

Bifunctional Allyl-Sulphonium Salt as a Novel Addition–Fragmentation Agent for Photoinitiated Cationic Polymerization

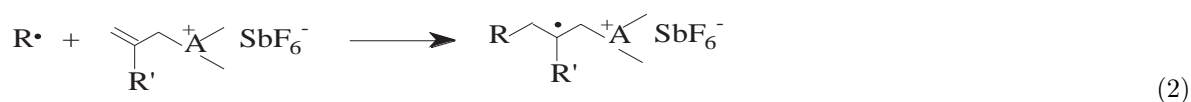
Utku KÜÇÜKTÖNBEKİCİ, Mustafa DEĞİRMENCİ, Yusuf YAĞCI
*İstanbul Technical University, Department of Chemistry,
Maslak 80620, İstanbul-TURKEY*

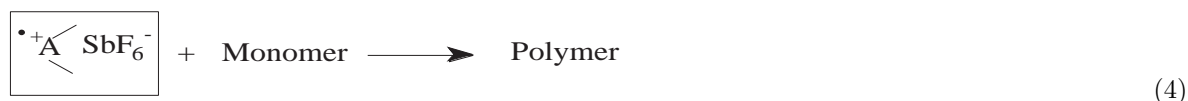
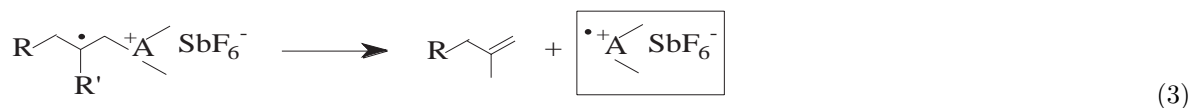
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Bifunctional allyl tetrahydrothiophenium hexafluoroantimonate was synthesized via a one-pot reaction of 3-chloro-2-chloromethylpropene with thiophene in the presence of sodium hexafluoroantimonate. The initiation capability of this salt, in conjunction with a photochemical free radical source such as 2,2-dimethoxy-2-phenyl acetophenone and benzophenone, via an addition-fragmentation mechanism in the cationic polymerization of cyclohexene oxide and butyl vinyl ether is investigated.

Introduction

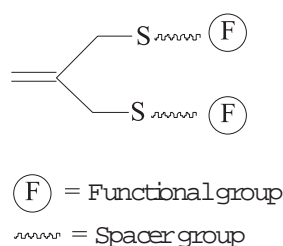
Photoinitiated cationic polymerization is of great practical interest due to its utilization, particularly for curing coatings based on technologically important epoxy and vinyl ether type monomers¹. Many efficient photoinitiators such as iodonium², sulfonium^{3,4}, alkoxy pyridinium salts^{5–8} and arene iron complexes⁹ were developed and their photochemistry has been studied in detail. In order to fulfill the practical requirements regarding the extension of their spectral sensitivity several direct and indirect activation of these photoinitiators were proposed¹⁰. One recent approach developed 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:



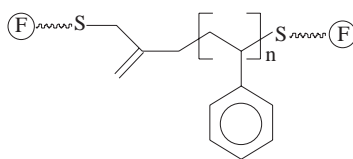


The mechanism involves the formation of radicals by irradiating the radical photoinitiator, the addition of these radicals to the allylic salt and the subsequent fragmentation reactions. The radicals thus produced initiate the polymerization either by reacting with the monomer directly or by producing protonic acids. Previously, sulfonium¹¹, pyridinium^{12,13}, alkoxy pyridinium^{14–20}, phosphonium²¹ and anilinium²⁷ with an allylic structure, and sulfonium and pyridinium salts with a dienic structure²⁸ 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 an appropriate free radical photoinitiator. Moreover, thermal initiators can also be used as the radical generating component of the system.

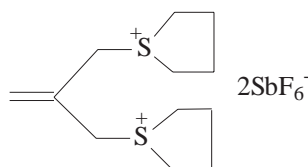
Recently, Sunder and Mulhaupt³¹ have reported the preparation and application of novel allylic dithio compounds of the following structure as addition-fragmentation chain transfer agents in free radical polymerization:



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



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



Experimental

Materials

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 use.

