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Photoinitiation of cationic polymerization by using poly(methyl phenyl silane) in combination with addition–fragmentation agents

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Abstract

Poly(methyl phenyl silane) $(PhMeSi)_n$ was used in combination with the addition–fragmentation agents (AFA), namely 2-ethoxycarbonyl-2-propenylpyridinium hexafluoroantimonate (EPP^+), ethyl-α-tetrahydrothiophenium methyl acrylate hexafluoroantimonate (ETM^+) and 2-ethoxycarbonyl-propenyl triphenyl phosphonium hexafluroantimonate (ethoxy carbonly allyl phosphonium salt) ($ECAP^+$) to photoinitiate the cationic polymerization of cyclic ethers such as cyclohexane oxide (CHO), alkyl ethers like *n*-buthyl vinyl ether (BVE) and vinyl monomers such as methoxy styrene (MOS). By using poly(methyl phenyl silane), the spectral response was extended to 330 nm at which the allyl onium salts are transparent. The feasible mechanism involves radical addition to the allylic bond and subsequent fragmentation to yield reactive species capable of initiating cationic polymerization of related monomers. An alternative mechanism which involves the oxidation of electron donor radicals is also discussed. The initiation efficiency of the salts was studied by determination of the conversion of CHO and BVE. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Poly(methyl phenyl silane); Addition–fragmentation; Polymerization

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1. Introduction

Cationic polymerizations which are induced by external stimulation such as heating or photoirradiation have great importance due to their applicability for curing of coatings and printing inks and resist technology [1]. Onium salts [2] such as diaryliodonium and triarylsulfonium salts are commercially important and well studied cationic photoinitiators. Recently, pyridinium [3] and mixed ligand arene cyclopentadienyl metal salts [4] have been developed as alternative cationic photoinitiators. Diaryliodonium and triarylsulfonium salts have poor spectral sensitivity at wavelengths where commercial lamp emits light. To extend their spectral response to longer wavelengths, photosensitizers [5] and free radical photoinitiators [6] have been used successfully. Electron transfer from the excited photosensitizer or photogenerated electron donor radicals to the onium salts results in the formation of reactive species which are capable of initiating the cationic polymerization of related monomers.

More recently, we investigated the use of addition–fragmentation type reactions for the initiation of cationic polymerization [7–9]. The advantage of addition–fragmentation reactions derives from the fact that virtually all sorts of thermal and light-sensitive radical initiators may be utilized to start cationic polymerizations, which enables an adaptation to most initiation conditions. In contrast to radical promoted cationic polymerization based on the oxidation of radicals by onium salts, there is not limitation to use oxidizable radicals.

Onium salts (pyridinium, sulfonium, thiophenium salts, etc.) contain organic cations which by themselves (without external stimulation like, e.g., heat or light) only scarcely initiate cationic polymerizations [10] due to the steric reasons. In order to make the presented allyl-onium salts able to initiate cationic polymerizations, they have to be reacted with free radicals. In previous work, by using benzoin and 2,4,6-trimethylbenzoyl diphenylacylphosphine oxide, photopolymerization of cyclohexene oxide was achieved at 340 and 380 nm, respectively [8].

High-molecular weight, soluble and formable polysilanes have found application as photoresist materials [11], photoconductors [12] and photoinitiators in radical polymerization [13–15].

These applications are mainly based on the polysilanes which have strong ultraviolet absorption in the 300–350 nm region depending on the nature of the organic substituents [16,17]. Upon irradiation at this band, polysilane undergo

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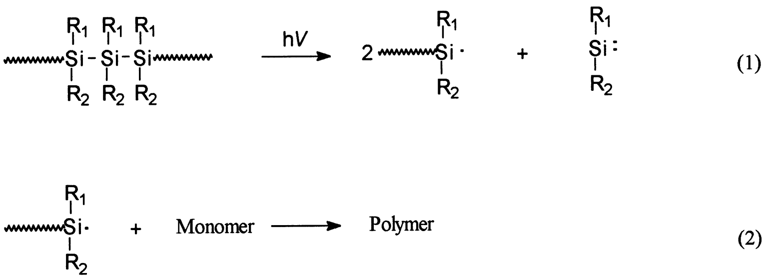


Scheme 1.

rapid photodegredation yielding both silyl radicals and silylenes [18,19] (Scheme 1).

