

Photochemically and thermally induced radical promoted cationic polymerization using allyl phosphonium salts

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Abstract

Three allylic triphenyl phosphonium salts, namely allylphosphonium (AP), methyl allylphosphonium (MAP) and ethoxy carbonyl allylphosphonium (ECAP) salts with a hexafluoroantimonate counter anion were synthesized and characterized. Their capability to act as initiators or coinitiators for the cationic polymerization of oxiranes such as cyclohexene oxide (CHO) and vinyl monomers such as butylvinyl ether and *N*-vinyl carbazole was examined. These monomers turned out to be polymerizable in the presence of ECAP provided free radicals are generated thermally at 70°C or photochemically at $\lambda > 350$ nm with the aid of appropriate radical sources. The polymerization of CHO was also induced thermally in the absence of radical sources only with ECAP at a very low rate, while all the three types of salts are ineffective in generating reactive species when irradiated at $\lambda = 268$ nm where the salts absorb the light. Regarding sources generating free radicals the mode of action of ECAP concerning promotion of the cationic polymerization seems to be based on the addition–fragmentation mechanism. Accordingly, a free radical adds to the carbon–carbon double bond and fragmentation of the adduct radical results in the formation of a reactive onium radical cation. The possibility of electron transfer mechanism was disregarded since nucleophilic triphenyl methyl radicals were not oxidized with the aid of phosphonium salts. © 2000 Elsevier Science Ltd. All rights reserved.

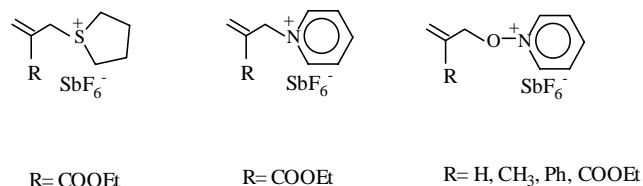
Keywords: Cationic polymerization; Phosphonium salts; Addition–fragmentation reactions

1. Introduction

Cationic polymerizations induced by heat or light are of great practical interest due to their applicability for the curing of coatings and printing inks, and for resist technology [1]. The major classes of photoinitiators which can successfully initiate cationic polymerization include diaryl iodonium [2,3] and triaryl sulphonium [4] salts. Phosphonium [5,6], *N*-alkoxy pyridinium [7] salts, and iron arene complexes [8] have also been reported as alternative cationic photoinitiators. Except iron arene complexes, most of these photoinitiators absorb mainly at wavelengths below 300 nm. Therefore, several indirect ways were reported to extend photopolymerization sensitivity to longer wavelengths. This way practical application of the photoinitiated cationic polymerization can become acceptable since medium and high pressure mercury lamps that are frequently used as light sources provide emission at 313 and 366 nm.

We, recently, introduced specially designed allyl-onium salts which initiate via addition–fragmentation reactions

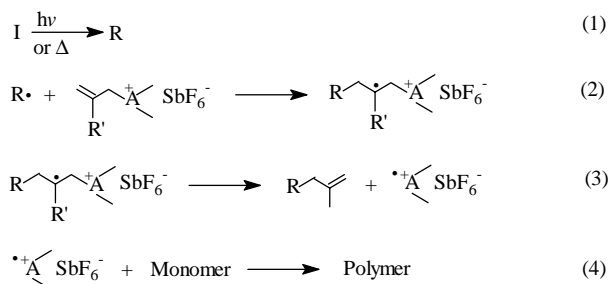
[9–17]. In these systems, the polymerization conditions can be tuned not only to the desired wavelengths but also to temperature ranges by choosing appropriate radical initiators. In the first step, photochemically or thermally generated free radicals add to the olefinic double bond of a specially designed addition fragmentation agent (AFA). The intermediate thus produced is relatively unstable and prone to fragmentation. In the second step a new radical cation is generated which initiates the polymerization (Scheme 1). AFAs found to be useful include thiophenium, pyridinium and alkoxy-pyridinium salts of the following structure:



No report has appeared on allylic phosphonium salts such as AFAs in cationic polymerization. Introduction of a phosphorus atom into the allylic salt is interesting from the viewpoint of the special effect on the initiation

