ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF DIENIC SALTS AND THEIR USE AS ADDITION-FRAGMENTATION TYPE INITIATORS FOR CATIONIC POLYMERIZATION

M.Sc. Thesis by

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DİEN TÜRÜ TUZLARIN SENTEZİ, KARAKTERİZASYONU VE KATYONİK POLİMERİZASYONDA KATILMA-BÖLÜŞME BAŞLATICISI OLARAK KULLANIMLARI

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LIST OF ABBREVIATIONS

AFA	:Addition-Fragmentation Agent
TPD	:5-Thiophenium-1,3-pentadiene hexafluoroantimonate
PPD	:5-Pyridinium-1,3-pentadiene hexafluoroantimonate
I	:Initiator
M	:Monomer
$\mathbf{R^{\cdot}}$	:Radical
$\mathbf{C^{+}}$	:Cation
$\mathbf{C^{-}}$	:Anion
$\mathbf{C^{+\cdot}}$	:Radical Cation
$\mathbf{On^{+}}$	:Onium Salt
$\mathbf{^{1}H}$**-NMR**	:Proton Nuclear Magnetic Resonance
CT	:Charge-Transfer
$\mathbf{S^{*}}$	:Sensitizer
$\mathbf{E^{*}(S)}$	:Excitation Energy of the Sensitizer
$\mathbf{E^{*}(I)}$	:Excitation Energy of the Photoinitiator
AIBN	:2,2'-Azobisisobutyronitrile
BPO	:Benzoyl Peroxide
PAT	:Phenylazotriphenyl methane
B	:Benzoin
TMDPO	:Trimethoxybenzoyldiphenylacylphosphine oxide
CHO	:Cyclohexene oxide
$\mathbf{M_{n}}$	:Number Average Molecular Weight

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SYNTHESIS AND CHARACTERIZATION OF DIENIC SALTS AND THEIR USE AS ADDITION-FRAGMENTATION TYPE INITIATORS FOR CATIONIC POLYMERIZATION

SUMMARY

In this study, diene-type addition-fragmentation agents namely, 5-thiophenium-1,3-pentadiene (TPD) and 5-pyridinium-1,3-pentadiene (PPD) salts with hexafluoroantimonate counter anion were prepared by reacting 5-bromo-1,3-pentadiene with tetrahydrothiophen and pyridine, respectively and subsequent counter anion exchange was performed with sodium hexafluoroantimonate. These salts were then characterized. They were used in the cationic polymerization of cyclohexene oxide (CHO), both thermally and photochemically. Polymerization was initiated upon thermolysis at 70°C or photolysis at 350 nm in bulk solutions containing one of the dienic salts (TPD or PPD) and a respective free radical initiator. Benzoyl peroxide (BPO), 2,2'-azobisisobutyronitrile (AIBN) and phenylazotriphenyl methane (PAT) were used as thermal, benzoin (B) and trimethoxybenzoyldiphenylacylphosphine oxide (TMDPO) were used as photochemical sources of free radicals. The addition-fragmentation reaction mechanism involves (a) the formation of radicals by heating or irradiating the radical initiator, (b) the addition of these radicals to an AFA molecule and (c) the fragmentation of the AFA. In step (c), radical cations are produced, which with high rates initiate the polymerization of CHO which can only be polymerized cationically. This study deals with contribution of addition-fragmentation and electron transfer mechanisms for the initiation and time-conversion curves indicate that such systems consisting of free radical initiator and dienic salt are suitable for thermally and photochemically induced cationic polymerization.

DİEN TÜRÜ TUZLARIN SENTEZİ, KARAKTERİZASYONU VE KATYONİK POLİMERİZASYONDA KATILMA-BÖLÜŞME BAŞLATICISI OLARAK KULLANIMLARI

ÖZET

Bu çalışmada, 5-brom-1,3-pentadien, tetrahidrotiyofen ve piridin ile ayrı ayrı raeksiyona sokulmuş, anyon değişimi sodyum hekzaflorantimonat ile gerçekleştirilerek dien türü katılma-bölüşme reaktifleri olan 5-tiyofenyum-1,3-pentadien (TPD) ile 5-piridinyum-1,3-pentadien (PPD) tuzları hekzaflorantimonat anyonu ile sentezlenmiştir. Elde edilen tuzlar karakterize edilmiş ve siklohekzen oksidin (CHO) termal ve fotokimyasal katyonik polimerizasyonunda kullanılmıştır. Polimerizasyon, çözücüsüz ortamda dien türü tuzlardan biri (TPD veya PPD) ile beraber uygun serbest radikal başlatıcı kullanılarak 70°C'de termoliz veya 350 nm'de fotoliz sonucu başlatılmıştır. Benzoil peroksit (BPO), 2,2'-azobisizobutironitril (AIBN) ve fenilazotrifenil metan (PAT) termal, benzoin (B) ve trimetoksibenzoildifenilaçilfosfin oksit (TMDPO) fotokimyasal radikal kaynağı olarak kullanılmıştır. Katılma-bölüşme reaksiyonları (a) radikal kaynağının ısıtılması veya aydınlatılması sonucu radikallerin oluşmasını, (b) bu radikallerin AFA molekülüne katılmasını ve (c) AFA'nın bölüşmesini içerir. En son adımda oluşan radikal katyonlar, sadece katyonik olarak polimerleşebilen siklohekzen oksidin polimerizasyonunu başlatır. Bu çalışmada katılma-bölüşme ve elektron transfer mekanizmalarının katyonik polimerizasyonun başlama aşaması üzerindeki etkileri incelenmiştir. Elde edilen veriler sonucunda çizilen zaman-dönüşüm eğrileri serbest radikal kaynağı ve dien türü tuz içeren sistemlerin, termal ve fotokimyasal yolla başlatılan katyonik polimerizasyon için uygun olduğunu göstermiştir.

1. INTRODUCTION

In the past decade, addition-fragmentation reactions turned out to be a versatile and exceptionally interesting tool for polymer synthesis. Addition–fragmentation reactions are applied in both free radical and cationic polymerizations [1]. Many reports have appeared on the application of the addition–fragmentation method for chain length control in free radical polymerization and for deriving end-functional polymers. Appropriately substituted allylic compounds such as sulphides, bromides, peroxides, vinyl ethers have been shown to be efficient addition-fragmentation agents (AFA) in free radical polymerizations [2,3].

Diene type AFAs were also found to exhibit chain transfer properties and to be used for diene functional macromonomers [4].

The initial process of the addition-fragmentation reactions is quite similar in both radical and cationic polymerizations. However, the addition-fragmentation reactions in cationic polymerization concerns only the initiation step [5-12]. With the aid of specially designed allyl-onium salts, cationic AFAs, in conjunction with conventional radical initiators, it is possible to very efficiently initiate cationic polymerizations. The mechanism involves (a) the formation of radicals by heating or irradiating the radical initiator, (b) the addition of these radicals to an AFA molecule and (c) the fragmentation of the AFA. In step (c), radical cations are produced, which with high rates initiate the polymerization of cationically polymerizable monomers (e.g., cyclohexene oxide, CHO).

The obvious advantage of using AFAs for cationic polymerization is that, depending on the nature of the radical source used, initiation can be triggered by either heat or light. Moreover, as far as photopolymerization is concerned, it is extremely easy to tune to a desired wavelenghts' range (the emission maximum of the irradiation source used) by choosing appropriate radical initiators.

This study describes the synthesis and activity of 5-thiophenium-1,3-pentadiene (TPD) and 5-pyridinium-1,3-pentadiene (PPD) salts with hexafluoroantimonate counter anion in conjunction with radical sources as thermally and photochemically initiating systems for cationic polymerization of cyclohexene oxide (CHO).

2. THEORY

2.1. RADICAL POLYMERIZATION

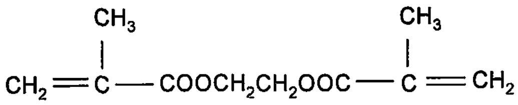
Today, free-radical polymerization has received more intensive study than any other chemical chain reaction; countless investigations have contributed to industry and to the chemistry of free radicals. Free-radical polymerization still accounts for a large proportion of mass produced polymers: in 1985 over 46% (by weight) of the total U.S. production of plastics involved this type of polymerization [13,14].

2.1.1. Monomers

Monomers in free-radical polymerization are commonly monosubstituted or unsymmetrically (1,1-) disubstituted ethylenes, $CH_2{=}CHX$ or $CH_2{=}CXY$.

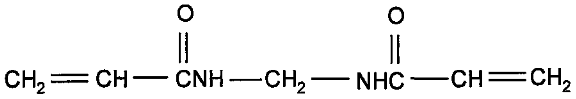
Symmetrically disubstituted (1,2-) ethylenes don't homopolymerize readily as a rule.

Dienes constitute an important class of vinyl monomers. Those having isolated double bonds are typified by *p*-divinyl benzene, ethylene glycol dimethacrylate (1), and N,N′-methylenebisacrylamide (2). Either one or both double bonds may participate in polymerization; when both react, cross-linked structures are generated.



$$CH_2{=}\overset{\overset{\textstyle CH_3}{|}}{C}{-}COOCH_2CH_2OOC{-}\overset{\overset{\textstyle CH_3}{|}}{C}{=}CH_2$$

(1)



$$CH_2{=}CH{-}\overset{\overset{\textstyle O}{\|}}{C}NH{-}CH_2{-}NH\overset{\overset{\textstyle O}{\|}}{C}{-}CH{=}CH_2$$

(2)

Divinyl monomers such as (1) and (2) are used increasingly for this purpose.

Examples of dienes containing conjugated double bonds are butadiene, isoprene, and chloroprene. These important monomers may react by 1,2 or 3,4 addition, or by 1,4 addition. In the former two cases polymerization gives chains with pendant vinyl groups, whereas 1,4 addition leads to unsaturation within polymer chains.

2.1.2. Component Reactions

A typical free-radical polymerization comprises four elementary steps: initiation, propagation, termination and chain transfer [15-17].

In *initiation* a free radical R_0 derived from an initiator, the "primary radical", adds to a monomer molecule to form an active center, a free radical that subsequently propagates :

$$R_0\cdot + CH_2{=}CXY \longrightarrow R_0{-}CH_2{-}\dot{C}XY \qquad (2.1)$$

Other initiating reactions, such as addition to the head of the molecule

$$R_0\cdot + CH_2{=}CXY \longrightarrow R_0{-}CXY{-}\dot{C}H_2 \qquad (2.2)$$

or hydrogen abstraction, are possible but less common; their importance depends on the structures of the radical and the monomer.

If M represents a monomer molecule, equations 2.1 and 2.2 may be summarised as

$$R_0\cdot + M \longrightarrow R_1\cdot \qquad (2.3)$$

The *propagation* or growth reaction consists of the (rapid) addition of monomer molecules to the radical species. Usually, it occurs in head-to-tail fashion:

$$R_0{-}CH_2{-}\dot{C}XY + CH_2{=}CXY \longrightarrow R_0{-}CH_2{-}CXY{-}CH_2{-}\dot{C}XY \qquad (2.4)$$

$$R_0\!\left[CH_2-CXY\right]_n\!CH_2-\dot{C}XY + CH_2=CXY \longrightarrow R_0\!\left[CH_2-CXY\right]_m\!CH_2-\dot{C}XY \tag{2.5}$$

However, as with initiation, alternatives are possible and head-to-head, tail-to-head, and tail-to-tail modes occur, usually to minor extents.

In *termination*, growth of polymer chains is brought to an end by the destruction of propagating radicals. Normally, in the absence of retarding species that destroy growing radicals, chain termination occurs by bimolecular interaction of radicals. These processes, analogous to those taking place with simple alkyl radicals, consist of radical combination or disproportionation:

$$R-CH_2-\dot{C}XY + R-CH_2-\dot{C}XY \longrightarrow R-CH_2-CXY-CXY-CH_2-R \tag{2.6}$$

$$R-CH_2-\dot{C}XY + R-CH_2-\dot{C}XY \longrightarrow R-CH_2-CHXY + R-CH=CXY \tag{2.7}$$

Disproportionation leads to two polymer molecules, one saturated and one containing a terminal double bond. Many monomers show both types of termination: thus in methyl methacrylate, disproportionation is approximately twice as rapid as combination at room temperature and increases in importance as the temperature is raised. On the other hand, styrene and acrylonitrile radicals terminate preponderantly by combination.

Atom (often hydrogen) abstraction from saturated molecules is a well-known reaction of free radicals and, as would be expected, is important in free-radical polymerization. It leads to the *chain-transfer* process, which brings about the cessation of growth of a propagating radical and at the same time produces a new small radical which may propagate. A great variety of species can participate in chain transfer, act as transfer agents. Chain transfer, therefore, occurs widely; it commonly involves reaction of growing chains with monomer or solvent or other additive and is well established for polymers and some initiators. Atoms other than hydrogen, notably halogens (except fluorine), may be transferred. Transfer to monomer and to carbon tetrachloride is illustrated in 2.8 and 2.9, respectively:

$$R_n\cdot + CH_2{=}CHX \longrightarrow R_n{-}H + CH_2{=}\dot{C}X \tag{2.8}$$

$$R_n\cdot + CCl_4 \longrightarrow R_n{-}Cl + \dot{C}Cl_3 \tag{2.9}$$

In general, the effect of chain transfer on the overall polymerization is determined by the reactivity of the transfer radical formed. If the latter is very reactive towards monomer, it rapidly reinitiates, begins to propagate.

Alkyl mercaptans are active transfer agents by virtue of the relative weakness of the S-H bond:

$$R_n\cdot + R{-}SH \longrightarrow R_n{-}H + R{-}\dot{S} \tag{2.10}$$

$$R{-}\dot{S} + CH_2{=}CXY \longrightarrow R{-}S{-}CH_2{-}\dot{C}XY \tag{2.11}$$

When the transfer radical is unreactive, reinitiation may not occur or be very slow. The transfer agent then behaves as a retarder and reduces the rate of polymerization by converting propagating radicals into unreactive species. The latter may ultimately disappear by reaction with propagating radicals or by dimerization.

Chain transfer to polymer normally gives rise to branched or cross-linked molecules.

2.1.3. Ideal Polymerization Mechanism

The four component reactions discussed are set out in the following:

Initiation

$$I \longrightarrow 2\,R_0\cdot \tag{2.12}$$

$$R_0\cdot + M \longrightarrow \dot{R}_1 \tag{2.13}$$

Propagation

$$\dot{R}_1 + M \longrightarrow \dot{R}_2 \tag{2.14}$$

$$\dot{R}_r + M \longrightarrow \dot{R}_{r+1} \tag{2.15}$$

Transfer to monomer or substrate

$$\dot{R}_r + M \longrightarrow P_r + \dot{M} \tag{2.16}$$

$$\dot{R}_r + S \longrightarrow P_r + \dot{S} \tag{2.17}$$

Reinitiation by transfer radicals

$$\dot{M} + M \longrightarrow \dot{R}_2 \tag{2.18}$$

$$\dot{S} + M \longrightarrow \dot{R}_1 \tag{2.19}$$

Termination

In these equations I, M, and S represent initiator, monomer, and solvent (or other substrate), respectively, and P, stands for a dead polymer molecule containing *r* monomer units.

$$\dot{R}_r + \dot{R}_s \longrightarrow P_{r+s} \tag{2.20}$$

$$\dot{R}_r + \dot{R}_s \longrightarrow P_r + P_s \tag{2.21}$$

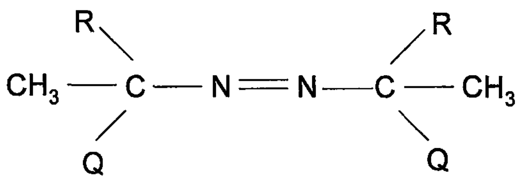
2.1.4. Initiation

Polymerization of a reactive vinyl monomer is initiated by free radicals having sufficiently high activity. These may be generated from initiators in diverse ways, among which thermal or photochemical intramolecular bond cleavage, redox reactions, and photochemical hydrogen abstraction are the commenest, but other processes such as use of γ-radiation or electron beams find applications.

2.1.4.1. Thermal Initiators: Intramolecular Bond Cleavage

Azo Initiators

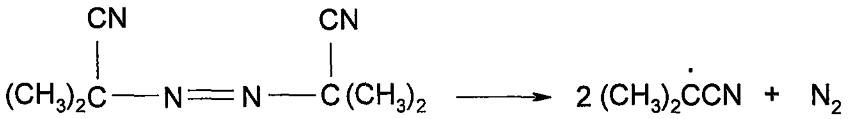
Most of the compounds are represented by the formula



$$CH_3-C(R)(Q)-N=N-C(R)(Q)-CH_3$$

where R = alkyl and Q is a simple carboxylic acid residue or a derivative (nitrile, ester). Azobisisobutyronitrile (AIBN) is very widely used as an initiator: 4,4′-azo-4-cyanopentanoic acid ($R=CH_3$, $Q=(CH_2)_2COOH$) has rather similar initiating properties and, unlike AIBN, is soluble in water.

Thermal decomposition of AIBN and its analogues is generally considered to produce cyanoisopropyl radicals (or analogues) according to the following reaction:

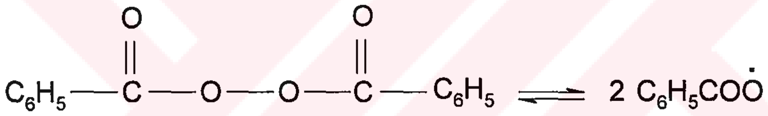


$$(CH_3)_2\overset{CN}{\overset{|}{C}}-N=N-\overset{CN}{\overset{|}{C}}(CH_3)_2 \longrightarrow 2\,(CH_3)_2\dot{C}CN + N_2$$

(2.22)

Peroxy Compounds

Benzoyl peroxide is a well-established initiator of polymerization. As with other peroxides, the primary step in the thermal decomposition is scission of the — O — O — bond to give two acyloxy radicals. A number of secondary processes may follow; in addition to reacting with monomer, benzoyloxy radicals may recombine or undergo β-scission to phenyl radicals and carbon dioxide. Further, recombination reactions giving biphenyl and phenyl benzoate may then occur.