It has been reported by West et al. [13,14] that polysilanes are effective photoinitiators for the free radical polymerization and it was assumed that the initiating process consists of the reaction of silyl-type radicals with vinyl monomers. Recently, it was shown that in conjunction with pyridinium [20] or iodonium salts [21], polysilanes can be used as photoinitiators for the cationic polymerization of cyclic ethers such as cyclohexene oxide and vinyl ethers, such as *n*-butyl vinyl ether.

This paper describes the photochemical initiation efficiency of the allylic type onium salts in conjunction with poly(methyl phenyl silane) as a radical source for the cationic polymerization of appropriate monomers.

2. Experimental

2.1. Materials

2-Ethoxycarbonyl-2-propenylpyridinium hexafluoroantimonate [9] (EPP^+) and ethyl-α-tetrahydrothiophenium methyl acrylate hexafluoroantimonate [8] (ETM^+) and 2-ethoxycarbonyl-propenyl triphenyl phosphonium hexafluoroantimonate [22] (ethoxy carbonly allyl phosphonium salt) ($ECAP^+$) were prepared as described previously.

Monomers and solvents were prepared by conventional drying and distillation procedures. Poly(methy phenyl silane) ($M_n = 14\,000$) was prepared , as described by Zhang and West [23], with the aid of the Wurtz coupling reactions using finely dispersed sodium and diphenyl methyl silane.

2.2. Polymerization

Bulk monomer, known amount allyl onium salt (EPP^+, ETM^+ and $ECAP^+$) and poly(methyl phenyl silane) were mixed in a pyrex tube. The mixture was purged with nitrogen before irradiation by a xenon lamp (XBO 75 W/2 and a mercury lamp (HBO 100 W/2) equipped with a monochromotor at 330 nm. In the case of $(PhMeSi)_n$, which was insoluble or scarcely soluble in the monomer, the polymerization was carried out in solution using purified CH_2Cl_2 as a solvent. Polymers were obtained from the reaction mixture by precipitation with methanol.

Table 1
Bulk photopolymerization of CHO initiated by poly(methy phenyl silane) as radical source in the presence of various ally-onium salts. $[(PhMeSi)_n)] = 15\,g\,l^{-1}$, $\lambda = 330\,nm$

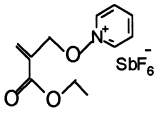
[Salt] ($mol\,l^{-1}$)	Irradiation time (min)	Conversion (%)	M_n	M_w/M_n
ETM^+ (4×10^{-3})	60	27	2800	1.4
EPP^+ (4×10^{-3})	60	22	7170	1.4
$ECAP^+$ (4×10^{-3})	60	17	7270	1.4

2.3. Analysis

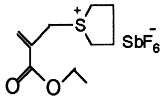
^1H-NMR measurements were performed in $CDCl_3$ solution using a Bruker 250 MHz instrument. Size Exclusion Chromatography (SEC) analyses were performed with a set up consisting of a Waters 600 pump and two ultrastyragel columns with porosities 500 and 104 Å with THF as the eluent at a flow rate of $1\,ml\,min^{-1}$ and a Waters differential refractometer (model 410). Molecular weights were calculated with the aid of polstyrene standards.

3. Results and discussion

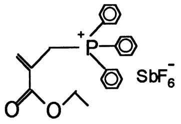
Allylic type onium salts with the following structures were used as addition-fragmentation agents.



(EPP^+)



(ETM^+)



($ECAP^+$)

Since these salts do not absorb the light at $\lambda > 300\,nm$, all irradiations were performed at $\lambda = 330\,nm$. At this wavelength, all the incident light was absorbed by polysilane (Fig. 1). Table 1 provides the results of the influence of the different salts on the initiation efficiency of the cationic polymerization of cyclohexane oxide (CHO). As can be seen from the Table 1 CHO was polymerized quite effectively

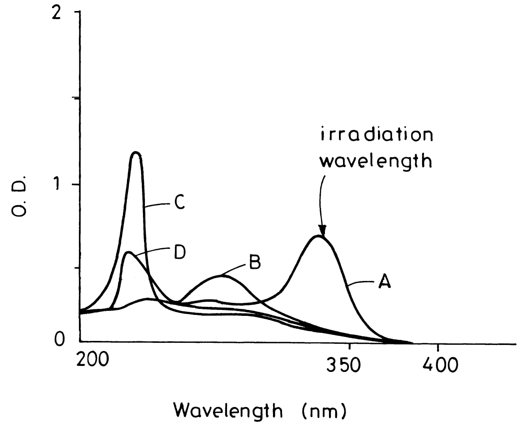


Fig. 1. UV absorption spectra of (a) poly(methyl phenyl silane), (b) EPP^+, (c) ETM^+ and (d) $ECAP^+$ in methylene chloride.