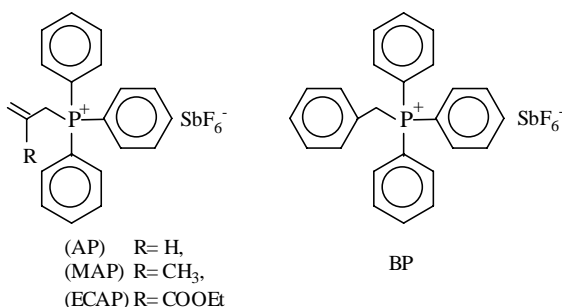
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Scheme 1.

efficiency of such salts. In the present work, the phosphonium salts, which have the following structure were synthesized and examined with respect to their reactivity towards photochemically and thermally generated radicals.



In order to demonstrate the role of addition–fragmentation type initiation, polymerization capability is viewed in comparison with triphenylbenzylphosphonium salt which is not able to undergo such reactions.

2. Experimental

2.1. Materials

Cyclohexene oxide (CHO) (Aldrich), isobutyl vinyl ether

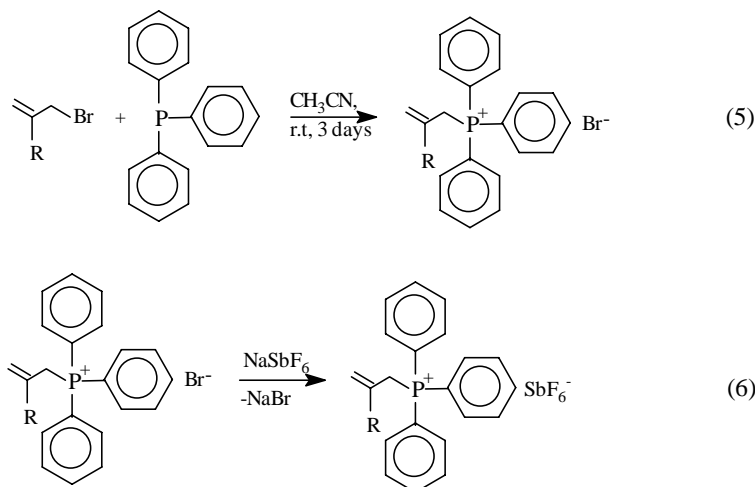
(IBVE) (Aldrich) and *n*-butyl vinyl ether (BVE) (Aldrich) were distilled from CaH₂ in vacuo. *N*-vinyl carbazole (NVC) (Fluka) was recrystallized from ethanol. Reagent grades solvents were used after distillation. 2,2'-Azobisisobutyronitrile (AIBN) (Fluka), benzophenone (Fluka) and benzoin (Merck) were recrystallized from ethanol. Dibenzoyl peroxide (Fluka) was recrystallized from diethyl ether. 2,4,6-Trimethylbenzoyl diphenylphosphine oxide (BASF) was recrystallized from ethanol/diethyl ether. Phenylazotriphenylmethane (PAT) was prepared as described previously [18]. The other chemicals (Aldrich) were reagent grade and used as received.

2.2. Synthesis of (2-ethoxycarbonyl-propenyl) triphenyl phosphonium hexafluoroantimonate (ethoxy carbonyl allyl phosphonium salt) (ECAP)

A mixture of 0.42 g (2.15 mmol) ethyl- α -(bromomethyl)-acrylate, which was prepared by the described procedure [19], and 0.56 g (2.15 mmol) triphenylphosphine in 5 ml dry acetonitrile was stirred at room temperature for 3 days. After evaporation of the solvent, the white bromide salt was isolated by filtration, washed copiously with diethyl ether, dried and then taken up in aqueous solution. To this aqueous solution was added 0.56 g (2.15 mmol) sodium hexafluoroantimonate. The white precipitate formed was filtered off, washed with water and dried in vacuo at room temperature. Yield: 1.01 g (77.4%), m.p.: 142°C. Elemental analysis: Found: C: 47.23; H: 4.11. Calculated: C: 47.31; H: 3.94. ¹H-NMR (CDCl₃, ppm) 7.9–7.6 (aromatic, *H*), 5.9, 6.5 (C=CH₂), 3.9–3.8 (–OCH₂), 4.4 (P–CH₂) 1.1 (–CH₃).