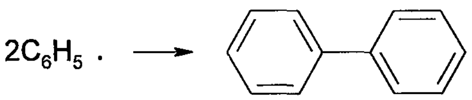


$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \rightleftharpoons 2\,C_6H_5CO\dot{O}$$

(2.23)

$$C_6H_5CO\dot{O} \longrightarrow C_6H_5\cdot + CO_2$$

(2.24)



(2.25)

$$C_6H_5CO\dot{O} + C_6H_5\cdot \longrightarrow C_6H_5COOC_6H_5$$

(2.26)

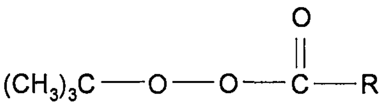
Di-t-butyl peroxide is useful as a thermal initiator at temperatures above 100°C. Since it also initiates photochemically, it may be employed for purely photochemical initiation at temperatures that bring about rapid decomposition of many initiators. The primary step in decomposition is rupture of the peroxide bond, yielding two *t*-butyloxy radicals, which may undergo β-scission into acetone and methyl or enter into hydrogen abstraction reactions with the peroxide or other substance present.

$$(CH_3)_3C-O-O-C(CH_3)_3 \longrightarrow 2\,(CH_3)_3C-\dot{O} \tag{2.27}$$

$$(CH_3)_3C-\dot{O} \longrightarrow (CH_3)_2C{=}O + \dot{C}H_3 \tag{2.28}$$

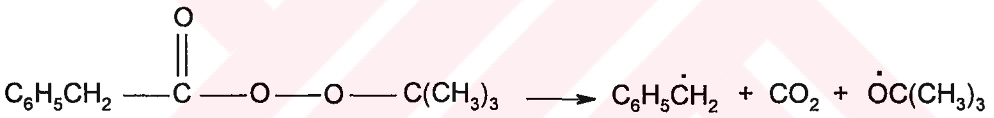
Peresters

The thermolysis of *t*-butyl peresters has received detailed attention [18-20].



$$(CH_3)_3C-O-O-\overset{\overset{\displaystyle O}{\|}}{C}-R$$

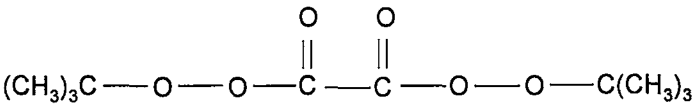
Evidence was adducted for the occurrence of concerted rupture of C — C and O — O bonds on thermolysis , for example with *t*-butyl phenylperacetate [21]:



$$C_6H_5CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-C(CH_3)_3 \longrightarrow C_6H_5\dot{C}H_2 + CO_2 + \dot{O}C(CH_3)_3 \tag{2.29}$$

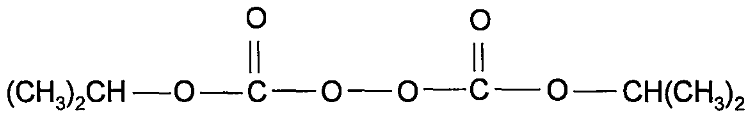
The driving force arises partly from formation of the very stable CO_2 and partly from the (resonance) stabilization of the hydrocarbon radicals (benzyl in the above) if this considerably exceeds that of the methyl or phenyl radical.

Peroxalates with the exception of di-t-butyl peroxyoxalate Y= $(CH_3)_3CO$, yield thermolysis products consistent with the carbalkoxy group (Y— O — CO) remaining intact: *t*-butyl alkyl carbonate, alkyl formate, and the ester YOOCR, derived from the solvent RH. No corresponding products arise from di-*t*-butyl peroxyoxalate, and it is possible that concerted three-bond cleavage occurs with this compound [22,23].



$$(CH_3)_3C-O-O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-C(CH_3)_3$$

Many of these peresters function as low-temperature initiators of free-radical polymerization. Although some of the stabilized radicals may not be effective initiators, the *t*-butoxy radical and its β-scission product, methyl, initiate readily. Di-*t*-butyl peroxyoxalate initiates well at 25°C. Di-isopropyl peroxydicarbonate is a familiar perester which initiates well at moderate temperatures [24].



$$(CH_3)_2CH-O-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-O-CH(CH_3)_2$$

2.1.4.2. Redox Initiation

Many oxidation-reduction reactions produce radicals that can be used to initiate polymerization. This type of initiation is referred as *redox initiation, redox catalysis,* or *redox activation.* A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular redox system, including initiation at moderate temperatures of 0-50°C and even lower. This allows a greater freedom of choice of the polymerization temperature that is possible with the thermal homolysis of initiators [25].

Types of Redox Initiators

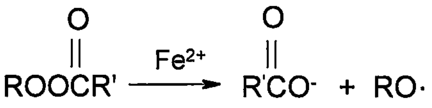
1. Peroxides in combination with a reducing agent are a common source of radicals, for example, the reaction of hydrogen peroxide with ferrous ion

$$H_2O_2 + Fe^{2+} \longrightarrow HO^- + HO\cdot + Fe^{3+} \tag{2.30}$$

Ferrous ion also promotes the decomposition of a variety of other compounds including various types of organic peroxides.

$$ROOR \xrightarrow{Fe^{2+}} RO^- + RO\cdot \tag{2.31}$$

$$ROOH \xrightarrow{Fe^{2+}} HO^- + RO\cdot \tag{2.32}$$



$$\mathrm{ROO\overset{\overset{\displaystyle O}{\|}}{C}R'} \xrightarrow{Fe^{2+}} \mathrm{R'\overset{\overset{\displaystyle O}{\|}}{C}O^{-}} + \mathrm{RO\cdot}$$

(2.33)

Other reductants such as Cr^{2+}, V^{2+}, Ti^{3+}, Co^{2+}, and Cu^{+} can be employed in place of ferrous ion in many instances.

2. The combination of a variety of inorganic reductants and inorganic oxidants initiates radical polymerization, for example,

$$^{-}O_3S—O—O—SO_3^{-} + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-}\cdot$$

(2.34)

$$^{-}O_3S—O—O—SO_3^{-} + S_2O_3^{2-} \longrightarrow SO_4^{2-} + SO_4^{-}\cdot + \cdot S_2O_3^{-}$$

(2.35)

Other redox systems include reductants such as HSO_3^{-}, SO_3^{2-}, $S_2O_3^{2-}$, and $S_2O_5^{2-}$ in combination with oxidants such as Ag^{+}, Cu^{2+}, Fe^{3+}, ClO_3^{-}, and H_2O_2.

3. Organic-inorganic redox pairs initiate polymerization, usually but not always by oxidation of the organic component, for example, the oxidation of an alcohol by Ce^{4+}:

$$R—CH_2—OH + Ce^{4+} \longrightarrow Ce^{3+} + H^{+} + R—\overset{\bullet}{C}H—OH$$

(2.36)

or by V^{5+}, Cr^{6+}, Mn^{3+}.

4. There are some initiator systems in which the monomer itself acts as one component of the redox pair. Examples are thiosulfate plus acrylamide or methacrylic acid and N,N-dimethylaniline plus methyl methacrylate.

2.1.4.3. Photoinitiators

Photoinitiators for free-radical polymerization fall into two classes: those which on irradiation undergo intramolecular bond cleavage with radical generation and those which when photoexcited abstract hydrogen atoms from H-donors and so form radicals.

Photoinitiation by Intramolecular Bond Cleavage

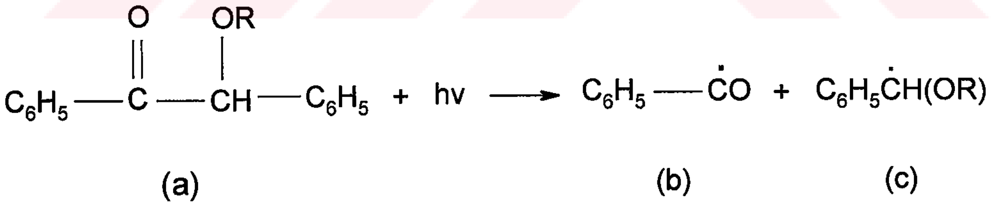
Most peroxy initiators yield radicals on photolysis and benzoyl peroxide has frequently been used as a photoinitiator [26,27]. They require shorter wavelengths than azo compounds (<300nm), a disadvantage since many monomers absorb in this region. The same remark applies to many simple ketones which photodissociate according to the Norrish type I mechanism [28].

$$\mathrm{RCOR'} + h\nu \longrightarrow \mathrm{R\dot{C}O} + \mathrm{\dot{R}'} \tag{2.37}$$

Ketones carrying alkyl chains three or more carbon atoms long may undergo the essentially nonradical Norrish type II fission:

$$\mathrm{CH_3CH_2CH_2COR'} + h\nu \longrightarrow \mathrm{CH_2{=}CH_2} + \mathrm{CH_3COR'} \tag{2.38}$$

Benzoin is a well-known photoinitiator [29,30]. Benzoin ethers (a) which are much used in photocuring process, undergo a type I photodissociation into two different radicals. It has been reported that both types of radicals can initiate the polymerization.



$$\underset{\text{(a)}}{\mathrm{C_6H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle OR}{|}}{C}H{-}C_6H_5}} + h\nu \longrightarrow \underset{\text{(b)}}{\mathrm{C_6H_5{-}\dot{C}O}} + \underset{\text{(c)}}{\mathrm{C_6H_5\dot{C}H(OR)}}$$

(2.39)

Photoinitiation by Hydrogen Abstraction

Photoinitiators of this group are generally aromatic ketones and include benzophenone, benzil, quinones, Michler's ketone, and thioxanthanes. When photoexcited these compounds do not dissociate but enter into bimolecular abstraction reactions with hydrogen donors such as alcohols, ethers, tertiary amines, and so on.

The classical example is benzophenone, of which the photochemistry is well-known [31]. The lowest excited singlet (S_1) is of $n \rightarrow \pi^*$ character and yields by intersystem crossing the lowest excited triplet (T_1). In the presence of a hydrogen donor RH the following reaction occurs:

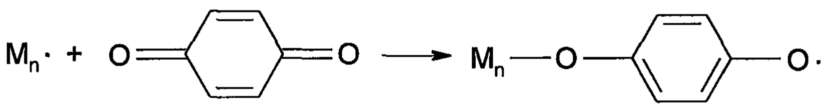
$$(C_6H_5)_2C{=}O + h\nu \longrightarrow \left[(C_6H_5)_2C{=}O\right](S_1) \longrightarrow \left[(C_6H_5)_2C{=}O\right](T_1) \tag{2.40}$$

$$\left[(C_6H_5)_2C{=}O\right](T_1) + RH \longrightarrow (C_6H_5)_2\dot{C}{-}OH + R\cdot \tag{2.41}$$

2.1.5. Types of Inhibitors and Retarders

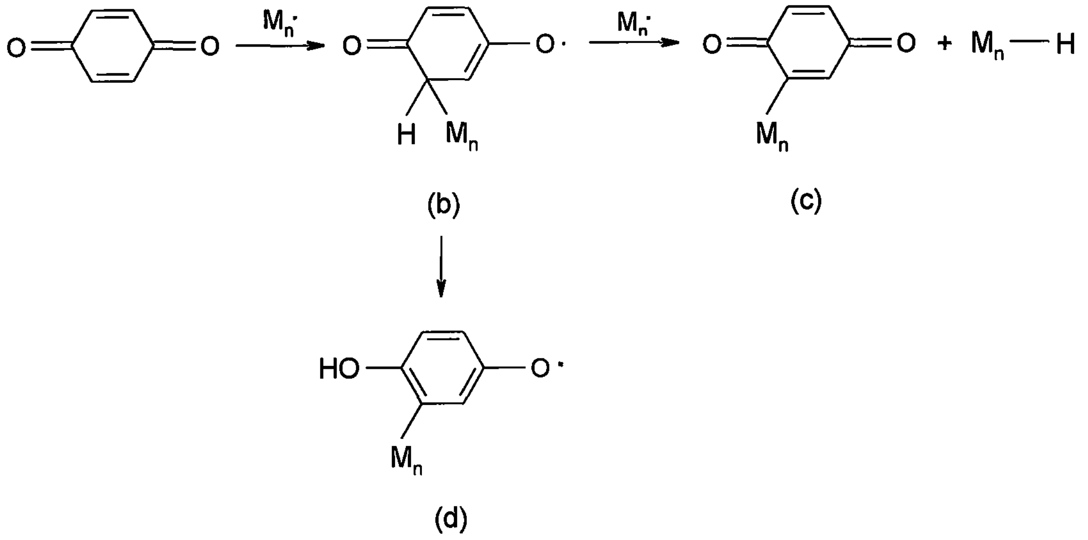
Various types of compounds act as inhibitors and retarders. Stable free radicals that are too stable to initiate polymerization but that can still react with radicals are one type of radical terminator. Diphenylpicrylhydrazyl (DPPH) is such a radical. The stoichiometry between the number of kinetic chains terminated and the number of DPPH radicals consumed is 1:1.

The most useful class of inhibitors are molecules that react with chain radicals to yield radicals of low reactivity. Quinones such as benzoquinone are an important class of inhibitor. The behaviour of quinones is quite complex. Two major types of products are obtained- quinone and ether- formed by the reaction at the C and O atoms of a quinone, respectively.



(a)

(2.42)



(2.43)

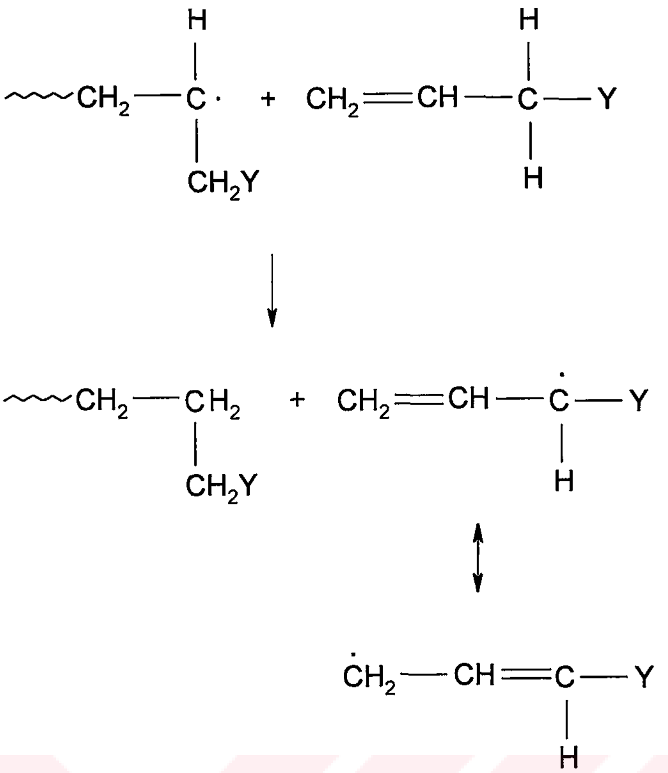
Oxygen is a powerful inhibitor. It reacts with radicals to form the relatively unreactive peroxy radical

$$M_n\cdot + O_2 \longrightarrow M_n{-}O{-}O\cdot \tag{2.44}$$

that reacts with itself or another propagating radical by coupling and disproportionation reactions to form inactive products (probably peroxides or hydroperoxides). Peroxy radicals can also slowly add monomer to yield an alternating copolymer.

2.1.6. Autoinhibition of Allylic Monomers

An especially interesting case of inhibition is the internal or *autoinhibition* of allylic monomers ($CH_2=CH-CH_2Y$). The propagating radical in the polymerization is very reactive, while the allylic C–H bond (the C–H bond alpha to the double bond) in the monomer is quite weak because of the high resonance stability of the allylic radical “f” formed. Therefore, facile chain transfer to monomer is observed.



(f)

(2.45)

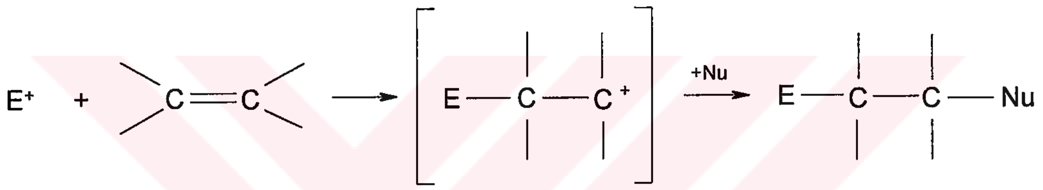
The allylic radicals which are formed are too stable to initiate polymerization . They undergo termination by reaction with each other or, more likely, with propagating radicals.

2.2. CATIONIC POLYMERIZATION

Within the context of polyaddition, cationic polymerization refers to chain growth reactions promoted by active species possessing electrophilic character: carbenium, carbonium, oxonium, sulfonium, ammonium and phosphonium ions, but also molecular chain carriers, ie, mostly esters, which are sufficiently polarized to induce propagation. In these systems, the intrinsic structure and reactivity of the active species are maintained throughout the growth of a polymer molecule. Typical examples of such polyadditions are the cationic polymerizations of alkenyl monomers through the opening of the C=C double bond and of saturated heterocyclic monomers through ring-opening. 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 [14].

