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**BIFUNCTIONAL ALLYL-SULPHONIUM SALT AS A
NOVEL ADDITION-FRAGMENTATION AGENT FOR
PHOTOINITIATED CATIONIC POLYMERIZATION**

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**İKİ FONKSİYONLU ALLİL-SULFONYUM TUZU İLE
FOTOKİMYASAL KATYONİK POLİMERİZASYON İÇİN YENİ BİR
KATILMA-BÖLÜŞME VASITASI**

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BIFUNCTIONAL ALLYL-SULPHONIUM SALT AS A NOVEL ADDITION-FRAGMENTATION AGENT FOR PHOTOINITIATED CATIONIC POLYMERIZATION

SUMMARY

Addition-fragmentation type initiation is a versatile route for cationic polymerization. Specially designed allylic salts have been shown to act as addition fragmentation agents (AFA) in the initiation of cationic polymerization. In this process, radicals regardless of their mode of generation, add to the double bond, thus generate radicals. Unstable radicals then undergo rapid cleavage to yield reactive radical cations. Either these radical cations themselves or protonic acids produced after hydrogen abstraction are responsible for the successful initiation. Obviously, AFAs are not actual initiators but act as co-initiators in conjunction with free radical sources.

In this study, bifunctional allyl tetrahydrothiophenium hexafluoroantimonate was synthesized via one-pot reaction of 3-chloro-2-chloromethylpropene with thiophene in the presence of sodium hexafluoroantimonate. The salt is not soluble in common organic solvents suitable for cationic polymerization except the polar solvent propylene carbonate. The initiation capability of this salt, in conjunction with a photochemical free radical source such as 2,2-dimethoxy-2-phenyl acetophenone (DMPA) and benzophenone (BP), via an addition-fragmentation mechanism in the cationic polymerization of cyclohexene oxide (CHO) and butyl vinyl ether (BVE) is investigated. Polymerization proceeded heterogeneously in both monomers due to the insolubility of the respective polymers in the solvent, propylene carbonate. It was postulated that the initiation mechanism in the case of the bifunctional salt is similar to that described for the usual AFAs.

İKİ FONKSİYONLU ALLİL-SULFONYUM TUZU İLE FOTOKİMYASAL KATYONİK POLİMERİZASYON İÇİN YENİ BİR KATILMA-BÖLÜŞME VASITASI

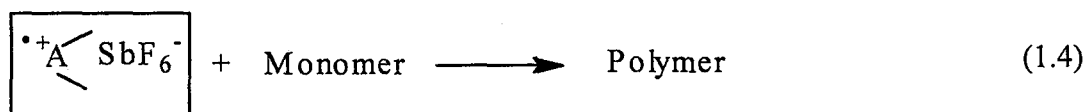
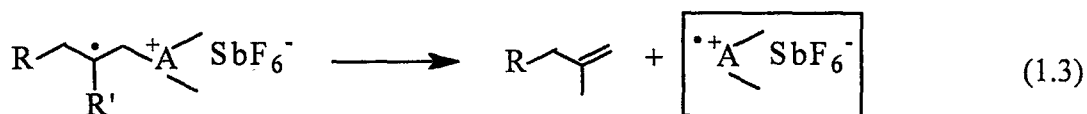
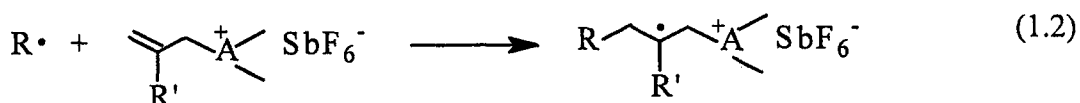
ÖZET

Katılma-bölüşme türü başlama katyonik polimerizasyon için uygun bir yöntemdir. Özel tasarlanmış katılma-bölüşme vasıtalarının katyonik polimerizasyonda etkin bir başlatıcı olduğu gösterilmiştir. Bu proste, elde edilme yöntemine bağlı olmaksızın radikaller çift bağa katılarak yeni radikaller oluştururlar. Bu karasız radikaller daha sonra hızlı bir bölünmeye uğrayarak reaktif radikal katyonları oluştururlar. Bu radikal katyonların kendileri veya hidrojen abstraksiyonu sonucu oluşan protonik asitler polimerizasyonu başlatır. Aslında, katılma-bölüşme vasıtalarının kendileri gerçek bir başlatıcı olmayıp, serbest radikal kaynakları birlikte yardımcı-başlatıcı (co-initiator) olarak görev yaparlar.

Bu çalışmada, iki fonksiyonlu başlatıcı, allil tetrahidrotiofenyum heksafloroantimonat, 3-kloro-2-metilpropen'in tetrahidrotiofen ile sodyum heksafloroantimonat varlığında tek aşamada gerçekleştirilen reaksiyon ile sentez edilmiştir. Bu tuz, polar bir çözücü olan propilen karbonat hariç, katyonik polimerizasyon için uygun olan organik çözücülerde çözünmemektedir. Bu tuzun, 2,2-dimetoksi-2-fenil asetofenon (DMPA) ve benzofenon (BP) gibi fotobaşlatıcılar varlığında sikloheksen oksit (CHO) ve butil vinil eter (BVE) in katyonik polimerizasyonundaki başlatıcı etkinliği incelenmiştir. Oluşan polimerlerin propilen karbonat çözücüsünde çözünmemesi nedeniyle polimerizasyon heteojen olarak gerçekleşmektedir. İki fonksiyonlu tuzun polimerizasyonu genel olarak kullanılan katılma-bölüşme vasıtalarına benzer bir mekanizma ile başlattığı varsayılmaktadır.

1. INTRODUCTION

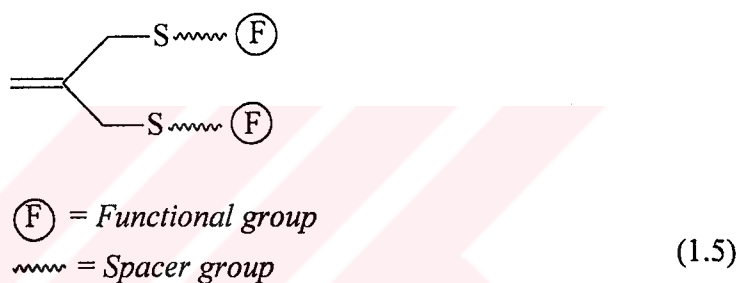
Photoinitiated cationic polymerization is of great practical interest due to their utilization particularly for curing of coatings based on technologically important epoxy and vinyl ether type monomers [1]. Many efficient photoinitiators such as iodonium [2], sulphonium [3,4], alkoxy pyridinium salts [5-8] and arene iron complexes [9] were developed and their photochemistry has been studied in detail. In order to fulfill the practical requirements regarding extension of their spectral sensitivity several direct and indirect activation of these photoinitiators were proposed [10]. One recent approach developed in author's laboratory concerns the use of specially designed allylic salts as co-initiators in conjunction with free radical photoinitiators [11-29]. In fact, these salts are not photoinitiators but participate in the addition fragmentation reaction with the initial free radicals being provided by a conventional photochemical initiator according to the following reactions.



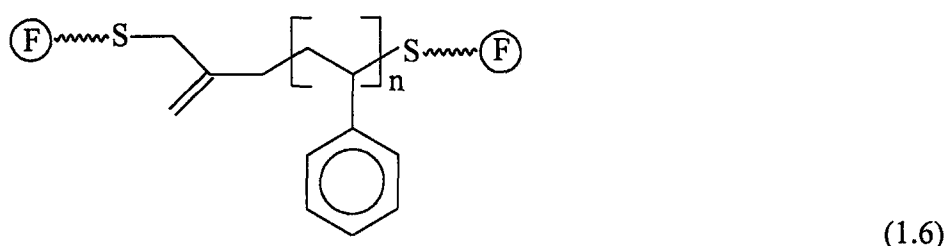
The mechanism involves the formation of radicals by irradiating the radical photoinitiator, the addition of these radicals to the allylic salt and the subsequent fragmentation reactions. The radicals thus produced initiate the polymerization either by reacting with monomer directly or by producing protonic acids. Previously, sulphonium [11], pyridinium [12,13], alkoxy pyridinium [14-20], phosphonium [21]

and anilinium [27] with allylic structure, and sulphonium and pyridinium salts with dienic structure [28] were shown to participate in such addition fragmentation reactions and efficiently initiate the cationic polymerization when used in conjunction with free radical photoinitiators. The most striking advantage of using these addition fragmentation agents (AFA) is the wavelength flexibility provided by choosing appropriate free radical photoinitiator. Moreover, thermal initiators can also be used as the radical generating component of the system.

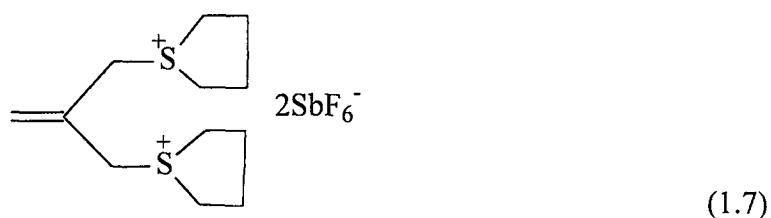
Recently, Sunder and Mulhaupt [30] have reported preparation and application of novel allylic dithio compounds of the following structure as addition-fragmentation chain transfer agents in free radical polymerization.



It was shown that the use these compounds lead to the formation of oligomers with two functional groups during free radical polymerization.



This article describes the synthesis and activity of novel bifunctional AFA of the following structure in conjunction with a photoinitiator in cationic polymerization of appropriate monomers such as cyclohexene oxide.



