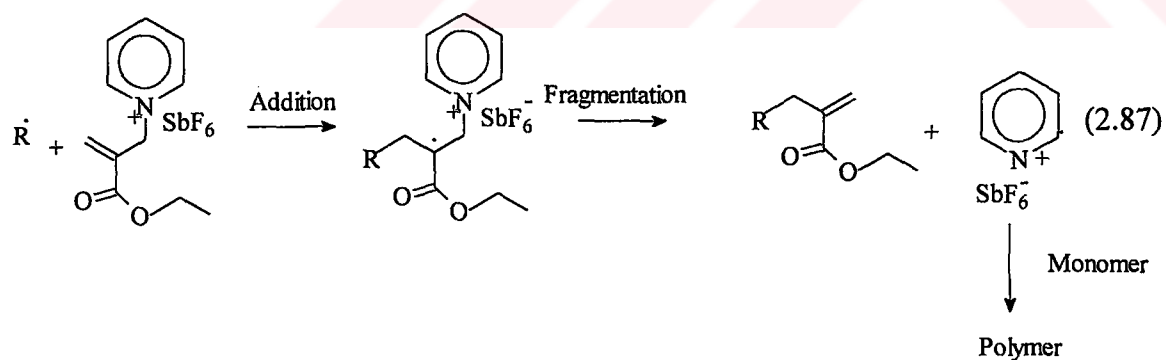


Phenylazotriphenyl methane (PAT) as a radical source, slightly different initiation behaviour is observed [43].



Allyl-Pyridinium based AFAs

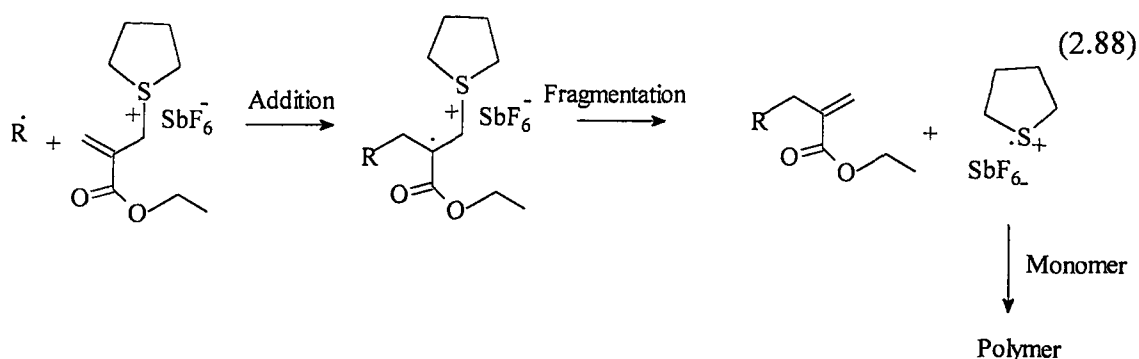
Allyl-pyridinium salt synthesis consists in the reaction of pyridinium with the respective bromo- allyl compound and a subsequent anion exchange for hexafluoro antimonate. Apart from allyloxy- pyridinium compounds, ally-pyridinium salts were developed as coinitiators for cationic polymerization [46].



The reaction mechanism resembles very much like allyloxy- pyridinium salts with the difference that allyl- pyridinium salts are somewhat less reactive. The circumstance is explained by relatively high bond dissociation energy of the $\text{N}^+\text{-C}$ bond in comparing with the $\text{N}^+\text{-O}$ bond.

Allyl- Sulphonium based AFAs

By the reaction of tetrahydrothiophen with the respective bromo- allyl compound, the bromine derivative allyl- sulphonium based AFA is obtained. In order to transform it to a coinitiator suitable for cationic polymerization, the anion has to be exchanged, eg. for hexafluoro antimonate [47-48].

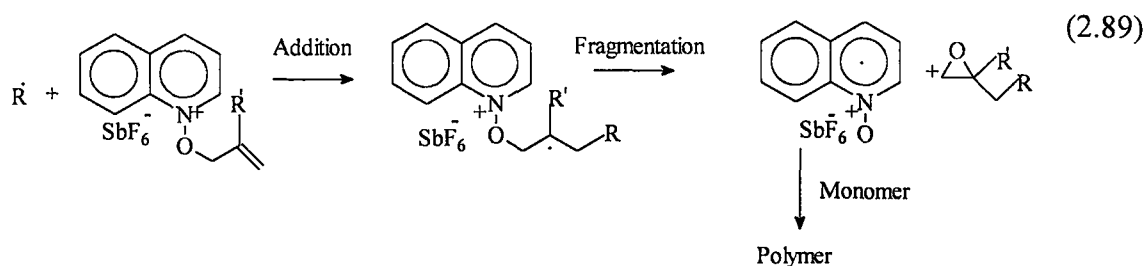


When **PAT** was used as a radical initiator, the initiation was exceptionally rapid. The reason is that the characteristic absorption of triphenylmethyl carbocations was formed (410 and 440nm), the oxidation of triphenyl methyl radicals by allyl-sulphonium based AFA has to be taken into account. Hence, cations from both the AFA and from **PAT** result in a high overall initiation rate.

As far as photoinitiation is concerned it has to be pointed out that this type of AFA does not possess suitable chromophoric group. An initiation of direct light can therefore be disregarded. However, with radical photoinitiators, such as benzoin and phosphine oxides, very fast cationic polymerizations are obtained. With these radical initiators polymerization are carried out at 340 and 380nm.

Allyloxy- Isoquinolium based AFA

Allyloxy-isoquinolium salt synthesis consists in the reaction of isoquinole with the respective bromo- allyl compound and a subsequent anion exchange for hexafluoro antimonate. Their polymerization mechanism is the same with allylox-pyridinium based AFAs. The reason is that N⁺-O bond is very weak and may easily be ruptured in the course of fragmentation giving rise to initiating isoquinolium radical cations [49].



According to radical source the polymerization rate $\text{PAT} > \text{AIBN} \cong \text{BPO}$. Moreover, the substituents on the double bond effect the polymerization rates. The reason is that if double bond contains electron-donating substituents then N^+-O bond would not be easily ruptured. If double bond contains electron-withdrawing substituents, N^+-O would be weak then this bond will be easily broken.