Synthesis of 1,1-ditetrahydrothiopheniummethyl ethylene hexafluoroantimonate (DTE)

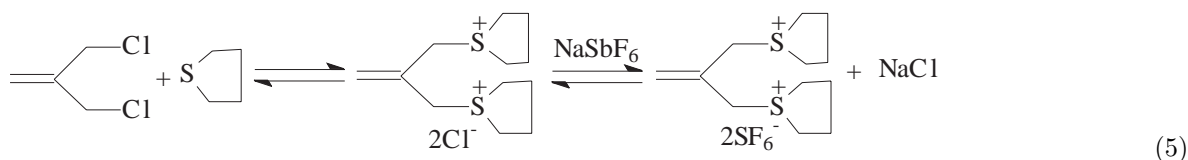
A mixture of 0.54 g (4.32 mmol) 3-chloro-2-(chloromethyl)-1-propene, 0.76 g (8.64 mmol) tetrahydrothiophene and 2.23 g (8.64 mmol) NaSbF₆ in 20 ml dry acetone was placed in a round bottom flask and stirred at 45 °C for 10 days. The white precipitate formed was filtered off and dissolved in 10 ml of acetonitrile 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} = 225nm (ε = 236.4 l mol⁻¹cm⁻¹).

Analysis

GPC analyses of the polymers were performed with a set-up consisting of a pump (Waters) and four ultrastryragel columns of different porosities. THF was used as the eluent (flow rate 1 ml min⁻¹) and detection was carried out with the aid of a differential refractometer. Average molecular weights were determined using polystyrene standards. ¹H-NMR spectra were recorded on a Bruker 250 instrument with CDCl₃ as solvent and tetramethylsilane (TMS) as the internal standard. UV-VIS spectra were taken on a Perkin Elmer Lambda 2 spectrophotometer. IR spectra were recorded on a Jasco FT/IR-3 spectrometer on a KBr disk.

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 NaCl 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 1). The IR spectrum also shows the peak characteristics of thiophene and allyl groups (1786 , 1417 , 1190 , 1050 , 950 , 660 cm^{-1}) (Figure 2).

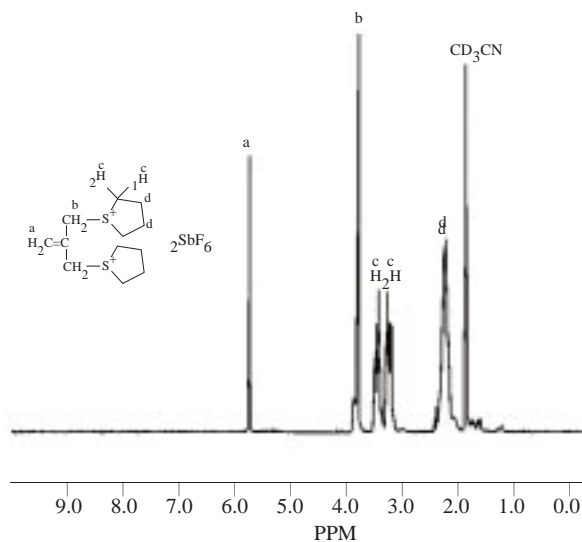


Figure 1. $^1\text{H-NMR}$ spectrum of DTE in CDCl_3 .

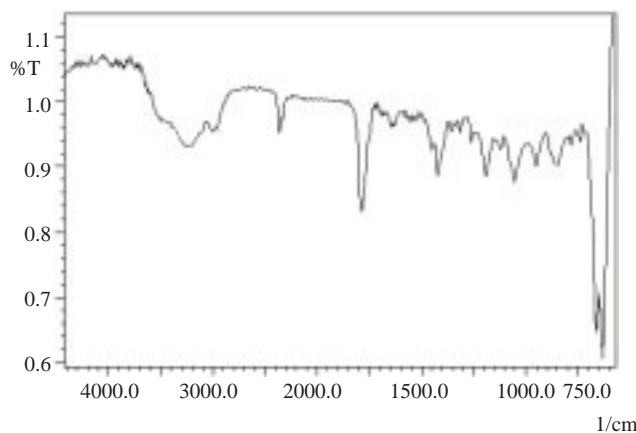


Figure 2. IR spectrum of DTE on KBr disk.

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 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 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. As can be seen from Table 1, the 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 1). As can be seen from Figure 4, the polymerization reached a limiting conversion within a 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.