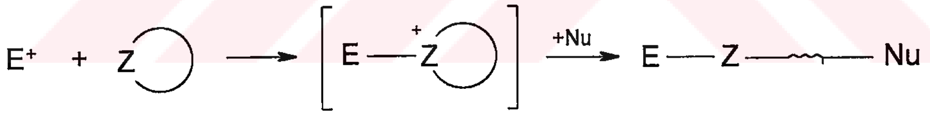
2.2.1. Electrophilic Addition Mechanism and Monomers

All polyadditions can be viewed as special cases of specific physical organic reactions in which the intermediate species manages to survive long enough to ensure the growth of a macromolecule instead of rapidly collapsing into inactive products. A cationic polymerization is a special case of electrophilic addition. Classical electrophilic additions to the two types of common monomers in cationic polymerization, ie, to the olefinic bond in alkenyl compounds and to the heteroatom in saturated heterocyclic compounds, can be represented as



(1)

(2.46)



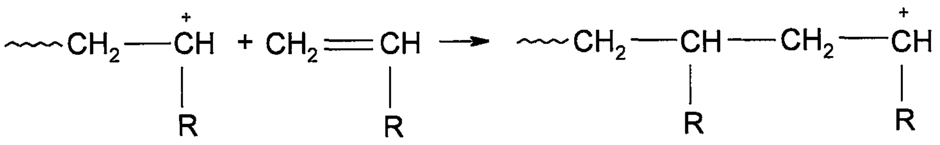
(2)

(2.47)

where Z = O, S, N—, P— etc. In cationic polymerization, the intermediates (1) and (2), shown as positively charged species must be prevented from collapsing through the reaction with an anion for long enough to allow them a large number of successive monomer additions.

2.2.1.1. 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.



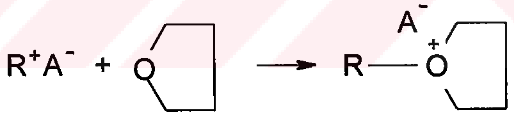
$$\sim CH_2-\overset{+}{\underset{R}{CH}} + CH_2=\underset{R}{CH} \longrightarrow \sim CH_2-\underset{R}{CH}-CH_2-\overset{+}{\underset{R}{CH}}$$

(2.48)

Solvents used in cationic polymerization 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 nitromethane or nitrobenzene and also dioxane.

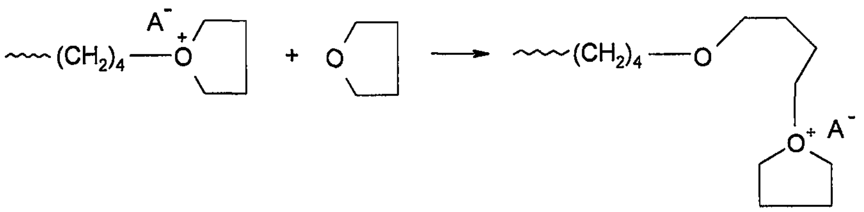
2.2.1.2. Cationic Polymerization of Heterocycles

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



(2.49)

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.

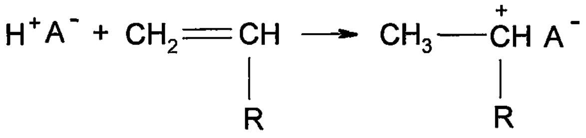


(2.50)

2.2.2. Initiators

2.2.2.1. Bronsted Acids

Sulphuric acid (H_2SO_4), perchloric acid ($HClO_4$), fluorosulphonic acid (FSO_3H), trifluoromethyl sulphonic acid (CF_3SO_3H) and even in some cases trifluoroacetic acid (CF_3COOH) have been employed. The initiation reaction proceeds by protonation;



$$H^+A^- + CH_2{=}\underset{\underset{R}{|}}{CH} \longrightarrow CH_3{-}\underset{\underset{R}{|}}{\overset{+}{C}H}\;A^-$$

(2.51)

2.2.2.2. Iodine

Like Bronsted acids, iodine is an initiator in the cationic polymerization of alkenyl monomers. Iodine solutions in chlorinated hydrocarbons are characterized by the following equilibria [32]:

$$I_4 \rightleftharpoons 2\,I_2 \rightleftharpoons I^+ + I_3^-$$

(2.52)

If alkenes are added to such a solution, diiodination of the double bond is the predominant reaction.

2.2.2.3. Inorganic Lewis Acids

The reactivity of Lewis acids is attributed to the intervention of an empty orbital.

A large number of complexes of variable strength between metal halides; such as $SnCl_4$, $AlCl_3$, BF_3; and water, alcohols, carboxylic acids, hydrogen halides (weak Bronsted acids) and ethers (Lewis bases) have been reported and characterized, eg, $BF_3.(CH_3CH_2)_2O$. These complexes play a dominat role in what is known as cocatalytic initiation of cationic polymerization.

$$AlCl_3 + RCl \rightleftharpoons R^+AlCl_4^-$$

(2.53)

$$BF_3 + H_2O \rightleftharpoons H^+ BF_3OH^- \tag{2.54}$$

2.2.2.4. Organic Lewis Acids

This category of initiators includes salts whose cations are organic entities and polarized molecules in which the electrophilic moiety is organic. Carbenium salts have been used as initiators of cationic polymerization for over 20 years. The more stable ones are triphenylmethylium (trityl, $(C_6H_5)_3C^+$ and analogues) and cycloheptatrienylium (tropylium, $C_7H_7^+$ and analogues) derivatives with anions arising from both strong inorganic acids (ClO_4^-, $CF_3SO_3^-$, etc) and Lewis acids (BF_4^-, SbF_6^-, PF_6^-, $SbCl_6^-$, etc). Given their limited reactivity, with few exceptions, they can polymerize only the more nucleophilic alkenyl monomers, and are quite efficient in the activation of a large number of heterocyclic monomers [33,34].

2.2.3. 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, 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 [35-37] and metal salts [22], molecular weights and percentage conversions increase in the order $BF_4^- \ll PF_6^- < AsF_6^- < SbF_6^-$.

Classical cationic initiators lack the following two disadvantages:

1. 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 the initiator at the beginning of the polymerization is not constant throughout the reaction mixture.

2. 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 are 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 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 that 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.

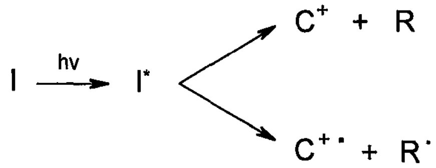
2.2.3.1. Onium Salts

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 [39].

2.2.3.2. 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 $C^{+\cdot}$, respectively.

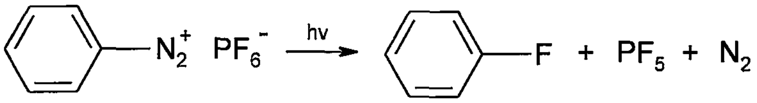


(2.55)

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 Bronsted 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 Bronsted 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 photons.



(2.56)

$$PF_5 + ROH \longrightarrow H^+ \ ROPF_5^-$$

(2.57)

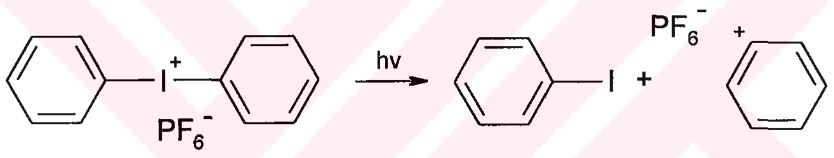
Simple benzyldiazonium salts absorb light only below 300 nm. By substituting the benzene ring, salts absorbing near UV and even visible light could be obtained. The decomposition quantum yields of aryldiazonium salts are relatively high, being usually between 0.3 and 0.6 [40]. However, these salts were, 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 sulphuric acid and acetic anhydride [41,42]. 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. While the heterolytic pathway generates a phenyl cation and an iodobenzene molecule (2.58), a phenyl radical and an iodobenzene radical cation are formed by homolytic cleavage (2.60). Both mechanisms involve the interaction with a hydrogen donating solvent or monomer yielding Bronsted acid which initiates the polymerization. Besides, the reaction of escaping phenyl cations or phenyl radicals with neighbouring iodobenzenes also produces protons and additionally various phenyliodobenzene derivatives.



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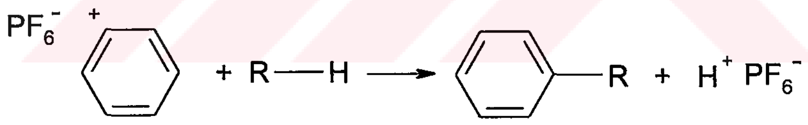

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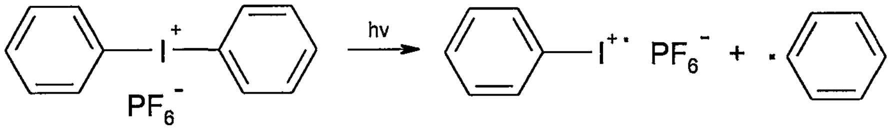

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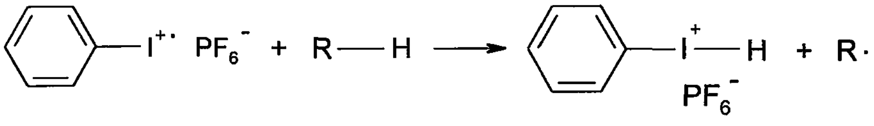

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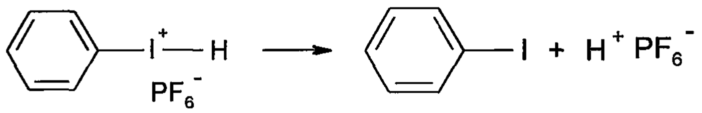


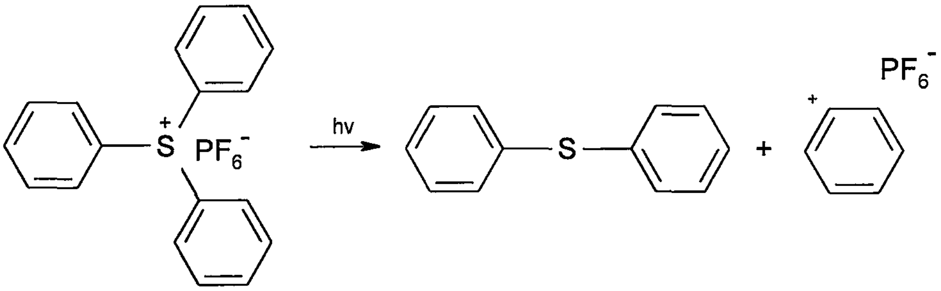
(2.62)

The photolytical formation of phenyliodonium radical cations has been evidenced by its transient absorption spectrum with maxima at 660 and 310 nm [43,44]. The heterolytic bond cleavage is the dominating reaction pathway for the direct irradiation of diaryliodonium salts [45,46]. Bronsted acid, formed upon the direct irradiation of diphenyliodonium salts has been used for the polymerization of many monomers.

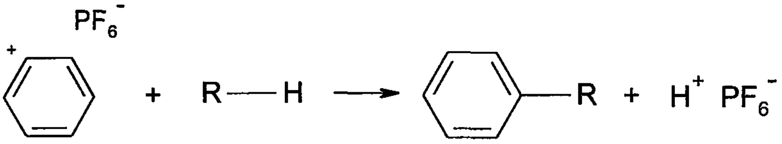
Sulphonium Salts

Regarding cationic photo polymerization, triaryl and alkylaryl sulphonium salts play the predominant role among all sulphonium salts [47]. Trialkyl sulphonium salts are less stable and initiate the polymerization of reactive monomers spontaneously [48].

Regarding the photolysis mechanism of triarylsulphonium salts, both heterolytic (2.63, 2.64) and homolytic (2.65, 2.67) 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 [49]. As in the case of diaryliodonium salts, in secondary reactions strong electrophilic Bronsted acid is produced. This acid initiates the cationic polymerization.



(2.63)



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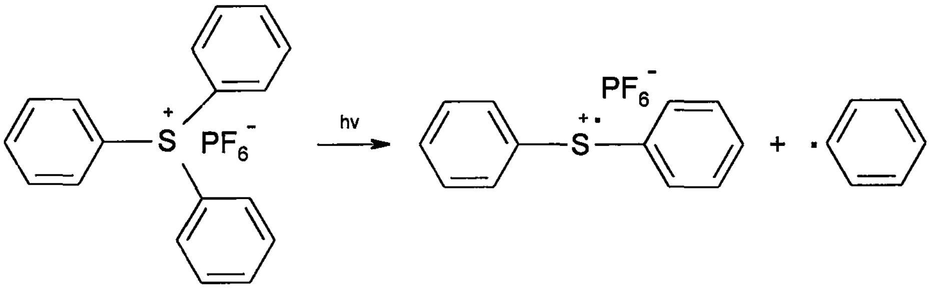

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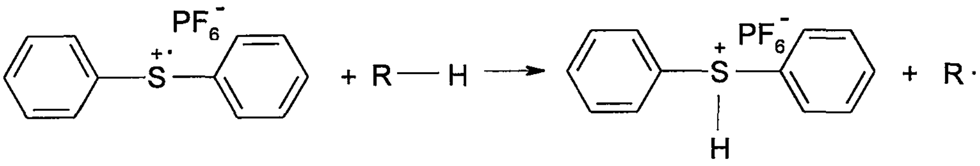

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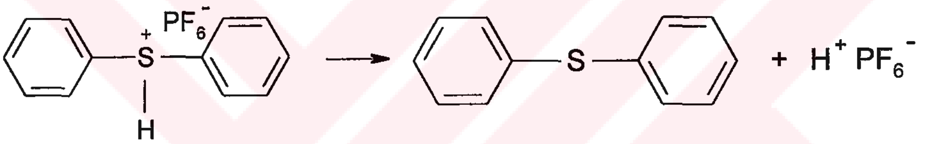
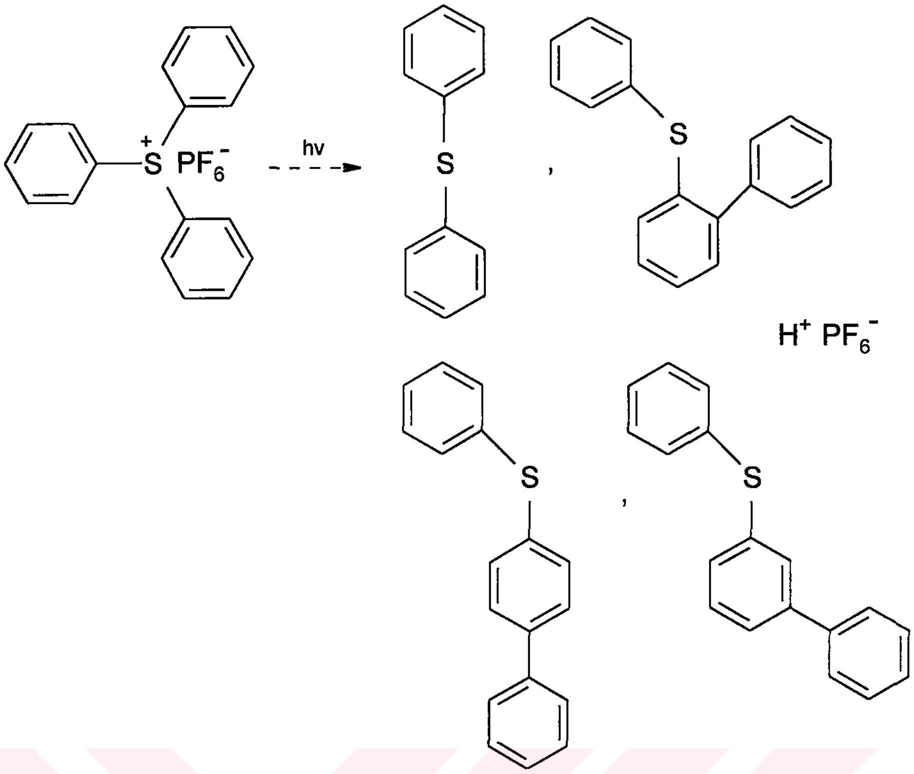


(2.67)

Mechanistic studies based on product analysis [50,51] 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 (2.68). The selectivity ortho > metha > 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.



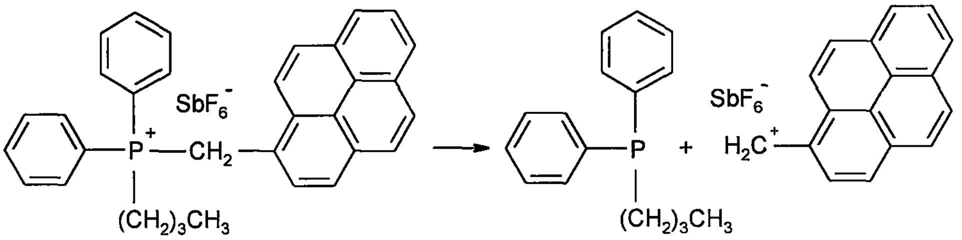
(2.68)

Cationic polymerizations following the direct photolysis of triarylsulphonium salts have been used for the industrially important UV curing of epoxy coatings [52]. Moreover, they were used in a number of investigations with reactive monomers with either epoxide [53-55] or vinyl groups [56].

Phosphonium Salts

The preparation of phosphonium salts is based on the reaction of chloromethylated or bromomethylated aryl compounds with the corresponding phosphines [57-59]. Phosphonium salts with absorptions acceptable for the direct photolysis have been synthesized.