3. EXPERIMENTAL WORK

3. 1. Materials and Chemicals

BDMP was obtained from CIBA Specialty Chemical Inc. and used without any purification.

PBr₃ was obtained from Fluka; no further purification was applied.

K₂CO₃ was a product of Fluka and used directly.

NaSbF₆, used as an anion exchanger in the synthesis of AFA, was obtained from Aldrich and used directly.

Cyclohexene oxide was used as a monomer and distilled with fractionation under calcium hydride. It was obtained from Aldrich.

Acetone used as solvent in the synthesis of AFA agents was a product of Merck.

Methanol (technical grade) was used in the precipitation processes.

Methylene chloride was used as solvent for dissolving the monomer and sometimes for polymerization. It was also used in UV measurements. It was first extracted with sulphuric acid then with water and with %5 sodium hydroxide solutions and finally again with water. Dried under sodium sulphate and distilled by fractionating-column.

Butyl vinyl ether, extracted with water and dried with sodium. Finally it was distilled.

3.2. Equipments

UV-visible spectra were recorded on a Perkin Elmer Lambda 2 spectrometer.

Merry-go-round type photoreactor with 16 Philips 8W/06 lamps, emitting $\lambda > 300\text{nm}$ or sometimes Amco monochromatic light source equipped with a xenon lamp (XB075W/2) and a mercury lamp (HB0100W/2) were employed according to selected wavelength range.

Elemental analysis were performed on a CHNS-932 (LECO) instrument.

^1H -NMR spectra were recorded on a Bruker 250MHz instrument. CDCl_3 used as a solvent.

Gel permeation chromatography (G.P.C) analyses were performed via set up consisting of a waters 600 pump and 2 ultra styragel columns with porosities 500 and $10^4 \text{ \AA}$ with THF as the fluent at a rate flow rate of 1ml/ Min and a Waters differential refractometer (model 410). Molecular weights were calculated with the aid of polystyrene standards.

3. 3. Synthesis of Ethyl- α -(bromomethyl) acrylate

To a mixture of triethyl phosphonoacetate (0.2 mol, 44.8 gr) and %40 aqueous solution of formaldehyde (0.8mol, 60ml) agitated at 1000 r.p.m at room temperature was added slowly (30min) a saturated solution of potassium carbonate (0.35 mol, 48gr). At the end of addition the temperature reached 30-35°C and agitation was continued for 1 hour. Then, saturated amonium chloride solution (75ml) was added and the mixture was extracted with ether (3x50ml). The combined organic layers were dried with magnesium sulphate, the solvents were evaporated under vacuo, and the remaining oil was distilled under 1.2 torr. Therefore ethyl- α -(hydroxy methyl) acrylate was obtained b.p: 80-85 °C n_D^{20} : 1.4495 with a yield of 63%.

Phosphorous (III) bromide (0.0048 mol, 4.6 ml) was added to a stirred solution of ethy- α -(hydroxy methyl) acrylate (0.104mol, 13.58gr) in dry ether (100ml) at -10°C and the mixture was extracted with technical-grade hexane (3x50ml). The organic phase was washed with saturated sodium chloride solution

(2x50ml) and dried with magnesium sulphate. The solvents were evaporated and the remaining oil was distilled in vacuo 20 torr. Therefore ethyl- α -(bromomethyl)acrylate was obtained 50.63% n_D^{20} : 1.475. The structure was confirmed by $^1\text{H-NMR}$ spectra.

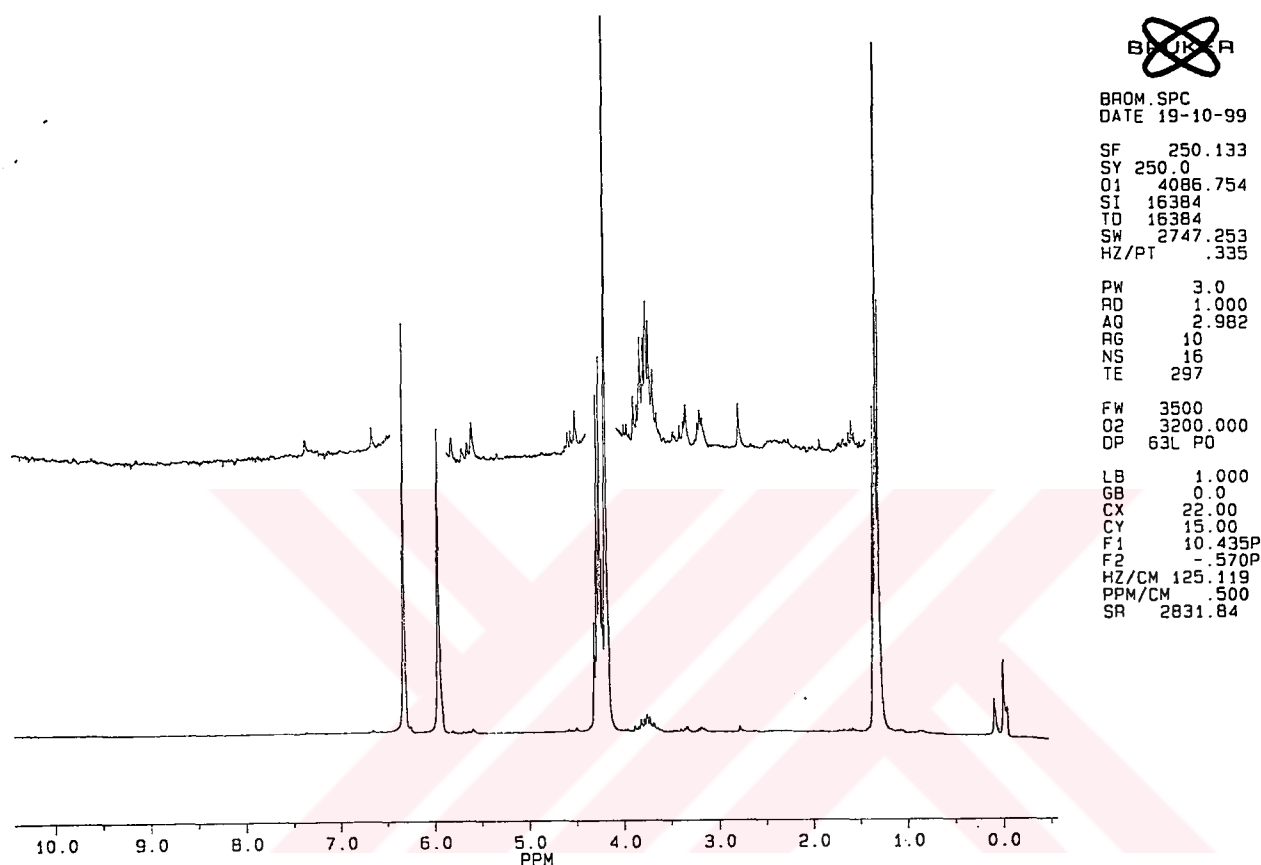
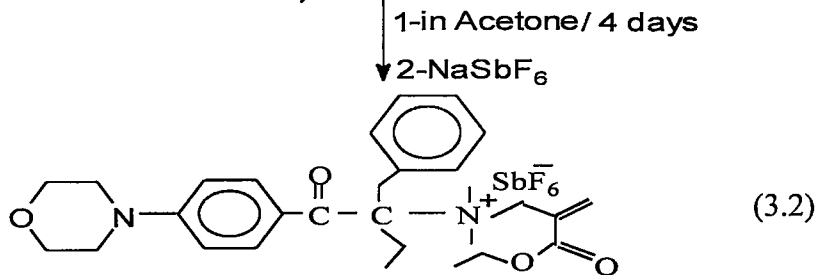
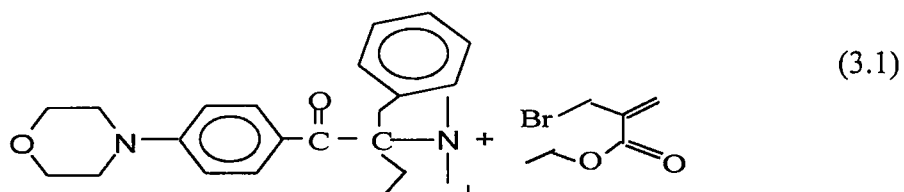