2.3. Synthesis of (2-methyl propenyl) triphenyl phosphonium hexafluoroantimonate (methyl allyl phosphonium salt) (MAP)

The above procedure was applied. 3-Bromo-2-methyl propene was used as the corresponding allylic bromide. Yield: 0.98 g (82.18%), m.p.: 158–160°C. Elemental



Scheme 2.

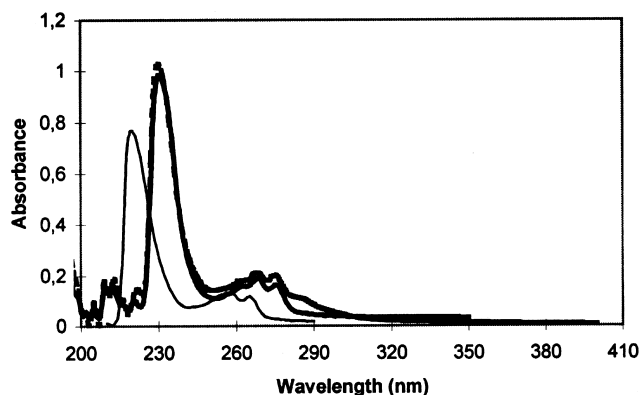


Fig. 1. UV spectra of phosphonium salts recorded in CH_2Cl_2 . [Phosphonium salts] = $1.25 \times 10^{-5} \text{ mol l}^{-1}$. (---, AP; —, MAP; —·—, ECAP.)

analysis: Found: C: 48.10; H: 4.11. Calculated: C: 47.85; H: 3.99. $^1\text{H-NMR}$ (CDCl_3 , ppm) 7.9–7.5 (Aromatic, *H*), 4.0 (P-CH_2), 4.8, 5.2 (C=CH_2), 1.6 ($-\text{CH}_3$).

2.4. Synthesis of propenyl triphenyl phosphonium hexafluoroantimonate (allyl phosphonium salt) (AP)

The above procedure was applied. Allyl bromide was used as the corresponding allylic bromide. Yield: 1.55 g (95.67%), m.p.: 140°C . Elemental analysis: Found: C: 47.39; H: 3.84. Calculated: C: 46.86; H: 3.71. $^1\text{H-NMR}$ (CDCl_3 , ppm) 7.9–7.5 (Aromatic, *H*), 5.8–5.6 (CH-CH_2), 4.0 (C=CH_2), 5.5–5.3 (P-CH_2).

2.5. Polymerizations

Thermal polymerization: Monomer solutions in bulk or in methylene chloride, in pyrex tubes, containing allyl phosphonium salts in the absence or presence of radical sources were deaerated by bubbling with nitrogen and immersed for a given time in an oil bath kept at constant temperature.

Photopolymerization: Monomer solutions in bulk or in methylene chloride, in quartz tubes containing phosphonium salts in the presence or absence of free radical photoinitiators were bubbled with nitrogen and subsequently irradiated in a merry-go-round type photoreactor equipped with lamps emitting at nominally 300 or 350 nm. In some cases, e.g. for selective irradiation of phosphonium chromophore at 268 nm, an Amco monochromatic light source was employed.

2.6. Characterization

Polymers were obtained from the reaction mixture by precipitation with a 10-fold excess of methanol. Size exclusion chromatography (SEC) analyses of the polymers were performed with a setup consisting of a pump (Waters) and four ultrastyrigel columns of different porosities. THF was used as the eluent (flow rate: 1 ml min^{-1}) and the detection