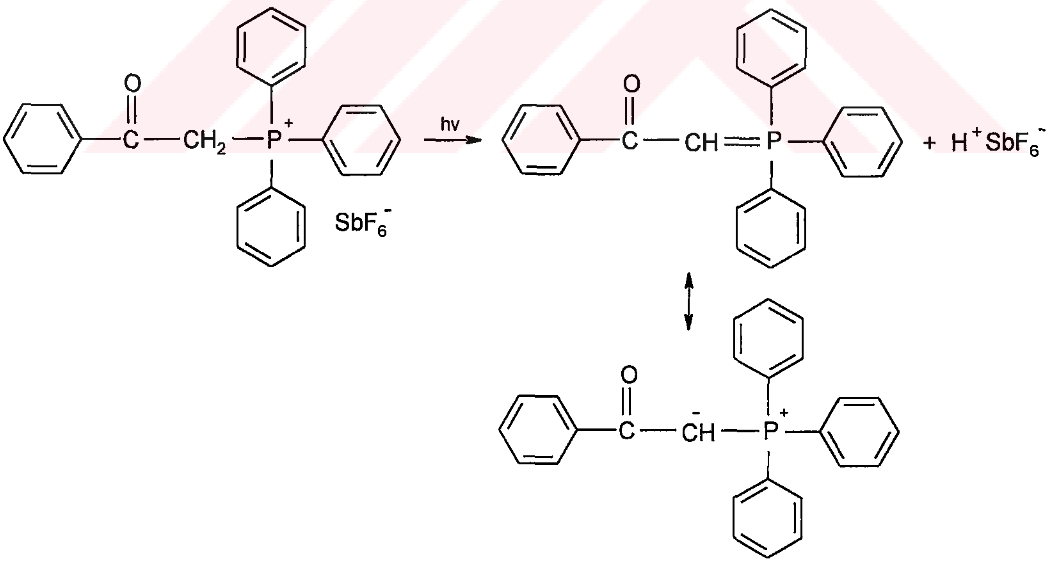
Benzyl or pyrenylmethyl group containing phosphonium salts produce the respective carbon centered cations after a heterolytic bond rupture according to the reaction (2.69) [60-62]. These cations are assumed to be the initiating species in cationic polymerization.



(2.69)

The excellent initiating ability of phosphonium salts containing pyrenylmethyl groups has been demonstrated for epoxides and vinyl monomers [63,64]. In the polymerization of butylvinyl ether, conversions of 100 % were achieved. UV-VIS and ^{1}H-NMR spectra of the polymers obtained gave a clear evidence for the presence of aromatic groups thus providing that, indeed carbocations with aromatic substituents start the chain reaction.

In the case of phenacyltriphenyl phosphonium salts, however, Bronsted acid is expected to initiate cationic polymerizations. They are used in the cationic polymerization of cyclohexene oxide [59,65], styrene [65] and *p*-methyl styrene [65].



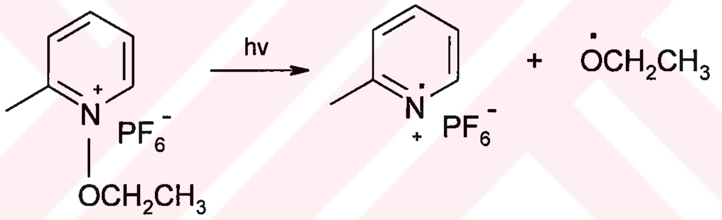
(2.70)

N-Alkoxy Pyridinium Salts

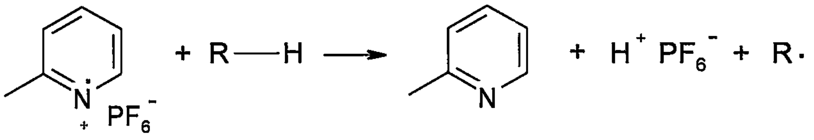
N-Alkoxy pyridinium salts are obtained with relatively high yields by a reaction of pyridine N-oxides with a triethyloxonium salt in methylene chloride or chloroform [66]. Quinolinium salts can also be prepared from the corresponding N-oxides [67]. In both cases, an anion exchange is not necessary since 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 shifts the absorption maximum towards higher wavelengths by 40 nm.

When absorbing UV light in the presence of a cationically polymerizable monomer, pyridinium type salts do readily initiate the polymerization [66,68]. The two initiation mechanisms described are depicted in (2.71-2.72) on the example of N-ethoxy-2-methylpyridinium hexafluorophosphate (EMP$^+$ PF_6^-).



(2.71)



(2.72)

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 higly reactive towards various nucleophilic monomers. Bronsted acid formed in the presence of hydrogen donors (monomer, solvent) may initiate the polymerization, as illustrated in (2.72).

2.2.3.3. Indirect Acting Systems

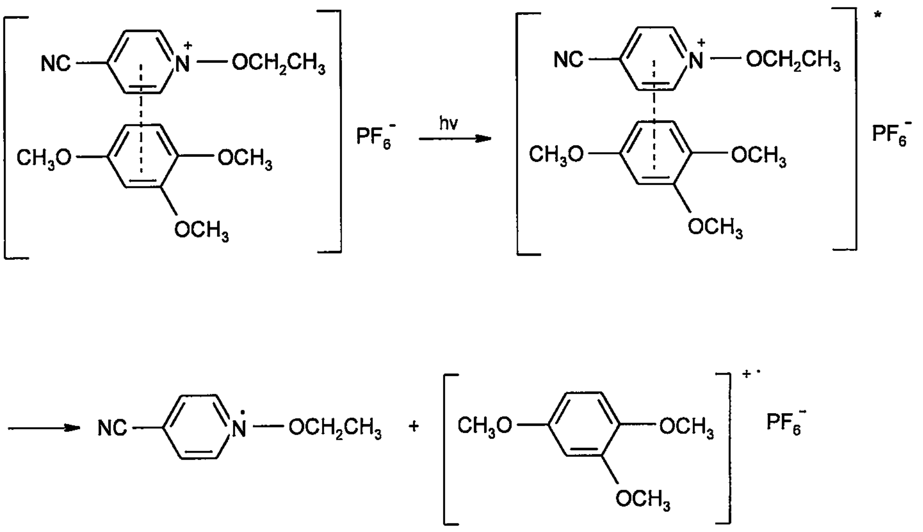
The spectral response of simple onium salts is only rarely acceptable for their practical application. One possibility in handling this problem is the chemical attachment of chromophoric groups to the onium salt making it absorb at higher wavelengths. Besides that, appropriate chemicals may be added to the polymerization mixture. In this manner, charge-transfer complexes, sensitization by energy transfer, oxidation of free radicals, electron transfer via exciplexes and addition-fragmentation reactions can be observed.

Charge-Transfer Complexes

Pyridinium salts are capable of forming ground state CT complexes with electron-rich donors such as methyl- and methoxy-substituted benzene [69]. 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.

Since the proton scavenger 2,6-di-tert-butylpyridine did not noticeably influence the polymerization, the initiation by Bronsted acid that could be formed after an interaction with hydrogen containing components can be excluded.

The following mechanism for the initiation of the cationic polymerization has been suggested:



(2.73)

Sensitization by Classical Energy Transfer

This mechanism involves the electronic excitation of the sensitizer, a molecule possessing a suitable absorption spectrum. 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.

$$S \xrightarrow{h\nu} S^* \tag{2.74}$$

$$S^* + I \longrightarrow S + I^* \tag{2.75}$$

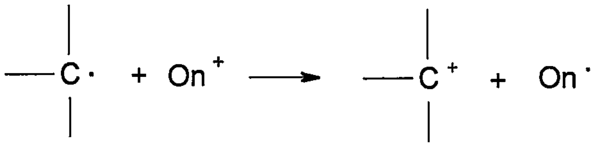
In consequence of the transfer process, the sensitizer returns to its ground state and excited onium salt species (I^*) are formed.

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 $E^*(I)$.

$$E^*(S) \geq E^*(I) \tag{2.76}$$

Oxidation of Free Radicals

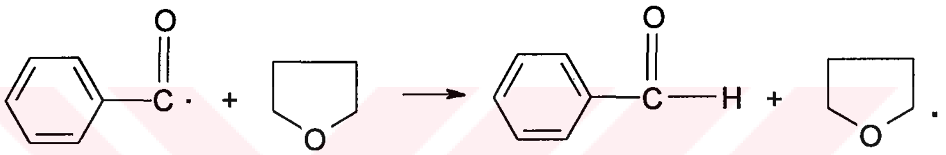
Onium salts may be used to oxidize free radicals according to the reaction (2.77) thus generating reactive cations.



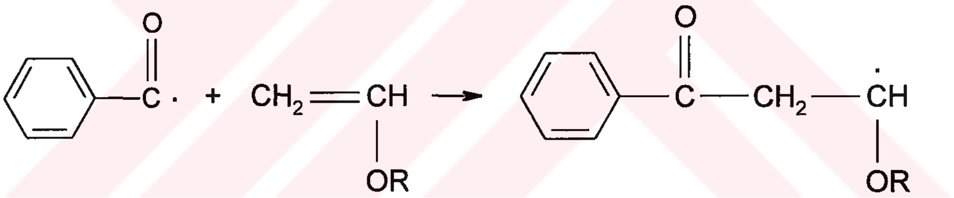
$$-\overset{|}{\underset{|}{C}}\cdot + On^+ \longrightarrow -\overset{|}{\underset{|}{C}}{}^+ + On^\cdot$$

(2.77)

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.



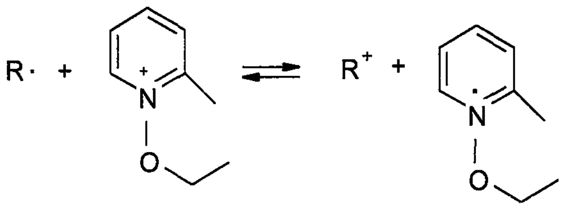
(2.78)



(2.79)

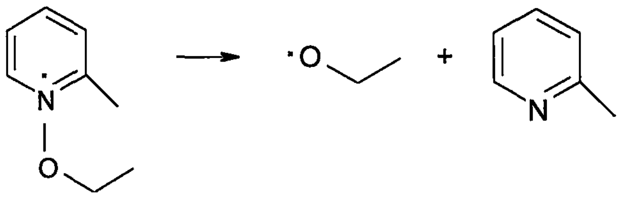
Thus formed, these radicals can easily be oxidized by onium salts yielding initiating species.

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 butyl vinyl ether and cyclohexene oxide [71].



(2.80)

It was found that the pyridinyl radical formed by reaction (2.80) is very short living, decomposing rapidly according to (2.81).



(2.81)

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.

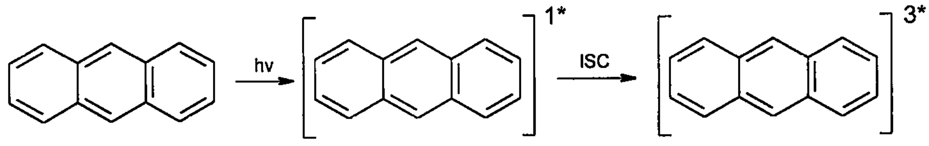
$$S \xrightarrow{h\nu} S^{*} \xrightarrow{On^{+}X^{-}} \left[S^{*} \cdots On^{+}X^{-}\right] \longrightarrow S^{+\cdot}X^{-} + On^{\cdot} \tag{2.82}$$

$$S^{+\cdot}X^{-} + R{-}H \longrightarrow HS^{+}X^{-} + R\cdot \tag{2.83}$$

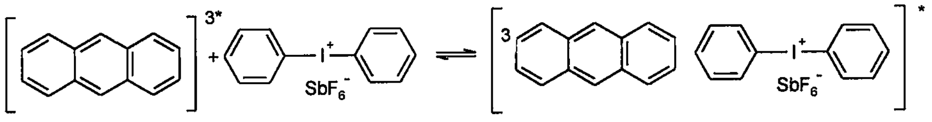
$$HS^{+}X^{-} \longrightarrow H^{+}X^{-} + S \tag{2.84}$$

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 Bronsted acid. In the case of alkoxy pyridinium salts, an additional mechanism has to be taken into account. Alkoxy radicals, which are generated by the decomposition of alkoxy pyridinium salts, react with sensitizer radical cations yielding initiating sulfur centered cations [72].

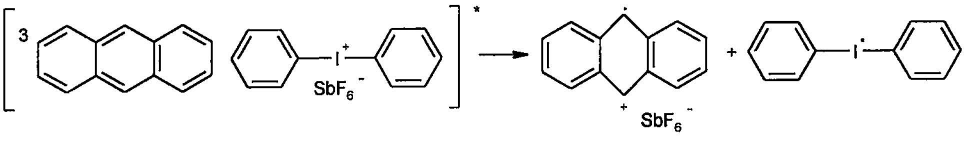
In the case of sensitization of onium salts (especially diphenyliodonium and triphenylsulphonium salts) by anthracene, exciplex formation is followed by a partly loss of anthracene's aromatic system as concluded from the decrease in the sensitizer fluorescence. The reactions are illustrated below on the example of diphenyliodonium salt.



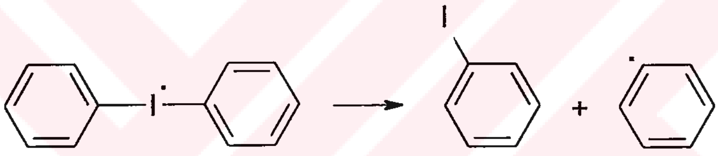
(2.85)



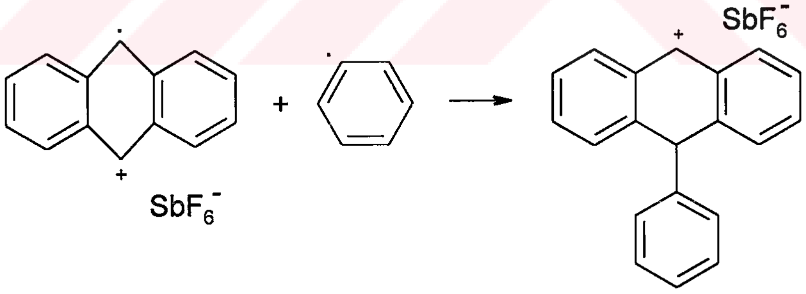
(2.86)



(2.87)



(2.88)



(2.89)

2.2.4. Thermolatent Systems in Cationic Polymerization

As far as cationic polymerization is concerned, it has to be said that some of the onium salts described in the previous section 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 the previous section 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 in 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 temperatures. The initiating compounds have to be stable at room temperature; otherwise their thermal latency would be lost.

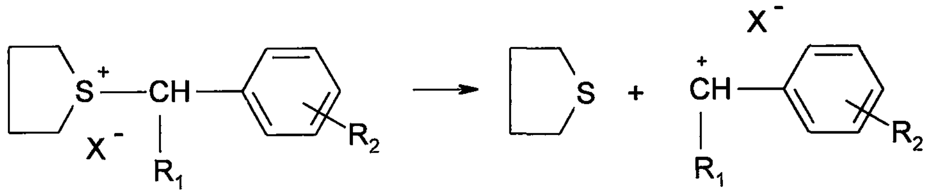
2.2.4.1. Direct Thermolysis

Sulphonium Salts

Sulphonium salts have a considerable potential as cationic photoinitiators. 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, alkylbenzylsulphonium and alkylarylbenzylsulphonium salts possess a high thermal sensitivity.

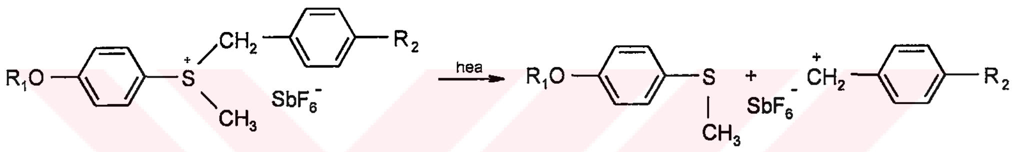
The synthesis of benzylthiophenium salts is achieved through a reaction of respectively substituted benzylhalides with tetrahydrothiophen and a subsequent anion exchange. As confirmed by ^{1}H-NMR analysis of polymer formed [73], the initiating species are thermolytically generated benzyl cations.



(2.90)

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 [74,75]. In this case, benzyl cations have been shown to initiate the polymerization.



(2.91)

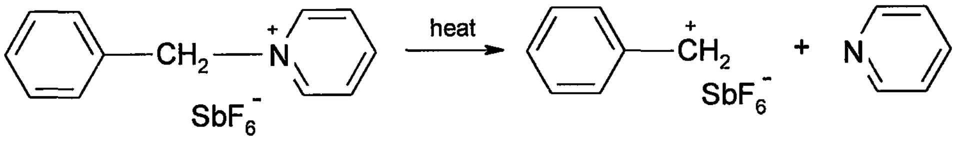
As far as the substituents in the benzyl group, R_2, are concerned, electron donating substituents were found to enhance the thermal sensitivity by stabilizing the benzyl cation. The reactivity diminishes in the order $CH_3 > H \approx Cl > NO_2$ [75]. Regarding phenyl ring substituents, R_1, electron withdrawing groups were found to increase the thermal sensitivity due to the destabilization of the sulphur centered cation. In the case of p-$CH_3OC(O)O$ derivative, 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.

N-Containing Onium Salts

Benzyl Pyridinium Salts

N-Benzyl pyridinium salts, the N- containing onium salts most frequently used for thermal cationic polymerization [76], are facile to prepare by reacting benzyl chlorides with corresponding pyridines [77].

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 is depicted in (2.92) [78].



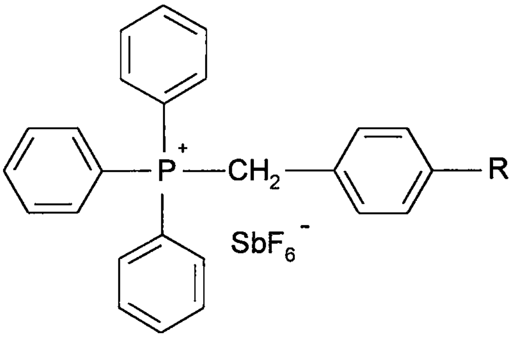
(2.92)

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) [78,79]. 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*-CH_3 > *p*-$N(CH_3)_2$. This order indicates that electron accepting groups stabilize the cation on the pyridinium moiety [79]. 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 [80,81]. The effect of the *o*-CN substituent was attributed to both steric and electronic factors.