2. THEORY

2.1. Radical Polymerization

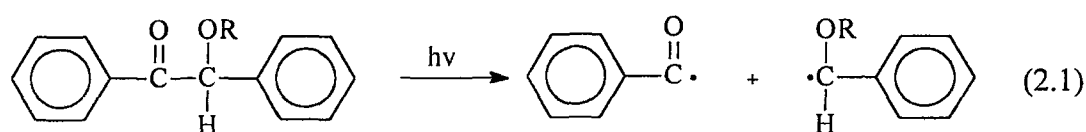
Today, free-radical polymerization has received more intensive study than any other chemical chain reaction; countless investigations have contributed to industry and to the chemistry of free radicals. Free-radical polymerization still accounts for a large proportion of mass produced polymers: in 1985 over 46% (by weight) of the total U.S. production of plastics involved this type of polymerization [31, 32].

2.1.1. Free radical photoinitiated polymerization

In these coatings, free radicals are photogenerated and initiate polymerization by adding to vinyl double bonds, primary acrylates. Two classes of photoinitiators are used: those that undergo unimolecular bond cleavage and those that undergo bimolecular hydrogen abstraction from some other molecule.

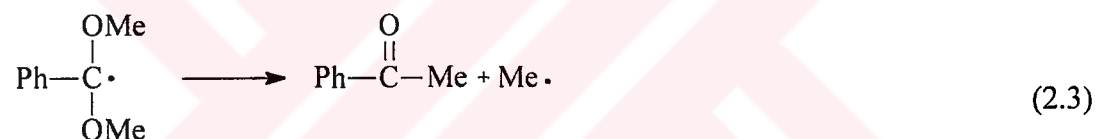
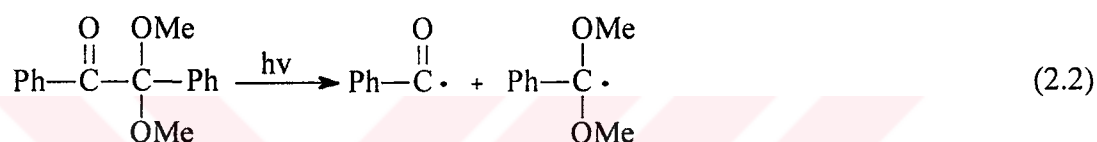
2.1.1.1. Unimolecular photoinitiators

A range of unimolecular photoinitiators has been studied (7). The first ones used on a large scale commercially were ethers of benzoin. Benzoin ethers undergo cleavage to form benzoyl and benzyl ether radicals:

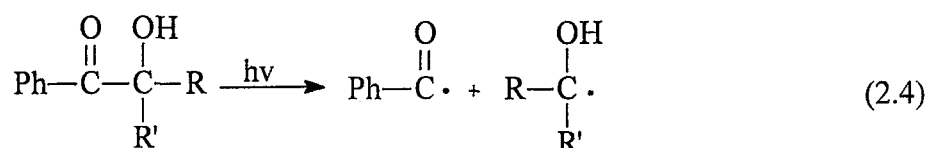


Both these radicals can initiate polymerization of acrylate monomers (8). There is doubt whether the benzyl ether radical can initiate the polymerization of styrene (7).

The package stability of UV cure coatings containing such benzoin ethers tends to be limited. Apparently, this is due to the ease of abstraction of the hydrogen on the benzyl ether carbon. Any organic material contains hydroperoxides that slowly decompose. The resulting radicals can abstract the benzylic hydrogen, leading to initiation of polymerization and, hence, poor package stability. Package stability is improved if the benzylic carbon is fully substituted. Accordingly, the ketal, 2,2-dimethoxy-2-phenylacetophenone, is an effective photoinitiator with good package stability. Photocleavage produces benzoyl and dimethoxy benzyl radicals. The latter is a sluggish initiator; however, it can undergo further cleavage to the highly reactive methyl radical; the extent of this cleavage increases with increasing temperature.

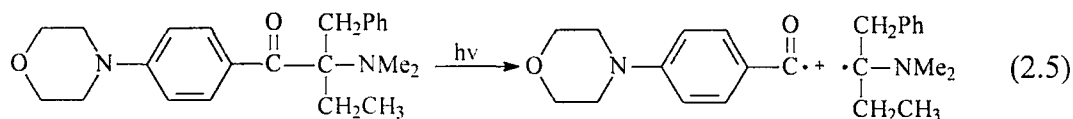


2,2-Dialkyl -2-hydroxyacetophenones are also commercially important photoinitiators with good package stability. These photoinitiators tend to give less yellowing than phenyl substituted acetophenones, including benzoin ethers as well as the above ketal, probably because benzylic radicals are not generated by photocleavage.



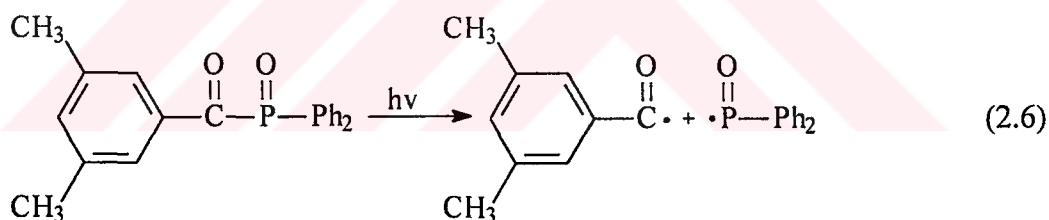
All these photoinitiators have an acetophenone chromophore, the absorptivity of which is enhanced by electron donating substituents on the benzoyl ring. This is

exemplified by the morpholino-substituted photoinitiator 2-dimethylamino-2-benzyl-1-(4-morpholinophenyl)-butan-1-one, which is recommended for pigmented coatings (9). Yellowing can be a problem in clear coatings.



Acylphosphine oxides are another class of unimolecular photoinitiators. Several acylphosphine oxides are available, for example, diphenyl 1-2,4,5-trimethylbenzoylphosphine oxide. Irradiation generates the corresponding benzoyl and phosphinyl radicals. Acylphosphine oxides tend to be no yellowing and give good package stability.

Bis(2,6-dimethoxybenzyl)-2,4,4-trimethylpentylphosphine oxide (BAPO) on irradiation is reported to generate four radicals that can initiate polymerization (10). The strong absorption of near UV radiation and short wavelength light makes possible curing of

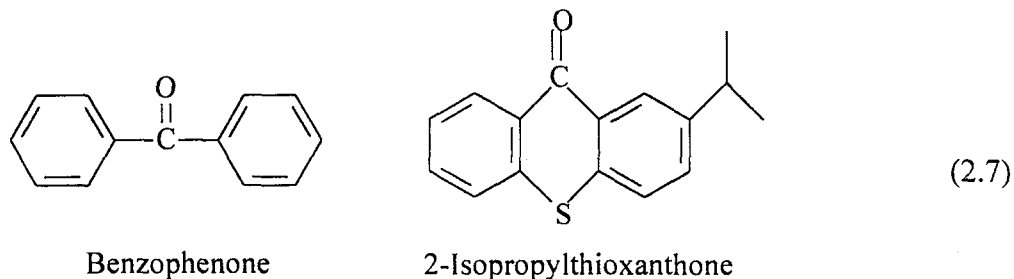


Relatively thick films of white-pigmented coatings. While BAPO is yellow, photocleavage results in reduced absorptivity (bleaching), so BAPO can be used in white coatings. The absorption spectrum can be broadened by using a blend with 2-hydroxy-2-methyl-1-phenylpropan-1-one (HMMP), providing combined surface and through cure at lower cost.

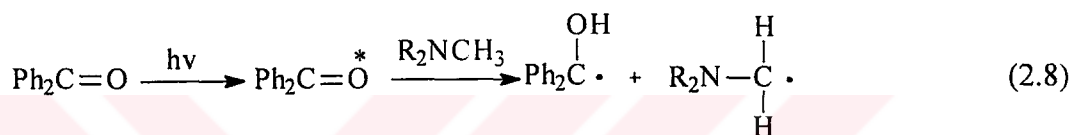
2.1.1.2. Bimolecular initiators

Photoexcited benzophenone and related diarylketones, such as xanthone and thioxanthone, do not cleave to give free radicals, but can abstract hydrogens from a hydrogen donor to yield free radicals that initiate polymerization. Thioxanthenes, such as 2-isopropylthioxanthone, are used when their high absorption in the very

near UV is desirable to permit absorption in the presence of pigments or dyes that absorb UV strongly in the shorter UV range.



Widely used hydrogen donors are tertiary amines with hydrogens on carbon atoms, such as 2-(dimethylamino) ethanol (DMAE) and, in printing inks, methyl p-(dimethylamino) benzoate. It has been shown that the accompanying ketyl free radical does not initiate polymerization.



An advantage of bimolecular initiators with amine coinitiators is reduced oxygen inhibition, as discussed in the next section. A disadvantage is that the excited states of these initiators are more readily quenched by oxygen, as well as by vinyl monomers with lower triplet energies.

2.2. Photoinitiated Cationic Polymerization

During the past decade, photoinitiated polymerization have received considerable attention and practically applied in variety of areas, including printing inks, adhesives, surface coating, microelectronics and printing plates [33-38]. The advantages of photoinitiated polymerization over conventional thermal polymerization lie in the high speed reaction at ambient temperature, low energy consumption and solvent free formulation. Photoinitiated polymerization is typically a process that transforms a monomer into polymer by a chain reaction initiated by reactive species (free radicals or ions), which are generated by UV irradiation.

Much effort has been devoted to free radical systems [34-37] mainly due to the availability of a wide range of photoinitiators and the great reactivity of acrylate-based monomers. Despite the most popular industrial application based on the photoinitiated free radical photopolymerization there are some drawbacks associated with this type polymerization such as the inhibition effect of oxygen and post-cure limitations which may affect the properties of the final product. UV initiated cationic polymerization holds considerable promise in future, particularly as a means of overcoming volatile emission, toxicity and molecular oxygen inhibition limitations.

Although the cationic polymerization exhibits several advantages it has not as yet achieved the commercial significance of radical polymerization in UV curing applications. This was mainly because of the limited choice of the cationic photoinitiators and monomers that were commercially available until recently. This situation changed with two significant improvements. First, cationically polymerizable important classes of monomers such as vinyl ethers and epoxides became commercially available. Second, a new class of cationic photoinitiators with non-nucleophilic counter ions such as SbF_6^- and AsF_6^- has been utilized [39].

