

**THE EFFECT OF CATIONIC SALT ON
PHOTOINITIATED FREE RADICAL POLYMERIZATION
USING POLYSILANES**

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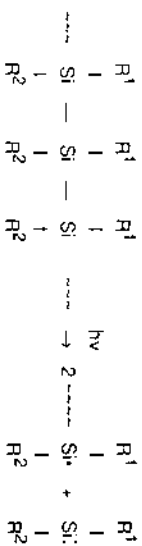
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SUMMARY

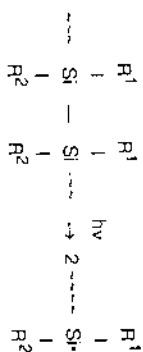
Photoinitiated free radical polymerization of methylmethacrylate (MMA), (N-isopropylcarbamate) ethylpropenoate (CL-960) and tripropylene glycol diacrylate (TPGDA) by using polysilanes in the presence of N-ethoxy-2-methyl pyridinium hexafluorophosphate (EMPF₆) and diphenyliodonium hexafluorophosphate (Ph₂I⁺ PF₆⁻) was studied. In the presence of the cationic salts the rate of photopolymerization was significantly increased. The effect was attributed to the oxidation of silyl radicals formed from the photoexcitation of polysilane by pyridinium or diphenyliodonium salts. The resulting radical species are more capable of initiating the radical polymerization.

INTRODUCTION

High molecular weight polysilanes are interesting materials due to their potential use as ceramic precursor photoresist, photoinitiators, dopable semiconductors, photoconductors and nonlinear optical media[1]. These polymers absorb light between 295-400 nm depending on the nature of the substituents. Upon irradiation these materials undergo rapid photodegradation according to the following reactions



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It has been reported [2,3] that silyl radicals from photolysis of polysilanes initiate free radical polymerization of vinyl monomers. The initiation efficiency of polysilanes is rather low compare to the commercial photoinitiators[2].

The objective of the present work is to examine the effect of cationic salts, namely N-ethoxy-2-methyl pyridinium hexafluorophosphate (EMP⁺ PF₆⁻) and diphenyliodonium hexafluorophosphate (Ph₂I⁺ PF₆⁻) on the photoinitiated free radical polymerization using polysilanes.

EXPERIMENTAL

Materials

Polysilanes, polymethylphenylsilane (PMPSi) and polyphenylbi-phenylsilane (PPBPSi) were prepared according to the method of Zhang and West[4] as described previously[5,6]. The optical absorption characteristics of polysilanes are listed in Table 1. N-ethoxy-2-methyl pyridinium hexafluorophosphate[7] (EMP⁺ PF₆⁻) and diphenyliodonium hexafluorophosphate[8] were prepared as described earlier. Methylmethacrylate (MMA) (Aldrich) was washed with aqueous NaOH solution, dried over CaH₂ and distilled. Dichloromethane (Aldrich) was dried over CaH₂ and distilled. Tripropylene glycol diacrylate (TPGDA) (Aldrich) and (N-isopropylcarbamate) ethylpropenoate [carbamate monoacrylate (CL-960)] (SNPE) were used as received.

Photoinitiated Free Radical Polymerization

Appropriate dichloromethane solutions containing polysilane and MMA or CL-960 in the absence and presence of EMP⁺ or Ph₂I⁺ ions were degassed with nitrogen prior to irradiation. At the end of irradiation at $\lambda=350$ nm (for PMPSi) or $\lambda=385$ nm (for PPBPSi) in AMKO LTI photoreactor equipped with HPO, the polymer was precipitated into methanol and diethyl ether was chosen for the monomer CL-960. In the case of TPGDA, similar experimental conditions were employed and gelation times were monitored.