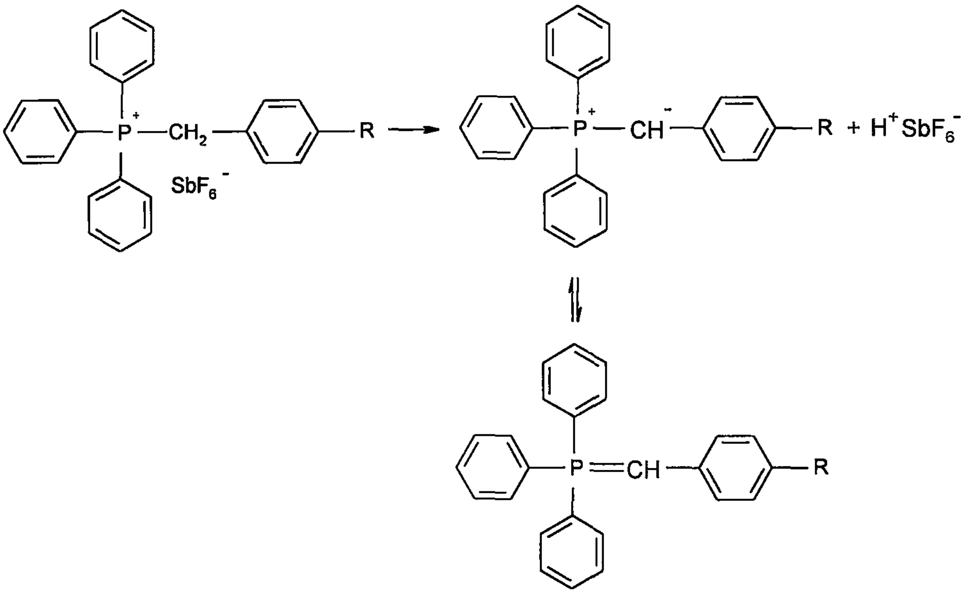
The substitution of the benzene ring by electron donating groups stabilizes the benzyl cation formed thermolytically, thus further enhancing the thermal activity. The activity of pyridinium salts with various *p*-substituents at the benzene ring decreases in the order CH_3O > Cl > *t*-C_4H_9 > CH_3 > H [82]. Notably, if the benzene ring is substituted by CH_3O, the thermal latency may be lost: with *p*-methoxybenzyl *o*-cyanopyridinium, polymerizations are observed already at room temperature [83].

Phosphonium Salts

Substituted benzylphosphonium salts of the general structure



with R being NO_2, Cl, H, CH_3, OCH_3 have been synthesized by the reaction of correspondingly substituted benzyl chlorides with triphenylphosphine. These salts have been used for the thermal polymerization of glycidyl phenyl ether and cyclohexene oxide at temperatures in the range between 100 and 170°C [84,85]. Interestingly, the activity of these compounds was found to increase by changing with more electron withdrawing substituents; the order of reactivity observed is $OCH_3 < CH_3 < H < Cl < NO_2$. This is a significant contrast when compared to benzylsulphonium and benzylpyridinium salts, where electron withdrawing substituents reduced the thermal sensitivity by destabilizing the benzyl cation formed upon thermolysis. The explanation for the unusual behaviour of benzylphosphonium salts was figured out in the initiating mechanism. As confirmed by ^{1}H-NMR and UV measurements of polymers and low molecular weight thermolysis products, benzyl groups are not the initiating species in the case of benzylphosphonium salts. Instead, protons liberated from the benzylic methylene have been assumed to initiate.

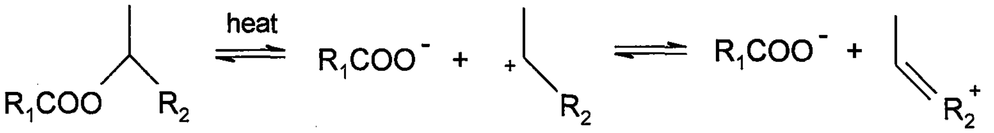


(2.93)

Salt Free Initiators

Since onium salt initiators are often not particularly soluble in common monomers and, furthermore, introduce inorganic impurities into the polymer, salt free thermolatent systems have been created.

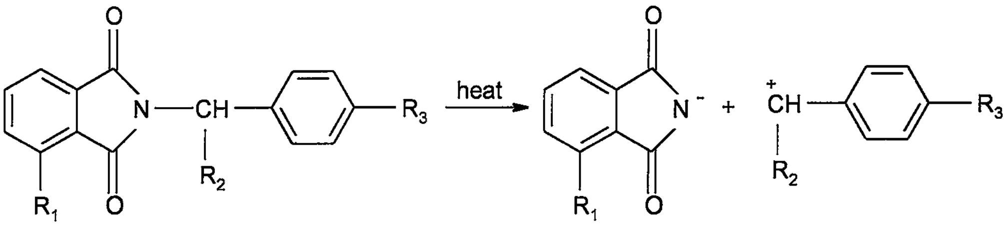
Recently, carboxylic acid esters have shown great potential in thermal cationic initiation [86]. The esters (with R_1 = CH_3, $CHCl_2$, CF_3, CCl_3 and R_2 = $OCH_2CH(CH_3)_2$, Ph) have been found to produce a resonance stabilized carbocation upon heating. The compound was used for the thermal bulk polymerizations of isovinyl ether.



(2.94)

The substituents R_1 and R_2 exert a srong 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 decreases in the following order: CF_3 > CCl_3 > $CHCl_2$ > 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 $OCH_2CH(CH_3)_2$ 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 [87]. These compounds undergo ion pair formation by heating, initiating benzyl cations with weak nucleophile phthalimide anions are produced. The initiation efficiency has been demonstrated on the polymerization of aziridines.



(2.95)

2.2.4.2. Indirect Acting Thermolatent Systems

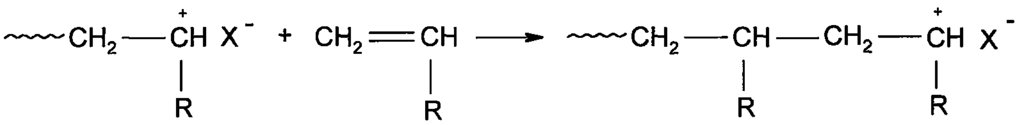
Thermally Induced Radical Promoted Polymerization

Free radicals produced upon external stimulation can be oxidized by onium salts. The mode of stimulations by which the radical is produced, such as heating or irradiating, 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 [88-92]. In the case of tetrahydrofuran polymerization, the molecular weight was found to depend strongly upon the thermal radical initiator used. For example, for AIBN, $M_n \approx 9x10^5$ was obtained, whereas for phenylazotriphenylmethane, the molecular weight was in the order $M_n \approx 5x10^4$. 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.

2.2.5. Propagation

The initiator ion pair (consisting of the carbocation and its negative counterion) produced in the initiation step proceeds to propagate by successive additions of monomer molecules. This addition proceeds by insertion of monomer between the carbocation and its negative counterion.



$$\sim\sim CH_2-\underset{R}{\overset{+}{CH}}\;X^- + CH_2{=}\underset{R}{CH} \longrightarrow \sim\sim CH_2-\underset{R}{CH}-CH_2-\underset{R}{\overset{+}{CH}}\;X^- \qquad (2.96)$$

The propagation reaction can be complicated in some cases by the occurence of intramolecular rearrangements due to 1,2-hydride ion ($H:^-$) or 1,2-methide ($CH_3:^-$) shifts. The extent of rearrangement during cationic propagation will depend on the relative stabilities of the propagating and rearranged carbocations and the relative rates of propagation and rearrangements. Both factors favor propagation without rearrangement for monomers such as styrene, indene, acenapthylene, coumarine, vinyl ethers, and isobutylene: the carbocations have no routes available for rearrangement to more stable carbocations.

2.2.6. Chain Transfer and Termination

2.2.6.1. Chain Transfer to Monomer

Chain transfer to monomer is probably the most important chain-breaking reaction for most monomers. There are a few polymerizations where it does not occur. Transfer to monomer involves transfer of a β-proton from the carbocation to a monomer molecule with the formation of terminal unsaturation in the polymer molecule, for example:

$$H\text{-}\left[CH_2C(CH_3)_2\right]_n\text{-}CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^- + CH_2{=}C(CH_3)_2 \longrightarrow$$

$$(CH_3)_3\overset{+}{C}(BF_3OH)^- + H\text{-}\left[CH_2C(CH_3)_2\right]_n\text{-}CH_2C(CH_3){=}CH_2 +$$

$$H\text{-}\left[CH_2C(CH_3)_2\right]_n\text{-}CH{=}C(CH_3)_2$$

(2.97)

Chain transfer to monomer is the principle reaction that limits polymer molecular weight for most monomers, especially at reaction temperatures higher than about 20°C. Since chain transfer to monomer generally has a higher activation energy than propagation, it is usually suppressed by working at lower temperatures.

2.2.6.2. Spontaneous Termination

Termination can also take place by rearrangement of the propagating ion pair. It involves regeneration of the initiator-coinitiator complex by expulsion from the propagating ion pair with the polymer molecule left with terminal unsaturation:

$$H\text{-}\left[CH_2C(CH_3)_2\right]_n\text{-}CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^- \longrightarrow$$

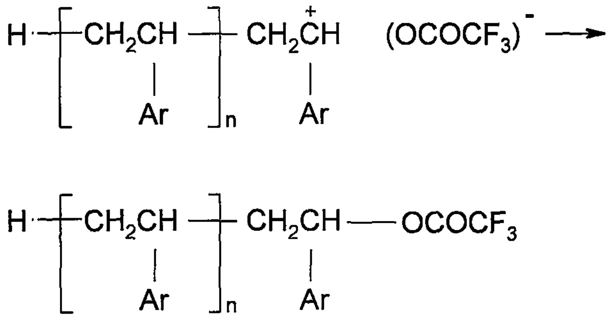
$$BF_3.OH_2 + H\text{-}\left[CH_2C(CH_3)_2\right]_n\text{-}CH_2C(CH_3){=}CH_2$$

(2.98)

This type of termination is also called chain transfer to counterion. It is almost never a dominant termination reaction compared to chain transfer to monomer.

2.2.6.3. Combination with Counterion

Termination by combination of the propagating center with the counterion occurs, for example, in trifluoroacetic acid initiated polymerization of styrene.



$$H-\left[CH_2\underset{Ar}{CH}\right]_n-CH_2\overset{+}{\underset{Ar}{CH}}\quad (OCOCF_3)^- \longrightarrow$$

$$H-\left[CH_2\underset{Ar}{CH}\right]_n-CH_2\underset{Ar}{CH}-OCOCF_3$$

(2.99)

Alternately, the propagating ion may combine with an anionic fragment from the counterion, for example

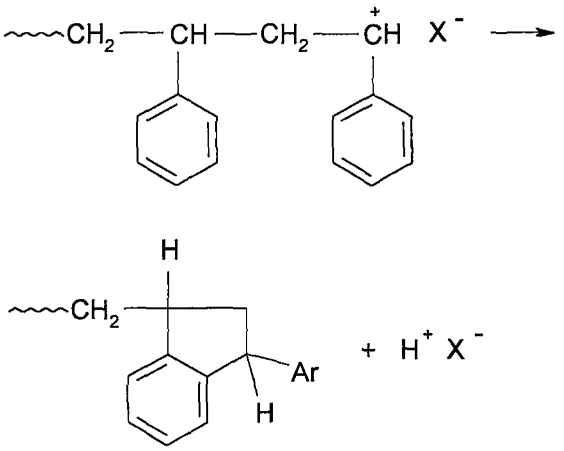
$$H-\left[CH_2C(CH_3)_2\right]_n-CH_2\overset{+}{C}(CH_3)_2\quad BF_3OH^- \longrightarrow$$

$$H-\left[CH_2C(CH_3)_2\right]_n-CH_2C(CH_3)_2OH + BF_3$$

(2.100)

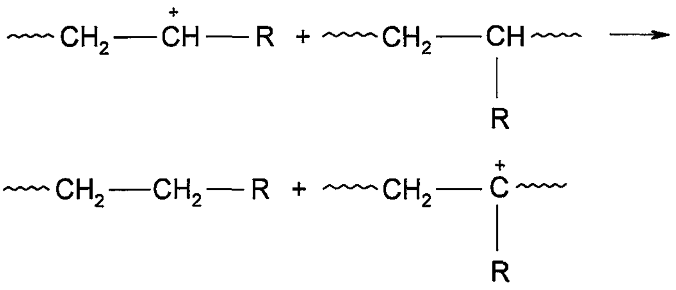
2.2.6.4. Chain Transfer to Polymer

Transfer of the cationic propagating center can occur either by electrophilic aromatic substitution or hydride transfer. Intramolecular electrophilic aromatic substitution (or backbiting) occurs in the polymerization of styrene as well as other aromatic monomers with the formation of terminal indanyl structures and regeneration of the initiator-coinitiator complex.



(2.101)

Intermolecular hydride transfer to polymer probably accounts for the short-chain branching found in the polymerizations of 1-alkenes such as propylene. The propagating carbocations are reactive secondary carbocations that can abstract tertiary hydrogens from the polymer. This reaction and the corresponding intramolecular transfers are responsible for the production of only low molecular products from 1-alkenes.



$$\sim CH_2-\overset{+}{C}H-R + \sim CH_2-\underset{\substack{|\\R}}{CH}\sim \longrightarrow$$

$$\sim CH_2-CH_2-R + \sim CH_2-\underset{\substack{|\\R}}{\overset{+}{C}}\sim$$

(2.102)

2.3. ADDITION-FRAGMENTATION REACTIONS

There are two important synthetic areas where addition-fragmentation processes occur:

1. *In radical chain transfer*; where addition-fragmentation agents (AFAs) are used as chain transfer agents. These reactions aim at gaining control over molecular weight and make it possible to synthesize end-functionalized polymers, often macromonomers, which may further be employed in block or graft copolymerization [93,94].

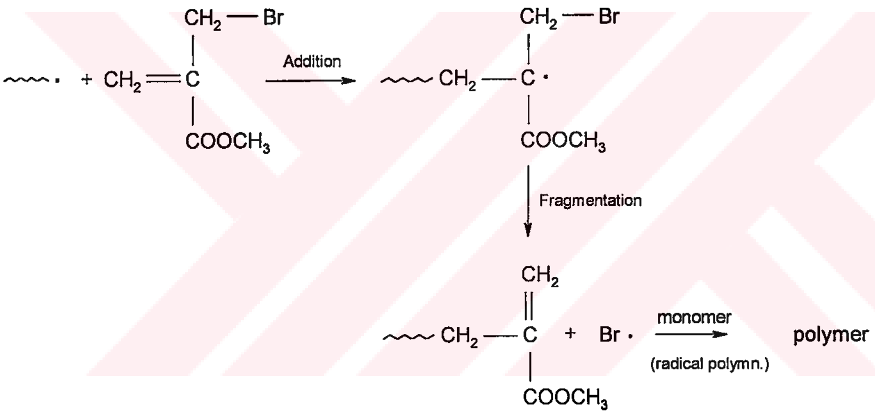
2. *In cationic photo or thermal polymerization*; where AFAs are used in conjunction with radical initiators for the production of initiating cations. Depending upon coinitiators used, cationic polymerization may be initiated by either heat or light [95].

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

The principle of addition-fragmentation type reactions can be described briefly as follows:

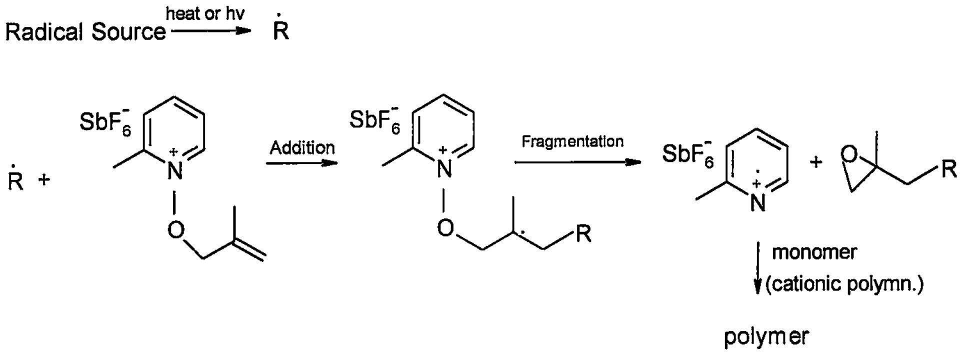
Free radicals (macro radicals in the case of chain transfer, low molecular weight radicals for cationic polymerization) add to olephinic double bonds of a specially designed addition-fragmentation agent (AFA). The intermediate thus produced is relatively unstable and prone to fragmentation, what mostly means β-fragmentation. In this step a new radical (cationic polymerization: radical cation) is generated, which initiates polymerization. As a result, a growing radical chain has been terminated and a new chain initiated (chain transfer) [96], or, a primarily formed radical led to the generation of a radical cation, which initiates cationic polymerization [95]. These reactions are illustrated in 2.103-2.104.

Chain Transfer:



(2.103)

Cationic Polymerization:



(2.104)

2.3.1. Addition-Fragmentation Agents for Chain Transfer

In technical polymer synthesis molecular weight has often to be controlled since very high molecular weight polymers are hard to process and in some cases undesired crosslinking may occur during polymerization. For lowering molecular weight, definite amounts of chain transfer agents, mostly thiols, or solvents with high chain transfer capability, eg., CCl_4, are used [97,98]. An interesting novel method is the application of high efficiency in chain transfer with the possibility of end-functionalizing the polymer. Furthermore, if sulphur free AFAs are used, there is no contamination of the polymer with thiols which would give an unpleasant odour and premature colour to the polymer.