Since the photoinitiator is one of the most important parts of a UV initiated polymerization, many research efforts have been devoted to understand what type of photoinitiators is applicable to generate cations. Among the various types of photoinitiators that can lead to the formation of cation as a result of UV light induced fragmentation, onium salts have found considerable application in UV curing and photorezist technology. The photochemistry of these novel classes of photoinitiators is well documented [33-38]. Upon photolysis, these thermally and hygroscopically stable initiators undergo irreversible photofragmentation to produce cation radicals and Brønsted acids.



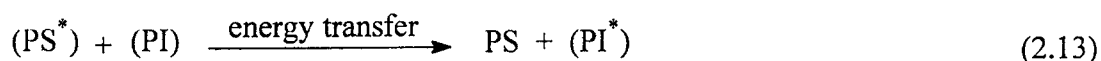
Reactive species thus produced photochemically with onium salts initiate the cationic polymerization of suitable monomers as illustrated below.



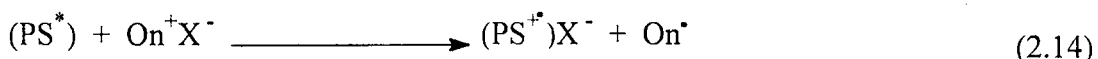
Onium salts used in cationic photopolymerization mainly absorb the wavelengths of light between 225 and 350 nm [33, 39-41]. Alkoxy pyridinium salts are also treated as onium salts since the chemistry of these salts resembles that of classical onium salt initiators, such as iodonium and sulphonium salts. For practical applications, onium salts should absorb light appreciably at wavelengths longer than 350 nm where the commercially available medium and high pressure mercury lamps emit much of their radiation. Since this requirement is not fulfilled for certain easily available onium salts several systems were developed to extend the applicability of the onium salt photoinitiators. In these case additives are present which participate in the reaction sequence to yield reactive species capable of initiating the cationic polymerization. In the following sections depending on the role played by the additives in the initiation of the polymerization three modes of indirect initiation will be discussed.

2.2.1. Photosensitization of cationic polymerization

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



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



Depending upon the two components involved the photosensitization can occur through energy transfer or electron transfer. The basic requirement for the energy transfer is the excitation energy of the sensitizer $E^*(PS)$ should be higher than that of excited onium salt $E^*(On^+)$. On the other hand the electron transfer (eq. 2.14) is energetically allowed, if ΔG calculated by (eq. 2.15) (extended Rehm- Weller equation) [42] is negative.

$$\Delta G = F [E_{ox}^{1/2}(PS) - E_{red}^{1/2}(On^+)] - E^*(PS) \quad (2.15)$$

where $E_{ox}^{1/2}$ and $E_{red}^{1/2}$ are half wave oxidation and reduction potential of photosensitizer and photoinitiator respectively, $F= 97 \text{ KJ.mol}^{-1} \text{ V}^{-1}$, is the conversion factor and $E^*(PS)$ is the excitation energy of photosensitizer.

2.2.1.1. Classical energy transfer

Energy may be transferred from excited sensitizer (PS^*) to onium salt (PI) by either resonance excitation or exchange energy transfer. Depending on the two components involved, energy transfer may proceed either excited singlet or in triplet state.

Table 2.1. Halfwave oxidation potentials $E_{1/2}^{\text{ox}}$ (PS) (vs SCE) and triplet or singlet energies $E^*(\text{PS})$ of commonly used photosensitizers.

Acetophenone	2.9	308 (E_t)
Benzophenone	2.7	290 (E_t)
Thioxanthone	1.7	277 (E_t)
Anthracene	1.1	319 (E_s)
Perylene	0.9	277 (E_s)
Phenothiazine	0.6	239 (E_t)
<i>m</i> -Trifluoromethyl acetophenone	2.7	305 (E_t)
Xanthone	-	311 (E_t)

Diphenyliodonium cations were excited to their first excited triplet state by energy transfer from *m*-trifluoromethyl acetophenone [43]. As can be seen from Tables 2.1 and 2.2, the energy transfer is energetically allowed. Electron transfer in the exciplex can be totally excluded, since the oxidation; potential of *m*-trifluoromethyl acetophenone is relatively low. In the case of triphenyl sulfonium salt energy, transfer may occur from sensitizers with triplet energies above 314 kJ mol^{-1} .

It has been shown that photosensitized decomposition of onium salt follows different route from that observed for direct photolysis of the onium salts [44, 45]. This can be attributed to the different spin multiplicities involved in the corresponding decompositions.

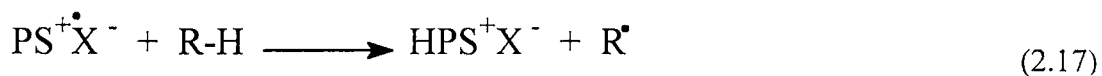
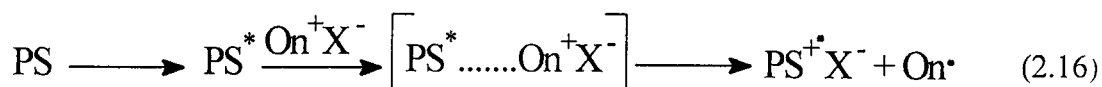
It should be pointed out that the energy transfer sensitization is not a technically useful process due to the high-energy requirements.

Table 2.2. Reduction potential and triplet excitation energies of selected onium ions

Onium cation	$E_{1/2}^{\text{red}}$ (V) (vs SCE)	E_i^* (kJ mol ⁻¹)
	0.35	-
	-0.2	268
	-1.1	314
	-0.7	-
	-0.5	-

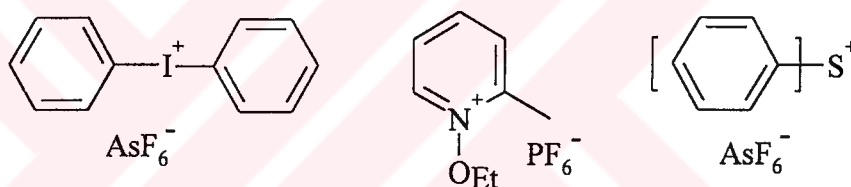
2.2.1.2. Electron transfer via exciplex

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



Since the oxidation potential of sensitizers $E_{1/2}^{\text{ox}}$ are easy to determine, the calculation of ΔG can indeed be applied in order to predict whether or not an oxidation would take place as presented for the example of typical onium salts in Table 2.3.

Table 2.3. Sensitization of onium salts; ΔG in kJ mol^{-1}



Sensitizer	ΔG	Sens ^a	ΔG	Sens ^b	ΔG	Sens ^a
Benzophenone	- 8	+	+ 39.8	-	+ 88	-
Acetophenone			+ 41.2	-		
Thioxanthone	-92	+	- 44.2	+	+4	-
Anthracene	- 193	+	-144.4	+	- 96	+
Perylene	- 171	+	- 121.8	+	- 71	+
Phenothiazine	- 159	+	- 112.9	+	- 63	+

^aPolymerization of the diepoxide, 3,4-epoxycyclohexylmethyl-3,4- epoxy cyclohexane carboxylate[46].

^bPolymerization of cyclohexene oxide [47].

However not all sensitizers are suitable in conjunction with onium salts. According to (eq 2.15) the requirements are low oxidation potentials, $E_{1/2}^{\text{ox}}(\text{PS})$, and relatively high excitation energies $E^*(\text{PS})$ of the sensitizer. It should also be noticed that only onium salts with high (low negative) reduction potentials $E_{1/2}^{\text{red}}(\text{On}^+)$, such as diphenyliodonium or alkoxy pyridinium salts are easily reduced by sensitizer.

The sensitization of onium salts (Ar_3S^+ and Ar_2I^+) by anthracene has been investigated in detail in a number of papers [48-50]. Exciplex formation is followed by a partly loss of anthracene's aromatic system as concluded from the decrease in the sensitizer fluorescence. These reactions are illustrated in equations 11-15 on the example of diphenyliodonium salt. Notably, similar coupling reactions of radical cations with the radicals formed from the salts were also observed with alkoxy pyridinium salts [51].

The sensitization of thioxanthone follows only partly the general mechanism described for the exciplex formation [51]. To some extent, this sensitization is based upon the oxidation of photolytically formed radicals.

2.2.2. Charge-transfer complexes initiated cationic polymerization

Pyridinium salts are capable of forming charge transfer (CT) complexes with electron rich donors such as methyl- and methoxy- substituted benzene. 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 at 270 and 265 nm for the pyridinium salt and trimethoxybenzene, respectively. It was found that the CT complexes formed between pyridinium salts and aromatic electron donors act as photoinitiators for the cationic polymerization of cyclohexene oxide and 4-vinyl cyclohexene oxide. The following mechanism for the initiation of the cationic polymerization has been suggested [52]:

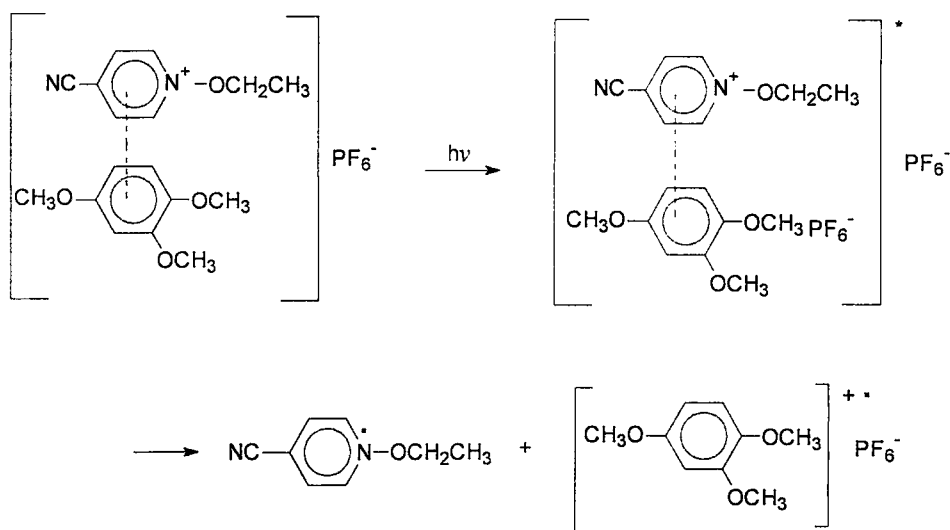


Figure 2.1: The initiation of the cationic polymerization by charge transfer complexes

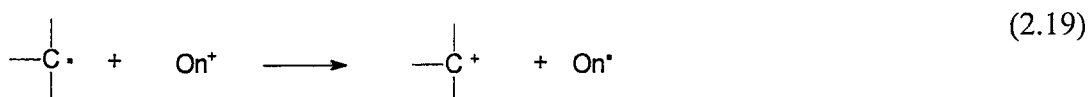
Since the proton scavenger 2,6-di-tert-butylpyridine did not noticeably influence the polymerization, the initiation by Brønsted acid that could be formed after an interaction with hydrogen donor components can be excluded. Notably, the CT complexes described above are applicable for the photoinitiation of epoxide monomers but not for the photoinitiation of vinyl ethers and N-vinyl carbazol. The latter monomers are already polymerized in a dark reaction upon addition of these complexes.