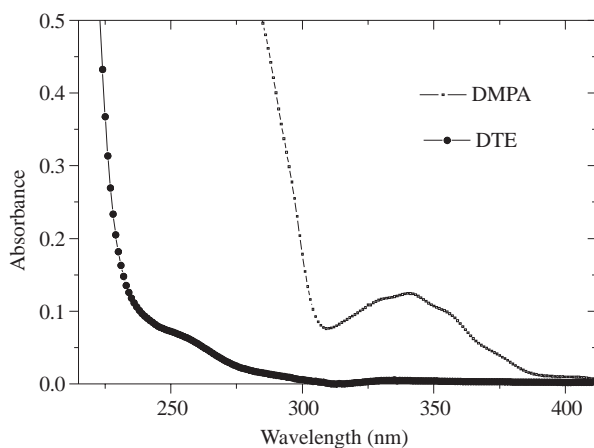


Figure 3. UV absorption spectra of DTE (●) and DMPA (---) in propylene carbonate.

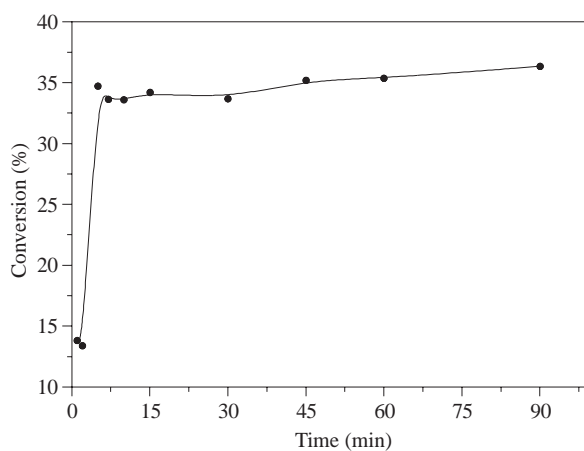
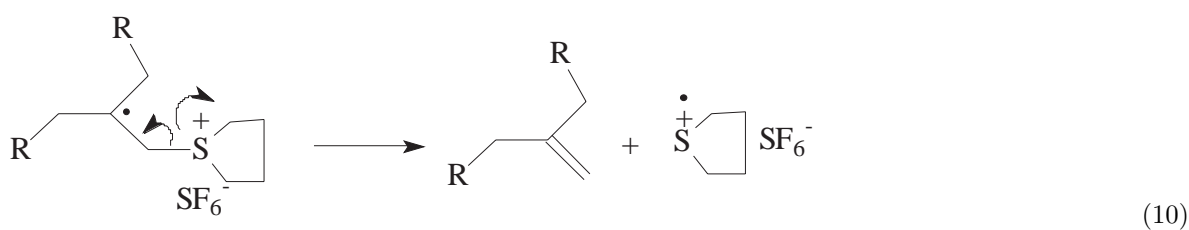
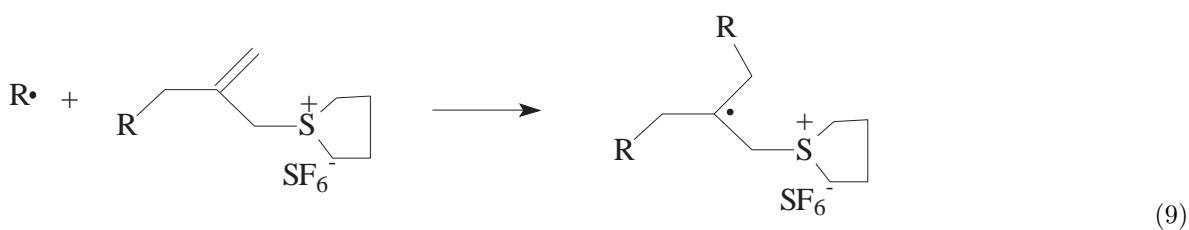
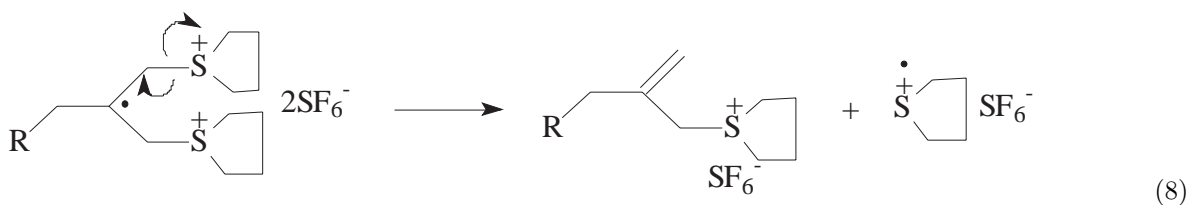
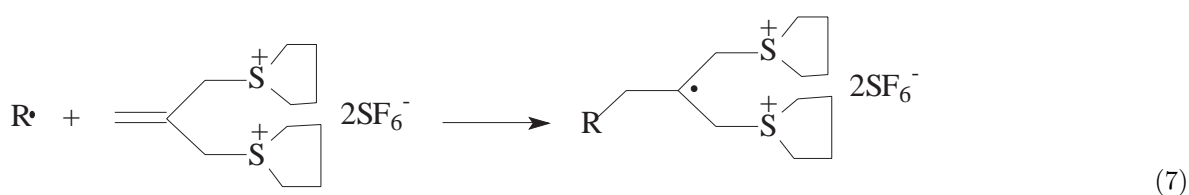
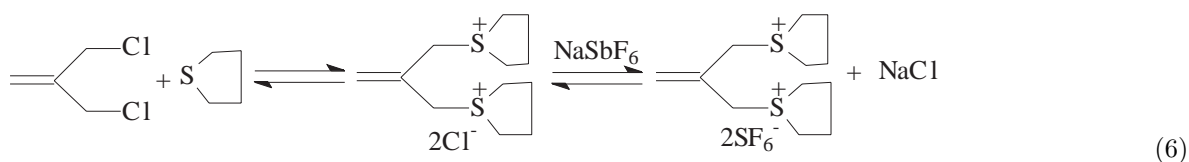