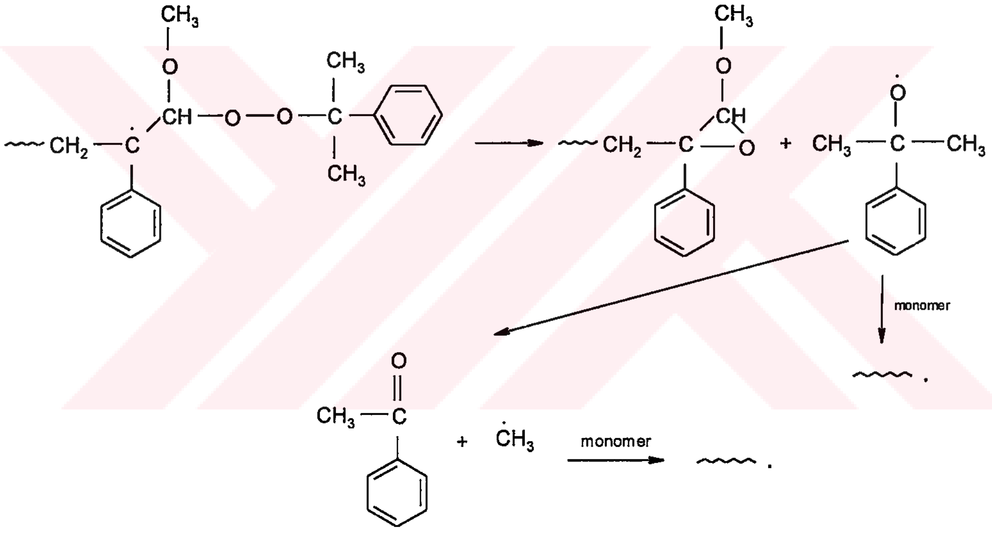
The efficiency of chain transfer is expressed in terms of the chain transfer constant (C_x), the ratio between the rate of chain transfer (reaction of chain radicals with AFA) to the rate of chain grow (reaction of chain radicals with monomer). By changing the AFA concentration it is possible to adjust a well-defined molecular weight, that is, lower than the one obtainable in the absence of AFA.

As far as addition-fragmentation reactions are concerned, there are two structural prerequisities for radical chain transfer. The double bond is the reactive site which free chain radicals are added to. Since the rate of radical addition does strongly depend upon the substitution pattern at the olefinic bond, substituents activating towards addition, like phenyl, alkoxy carbonyl or nitrile are frequently used [99]. The second structural principle is a weak bond in proximity to the double bond. Often, O-O, C-Br, C-S, C-O are chosen for their relatively easy cleavability. As a consequence of bond rupture, generally a double bond (at the end of the newly terminated chain) and a leaving radical (initiating a new chain) are produced. By creating energitically favourable leaving groups, which could be stabilized by, e.g., hyperconjugation (secondary or tertiary radicals) or resonance (e.g., benzyl radical), fragmentation can be tremendously facilitated.

Activation of the double bond towards addition is essential for a high efficiency in chain transfer. It is commonly assumed that with AFAs for chain transfer, it is the addition step that is rate determining [100], the fragmentation is a comparably fast process in these systems.

AFAs are also important for the synthesis of tailor made block and graft copolymers, often with definite molecular weights and narrow molecular weight distribution. As far as block copolymers are concerned, macromonomers are reacted with growing polymer chains, sometimes even two cycles of addition-fragmentation reactions take place [101]. For graft copolymerization, the adjacent radicals produced upon the addition of macromonomer to a growing chain are used to attach a second monomer to the chain.

An interesting variation of addition-fragmentation is that based on recently described peroxyketals [102]. It consists of a first fragmentation by O-O bond rupture. The oxygen centered free radical thus generated may directly react with monomer or, alternatively, undergo a second fragmentation yielding alkyl radicals which are also potential chain initiators.

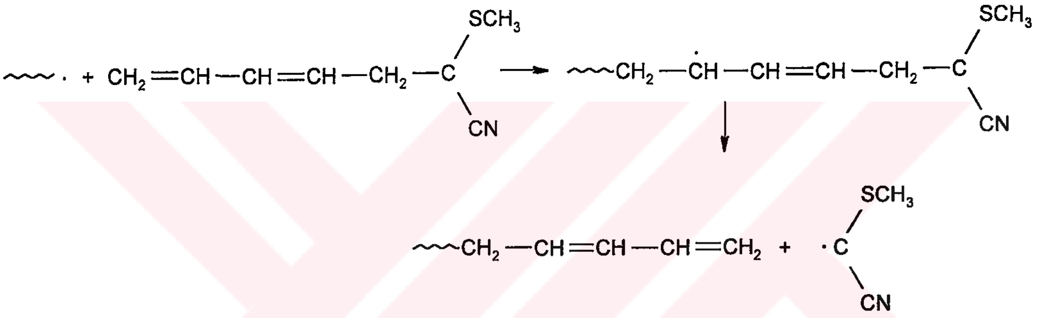


(2.105)

Some α-substituted monomers, like methyl α-(phenoxymethyl)acrylate, may be polymerized or copolymerized, but when the monomer is added to a chain, the newly formed radical with a certain probability (which rapidly rises with increasing temperature) undergoes fragmentation [103]. This circumstance may also be utilized for the production of polymers or copolymers with unsaturated end groups.

In the case of the bromine containing acrylate, there is an efficient transfer to monomer, owing to the ease in C-Br bond rupture. In fact, ethyl α-(bromomethyl)acrylate is a highly active AFA which may be used for controlling molecular weight.

Generally, the bond ruptured during fragmentation is in the β-position (peroxides: γ-position) to the double bond. However, if conjugated double bonds are present, there may be a distance of several bonds and still a high efficiency in transfer. The high chain transfer activity is in this case explainable in terms of the terminated polymer. With these pentadienyl derivatives, diene end-capped polystyrene and poly(methyl methacrylate) were obtained which are promising for the generation of tailor made graft and block copolymers. Notably, the unsaturated end groups (of allylic, α-substituted acrylic or styrylic type) prepared with AFAs that contain only a single double bond, usually have relatively bulky substituents, which by steric reason often affect the polymerizability. The macro diens prepared with pentadienyl based AFAs are not sterically hindered and are, therefore, easily polymerizable [104].



$$\sim\!\sim\cdot + CH_2{=}CH{-}CH{=}CH{-}CH_2{-}C(SCH_3)(CN) \longrightarrow \sim\!\sim CH_2{-}\dot{C}H{-}CH{=}CH{-}CH_2{-}C(SCH_3)(CN) \downarrow \sim\!\sim CH_2{-}CH{=}CH{-}CH{=}CH_2 + \cdot C(SCH_3)(CN)$$

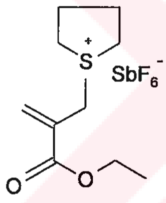
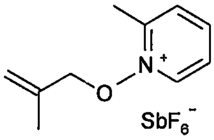
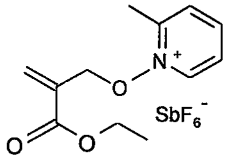
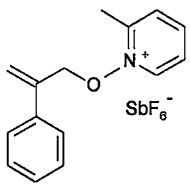
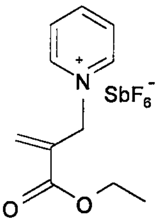
(2.106)

2.3.2. Addition-Fragmentation Agents for Cationic Polymerization

Polymerizations which are induced by external stimulation 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. Many technologically important monomers (vinyl ethers, oxiranes) are only polymerizable in a cationic mode which was the reason for the development of cationic photo- and thermal initiators [105]. Among these, specially designed allyl-onium salts which initiate via the addition-fragmentation scheme are a promising novelty. Onium salts (pyridinium, sulfonium, thiophenium salts etc.) contain organic cations, which by themselves (without external stimulation like, e.g., heat or light) by steric reasons do not or only scarcely initiate cationic polymerizations [106].

For cationic polymerization, thermal radical initiators, like AIBN, benzoyl peroxide, or radical photo initiators, such as benzoin or acylphosphine oxides, are used to produce free radicals. These radicals add to the double bond of the allyl onium salt and subsequently an onium radical cation is released, which initiates the polymerization (see reaction 2.104). Thus, fragmentation brings about the elimination of substituents that formerly prevented the cationic center from reacting with monomer, 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. Again, the substitution of the allylic double bond towards addition by, e.g., alkoxy ethyl or phenyl, facilitates the addition step. Furthermore, the bond to be ruptured should be one of the weakest bonds in the molecule.

Table 2.1. AFAs for Cationic Polymerization

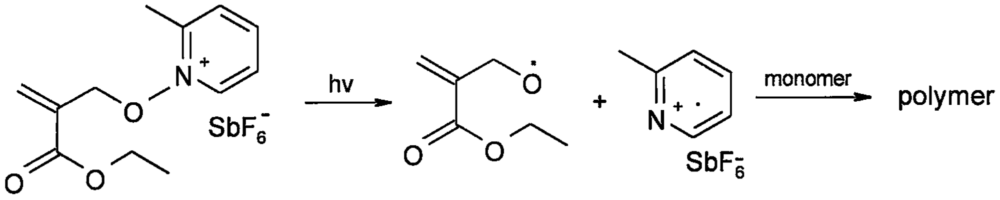
 1	 2
 3	 4
 5	 6

As seen in Table 2.1, it is S^+-C, N^+-O, and N^+-C bonds that are cleaved.

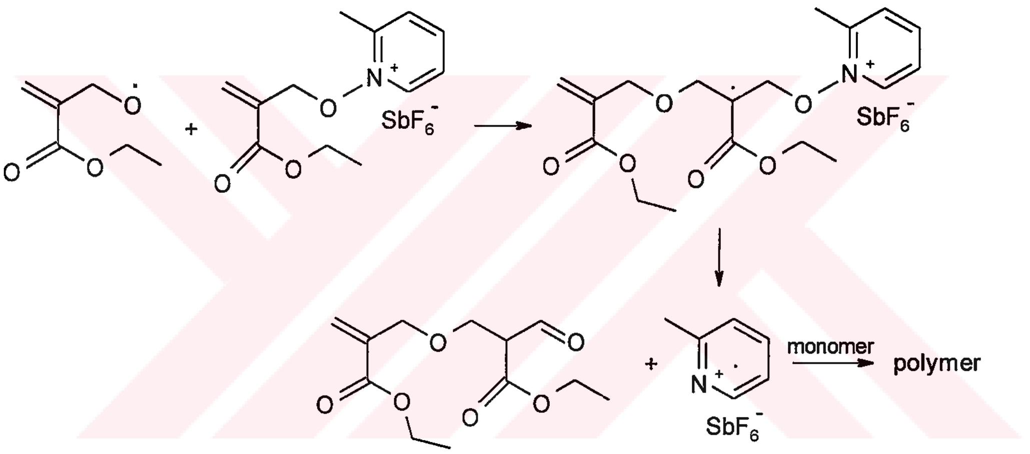
The obvious advantage of using AFAs for cationic polymerization is that, depending on the nature of the radical source used, initiation can be triggered by either heat (e.g., with AIBN or benzoyl peroxide) or light (with, e.g., benzoin). Moreover, as far as photopolymerization is concerned, it is extremely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

In Table 2.1, successful candidates of AFAs for cationic polymerization are compiled. The reactivity of allyloxy pyridinium derivatives (AFAs 2-5 in Tab. 2.1) and of the tetrahydrothiophenium based AFA 1 (Tab. 2.1) are as high as compared with the allyl pyridinium salt owing surely to the fact that N^+-O and S^+-C bonds are relatively weak. Interestingly, with the allyloxy pyridinium derivatives investigated (AFAs 2-5 in Tab. 2.1) there is no remarkable influence of the substituent at the double bond, it is clear that addition is not the rate determining step. Most probably, fragmentation is rate determining. The very initiation, i.e., the reaction of pyridinium radical cations with monomer, is a relatively fast process with bimolecular rate constants being $k = 10^6 - 10^7\ l\ mol^{-1}\ s^{-1}$ for CHO [107]. As a consequence, the search for even more efficient AFAs should be directed towards the introduction of more labile bonds in proximity to the allylic group and energetically favourable leaving groups formed by fragmentation. Interestingly, with some AFA / radical initiator pairs apart from addition-fragmentation, there are also oxidation reactions that account for the initiation. E.g., with phenylazo triphenylmethane, triphenylmethyl radicals are formed with high yield upon heating or irradiation. These radicals are relatively easily oxidizable, giving rise to the respective cations which may react with monomer and thus initiate chain grow. As a result, oxidation competes with addition-fragmentation resulting in the formation of additional initiating cations.

Allyloxy pyridinium salts may also be used as direct photoinitiators. Comparative studies have shown that being exposed to UV light (absorption reaches up to $\lambda \leq 290$ nm) allyloxy pyridinium salts initiate cationic polymerizations with rates that compare favorably with ethoxy pyridinium. From this high reactivity, the conclusion is drawn that also in direct photolysis addition-fragmentation reactions take place. Formed primarily after photolytical N-O bond rupture, allyloxy radicals add to intact salts species thus triggering the formation of initiating pyridinium radical cations. Thus, apart from the primarily formed pyridinium radical cation (N-O bond dissociation), another portion of initiating species is formed by addition-fragmentation. This interesting addition-fragmentation is outlined in 2.107-2.108.



(2.107)



(2.108)

With the initiators shown in Tab. 2.1, all sorts of cationically polymerizable monomers may be subjected to polymerization. Hence, most experiments were carried out with cyclohexene oxide, since this monomer may not be polymerized by a radical mode and it does not form radicals in the course of polymerization. With, e.g., butylvinyl ether and N-vinyl carbazole, redox processes between the monomer and the initiator take place accounting for an undesired polymerization in the dark at room temperature.

3. EXPERIMENTAL WORK

3.1. Materials and Chemicals

3-Hydroxy-1,4-pentadiene was a product of Aldrich, no further purification was applied.

Dry ether which was used in the synthesis of 5-bromo-1,3-pentadiene was obtained by distillation over sodium wire. (Diethyl ether was a product of Lab-Scan).

Phosphoroustribromide was a product of Aldrich, it was used as receieved.

Magnesium sulphate was a product of Fluka, it was used as received.

Tetrahydrothiophen was a product of Aldrich, it was used as received.

Pyridine was a product of Aldrich, it was used as received.

Acetonitrile which was used as solvent in the synthesis of AFAs, was a product of Lab-Scan.

Sodium hexafluoroantimonate, used as anion exchanger in the synthesis of AFAs, was a product of Aldrich. It was used as received.

Cyclohexene oxide, used as monomer, was a product of Fluka. It was distilled with fractination under calcium hydride.

Benzoin was a product of Fluka and it was recrystallized from ethanol.

Trimethoxybenzoyl diphenylacylphosphine oxide (TMDPO) was a product of BASF, it was recrystallized from diethyl ether / ethanol.

Benzoyl peroxide (BPO) was a product of Fluka and it was recrystallized from diethyl ether.

2,2'-Azobisisobutyronitrile (AIBN) was a product of Fluka and it was recrystallized from ethanol.

Phenylazotriphenylmethane (PAT) was a product of Fluka and it was used as received.

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

Methylene chloride was used as solvent for dissolving bulky polymer formations, also in UV measurements. It was first extracted with sulphuric acid, washed with water, then extracted with 5 % NaOH solution, and again washed with water. It was dried over calcium chloride and distilled by fractination column.

3.2. Equipments

3.2.1. Photoreactor

A merry-go-round type photo reactor with 16 Philips 8W / O6 lamps emitting light nominally at 350 nm was used.

3.2.2. UV Spectrophotometer

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

3.2.3. Elemental Analysis

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

3.2.4. Nuclear Magnetic Resonance Spectra

^{1}H-NMR spectra were recorded on an Bruker 250 MHz instrument.

3.2.5. Gel Permeation Chromatography (G.P.C.)

GPC analysis were performed via set-up consisting of a Waters pump and 3 styragel HR3, HR4, HR4E columns with THF as the eluent, at a flowrate of 1 ml min^{-1} and detection was carried out with a differential refractometer. Molecular weights were calculated with the aid of polystyrene standards.

3.3. Synthesis of 5-Bromo-1,3-pentadiene

3-Hydroxy-1,4-pentadiene (2.595 g, 0.03 mole) taken in dry ether (7.5 ml) was cooled to -10°C and to this, a solution of PBr_3 (4.1823 g, 0.015 mole) in 7.5 ml of dry ether was added dropwise. After addition, the system was kept agitated at room temperature for 12 hr. It was cooled to -20°C and 30 ml of distilled water was added carefully. The product was isolated with ether and dried over $MgSO_4$. Finally, solvent was evaporated. The structure was confirmed by ^1H-NMR spectra.

3.4. Synthesis of Addition-Fragmentation Agents

3.4.1. Synthesis of 5-Thiophenium-1,3-pentadiene hexafluoroantimonate (TPD)

A mixture of 5-bromo-1,3-pentadiene (0.4048g, 2.756 mmole) and tetrahydrothiophen (0.243 g, 2.756 mmole) in acetonitrile was stirred for 24 h in room temperature. Acetonitrile was evaporated and the residue was extracted with ether/water (20 ml / 4 ml). Then, an equimolar amount of $NaSbF_6$ (0.713 g, 2.756 mmole) was added to the aqeous layer. Yellowish crystals were precipitated after the addition of ethanol (m.p. 152°C).

3.4.2. Synthesis of 5-Pyridinium-1,3-pentadiene hexafluoroantimonate (PPD)

A mixture of 5-bromo-1,3-pentadiene (0.2980 g, 2.03 mmole) and pyridine (0.1606 g, 2.03 mmole) in acetonitrile was stirred for 24 h in room temperature. Acetonitrile was evaporated and the residue was extracted with ether/water (20 ml / 4 ml). Then, an equimolar amount of $NaSbF_6$ (0.5252 g, 2.03 mmole) was added to the aqeous layer. Yellowish crystals were precipitated after the addition of ethanol (m.p. 56°C).