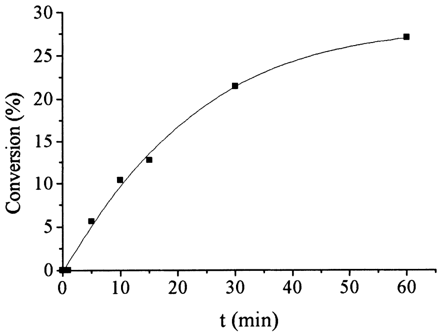
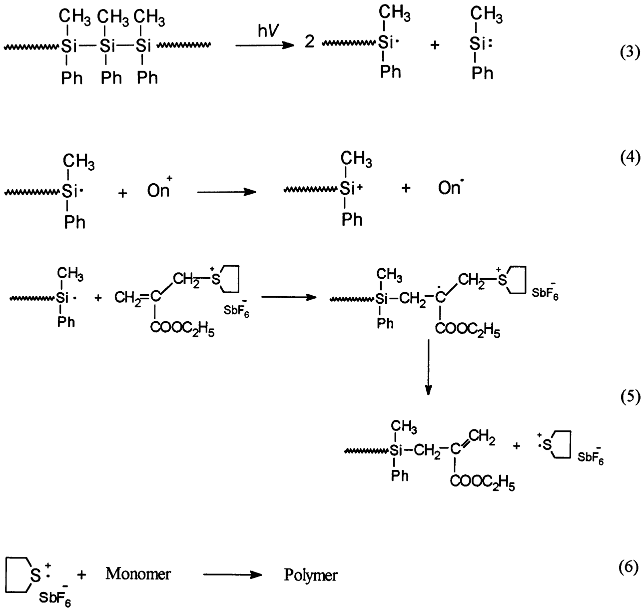
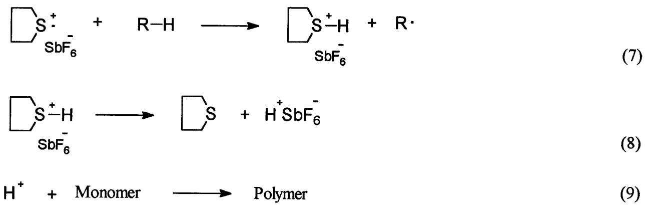


Fig. 2. Bulk photopolymerization of cyclohexene oxide using ETM^+ ($4\times10^{-3}\,mol\,l^{-1}$) and $(MePhSi)_n$ as a radical source ($15\,g\,ml^{-1}$) at $\lambda = 330\,nm$.



Scheme 2.



Scheme 3.

with the all salts which used in combination poly(methyl phenyl silane). In the case of sulphonium salt, ETM, the highest polymer yield was observed. As seen in Fig. 2, with poly(methyl phenyl silane) as a radical source, in conjunction with ETM^+, the polymerization rates of CHO increase with time of irradiation.

In the previous studies [20,21] conducted on the photoinitiated cationic polymerization by using polysilanes and simple onium salts, the mechanism is assumed to involve silyl radical oxidation yielding initiating silicon centered cations. Therefore, at present, a mechanism explaining the role of the allylic salts should also consider a redox reaction.

An alternative mechanism might be based on the addition–fragmentation type initiation which is consistent with the recent reports [7–9,24] on the reaction of free radicals with olefins containing leaving groups in the allylic position as shown below (Scheme 2) for the case of sulphonium salt.

The type of the initiating species depends on the heteroatom of the alylic salt employed, i.e., sulphonium, pyridinium and phosphonium radical cations are formed in the case of ETM^+, EPP^+ and $ECAP^+$, respectively.

The radical cations may also abstract hydrogen from the solvent or the monomer. Protons generated in this way add to the monomer and initiate the cationic polymerization (Scheme 3).