Figure 1: $^1\text{H-NMR}$ spectrum of Ethyl- α -(bromo methyl)acrylate

3. 4. Synthesis of AFA salts

AFA was synthesized by reacting a mixture of ethyl- α -(bromomethyl)acrylate (2.08×10^{-3} mol) and 2-benzyl-2-dimethylamino-1-(morpholinophenyl)-butane-1-one (BDMP) (2.08×10^{-3} mol) in acetone (4ml) for 4 days at room temperature. Acetone was evaporated and the residue was extracted with ether/water (20ml / 4ml). Then an equimolar amount of NaSbF_6 (2.08×10^{-3} mol) was added to the aqueous layer and light yellow precipitates, namely 2-benzyl-2-(N,N-dimethyl-2-ethoxycarbonyl-1-propenyl) amonium hexafluoroantimonate-1- (4-morpholinophenyl)-butane-1-one (AFA), was obtained %8, m.p:96-105°C. Elemental analysis and $^1\text{H-NMR}$ of this salt confirmed its structure.



AFA Salt

Table 1: Elemental Analysis of AFA salt

	C %	H %	N %
Calculated	48.65	5.31	3.91
Found	48.62	5.31	4

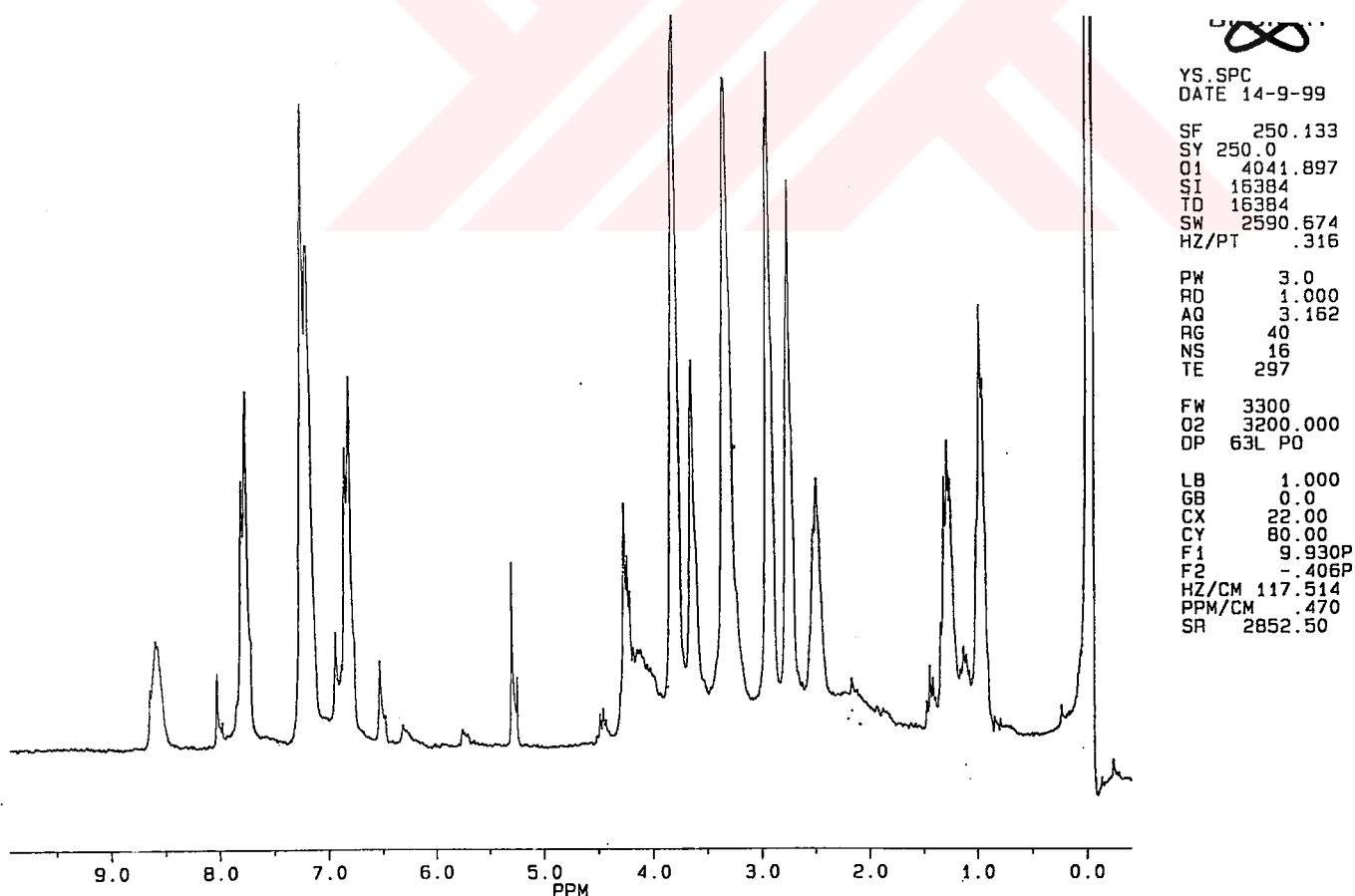


Figure 2: ^1H -NMR spectrum of AFA salt

3. 5. Polymerization

Appropriate solution of monomer and AFA salts were degassed with nitrogen which was passed through firstly from molecular sieve, secondly from P_2O_5 and finally from silica-gel and H_2SO_4 , prior to irradiation. In some cases, the polymerization was carried out in solution using CH_2Cl_2 as a solvent. Merry-go-round type photoreactor $\lambda > 300\text{nm}$ or Amco monochromatic light sources were