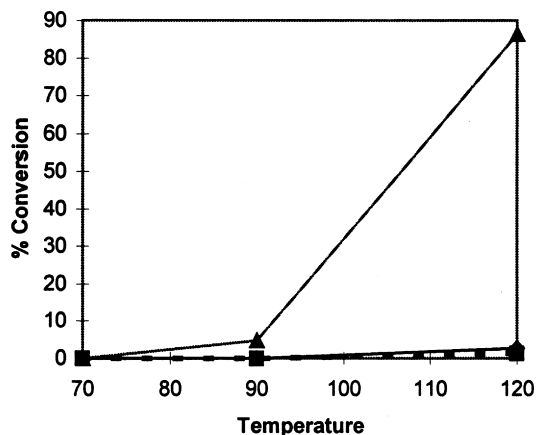


Fig. 2. Thermal polymerization of CHO with different phosphonium salts. [Phosphonium salts] = $5 \times 10^{-3} \text{ mol l}^{-1}$, $[\text{CHO}] = 9.89 \text{ mol l}^{-1}$, reaction time 2 h. (◆, AP; ■, MAP; ▲, ECAP.)

was carried out with the aid of a differential refractometer. The number average molecular weights were determined by using polystyrene standards. $^1\text{H-NMR}$ spectra were recorded on a Bruker 250 instrument with CDCl_3 as the solvent and tetramethylsilane as the internal standard. UV/Vis spectra were taken on a Perkin Elmer Lambda 2 spectrometer. Elemental analyses were performed on a CHNS-932 LECO instrument.

3. Results and discussion

3.1. Synthesis

The allylic phosphonium salts used in this study were prepared by the reaction of the corresponding allyl bromide with triphenylphosphine. In a second reaction step, the counter anion has been exchanged for the low nucleophilic hexafluoro antimonate (Scheme 2). The structure of the phosphonium salts was confirmed by elemental analysis as well as spectroscopic investigations (see Section 2). One particular interest concerns the UV absorptivity of the salts. Notably, all salts have absorption maxima at around 268 nm and are transparent above 300 nm (Fig. 1).

3.2. Polymerization

For the polymerization experiments, cyclohexene oxide (CHO) was deliberately chosen as a model monomer since it is not polymerizable by a radical mechanism and does not form oxidizable radicals in the course of polymerization. Also, it is not polymerizable by phosphonium salts in the dark at room temperature.

3.3. Thermal polymerization

3.3.1. Direct polymerization

As seen in Fig. 2, in the absence of additional radical

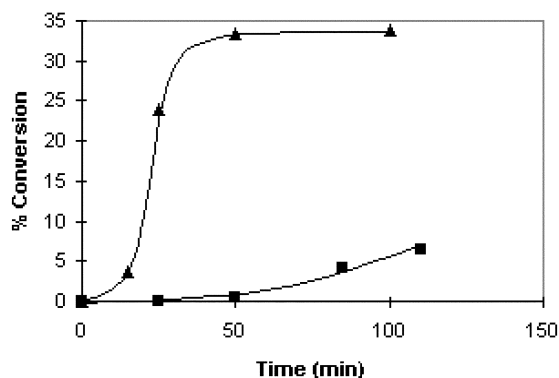


Fig. 3. Thermal polymerization of CHO initiated by PAT and AIBN as radical sources in the presence of ECAP at 70°C. [ECAP] = [PAT] = [AIBN] = $5 \times 10^{-3} \text{ mol l}^{-1}$, [CHO] = 9.89 mol l^{-1} . (▲, PAT; ■, AIBN.)

Table 1

Thermal polymerization of CHO initiated by various radical initiators in the presence of ECAP at 70°C. [Radical source] = $5 \times 10^{-3} \text{ mol l}^{-1}$, [CHO] = 9.89 mol l^{-1} , [ECAP] = $5 \times 10^{-3} \text{ mol l}^{-1}$

Radical source	Time (min)	Conversion (%)	M_n (g mol ⁻¹)	M_w/M_n
–	120	–	–	–
AIBN	100	5.90	7957	1.50
PAT	100	33.82	7813	1.56
BPO	100	14.44	5848	1.25

initiator the polymerization of CHO takes place only at relatively high temperatures with satisfactory yields only with ECAP salt. The efficiency in this mode of cationic polymerization rises in the order of ECAP \gg AP > MAP. Notably, with benzyl derivative (BP) no polymer is formed at temperatures up to 120°C after 2 h.