2.2.3. Sensitization by free radical photoinitiators

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

2.2.3.1. Oxidation of radicals

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



The cations thus generated are used as initiating species for cationic polymerization. This process is usually termed as the free radical promoted cationic polymerization.

This so-called free radical promoted cationic polymerization is an elegant and flexible type of sensitized cationic polymerization [53-54]. Free radicals may be produced by various modes: photochemically, thermally or by irradiating the system with high-energy rays. Table 2.4 shows free radical photoinitiator and onium salt combinations generally used in free radical promoted cationic polymerization.

Table 2.4. Initiating systems for free radical promoted cationic polymerization

Free Radical Source	Onium Salt	Reference
Benzoin Derivatives	Iodonium /pyridinium salts	[55,56]
Benzophenone	Iodonium /pyridinium salts	[55,56]
Acylphosphine oxides	Iodonium /pyridinium salts	[57,58]
Dye-Amine	Iodonium salt	[59]
Vinyl Halides	Sulphonium/pyridinium salts	[60,61]
<i>o</i> -Phtaldehyde	Pyridinium salts	[62]
Azo compounds	Iodonium /pyridinium salts	[55,56]
Polysilanes	Iodonium /pyridinium salts	[63,64]

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

The efficiency of onium salts in this mode of polymerization rises in the order of trialkylsulphonium salts < alkoxy pyridinium salts < diaryliodonium salts < aryldiazonium salts (see Table 2.4). Aryldiazonium salts are most suitable for the oxidation of radicals. However, their practical application is hampered by the lack of thermal stability. Diphenyliodonium salts have also a relatively high reduction potential. Being very suitable for the oxidation of free radicals, these salts have been most frequently used for the oxidation of photogenerated free radicals. On the other hand, triphenylsulphonium salts have only limited potential for radical induced cationic polymerizations due to their low reduction potential. However, some highly nucleophilic radicals could be oxidized with sulphonium salts.

Provided the oxidation and reduction potentials of the free radical and the onium ion, respectively, are known, it can be estimated on the bases of the Rehm-Weller equation (2.20) whether a radical can be oxidized by a given onium salt or not.

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

F... Faraday constant

(2.20)

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

2.2.3.2. Addition of free radicals and fragmentation

As the second way of cationic polymerization induced by free radicals, the addition-fragmentation reactions seem to be promising. The following discussion serves to illustrate the importance of such reaction in polymer chemistry in a comprehensive way.

2.3. Addition Fragmentation Reactions

In the past decade addition - fragmentation reactions turned out to be a versatile and exceptionally interesting tool for polymer synthesis. There are two synthetic areas where addition - fragmentation reactions are of importance:

In Chain Transfer

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 [65, 66].

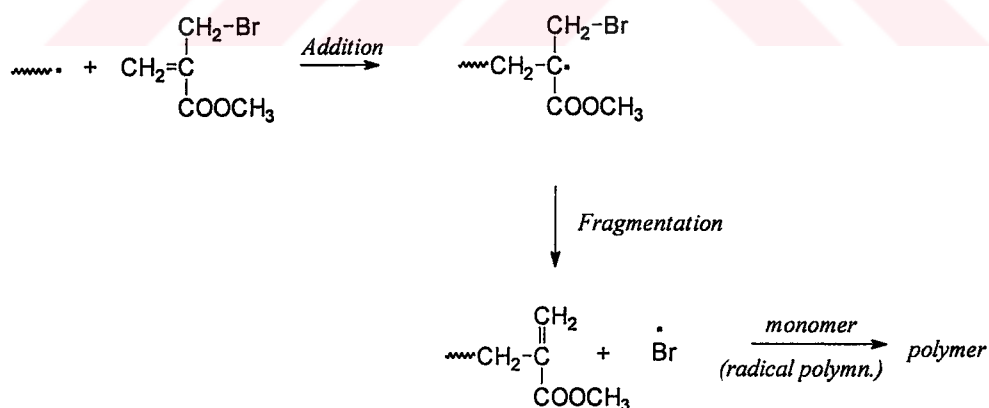
In cationic polymerization

Depending upon coinitiators used cationic polymerization may be initiated by either heat or light [67].

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 olefinic 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) [67], or, a primarily formed radical led to the generation of a radical cation, which initiates cationic polymerization [66]. In Figure 2.2 these reactions are illustrated on two typical examples.

Chain Transfer



Cationic Polymerization

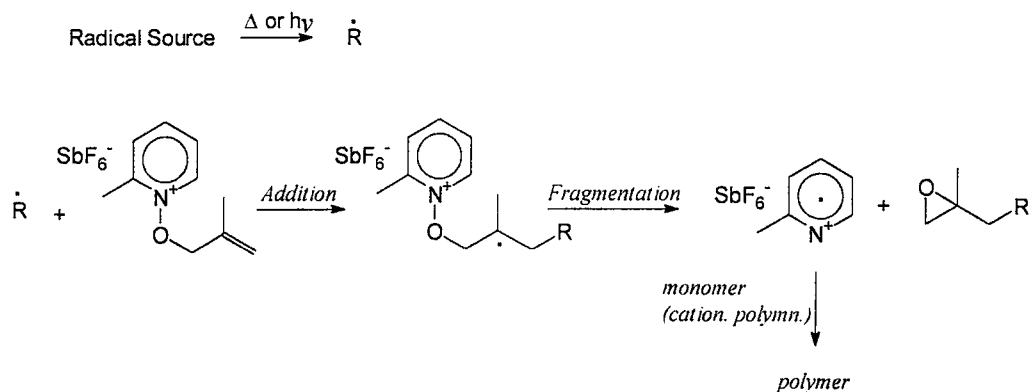


Figure 2.2. Use of Addition-Fragmentation Reactions in Chain Transfer and Cationic Polymerization.

The scope of this review is to show that how great the variety in applications of addition fragmentation reactions are, there are always certain functional groups or structural criteria that AFAs have to meet in order to facilitate both addition and fragmentation.

2.3.1. Addition - fragmentation agents for chain transfer reactions

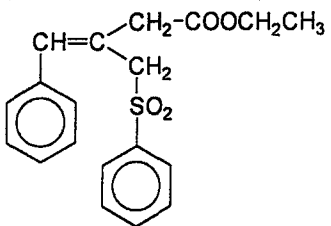
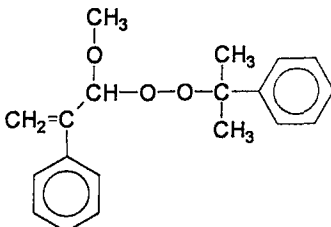
In technical polymer synthesis molecular weight has often to be controlled since very high molecular weight polymers are hard to process (e.g., since they possess a high melt viscosity) and in some cases undesired crosslinking may occur during polymerization. For lowering molecular weight definite amounts of chain transfer agents, mostly thiols, or solvents with high chain transfer capability, e.g., CCl_4 , are used [68,69]. An interesting novel method is the application of addition fragmentation reactions for chain transfer. These reactions combine the advantage of high efficiency in chain transfer with the possibility of end- functionalizing the polymer. Furthermore, if sulfur free AFAs are used there is no contamination of the polymer with thiols which would give an unpleasant odor and premature color to the polymer.

The efficiency of chain transfer is expressed in terms of the chain transfer constant (C_x), i.e., 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

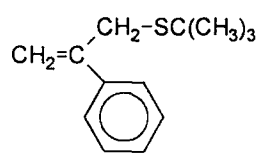
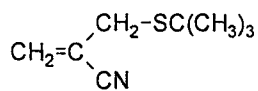
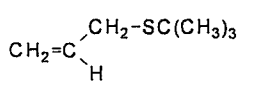
changing the AFA concentration, it is possible to adjust a well-defined molecular weight, that is, of course lower than the one obtainable in the absence of AFA. If C_x is unity one speaks of azeotropic chain transfer, a situation by which especially narrow molecular weight distributions are accessible. Chain transfer constants are calculated from sets of $[AFA]$, M_w data.

As far as addition - fragmentation reactions are concerned; there are two structural prerequisites for radical chain transfer. The double bond is the reactive site to which free chain radicals are added. 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 [70]. 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. Because 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 energetically favorable leaving groups, which could be stabilized by, e.g., hyper conjugation (secondary or tertiary radicals) or resonance (e.g., benzyl radical), fragmentation can be tremendously facilitated. Examples of AFAs for chain transfer with good transfer properties are depicted in Table 2.5.