employed according to the selected wavelength range. After a given time polymers were precipitated into methanol filtered and dried in vacuo. Sometimes methylene chloride was used as solvent for dissolving the monomer and for polymer. In some cases, the polymerization was carried out in solution using CH_2Cl_2 as a solvent. The conversion can be calculated according the following equations.

$$\% \text{ Conversion} = (P/M) \times 100$$

P: amount of the polymer obtained

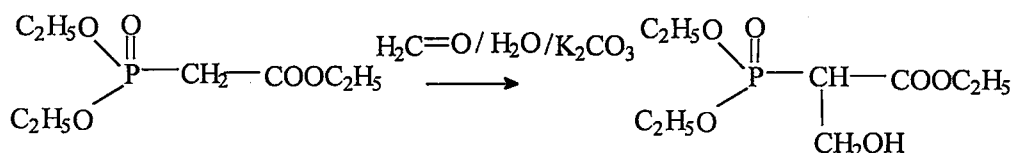
M: amount of the monomer consumed

4. RESULTS AND DISCUSSION

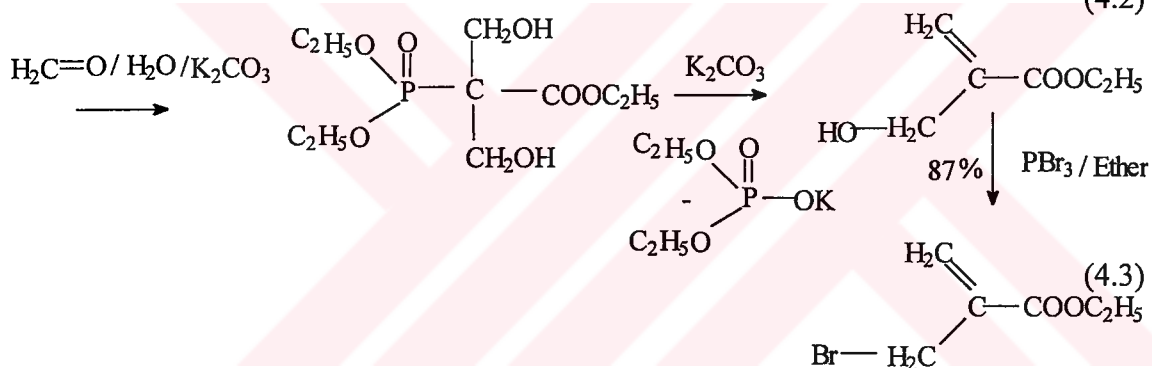
4. 1. Synthesis of Ethyl- α -(bromomethyl)acrylate

Ethyl- α -(bromomethyl)acrylate is the starting material for the synthesis of AFA salt used in this study was performed according to the following mechanism.

(4.1)



(4.2)

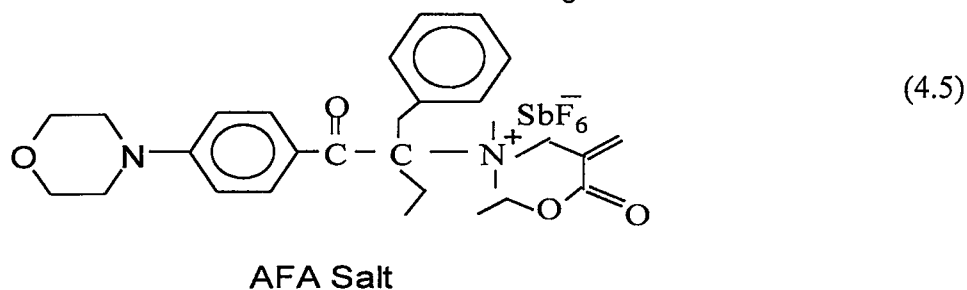


(4.3)

The structure of Ethyl- α -(bromomethyl)acrylate was confirmed by spectral analysis (see experimental section).

4. 2. Synthesis of AFA salts

AFA salt was prepared by the alkylation of the amino groups of BDMP with the Ethyl- α -(bromomethyl)acrylate according to the following reaction.



Notably, the bromo counter anion was exchanged by non-nucleophilic one, i.e. SbF_6^- , by using corresponding sodium salt. The Structure of the AFA was confirmed by elemental and ^1H -NMR measurement (see table 1.)