3.3.2. The effect of added radical initiator

No polymer is formed when CHO containing AP or MAP salts in the presence of radical initiators azoisobutyronitrile (AIBN) and phenyl azotriphenyl methane (PAT) are heated at 70°C for 4 h. However, the polymerization of CHO is induced upon the addition of free radical initiators using ECAP salt at the same temperature (Table 1 and Fig. 3). The monomer conversion commences after an induction period.

Table 2

Photopolymerization of CHO initiated by various radical photoinitiators in the presence of ECAP at room temperature. O.D. = 0.95 for all photoinitiators at the selected wavelength, [ECAP] = $5 \times 10^{-3} \text{ mol l}^{-1}$, [CHO] = 9.89 mol l^{-1}

Radical source	[Radical source] (mol l ⁻¹)	Irradiation wavelength (nm)	Time (min)	Conversion (%)	M_n (g mol ⁻¹)	M_w/M_n
PAT	4.3×10^{-3}	417	60	1	5023	1.15
TMDPO	1.7×10^{-3}	380	180	1.52	5280	1.18
Benzophenone	5×10^{-3}	333	90	18.54	5560	1.25

3.4. Photopolymerization

3.4.1. Excitation of the phosphonium moiety

The wavelength of incident light chosen in this study for directly exciting the phosphonium moiety is 268 nm. The salt concentrations were adjusted in order to obtain identical optical density values ($O.D._{268} = 0.95$). No polymerization took place with any of the phosphonium salts after 4 h of irradiation.

3.4.2. Use of additional radical photoinitiators

In photopolymerization with phosphonium salts, additional radical initiators may not only induce the polymerization, they also enable light of higher wavelengths to be used for initiating polymerization. Indeed, the polymerization of CHO is induced rapidly upon the addition of a compound acting as a free radical source, i.e. decomposing into free radicals upon irradiation at $\lambda_{inc} > 350 \text{ nm}$. Results obtained from experiments performed with CHO containing various photoinitiators and ECAP are shown in Table 2. The low conversions are due to the monochromatic light irradiation with lower light intensity.

It is interesting to note that AP and MAP salts in conjunction free radical photoinitiators are ineffective for the polymerization of CHO as was observed with the thermal radical initiators. As can be seen from Fig. 4, the conversion-time profile, illustrated for the benzoin ECAP initiating system, is S-shaped: a pronounced increase in monomer conversion sets in after an induction period and almost complete conversion is reached within 3 min after the irradiation was started.

Apart from CHO, several other cationically polymerizable monomers, namely IBVE, BVE and NVC, were also examined. All monomers polymerized readily in solutions containing ECAP and benzoin. Typical results are shown in Table 3.

4. Discussion

The results reported in this paper demonstrate that the thermal and photochemical initiation of the cationic polymerization of CHO is accelerated or promoted provided a phosphonium salt, ECAP, and in addition, a compound generating radicals upon heating or irradiation are present. Two mechanisms for the initiation are feasible: (a) the addition–fragmentation mechanism and (b) the

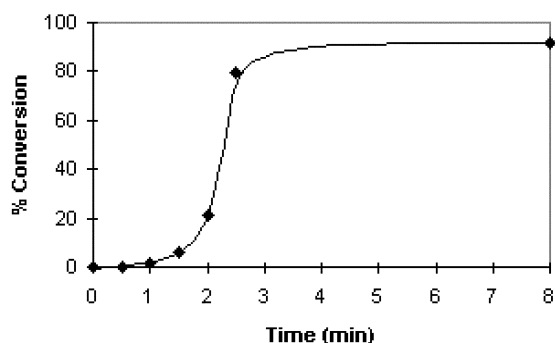
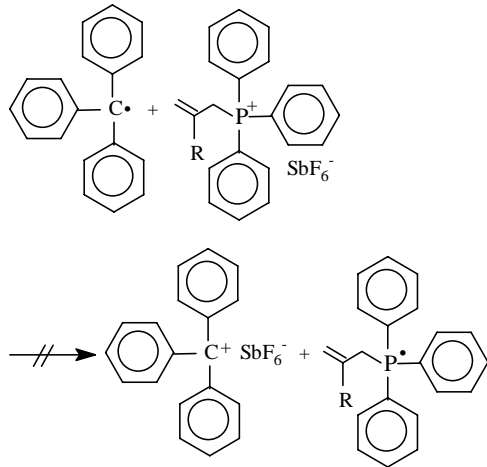