Table 2.5. Selected AFAs for Chain Transfer. C_x -Chain Transfer Constant at 60°C. St -Styrene. MMA - Methyl Methacrylate

Nr.	AFA	$C_x(\text{St})$	$C_x(\text{MMA})$	Ref.
1		0.37	-	8
2		0.92	0.49	9

3	<chem>CC(C)(C)c1ccc(OCC=C(c2ccccc2)OC(C)(C)C3=CC=CC=C3)cc1</chem>	0.90	-	9
4	<chem>CCOC(=O)C=C(C)COOSi(C)(C)C</chem>	0.90	0.15	10
5	<chem>c1ccc(cc1)COCC=C(c2ccccc2)</chem>	0.26	0.76	11-13
6	<chem>CC(C)C=C(C)C(=O)OCCSC(C)C</chem>	1.51	0.33	14
7	<chem>CSCC=C(C)C#N</chem>	1.7	0.66	14
8	<chem>CCOC(=O)C=C(C)SC</chem>	1.98	0.33	14
9	<chem>CN(C)C(C(=O)c1ccccc1)C=C(c2ccccc2)C(=O)OCC</chem>	1.87	0.14	14
10	<chem>CCOC(=O)C=C(c1ccccc1)COCC(=O)c2ccccc2</chem>	0.54	0.06	14
11	<chem>CCOC(=O)C=C(C)SC(C)(C)C</chem>	1.18	0.49	15

12		1.24	0.8	15
13		1.9	1.35	15
14		≈ 0	≈ 0	15

The AFAs 11-14 shown in Table 2.5 illustrate that an activation of the double bond towards addition is essential for a high efficiency in chain transfer. The unsubstituted representative (AFA 14) is no chain transfer agent. It is commonly assumed that with AFAs for chain transfer it is the addition step that is rate determining, the fragmentation is a comparably fast process in these systems.

As already mentioned, 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 [71]. 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 [72]. 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. The chain transfer is very efficient: e.g., in styrene polymerization the molecular weight (M_n) is lowered from 2×10^5 to 4×10^4 by a AFA (AFA 2 in Table 2.5.) concentration of $2.8 \times 10^{-3} \text{ mol l}^{-1}$ [72]. With AFA 3 (see Table 2.5.), peroxy functionalized polystyrene may be obtained which can serve as macroinitiator for thermally induced block copolymerization. By using AFAs containing peroxide groups polymers with epoxide functionalization at their ω -

termini are generated. The presence of epoxides at the end has been shown by NMR and by functional group modification from epoxide to aldehyde. These telechelic polymers could be useful for the production of block copolymers by a cationic mechanism. For the initiation with peroxyketals, a detailed kinetic model allowing the prediction of molecular masses after chain transfer has been derived.

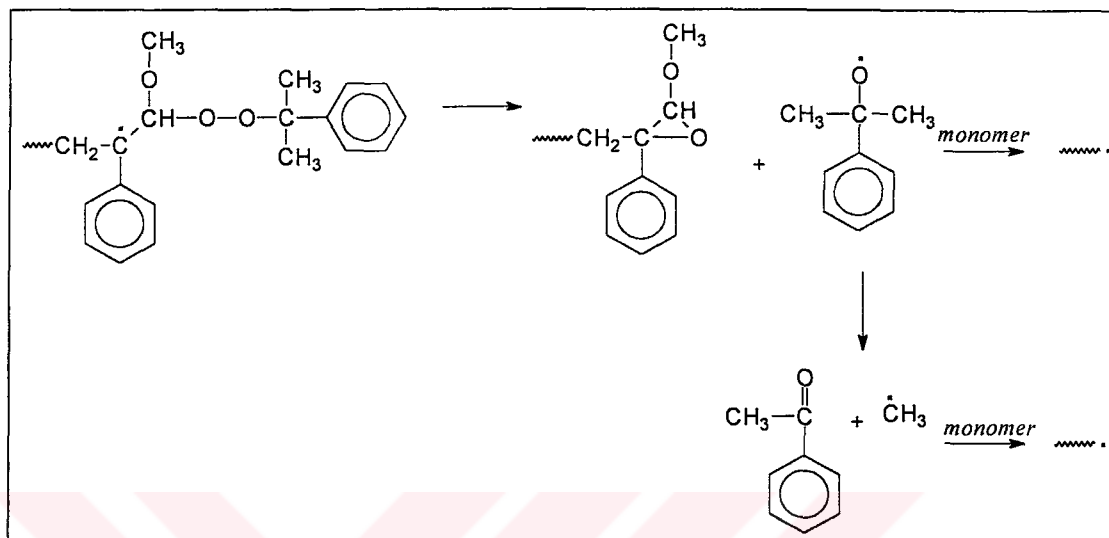


Figure 2.3. Peroxyketals as AFA

Recent investigations with dimers and crossdimers of various α -methylvinyl monomers carried out by Yamada et al. aimed at forming polymers with substituted allyl end groups. In these studies, dimers were synthesized and subsequently used in the polymerization of styrene and methyl methacrylate. It turned out that with many of them effective chain transfer takes place giving rise to the respective polymer with allylic end groups. Especially, the dimer of α -methyl styrene and cross-dimers of α -methyl styrene with other monomers were noted as highly reactive in lowering the molecular weight (see Figure 2.4.). The presence of unsaturated end groups, which might be utilized for the synthesis of block copolymers, has been proven by $^1\text{H-NMR}$ spectroscopy. Additional evidence for the occurrence of addition - fragmentation was found from ESR measurements.

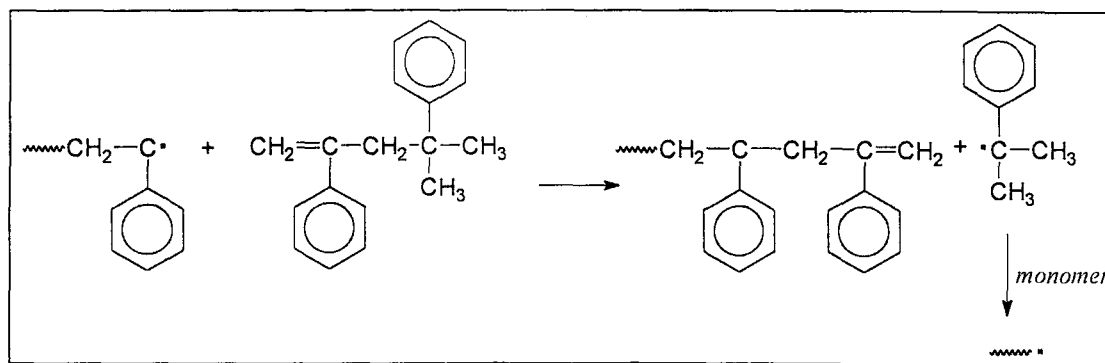


Figure 2.4. Dimers of α -Methyl Styrene as AFAs

Some α -substituted monomers, like methyl α -(phenoxyethyl) 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 [73]. This circumstance may also be utilized for the production of polymers or copolymers with unsaturated end groups. Interestingly, as far as copolymers are concerned the extent of fragmentation drops when the monomer radical of the fragmenting monomer is reactive towards the comonomer. E.g., for styrene, which efficiently adds to methyl α -(phenoxyethyl)acrylate radicals there is only little fragmentation. Another group of such monomers are ethyl α -(halomethyl)acrylates. From the 3 monomers depicted in Table 2.3., only the fluorine and chlorine derivative may be homopolymerized [74]. Although still polymerizable, with ethyl α -(chloromethyl)acrylate there is already a strong proneness to fragmentation (i.e., transfer to monomer): the ratio of rate constants of propagation to fragmentation (k_p/k_f) drops from 11 l mol⁻¹ at 60°C to 5.7 l mol⁻¹ at 80°C. In the case of the bromine containing acrylate there is an efficient transfer to monomer, owing to the ease in bond of C-Br bond rupture. In fact, ethyl α -(bromomethyl)acrylate is a highly active AFA which may be used for controlling molecular weight. Using the bromine containing AFA, poly(methyl methacrylate) and copolymers of methyl methacrylate and styrene with relatively low molecular weight bearing overwhelmingly bromine and the 2-carbomethoxyallyl group at the α - and ω - chain ends were produced.

Table 2.6. Homopolymerization of Ethyl α -(Halomethyl)acrylates at 50°C in Benzene

Ethyl α -(Halomethyl) acrylate	$\begin{array}{c} \text{CH}_2\text{-F} \\ \\ \text{CH}_2=\text{C} \\ \\ \text{COOCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{-Cl} \\ \\ \text{CH}_2=\text{C} \\ \\ \text{COOCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{-Br} \\ \\ \text{CH}_2=\text{C} \\ \\ \text{COOCH}_3 \end{array}$
Conversion (%)	52	9	0
M_w	5.2×10^4	1.2×10^4	-

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, as AFAs 6 and 7 in Table 2.5 demonstrate. The high chain transfer activity is in this case explainable in terms of the formation of thermodynamically favorable dienes at the end 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 [84].

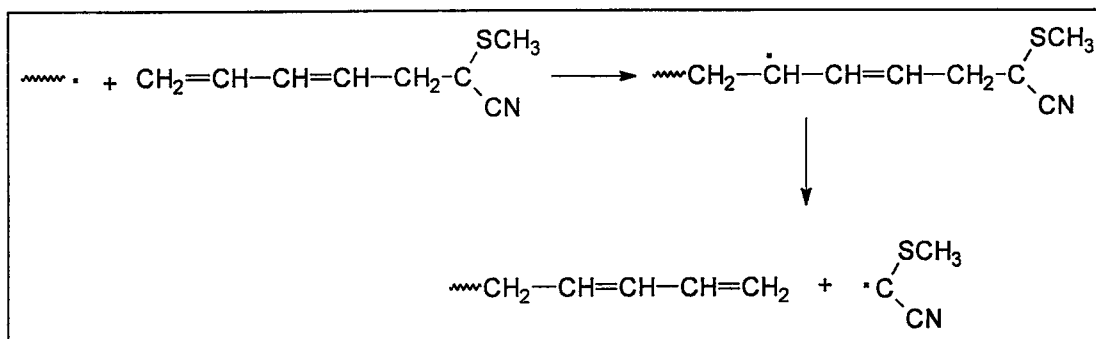


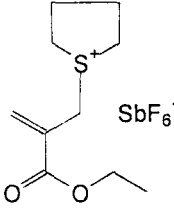
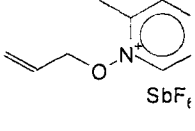
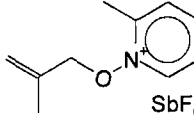
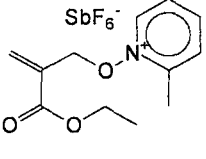
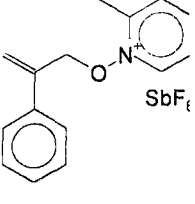
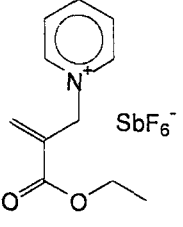
Figure 2.5. Addition Fragmentation Chain Transfer with Pentadiene Derivatives

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 what was the reason for the development of cationic photo- and thermal initiators [75]. 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 [76].