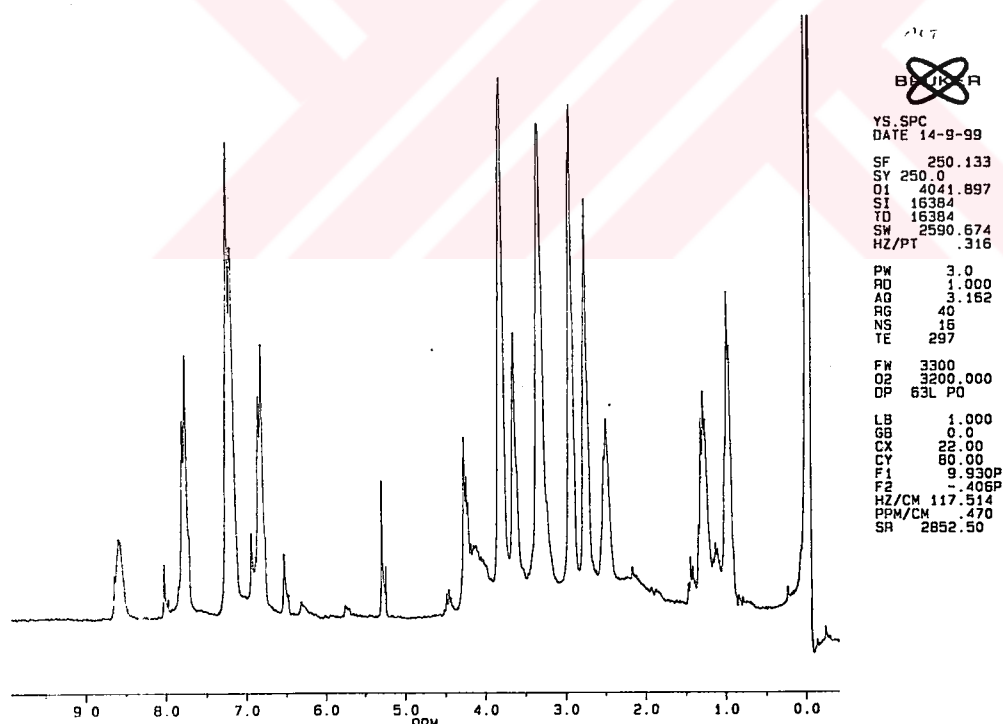


Figure 3 : ^1H -NMR spectrum of AFA salt

^1H -NMR spectrum of the AFA salt showed characteristic allyl protons at 6.5 ppm, aromatic protons of morpholino and phenyl groups between 7-8 ppm.

4. 3. Photolysis of AFA salt

Compared to the UV spectra of the salt the precursor photoinitiator BDMP, the main absorption bond of the salt is red shifted in the case of the AFA salt. However, since the photochromophoric groups of both compounds are the same, it is expected that they undergo α -cleavage upon photolysis as shown below.

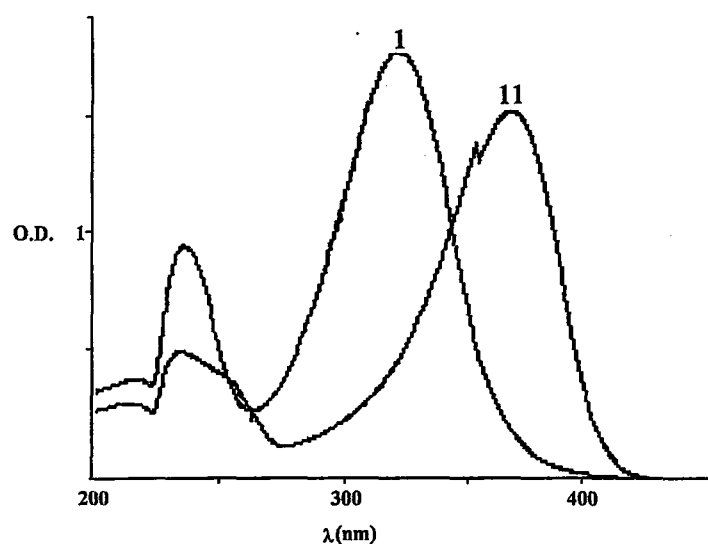
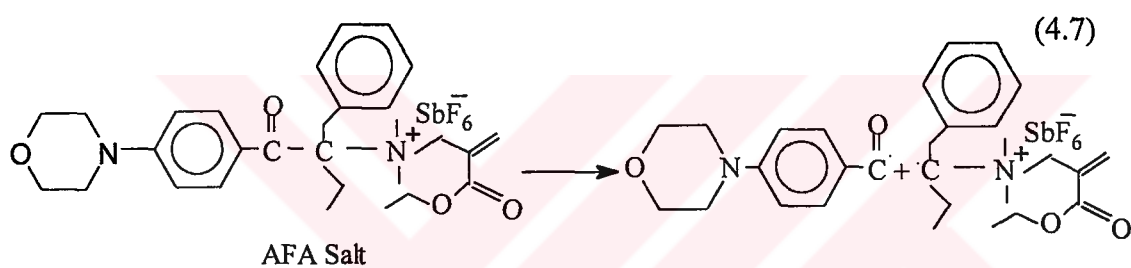
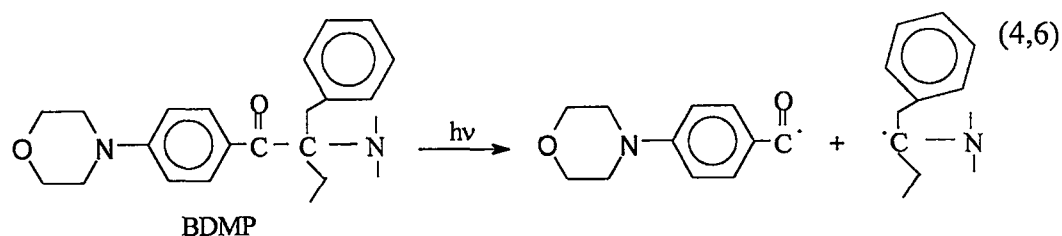
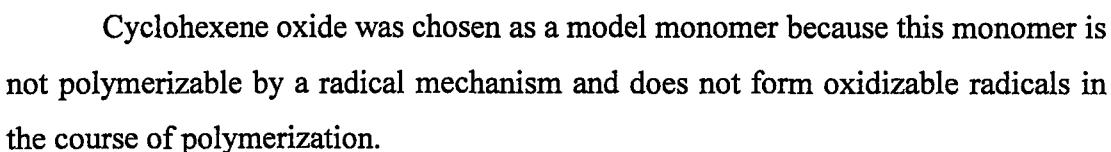


Figure 4: UV spectrum of 8×10^{-5} mol/L CH_2Cl_2 solutions of
a) BDMP (I) b) AFA salt (II)

(4.8)

(4.8)



45

Table 2: Polymerization of CHO^a in the presence of Allylic Salt AFA at different wavelengths

Wavelength $\lambda(\text{nm})$	Conversion (%)	Mn (g mol ⁻¹)
350	5.58	1300
380	21.46	6845
400	11.47	1300