A support for the initiation by radical addition–fragmentation processes in the polymerization was obtained by extracting the poly(cyclohexene oxide) using *n*-hexane. After filtration of the solution, the polymer was reprecipitated into methanol. This procedure was employed to separate unreacted poly(methyl phenyl silane) which does not dissolve in *n*-hexane, from poly(cyclohexene oxide) (PCHO). As can be seen from the ^{1}H-NMR spectrum of the extracted poly(cyclohexene oxide) the polymers obtained in this way do not contain polysilane chains (Fig. 3). Since polysilanes are not incorporated into poly(cyclohexene oxide), the occurrence of the electron transfer mechanism according to reactions seems to be unlikely, and the polymerization is initiated via addition–fragmentation mechanism.

Apart from CHO, the polymerization of other cationically polymerizable monomers with using these dual system was studied. Polymerization conditions and results are shown in Tables 2 and 3. As seen from Table 2, BVE and MOS polymerized very efficiently due to the electron donating nature of the susbtituents. In the case of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (EEC), which possesses two epoxide groups, an insoluble network polymer was readily formed.

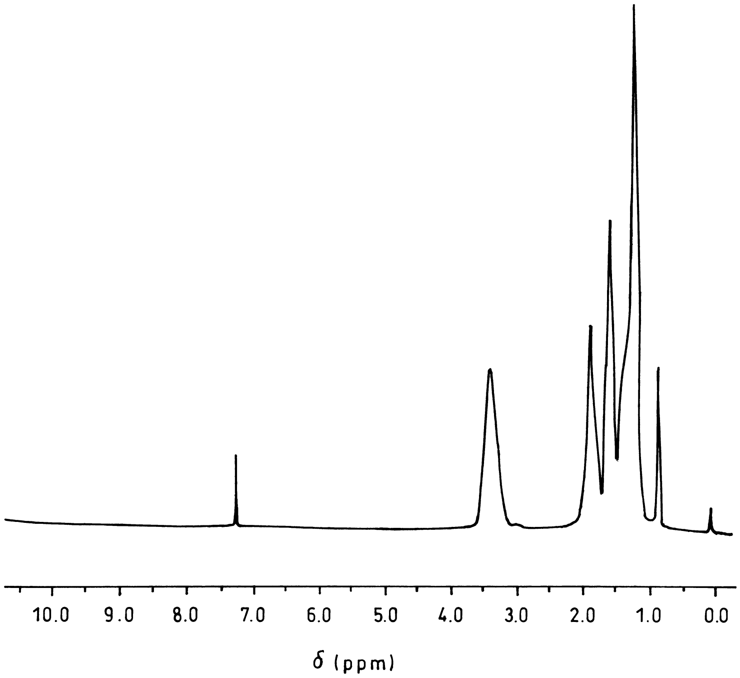


Fig. 3. ^{1}H-NMR spectrum of *n*-hexane soluble portion of poly(cyclohexene oxide) obtained by using polysilane and ETM.

Table 2
Photopolymerization of several cationically polymerizable monomers initiated by poly(methy phenyl silane) as radical source in the presence of ETM$^+$. [(PhMeSi)$_n$)] = 15 g l^{-1}, [ETM$^+$] = 4 × 10^{-3}, λ = 330 nm

Monomer (mol l^{-1})	Solvent	Irradiation time (min)	Conversion (%)	M_n	M_w/M_n
CHO (9.9)	Bulk	60	27	2800	1.4
N-BVE (5.17)	CH_2Cl_2	2	83	9120	1.6
MOS (3.75)	CH_2Cl_2	5	80	460000	1.2
CY179	CH_2Cl_2	36	Gel	–	–

Table 3
Photopolymerization of BVE initiated by poly(methy phenyl silane) as radical source in the presence of various ally-onium salts. [(PhMeSi)$_n$)] = 15 g l^{-1}, solvent = CH_2Cl_2, λ = 330 nm

[Salt] (mol l^{-1})	Irradiation time (min)	Conversion (%)	M_n	M_w/M_n
ETM$^+$ (4 × 10^{-3})	2	74	9120	1.6
ECAP$^+$ (4 × 10^{-3})	5	90	13600	1.9
EPP$^+$ (4 × 10^{-3})	5	35	10900	1.8

In conclusion, these results indicate that polysilanes with appropriate absorption characteristics can be used successfully as a radical source in conjunction with the specially designed allylic salts to initiate cationic polymerizations via addition fragmentation mechanism..

Acknowledgements

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