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 Figure 2.5). 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. As seen in Table 2.7, it is S^+-C , N^+-O , and N^+-C - bonds that are cleaved.

Table 2.7. AFAs for Cationic Polymerization

 <p>1</p>	 <p>2</p>	 <p>3</p>
 <p>4</p>	 <p>5</p>	 <p>6</p>

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 photo polymerization 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 leads to numerous radical initiators with excellent radical yields and good storage stability.

In Table 2.7 successful candidates of AFAs for cationic polymerization are compiled. The reactivity of allyloxy pyridinium derivatives (AFAs 2-5 in Tab 2.7.) and of the tetrahydrothiophenium based AFA 1 (Table 2.7.) are 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 Table 2.7.) there is no remarkable influence of the substituent at the allylic double bond. Since addition reactions are very much affected by the substituents 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 $k = 10^6-10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ for CHO [77]. 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 favorable 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. Spectroscopic investigations showed that EAP and AP are able to oxidize triphenylmethyl radicals, what is explainable on the bases of their relatively high oxidation potentials. 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 Figure 2.6.

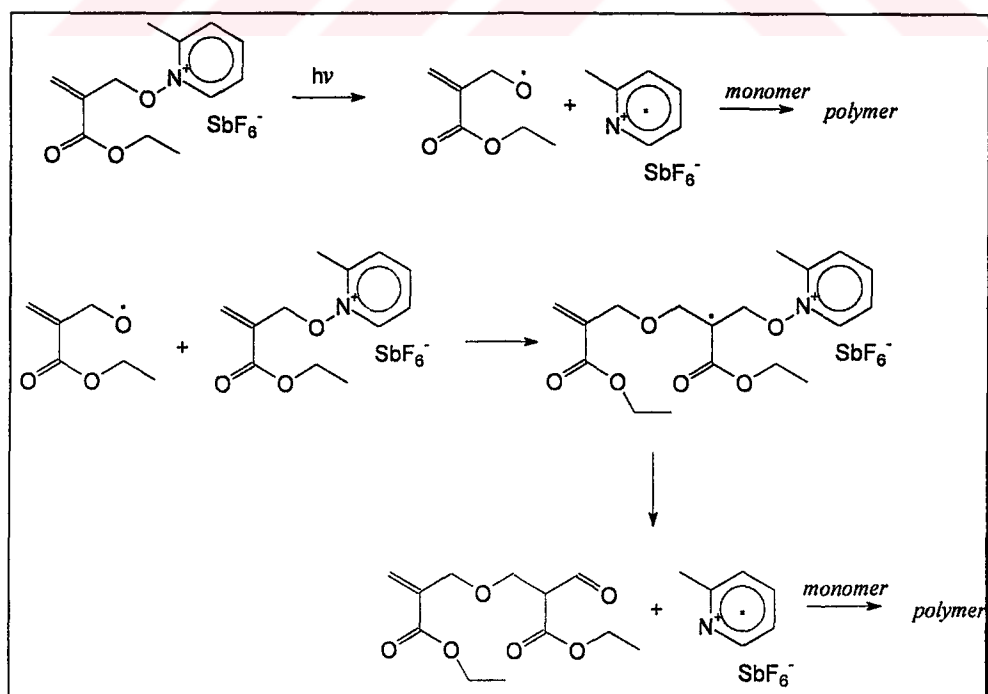


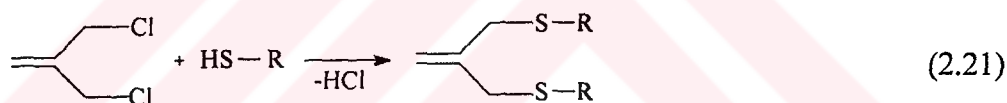
Figure 2.6. Cationic Photopolymerization with Allyloxy-Pyridinium Salts

With the initiators 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., butyl vinyl ether and N-vinyl carbazol redox processes between the monomer and the initiator take place accounting for an undesired polymerization in the dark at room temperature. Bifunctional oxirans have successfully been polymerized, what led to the formation of insoluble networks.

2.3.3. Bifunctional free radical addition-fragmentation agents

Free radical addition-fragmentation agents were used to prepare telechelic polymers as discussed in the previous section. If these molecules possess bifunctionality and participate in addition-fragmentation chain transfer reaction, they lead to the formation of oligomers with two end groups. For this purpose, Sunder and Mulhaupt synthesized novel symmetrically substituted dithioesters derived from 2-methylene-propane-1,3 thiol according to the following reaction :

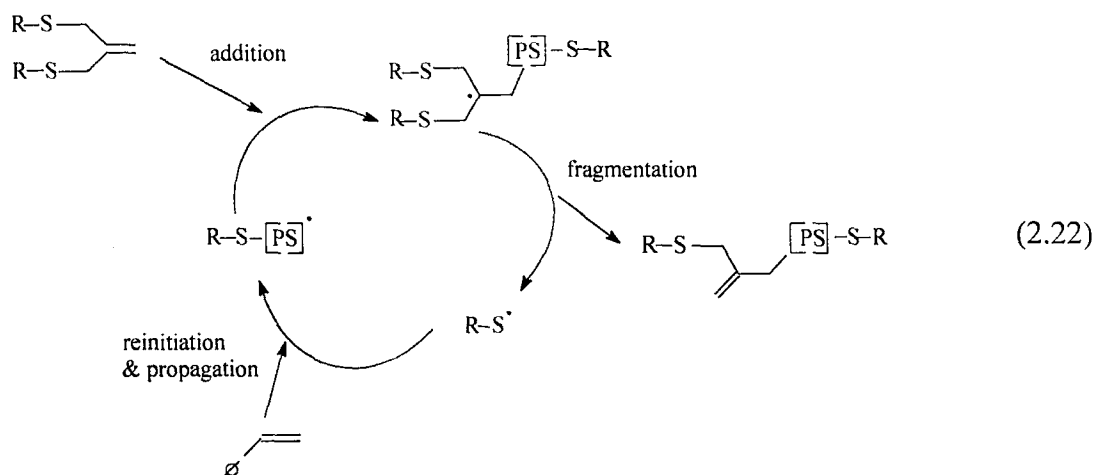
(3,4 by subsequent reaction from 1)



1 R=C₂H₄-CO₂CH₃ 2 R=CH₂-CO₂CH₃ 3 R=C₃H₆-OH 4 R=C₂H₄-CONH-C₂H₄-OH

Ester and hydroxy function thioethers were used in styrene polymerization and chain transfer constants were determined.

The typical reactions occurring during free radical styrene polymerization are illustrated in reaction 2.22 (mechanism of chain transfer in styrene polymerization with symmetrical addition-fragmentation agents in steady state):



The polymer radical (PS•) adds to the olefin group and fragments to yield mono vinyl and two R• functional polymers. Thiyl radical who is also formed, further initiates the polymerization to produce new polymeric chains. It was also expected that vinyl terminated polystyrene would further radical addition-fragmentation reaction.

3. EXPERIMENTAL WORK

3.1. Materials and Chemicals

3-Chloro-2-(chloromethyl)-1-propene (Aldrich), tetrahydrothiophene (Fluka) sodium hexafluoroantimonate (Aldrich) and 2,2-dimethoxy-2-phenyl acetophenone (DMPA) (Ciba Specialty Chemicals), were used as received.

Cyclohexene oxide (CHO) (Fluka), n-butyl vinyl ether (BVE) (Aldrich), acetone (Lab-scan) and propylene carbonate (Aldrich) were purified by conventional drying and distillation procedures.

Benzophenone (Fluka) was recrystallized from ethanol before used.

3.2. Equipment

3.2.1. Photoreactors

A merry-go-round type photoreactor equipped 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

¹H-NMR spectra were recorded on a Bruker 250 MHz instrument.

3.2.5. Gel permeation chromatography (G.P.C.)

GPC analyses were performed via set-up consisting of a Waters pump and three styragel HR3, HR4, HR4E columns with THF as the eluent, at a flow rate of 1 ml min⁻¹ and detection was carried out with a differential refractometer. Molecular weights were calculated with the aid of polystyrene standards.

3.2.6. Infrared spectrophotometer (FT/IR)

IR spectra were recorded on a Jasco FT/IR-3 spectrometer on a KBr disc.

3.3. Synthesis 1,1-ditetrahydrothiophenium methyl ethylene hexafluoroantimonate (DTE)

A mixture of 0.54g (4.32 mmol) 3-chloro-2-(chloromethyl)-1-propene, 0.76g (8.64 mmol) tetrahydrothiophene and 2.23g (8.64 mmol) NaSbF₆ in 20 ml dry acetone was placed in a round bottom flask and stirred at 45 °C for 10 days. The white precipitate formed was filtered off and dissolved in 10 ml of acetonitrile in order to remove unreacted NaSbF₆. After the evaporation of the solvent, the white precipitate was washed with water and recrystallized from ethanol. Yield: 0.34 g (12%), m.p.: 142 °C Elemental analysis: C₁₂H₂₂S₂ (SbF₆)₂ (700.34 g.mol⁻¹) Found: C:20.62, H:3.27 Calculated: C:20.56, H:3.14 UV: λ_{max}=225 (ε = 236.4 l mol⁻¹ cm⁻¹).