^a[CHO]=9.88 mol/L, [AFA] = 5×10^{-3} mol/L, Time = 6min

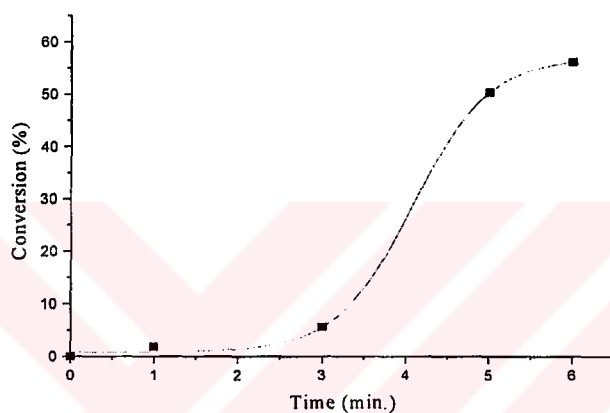


Figure 5: Photopolymerization of CHO in the presence of AFA Salt

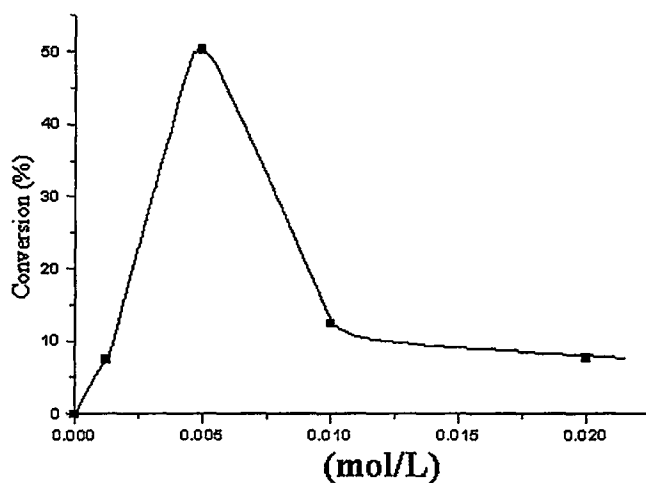


Figure 6: .Photopolymerization of CHO at different concentrations of AFA, [CHO] = 9.88 mole/L, $\lambda > 300\text{nm}$, Time = 6min.

As can be seen the conversion to poly (cyclohexene oxide) was found to increase rapidly up to a certain concentration of the salt from which point a marked reduction in apparent rate of polymerization is observed, probably owing to total completion absorption of irradiation by the salt. It may also indicate the occurrence of termination reactions.

In addition to CHO some other cationically polymerizable monomers were also tested.

Table 3. Photopolymerization of various monomers in the presence of Allyl salt AFA, in CH₂Cl₂ at room temperature

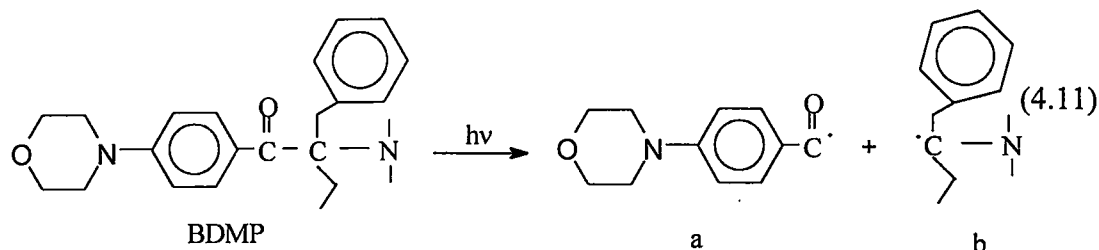
Monomer	[AFA]x10 ³ (mol/L)	[BDMP] x10 ³ (mol/L)	Time (min.)	Conversion (%)
NVC	5	-	0.016	74.81
NVC	-	5	12	42.70
BVE	5	-	35	62.31
CHO	5	-	20	38.97
EEC ^b	5	-	120	-

^a [Monomer] = 4 mol/L, $\lambda > 300\text{nm}$

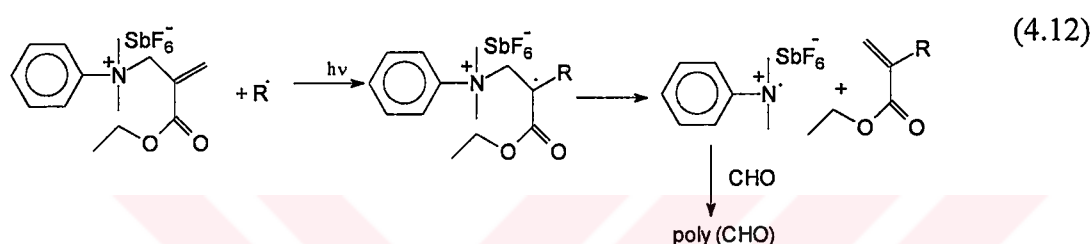
^b 3',4'-epoxycyclohexyl-3',4'-epoxycyclohexene carboxylate

As can be from the table, n-butyl vinyl (BVE) ether was polymerized to quite high yields while the spontaneous polymerization occurred with a more powerful monomer, N-vinyl carbazole (NVC). It should be pointed out that NVC is also polymerizable via a free radical mechanism. For comparison, free radical polymerization of NVC with the precursor photoinitiator, BDMP, was also included. The efficiency of the cationic system under the same absorptivity and experimental conditions was much higher. Notable, bifunctional monomer, 3',4'-epoxycyclohexyl-3',4'-epoxycyclohexene carboxylate (EEC) did not polymerize with the salt.

In order to gain more insight to the mechanism of initiation and comparison, cyclohexene oxide was polymerized with the combination of radical generating compound BDMP and allyl amonium salt (N,N-Dimethyl-2-Ethoxycarbonyl-1-Propenyl)aniline at the same experimental conditions.



$R^\cdot = a \text{ or } b$



Although at lower rate, the combined system also initiated the polymerization via addition fragmentation scheme. In this case radicals are formed independently and subsequently added to the free salt for the generation of reactive cations.