Fig. 4. Photopolymerization of CHO initiated by benzoin in the presence of ECAP at room temperature. $\lambda_{\text{inc}} \approx 350 \text{ nm}$, $\text{O.D.}(\text{benzoin})_{350 \text{ nm}} = 0.10$. $[\text{ECAP}] = 6 \times 10^{-3} \text{ mol l}^{-1}$, $[\text{Benzoin}] = 2.4 \times 10^{-2} \text{ mol l}^{-1}$.

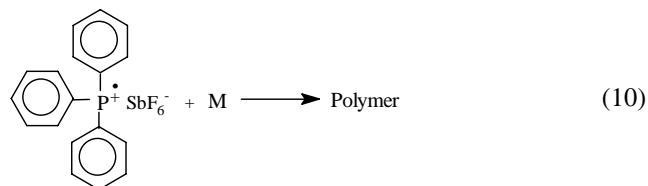
electron transfer mechanism [20]. In the present case it is unlikely that mechanism (b) contributes essentially to the initiation. Upon heating at 70°C or irradiation at $\lambda = 350 \text{ nm}$ of a solution containing PAT ($7.5 \times 10^{-3} \text{ mol l}^{-1}$) and ECAP for 90 min, the optical absorption spectrum changed. Notably, the new spectrum does not contain new bands around 420 and 450 nm, where characteristic absorption bands of trityl cations are located [21]. This implies that PAT undergoes thermolysis or photolysis. But the trityl radicals generated in this way do not react with the phosphonium salt according to the following reaction.



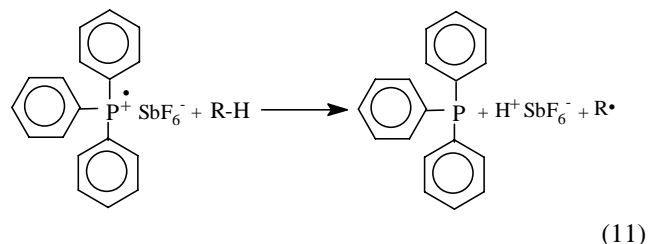
Moreover, free radicals generated from AIBN, BPO and TMDPO, i.e. $(\text{CH}_3)_2(\text{CN})\cdot$, $\text{PhCOO}\cdot$, $\text{Ph}\cdot$, $\text{PhCO}\cdot$ and $\text{Ph}_3\text{PO}\cdot$

are non-nucleophilic and, therefore, unreactive towards even strong oxidants such as iodonium salts [22].

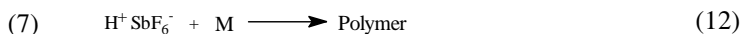
Therefore, it appears that the initiation is predominantly based on the addition–fragmentation mechanism. Accordingly, radicals generated by the thermolysis or photolysis of the corresponding initiator are supposed to add to the allylic double bond of the phosphonium salt. The subsequent spontaneous decomposition of the adduct radical yields phosphinium radical cations as illustrated by Scheme 3. The phosphinium radical cation may directly initiate the cationic polymerization of monomer M:



Alternatively, protons can be formed when the radical cation abstracts hydrogen from the solvent or the monomer:



Protons generated in this way then initiate the polymerization of M:

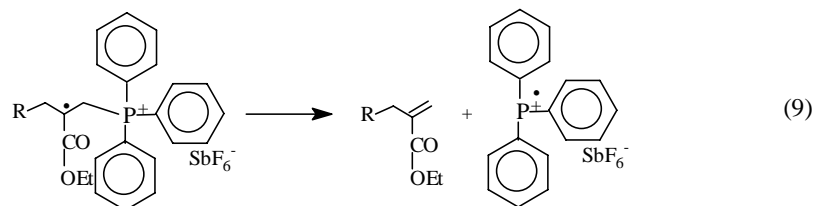
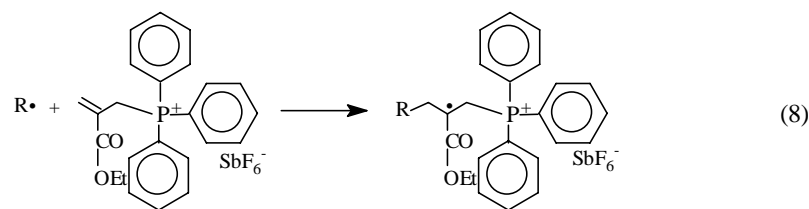


It is interesting to note that the polymers obtained with phosphonium type AFAs contain aromatic moieties as was confirmed by NMR spectra indicating the incorporation of triphenylphosphine groups into polymers. However, further studies are necessary to conclude if the incorporation is due to the initiation or termination mechanisms since nucleophilic triphenylphosphine, liberated according to reaction (11), may terminate the growing chains.

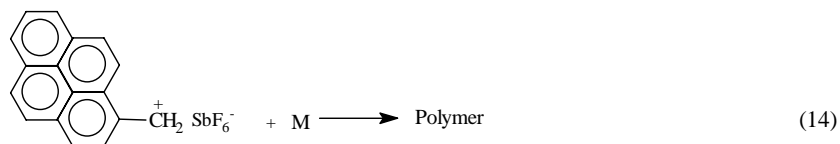
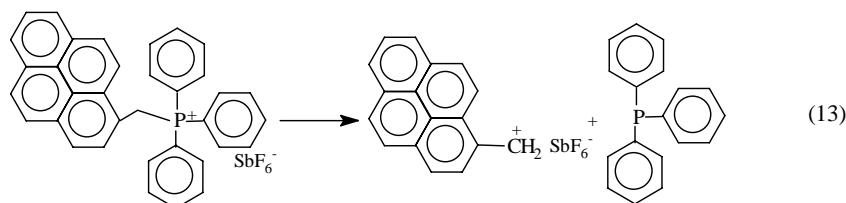
Table 3

Photopolymerization of several cationically polymerizable monomers initiated by benzoin as the radical source in the presence of ECAP. $\text{O.D.}_{370 \text{ nm}}(\text{Benzoin}) = 0.10$, $[\text{Benzoin}] = 2.4 \times 10^{-2} \text{ mol l}^{-1}$, $[\text{ECAP}] = 6 \times 10^{-3} \text{ mol l}^{-1}$

Monomer	Time (min)	Solvent	$c_{\text{mon}} (\text{mol l}^{-1})$	% Conversion	$M_n (\text{g mol}^{-1})$	M_w/M_n
CHO	8	Bulk	9.9	91.76	5633	1.25
BVE	4	CH_2Cl_2	5.7	63.78	23 600	3.0
IBVE	3	CH_2Cl_2	5.7	77.48	18 077	2.64
NVC	8	CH_2Cl_2	1	85.39	36 000	2.5



Scheme 3.



Scheme 4.

In this connection it should be pointed out that benzyl or pyrenylmethyl groups containing phosphonium salts initiate the cationic polymerization thermally and photochemically. In this case carbon centered cations formed after a heterolytic cleavage are assumed to be the initiating species (Scheme 4) [23].

Obviously, the polymerization of CHO, though at a very low rate, is induced by heating CHO containing ECAP in the absence of additional radical forming compound to above 90°C. Notably, the polymerization takes place only insignificantly even at relatively high temperatures with the unsubstituted and methyl substituted allyl phosphonium salts. In discussing the mechanism of this process, it can be anticipated that the initiation is not due to the breakage of the C–P bond. In contrast, the methyl acrylate moiety in the phosphonium salt under investigation is likely to undergo a purely thermal radical generation process and the radicals formed in this way undergo cation generating reactions via addition–fragmentation process.

In summary, allylic phosphonium salts with the methyl acrylate moiety were found to possibly behave as AFAs for cationic polymerization.

Acknowledgements

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