Figure 4. Photoinitiated polymerization of CHO (4.95 mol L^{-1}) in the presence of DMPA ($5 \times 10^{-3} \text{ mol L}^{-1}$) and DTE ($5 \times 10^{-3} \text{ mol L}^{-1}$) in propylene carbonate at room temperature.

A mechanism for initiation, consistent with the recent report on the bifunctional free radical AFAs³¹ and our previous investigations^{11–30}, is depicted below. Photochemically produced radicals add to the double bond and fragmentation occurs subsequently. Addition of another radical to the olefinic product formed would also lead to the formation of a tetrahydrothiophenium radical cation.

Table 1. Photoinitiated polymerization of CHO (4.95 mol L⁻¹), in propylene carbonate containing the allylic salt, DTE (5 x 10⁻³ mol L⁻¹) at room temperature.

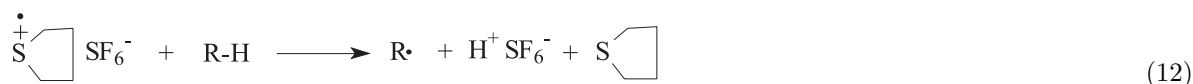
Radical Source (5 x 10 ⁻³ mol L ⁻¹)	Time (min)	Conversion (%)	\overline{M}_n (g.mol ⁻¹)	$\overline{M}_w/\overline{M}_n$
DMPA	1	13	2400	1.28
DMPA	2	14	3200	1.49
DMPA	5	35	3650	1.35
DMPA	10	34	2950	1.29
DMPA	15	34	3100	1.49
DMPA	30	34	3400	1.42
DMPA	60	35	3000	1.27
BP	60	36	3060	1.28



The resulting sulfonium radical cations may directly initiate cationic polymerization, as was shown by Ledwith et al.³²



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 examined (Table 2). While butyl vinyl ether (BVE) polymerized readily the 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 a chain transfer reaction dominating the polymerization of this particular monomer.

Table 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.

Radical Source ($5 \times 10^{-3} \text{ mol L}^{-1}$)	Time (min)	Conversion (%)	\overline{M}_n (g.mol^{-1})	$\overline{M}_w/\overline{M}_n$
CHO	4.95	35	3000	1.27
BVE	5	80	3050	2.25
NVC	5	-	-	-

In conclusion, bifunctional allylic salt, DTE, initiates heterogeneous cationic polymerization of CHO and BVE in the presence of free radical photoinitiators.

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