Table.4. Photopolymerization of CHO^a in the presence of Allyl salts (AFA)

Salt	BDMP (mol/L)	Time (min)	Conversion (%)
AFA	--	20	38.97
Allyl amonium	5×10^{-3}	35	28.60

^a [CHO] = 9.88 mol/L, [Salt] = 5×10^{-3} mol/L, $\lambda > 300\text{nm}$

Free radical generating capacity of AFA salt was also tested and compared with that of BDMP in methyl methacrylate (MMA) polymerization;

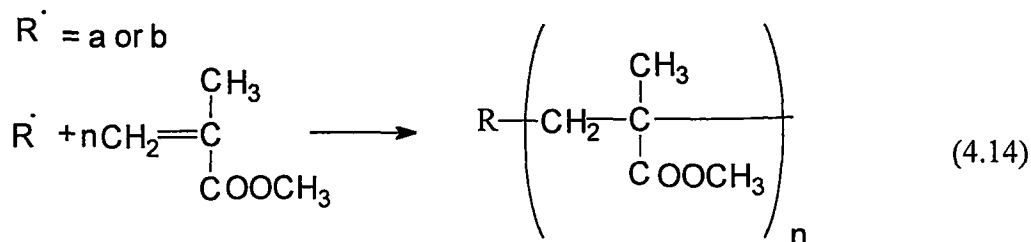
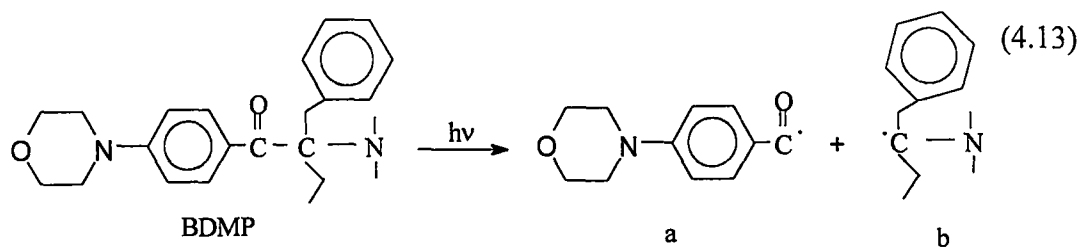
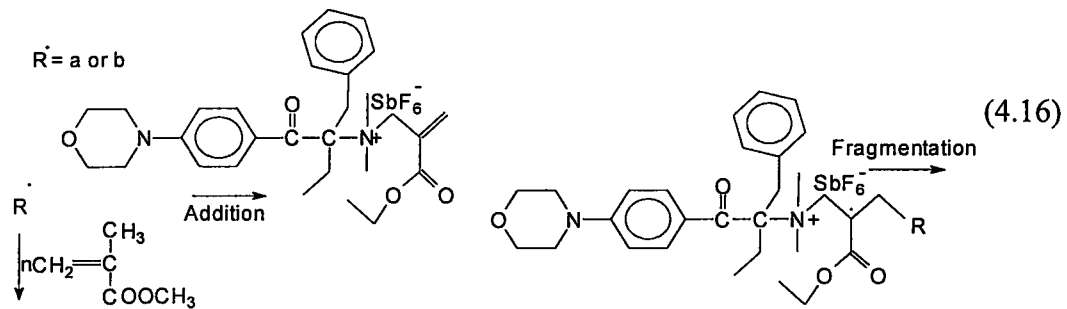
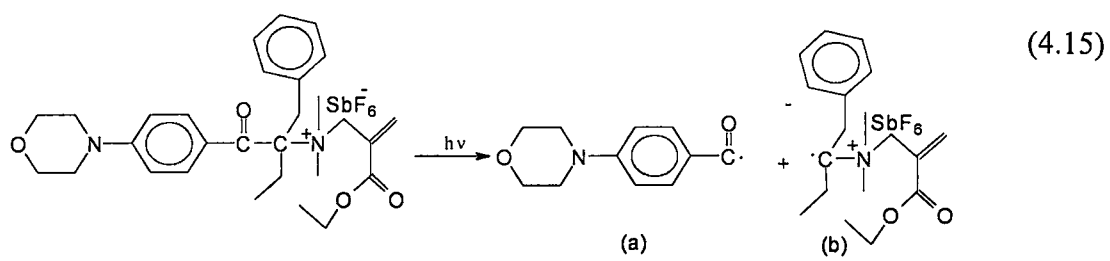


Table 5. Photoinitiated Free Radical Polymerization of Methyl Methacrylate in bulk with BDMP and Allylic Salt (AFA), Photoinitiator = 5×10^{-3} mol/L, $\lambda > 300\text{nm}$.

Photoinitiator	Irradiation time (min)	Conversion (%)	$M_n \times 10^{-3}$ g/mol
BDMP	60	14.3	237 ^a
AFA	60	>1	-
AFA	120	6.5	214

^aBimodal molecular weight distribution

It is clear that BDMP is much efficient photoinitiator for free radical polymerization. The lower efficiency of the allylic salt, (AFA), may be attributed to the participation of some of the radicals in addition fragmentation reactions instead of initiation.



CONCLUSION & SUGGESTIONS

In this study a novel addition-fragmentation agent (AFA), 2-benzyl-2-(N,N-dimethyl-2-ethoxycarbonyl-1-propenyl) amonium hexafluoroantimonate-1-(4-morpholinophenyl)-butane-1-one, for photoinitiated cationic polymerization was synthesized and characterized. With this compound it is possible to initiate the cationic polymerization of cyclohexene oxide (CHO), n-butyl vinyl ether (BVE), and N-vinyl carbazole photochemically at $\lambda=380\text{nm}$. The initiator possesses intrinsic chromophoric group for radical generation and allylic salt for the addition fragmentation scheme. Therefore, photoinitiation induced in the absence of additional radical initiators. Moreover, our AFA was compared with the combination of radical generating compound, BDMP with allyl amonium salt and found that this salt was more efficient than the other AFA reagents that need additional radical source.

With this compound it is possible to initiate both radically and cationically photopolymerizable monomers to bring polymer. However, the efficiency of photo radical initiation is much lower than the cationic one. The reason may be attributed to acting as both radical photoinitiation and addition-fragmentation mechanism.