Table 3.1. Elemental Analysis Results of AFAs

	TPD		PPD	
	C %	H %	C %	H %
Calculated	27.63	3.83	31.44	3.14
Found	27.04	3.81	30.59	3.02

3.5. Polymerization Techniques

3.5.1. Thermal Polymerization

Monomer, diene-onium salt and respective radical initiator were mixed in pyrex tubes that were closed with a teflon stopcock after bubbling through with nitrogen. These tubes were immersed in a water-bath for a given time, at a constant temperature (70°C). With respect to adjusted time, resulting polymers were precipitated in methanol, filtered off, dried in vacuum oven and weighed. Conversion percentages were calculated by using the equation indicated below:

Conversion % = (W / M) x 100
Where: W = amount of polymer obtained;   M = amount of monomer used

3.5.2. Photopolymerization

Monomer, diene-onium salt and respective radical initiator were mixed in pyrex tubes that were closed with a teflon stopcock after bubbling through with nitrogen. These tubes were irradiated in a merry-go-round type photoreactor with 16 Philips

8W/06 lamps, emitting light nominally at 350 nm. With respect to adjusted time, resulting polymers were precipitated in methanol, filtered off, dried in vacuum oven and weighed. Conversion percentages were calculated according to the equations indicated above.

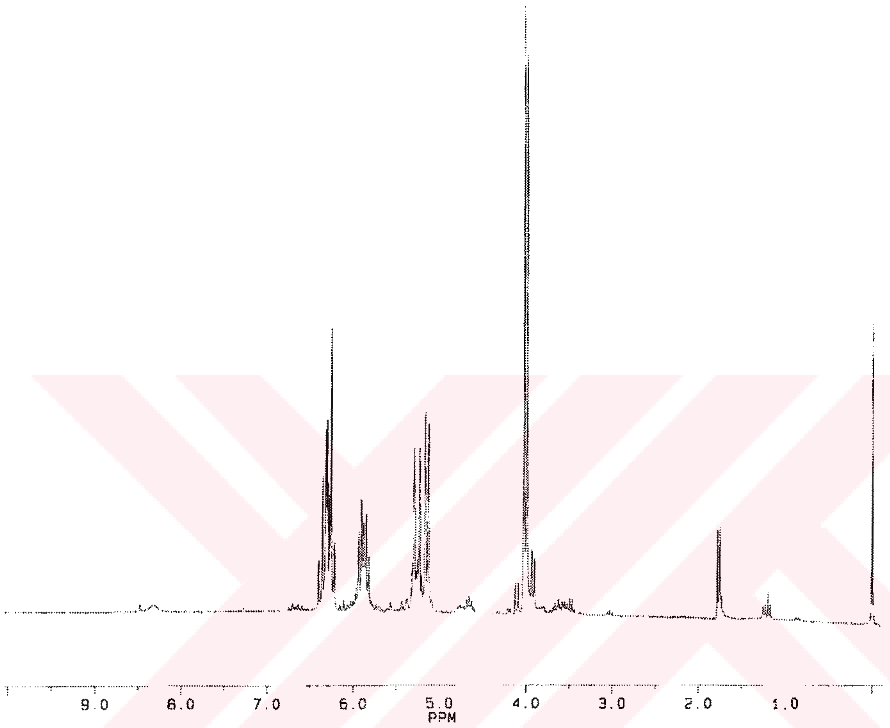


Figure 3.1. ^{1}H-NMR Spectrum of 5-Bromo-1,3-pentadiene

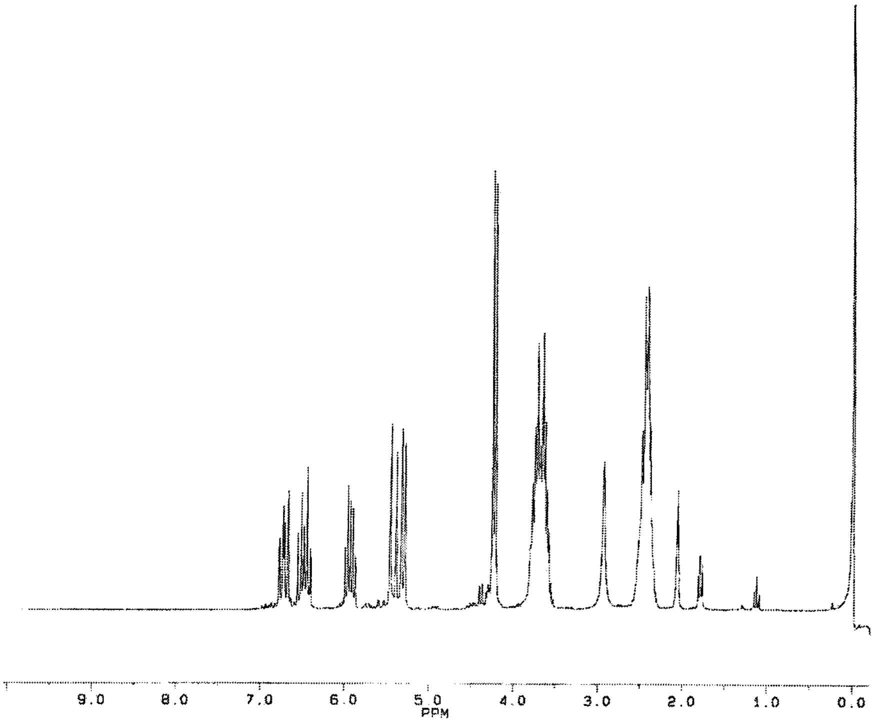


Figure 3.2. ^{1}H-NMR Spectrum of TPD

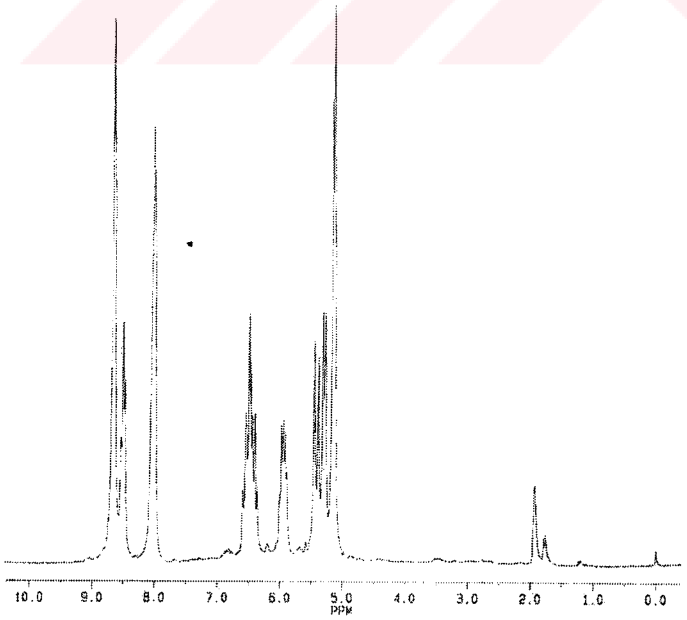
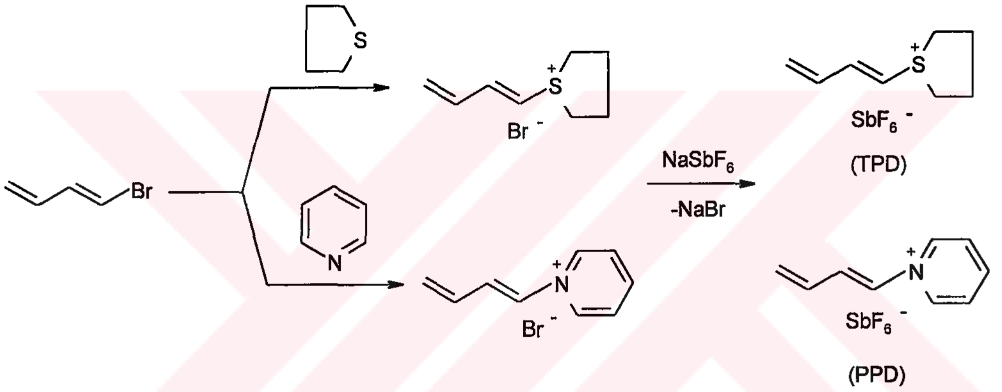


Figure 3.3. ^{1}H-NMR Spectrum of PPD

4. RESULTS AND DISCUSSION

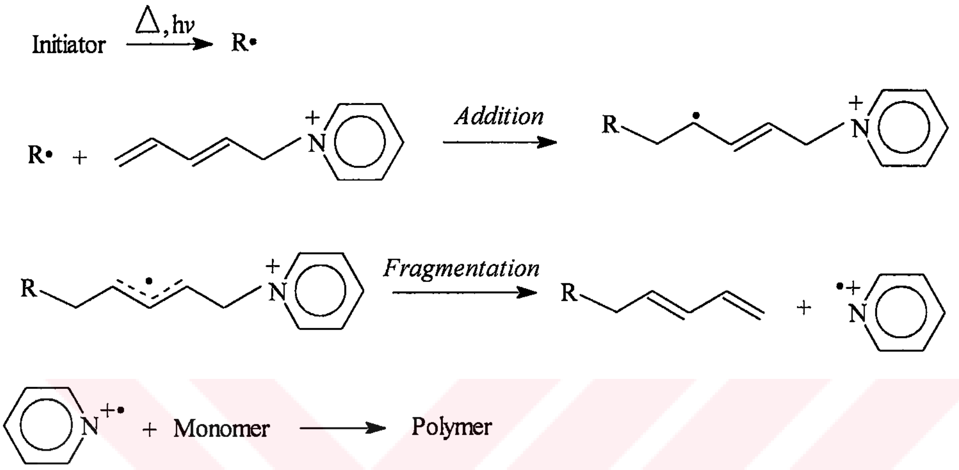
Two diene type AFAs namely, 5-thiophenium-1,3-pentadiene hexafluoro antimonate (TPD) and 5-pyridinium-1,3-pentadiene hexafluoro antimonate (PPD) were synthesized by the reaction of 5-bromopenta-1,3-diene with thiophene and pyridine, respectively and subsequent counter anion exchange of bromide with nonnucleophilic hexafluoro antimonate anion according to the following reactions.



(4.1)

The structures of TPD and PPD were confirmed by means of spectral and elemental analysis (see Chapter 3).

For the investigations described here, cyclohexene oxide (CHO) was selected as the cationically polymerizable monomer because of its inertness towards radicals and polymerizability only by a cationic mechanism. For the radical generation process, both thermal and photochemical sources of free radicals were employed. As can be seen from Table 4.1, thermolysis of 2,2'- azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO) and phenylazotriphenyl methane (PAT) and photolysis of benzoin (B) and trimethoxybenzoyldiphenylacylphosphine oxide (TMDPO) readily promotes the cationic polymerization of CHO in the presence of TPD and PPD. In this case, initiating species are produced by a radical addition-fragmentation mechanism in a manner similar to that described for allylic AFAs. Together with dienic addition fragmentation products, pyridinium (or thiophenium) radical cations are presumably formed. These species are potentially able to initiate the cationic polymerization of CHO present in the system. Previously, the reactivity of pyridinium radical cations towards nucleophilic monomers such as CHO was deduced from laser flash photolysis studies [107]. The initiation mechanism is illustrated on the example of the pyridinium salt in 4.2 and 4.3.



(4.2)

(4.3)

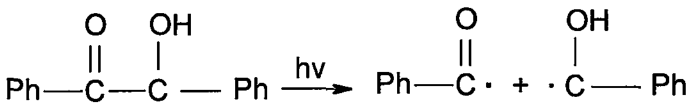
(4.4)

(4.5)

Table 4.1. Thermal and Photochemical Polymerization of CHO by using Dienic AFAs in the Presence of Free Radical Sources

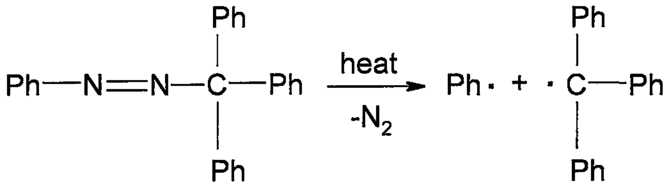
Method	Radical Source (mol l $^{-1}$)	AFA (5x10^{-3} moll^{-1})	Time (min.)	Conversion (%)	M$_n$x10^{-3}
Thermal	AIBN (5x10^{-3})	TPD	30	60	8.3
Thermal	AIBN (5x10^{-3})	PPD	30	5	-
Thermal	BPO (5x10^{-3})	TPD	30	8	-
Thermal	BPO (5x10^{-3})	PPD	30	6	-
Thermal	PAT (5x10^{-3})	TPD	30	65	-
Thermal	PAT (5x10^{-3})	PPD	30	17	-
Photo	B (2.4x10^{-2})	TPD	4	60	4.8
Photo	B (2.4x10^{-2})	PPD	4	10	-
Photo	TMDPO (1.7x10^{-3})	TPD	210	7	3.5
Photo	TMDPO (1.7x10^{-3})	PPD	210	5	-

As seen in Table 4.1 and the time-conversion curves of CHO, represented in Appendix A, for all free radical sources, B and PAT exhibit significantly higher initiation activity than that of the others. These compounds decompose upon photolysis and thermolysis, yielding nucleophilic hydroxybenzyl and triphenylmethyl radicals, respectively.



$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle OH}{|}}{C}{-}Ph \xrightarrow{hv} Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}\cdot + \cdot\overset{\overset{\displaystyle OH}{|}}{C}{-}Ph}$$

(4.6)



$$\mathrm{Ph{-}N{=}N{-}\underset{\underset{\displaystyle Ph}{|}}{\overset{\overset{\displaystyle Ph}{|}}{C}}{-}Ph \xrightarrow[-N_2]{heat} Ph\cdot + \cdot\underset{\underset{\displaystyle Ph}{|}}{\overset{\overset{\displaystyle Ph}{|}}{C}}{-}Ph}$$

(4.7)

Whilst the other radicals (benzoyl and phenyl radicals) are expected to participate in addition-fragmentation type initiation, these radicals (hydroxybenzyl and triphenylmethyl) are oxidized by the salt, thus forming additional initiating species. The effectiveness of such electron transfer reaction is related to the redox potentials of both radicals and salts used in the system. From the previous studies performed by using allylic AFAs, it was evident that the thiophenium salts participate more readily in these reactions due to the more favourable thermodynamical properties.

As can be seen from Figures A.1, A.3, A.5, A.7 and A.9, in the case of TPD there is some induction period in almost all polymerizations. This may be due to the impurities present in the initiator itself.

5.CONCLUSIONS AND SUGGESTIONS

In this study, diene-type addition-fragmentation agents namely, 5-thiophenium-1,3-pentadiene (TPD) and 5-pyridinium-1,3-pentadiene (PPD) salts with hexafluoroantimonate counter anion were synthesized effectively. In conjunction with suitable free radical initiators, these salts were used in the cationic polymerization of CHO.

In photopolymerization experiments, benzoin showed higher activity than that of TMDPO. Benzoin is known to produce two radicals; one of them being oxidizable hydroxyl benzyl radical. These electron donating radicals may be oxidized to the corresponding cations which results in the formation of additional initiating species.

Similar redox behaviour may also be suggested in the case of PAT as the thermal radical initiator.

In conclusion, mechanistic studies stil remain to be evaluated for each individual system consisting of free radical initiator and dienic salt. Such combination is highly suitable for thermally and photochemically induced cationic polymerization. Depending on the nature of the free radicals, formed by thermolysis and photolysis, both addition-fragmentation and electron transfer mechanisms may be operative.

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APPENDIX A

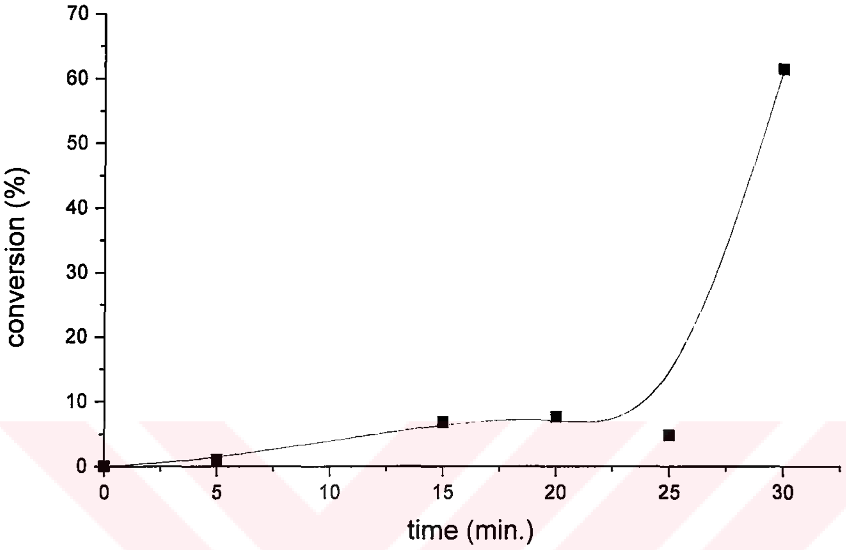

Figure A.1. Thermal Polymerization of CHO by using TPD in conjunction with PAT as the radical source, [TPD] = [PAT] = $5x10^{-3}$ mol l^{-1} at 70°C.