3.4. Polymerization Techniques

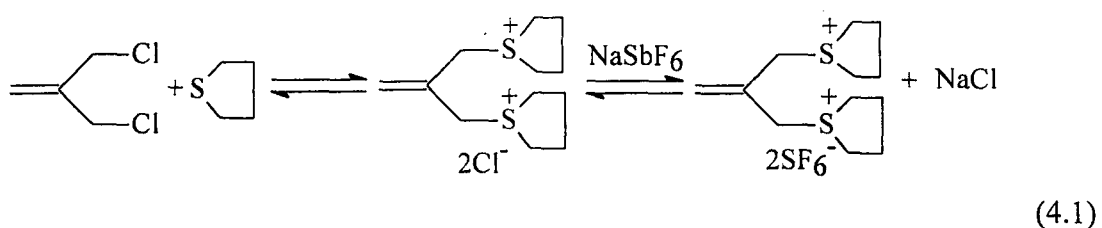
3.4.1. Photopolymerization

Appropriate solutions of monomer and DTE were mixed in quartz tubes and degassed with nitrogen prior to irradiation by a merry-go-round type reactor equipped with 16 Philips 8W/06 lamps emitting light at λ>300 nm. At the end of a given time, polymers were precipitated into methanol, filtered, dried in vacuum oven and weighed. Conversion percentages were calculated according to the equations (W=amount of polymer obtained M=amount of monomer used) indicated below:

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

4. RESULTS AND DISCUSSION

Bifunctional AFA namely, 1,1-ditetrahydrothiopheniummethyl ethylene hexafluoroantimonate (DTE) was synthesized by the reaction of 3-chloro-2-chloromethylpropene with thiophene in the presence of sodium hexafluoroantimonate.



The precipitation of insoluble NaBr, in this simple one-pot reaction, shifts the two simultaneous equilibrium reactions towards the desired final product. The structure of the salt was confirmed by spectral and elemental analyses. The $^1\text{H-NMR}$ spectrum, recorded in CDCl_3 evidenced $-\text{CH}_2=\text{C}$, $\text{C}-\text{CH}_2$, $\text{S}-\text{CH}_2$ and $-\text{CH}_2$ protons of relative intensities corresponding to the number and type of protons (Figure 4.1). The IR spectrum also shows peaks characteristics to thiophene and allyl groups ($1786, 1417, 1190, 1050, 950, 660 \text{ cm}^{-1}$) (Figure 4.2)

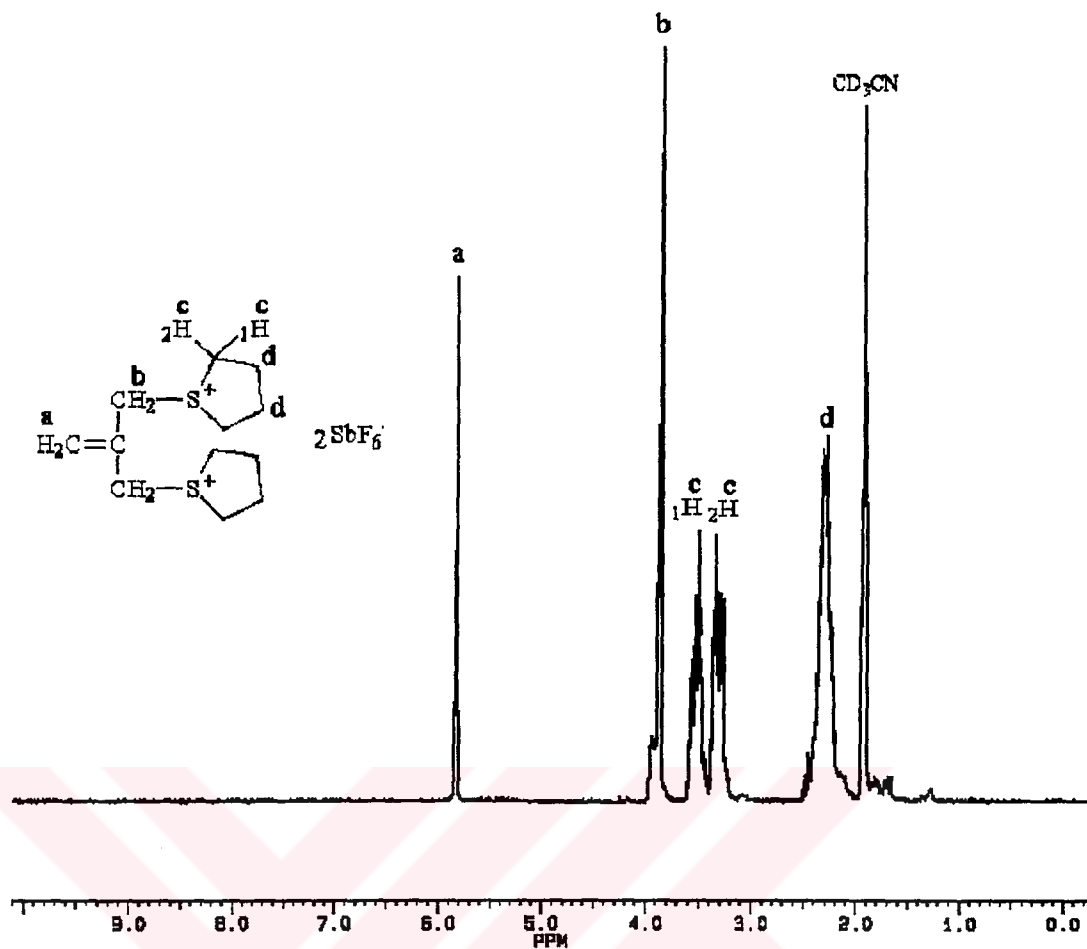


Figure 4.1. ¹H-NMR spectrum of DTE in CDCl₃.

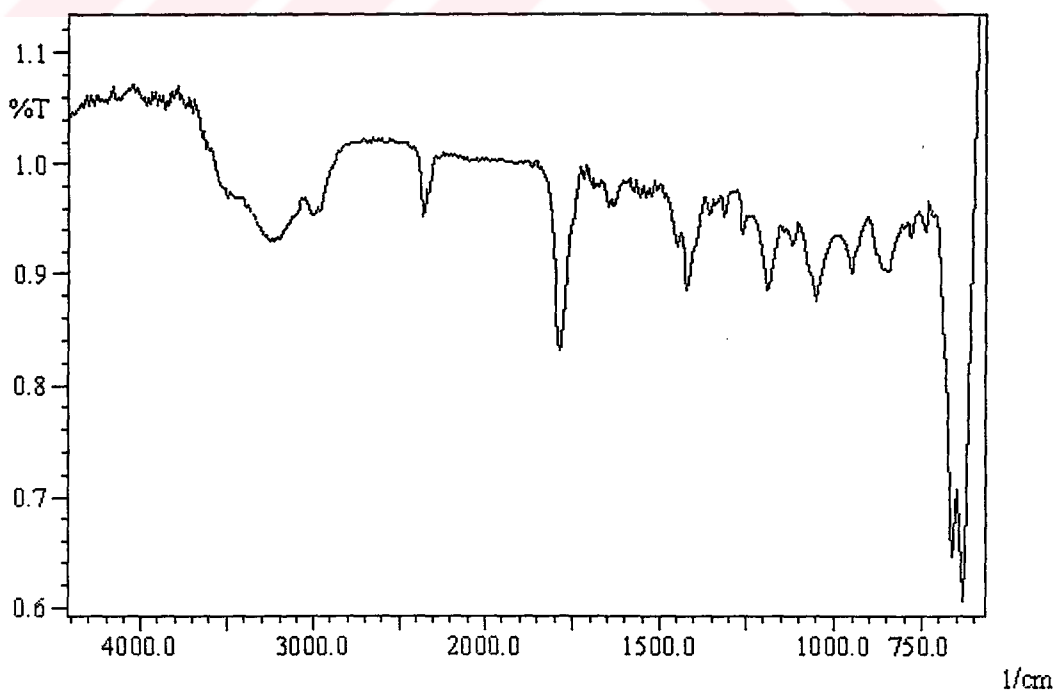


Figure 4.2. IR spectrum of DTE on KBr disc.

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, we have employed 2,2-dimethoxy-2-phenyl acetophenone (DMPA) as the free radical photoinitiator. DMPA was deliberately chosen as the radical initiator because it absorbs light in the near UV region and undergoes scission with high quantum efficiency. The light is absorbed only by DMPA since the allylic salt, DTE, is transparent at the irradiation wavelength (Figure 4.3). Polymerization was performed in a polar solvent (propylene carbonate) because DTE is either insoluble or poorly soluble in common organic solvents suitable for cationic polymerization. Polymerization proceeded heterogeneously as the poly(cyclohexene oxide) precipitated during irradiation.

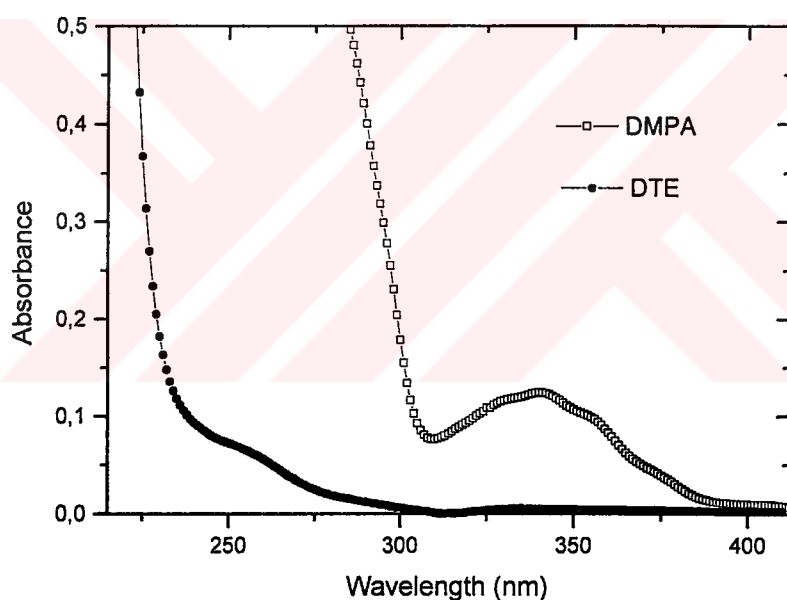


Figure 4.3. UV absorption spectra of DTE (1,1 ditetrahydrothiopheniummethyl ethylene hexafluoroantimonate) and DMPA (2,2-dimethoxy-2-phenyl acetophenone) in propylene carbonate

Table 4.1. Photoinitiated polymerization of CHO (4.95 mol L^{-1}) in propylene carbonate containing the allylic salt, DTE ($5 \times 10^{-3} \text{ mol L}^{-1}$) at room temperature.