REFERENCES

- [1] **Dietliker, K.**, 1991. "Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints, SITA Technology Ltd., London, Vol. III.
- [2] **Desorby, Y., Dieklier, K., Misev, L., Rembold, M., Rist, G and Rutssch, W.**, 1990. in Radiation Curing of Polymers, C. E. Hoyle, J.F.Kinstle (Eds.) Am. Chem. Soc., Washington D.C., p.92
- [3] **Yagci, Y and Reetz, I.**, 1998. Prog. Polym. Sci. **23**, 1485
- [4] **Denizligil, S., Yagci, Y and McArdle, C .**,1995. Polymer **36**, 3093
- [5] **Odian, G.**, 1981. "Principles of Polymerization", 2nd Ed. John Wiley and Sons, Inc. New York
- [6] **Rempp, P and Merrill, E.W.**, 1991. "Polymer Synthesis", 2nd Ed. Basel, New York
- [7] **Matyjaszewski, K.**, 1996. "Cationic Polymerizations, mechanisms, Synthesis and Applications", Marcel Dekker, USA
- [8] **Hsieh, H.L and Quirk, R.P.**,1996. "Anionic Polymerization Principles and Applications", Marcell Dekker Inc.,USA
- [19] **Lahse, F and Zwelfel, F. H.**, 1986. Adv. Poly. Sci., **78**, 61
- [10] **Rabek, R.**, 1975. "Photodegradation, Photooxidation and Photosensitization of Polymers", J. Willey & Sons, Britain
- [11] **Kucera, M.**, 1992. "Mechanism and Kinetics of Addition Polymerization" 2nd Rev. Ed., Academia Praha
- [12] **Yagci, Y.**, 1999. "Photoinitiated Cationic Polymerization", J. E. Puskas et. All. (Eds), "Ionic Polymerizations and Related Processes", 205-207, Kluwer Academic Publishers, Netherlands
- [13] **Smeets, G., Aerts, A and Von Erum, J.**, 1980. Polym. J., **12**, 539
- [14] **Crivello, J.V. and Lam, J.H.W.**,1976. J. Polym. Sci. Symp. No :**56**, 383
- [15] **Crivello, J.W and Lam, J.H.W.**, 1997. Macromolecules, **10**, 1307

- [16] **Fauossier, J.P., Burr, D and Crivello. J.W.**, 1994. J. Macromol. Chem. Pure. Appl. Chem **A31**, 677
- [17] **Dektar, J.L and Hacker, N.P.**, 1990. J. Org. Chem, **55**, 639
- [18] **Dektar, J.L. and Hacker, N.P.**, 1991. J. Org. Chem, **56**, 1839
- [19] **Crivello, J.V. and Varleman, U.**, 1995. J. Polym. Sci. Part A: Polym. Chem, **33**, 2463
- [20] **Crivello, J. V and Kim, W.G.**, 1994. J. Polym. Sci Part A: Polym. Chem, **32**, 1639
- [21] **Mah, S and Chai, C.**, 1994. Han'guk samyu Kong, **31**, 768
- [22] **Crivello, J.V and Narayan, R.**, 1996. Macromolecules, **29**, 439
- [23] **Crivello, J.V.**, 1983. Org. Coat, **5**, 35
- [24] **Honhsed, W.J.**, US Pat 3, 418, 289 (prior to 24. 12. 69) to Du Pont de Nemours Co
- [25] **Dektar, J.L. and Hacker, N.P.**, 1990. J. Am. Chem. Soc, **112**, 6004
- [26] **Hacker, N.P. and Dektar, J.L.**, 1989. Polym. Mater. Sci. Eng, **61**, 76
- [27] **Dektar, J.L. and Hacker, N.P.**, 1987. J. Am. Chem. Soc. Chem. Commun , 1591
- [28] **Hacker, N.P. and Dektar, J.L.**, 1989. Polym. Mater. Sci. Eng, **61**, 76
- [29] **Uno, H., Takata, T. and Endo, T.**, 1991. Macromol. Chem, **192**, 655
- [30] **Gupta, S., Thijs, L. and Neckers, D.C.**, 1980. Macromolecules, **13**, 1037
- [31] **Abu- Abdoun, I.I. and Alae- Ali.**, 1992. Eur. Polym. J., **28**, 73
- [32] **Takata, T., Takuma, K. and Endo, T.**, 1993. Macromol. Chem Rapid Commun, **14**, 203
- [33] **Takuma, K., Takata, T. and Endo, E.**, 1993. J. Photopol. Sci. Technol., **6**, 67
- [34] **Abu- Abdoun, I.I. and Alae- Ali.**, 1993. Eur. Polym. J. ,**29**, 1445
- [35] **Yagci, Y.**, 1989. J. Rad. Curing, **9**, 16
- [36] **Yagci, Y. and Schnabel, W.**, 1992. Macromol. Chem., Macromol Symp. **60**, 133
- [37] **Bauman, H. and Timpe, H.J.**, 1984. Z. Chem, **24**, 18

- [38] **Böttcher, A., Hasebe, K., Hızal, G., Yagci, Y., Stellberg, P. and Schnabel, W.**, 1991. *Polymer*, **32**, 2289
- [39] **Dektar, J.L. and Hacker, N.P.**, 1988. *J. Org. Chem*, **53**, 1833
- [40] **Dossow, D., Yagci, Y. and Schnabel, W.**, 1996. *Polymer*, **37**, 2821
- [41] **Devoe, R.J., Sayhun, M.R.V., Schmidt, E., Serpane, N. and Sharma, D.K.**, 1988. *Can. J.Chem*, **66**, 319
- [42] **Hızal, G., Yagci, Y. and Schnabel, W.**, 1994. *Polymer*, **35**, 2428
- [43] **Yagci, Y., and Reetz, I.**, 1994. *Macromol. Symp.*, **132**, 153
- [44] **Reetz, I., Bacak, V., and Yagci, Y.**, 1997. *Macromol. Chem. Phys.*, **198**, 19
- [44] **Reetz, I., Bacak, V., and Yagci, Y.**, 1997. *Polymer International*, **43**, 27
- [46] **Yagci, Y. and Önen, A.**, 1996. *J. Polym. Sci. Part A: Polym. Chem*, **34**, 3622
- [47] **Denizligil, S., Yagci, Y. and Mc Ardle, C.**, 1995. *Polymer*, **36**, 3093
- [48] **Denizligil, S., Resul, R., Yagci, Y., Mc Ardle, C. and Fouassier, J.P.**, 1996. *Macromol. Chem. Phys.*, **197**, 1233
- [49] **Atmaca, L.**, 1999. M. Sc Thesis of Institute of Science And Arts Istanbul Tech. University, Department of Chemistry, Istanbul

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