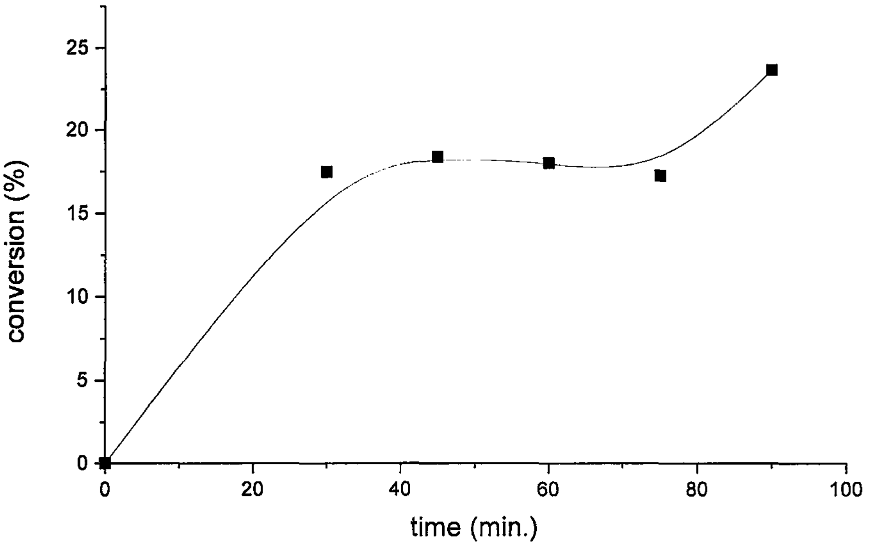

Figure A.2. Thermal polymerization of CHO by using PPD in conjunction with PAT as the radical source, [PPD] = [PAT] = $5x10^{-3}$ mol l^{-1} at 70°C.

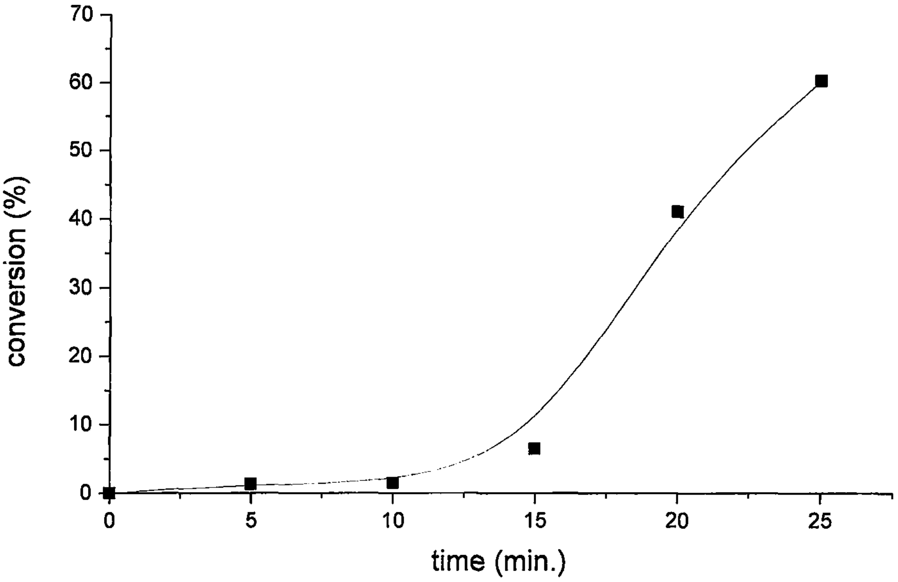

Figure A.3. Thermal polymerization of CHO by using TPD in conjunction with AIBN as the radical source, [TPD] = [AIBN] = $5x10^{-3}$ mol l^{-1} at 70°C.

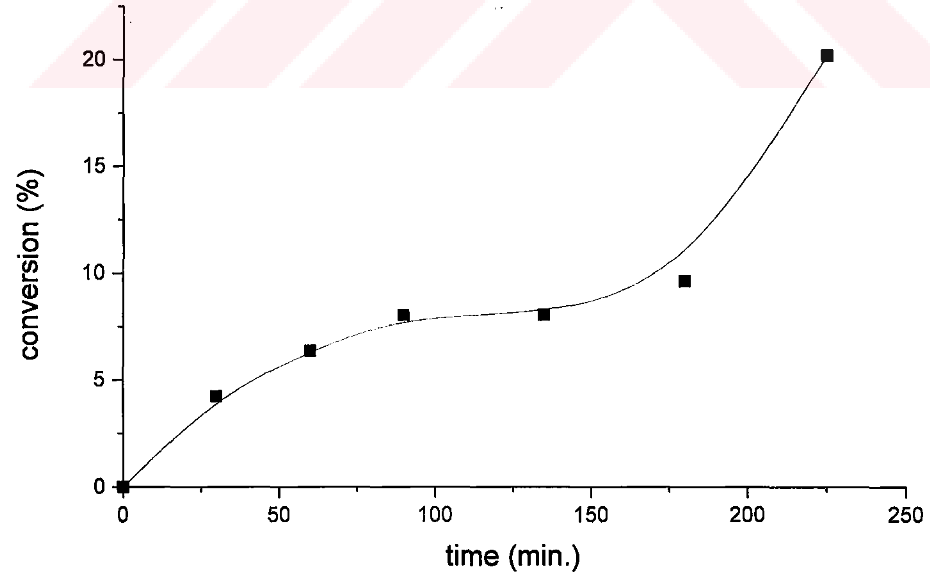

Figure A.4. Thermal polymerization of CHO by using PPD in conjunction with AIBN as the radical source, [PPD] = [AIBN] = $5x10^{-3}$ mol l^{-1} at 70°C.

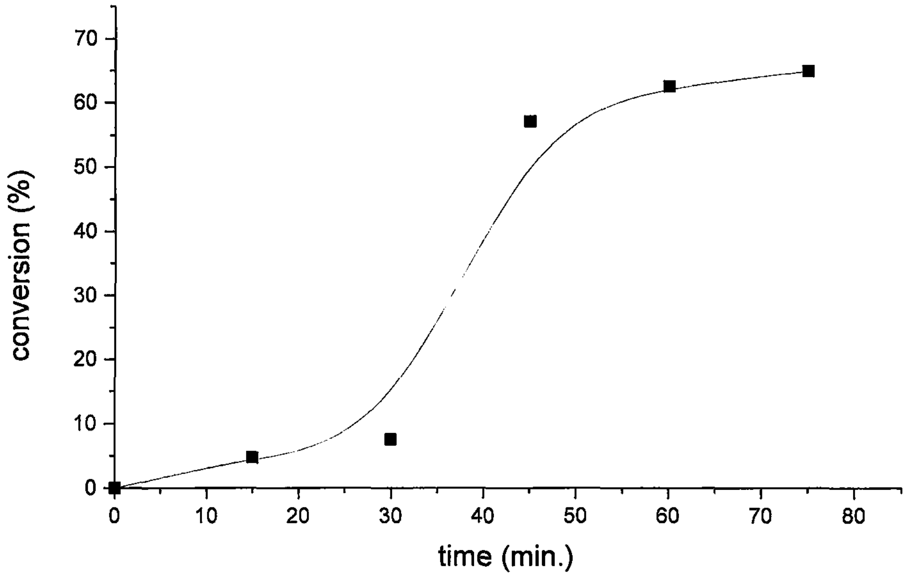

Figure A.5. Thermal polymerization of CHO by using TPD in conjunction with BPO as the radical source, [TPD] = [BPO] = 5x10^{-3} mol l^{-1} at 70°C.

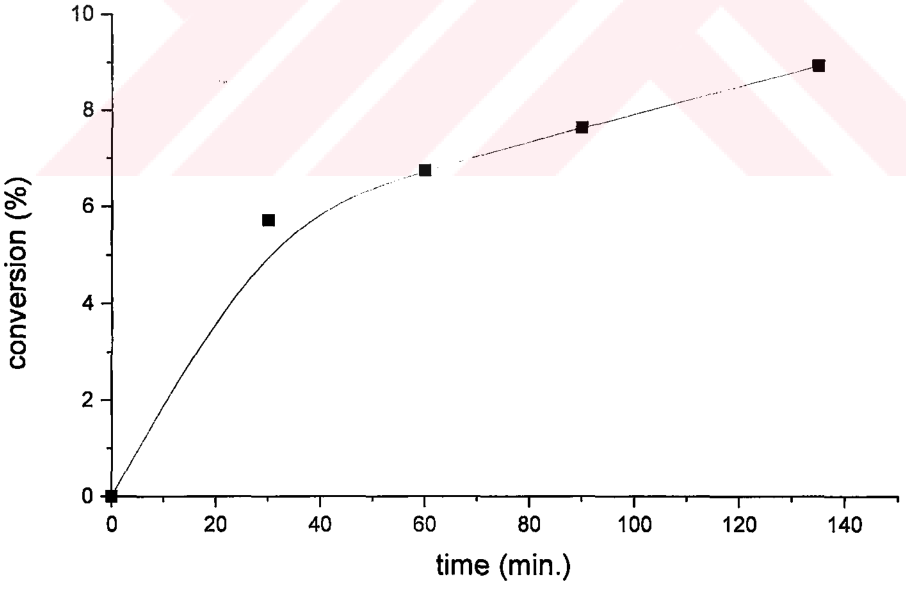

Figure A.6. Thermal polymerization of CHO by using PPD in conjunction with BPO as the radical source, [PPD] = [BPO] = 5x10^{-3} mol l^{-1} at 70°C.

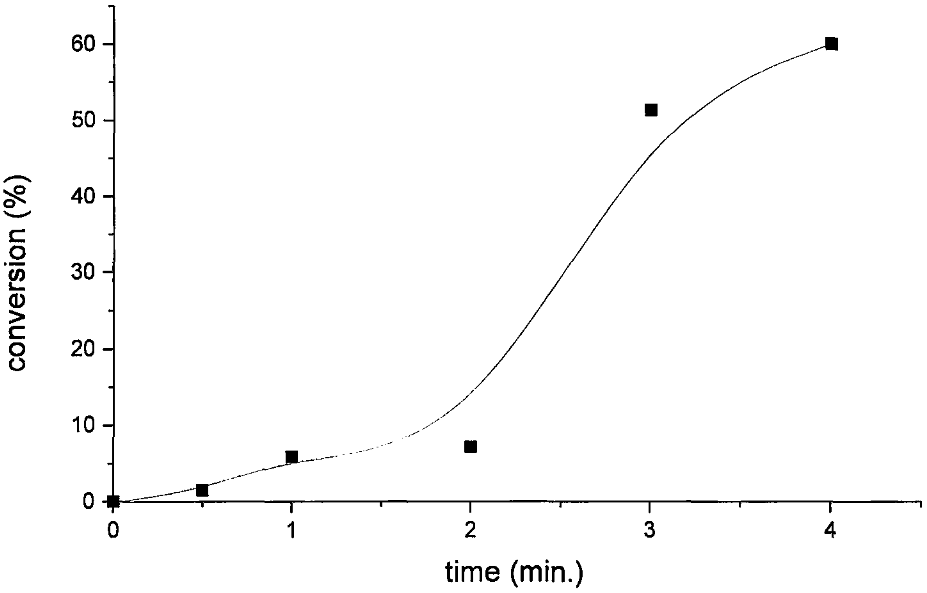

Figure A.7. Photopolymerization of CHO by using TPD in conjunction with benzoin as the radical source, [TPD] = 5x10^{-3} mol l^{-1}, [benzoin] = 2.4x10^{-2} mol l^{-1}.

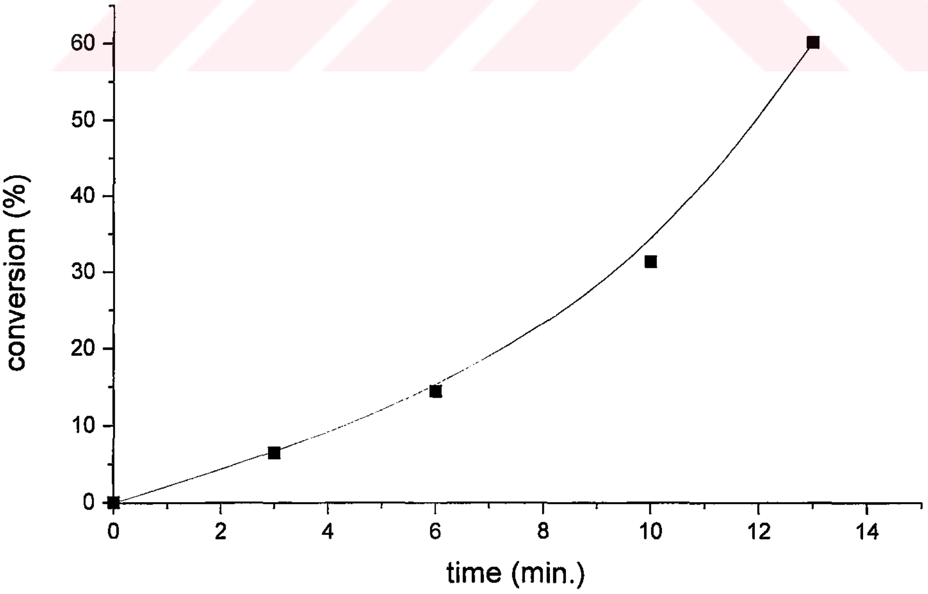

Figure A.8. Photopolymerization of CHO by using PPD in conjunction with benzoin as the radical source, [PPD] = 5x10^{-3} mol l^{-1}, [benzoin] = 2.4x10^{-2} mol l^{-1}.

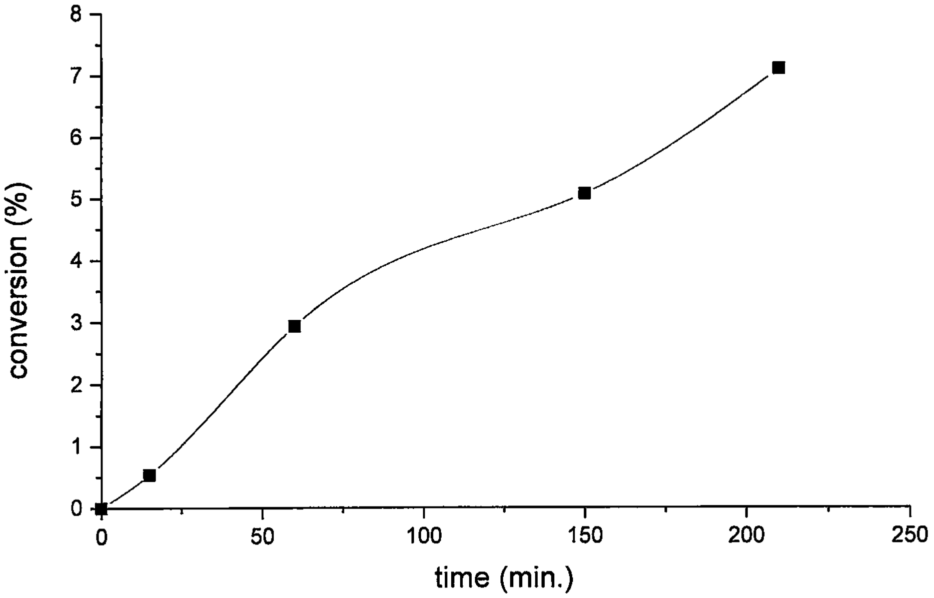

Figure A.9. Photopolymerization of CHO by using TPD in conjunction with TMDPO as the radical source, [TPD] = 5x10^{-3} mol l^{-1}, [TMDPO] = 1.7x10^{-3} mol l^{-1}.

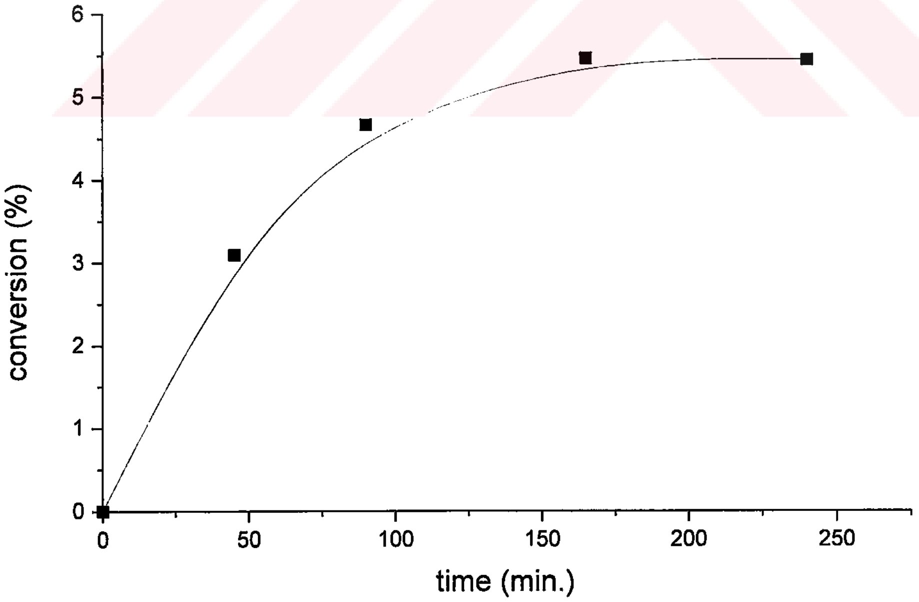

Figure A.10. Photopolymerization of CHO by using PPD in conjunction with TMDPO as the radical source, [PPD] = 5x10^{-3} mol l^{-1}, [TMDPO] = 1.7x10^{-3}.

BIOGRAPHY

Z. Berfu Yöneyman was born in Istanbul in 1978. She graduated from Eyüboğlu High School in 1995 and Istanbul Technical University, Department of Chemistry, in 1999.

She was registered as a M. Sc. Student in Polymer Science and Technology graduate program in Istanbul Technical University in 1999. She is the co-author of a research paper submitted to "Designed Monomers and Polymers".