Radical Source ($5 \times 10^{-3} \text{ mol L}^{-1}$)	Time (min)	Conversion (%)	\overline{M}_n ($\text{g}\cdot\text{mol}^{-1}$)	$\overline{M}_w / \overline{M}_n$
DMPA	1	13	2400	1.28
DMPA	2	14	3200	1.49
DMPA	5	35	3650	1.35
DMPA	10	34	2950	1.29
DMPA	15	34	3100	1.49
DMPA	30	34	3400	1.42
DMPA	60	35	3000	1.27
BP	60	36	3060	1.28

As can be seen from Table 4.1, photolysis of DMPA readily promotes the cationic polymerization of CHO in the presence of DTE, because the polymerization did not take place in the absence of DMPA. The number average molar mass of the polymers thus obtained were in the range of $2.4 \times 10^3 - 3 \times 10^3 \text{ g mol}^{-1}$. Beside DMPA, a hydrogen abstraction type photoinitiator such as benzophenone (BP) was also employed (Table 4.1).

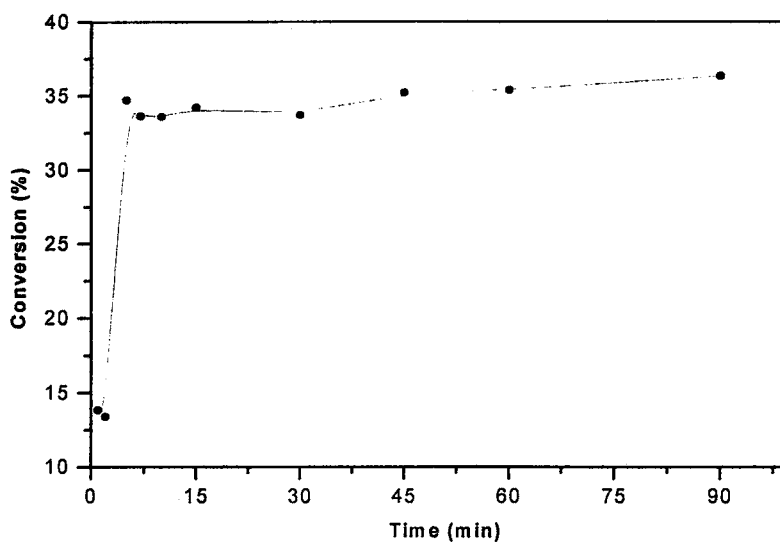
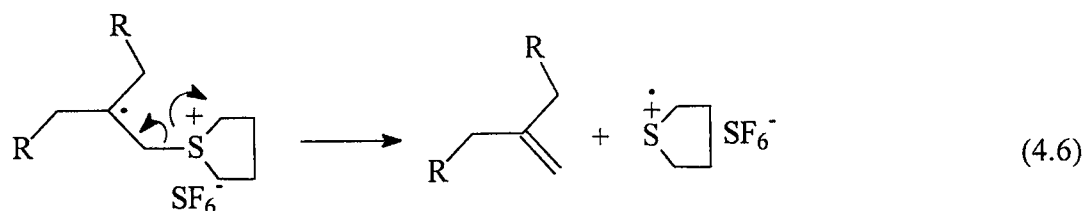
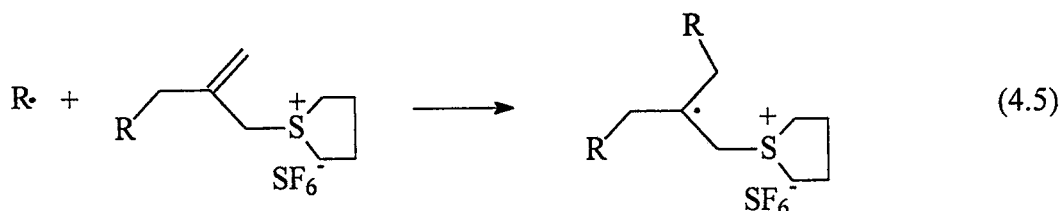
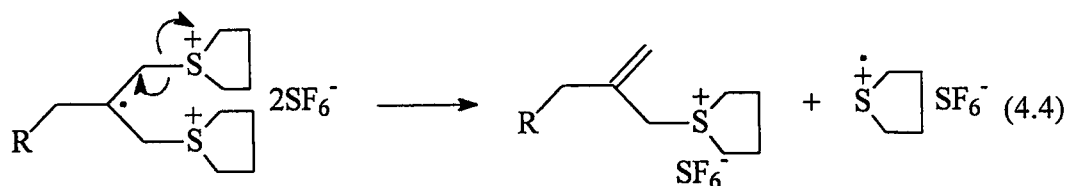
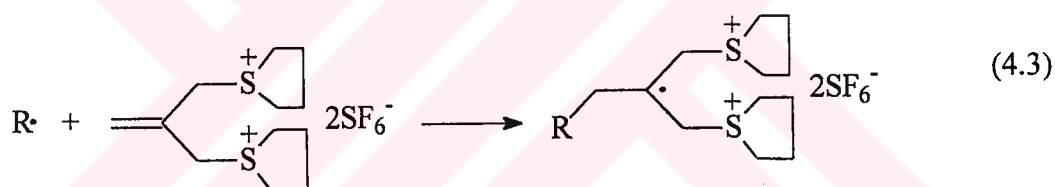
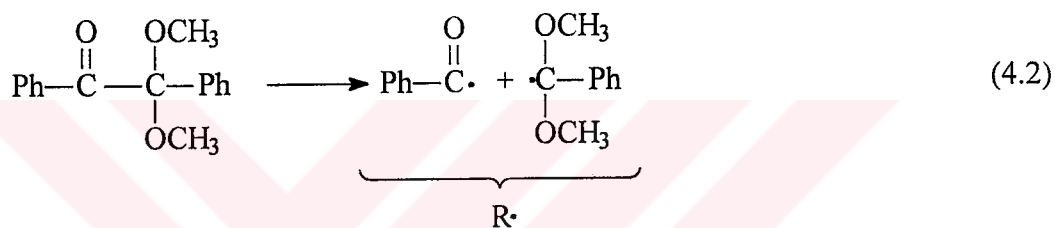


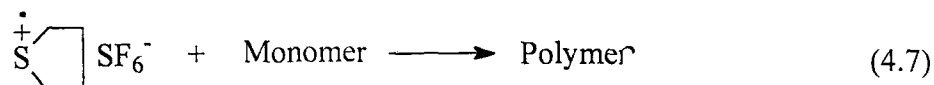
Figure 4.4. Photoinitiated polymerization of CHO (4.95 mol L^{-1}) in the presence of DMPA ($5 \times 10^{-3} \text{ mol L}^{-1}$) and DTE ($5 \times 10^{-3} \text{ mol L}^{-1}$) in propylene carbonate at room temperature.

As can be seen from Figure 4.4 the polymerization reached a limiting conversion within few minutes of irradiation and conversion remained constant thereafter. This behavior may be due to the limited diffusion of light in the heterogeneous medium as the polymer is insoluble in propylene carbonate.

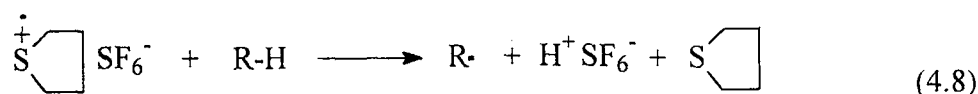
A mechanism for initiation, consistent with the recent report on the bifunctional free radical AFAs [30] and our previous investigations [11-29], is depicted below. Photochemically produced radicals add to the double bond and subsequently fragmentation occurs. Addition of another radical to the olefinic product formed would also lead to the formation of tetrahydrothiophenium radical cation.



The resulting sulphonium radical cations may directly initiate cationic polymerization, as was proved by Ledwith et al. [78].



Alternatively, the radical cations may abstract a hydrogen atom from the solvent, the monomer or the initiator, and the resulting intermediate dissociates to liberate a strong acid:



Protons generated in this way add to the monomer, thus forming species capable of initiating cationic polymerization:



Apart from CHO, two other cationically polymerizable monomers were also examined (Table 4.2). While butyl vinyl ether (BVE) polymerized readily, irradiation of N-vinyl carbazole (NVC) containing DMPA and the salt under the same experimental conditions failed to produce any precipitable polymer due to the insolubility of the monomer in propylene carbonate. Higher molecular weight distribution observed with the polymer of BVE indicates chain transfer reaction dominating the polymerization of this particular monomer.

Table 4.2. Photoinitiated polymerization of various cationically polymerizable monomers using DTE in the presence of DMPA ($5 \times 10^{-3} \text{ mol.L}^{-1}$) in propylene carbonate for 60 min at room temperature

Monomer	[M] (mol L ⁻¹)	Conversion (%)	\bar{M}_n (g mol ⁻¹)	\bar{M}_w / \bar{M}_n
CHO	4.95	35	3000	1.27
BVE	5	80	3050	2.25
NVC	5	-	-	-

5. CONCLUSIONS AND SUGGESTIONS

In conclusion, bifunctional allylic salt, DTE initiate heterogeneous cationic polymerization of CHO and BVE in the presence of free radical photoinitiators. In this case the AFA provides two reactive sites, namely double bonds for the radical addition. Consequently two sulphonium radical cations are produced from one molecule of the salt. The poor solubility of the salt is the major drawback for its use in practical applications. Further studies in this line are in progress.



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