Analyses

UV spectra were recorded on a Philips PU 8740 spectrophotometer. Molecular weights were determined by GPC on a Waters liquid chromatography system equipped by 600E system controller and 410 differential refractometer, using

Table 1

Polysilane	Polysilanes Used in the Experiments	
	Denotation	λ_{max} nm
Polymethylphenylsilane	PMPSi	340
Polyphenylbi-phenylsilane	PPBPSi	382

polytetrahydrofuran standard samples and tetrahydrofuran as eluent. The flow rate was 1 ml min⁻¹. The reaction mixtures in some cases after photolysis were analysed by HPLC (Cecil 1100) employing a Spherisorb HICHRON S5 005 [Length 25 cm (A, 4.6 mm Eluent 85:15 (MeOH: H₂O) (v/v)] column and UV detector.

Synthesis of Pyridinium Ion Terminated PTHF

A three-necked flask equipped with an argon inlet and a rubber septum was connected to a vacuum line. The flask was dried at 130°C under vacuum. After cooling to room temperature, THF (50 ml) was distilled into the flask. The flask was then disconnected under argon and placed in a thermostatically controlled bath. The initiation of the polymerization was induced by adding triflic anhydride (0.104 ml, 0.62 mmol) under stirring at 25°C. After 30 minutes an aliquot sample was removed for g.p.c. characterization by a syringe and the polymerization was terminated by the addition of methanol. The remaining part of the living PTHF was terminated by the addition of a solution of an N-oxide (12.3 mmol) in dichloromethane (CH₂Cl₂, 10 ml). The polymerization mixture was stirred for 15 min at 25°C, poured into methanol and cooled to -20°C. Finally, the precipitated polymer was filtered off and dried in vacuo.

RESULTS AND DISCUSSION

As mentioned in the introduction, silyl radicals formed upon irradiation of polysilanes, do not efficiently add to the double bonds of monomers[2]. We have previously shown [5] that silicon centered free radicals can be oxidized by EMP⁺ ions and this process may conveniently be used to initiate cationic polymerization of appropriate monomers. It seemed, therefore, appropriate to use EMP⁺ ions in free radical polymerizing systems in order to convert silyl radicals to more reactive initiating species.

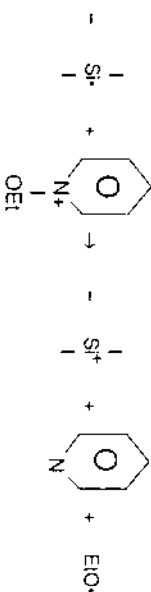
The results of experiments on the photoinitiated polymerization of MMA and CL-960 initiated by polysilane in the absence and presence of a cationic salt are presented in Table 2. These preliminary data are interesting in illustrating the dependence of the rate of the polymerization on the cationic salt.

Table 2
Photoinitiated free radical polymerization in the presence and absence of cationic salts by using of polysilanes in CH_2Cl_2

Monomer	[Monomer] (mol l ⁻¹)	t (min)	Polysilane (g l ⁻¹)	Cationic Salt (mol l ⁻¹)	Rp. 10 ³ (mol l ⁻¹ s ⁻¹)
MMA	4.68	60	PMPSi (1.10 ⁻⁵)	-	8.242
MMA	4.68	60	PMPSi (1.10 ⁻⁵)	EMP ⁺ (1.10 ⁻²)	9.1
MMA	1.86	60	PMPSi (1.10 ⁻⁵)	-	0.9
MMA	1.86	60	PMPSi (1.10 ⁻⁵)	EMP ⁺ (1.10 ⁻²)	2.89
MMA	4.68	60	PPBPSi (1.10 ⁻⁵)	-	7.04
MMA	4.68	60	PPBPSi (1.10 ⁻⁵)	Ph ₂ I ⁺ (1.10 ⁻²)	15.4
MMA	1.10	3	PMPSi (1.10 ⁻⁵)	-	198
CL-960	1.10	3	PMPSi (1.10 ⁻⁵)	EMP ⁺ (1.10 ⁻²)	228
CL-960	1.10	10	PMPSi (2.10 ⁻⁵)	-	96.03
CL-960	1.10	10	PMPSi (2.10 ⁻⁵)	EMP ⁺ (1.10 ⁻²)	115.02
CL-960	1.10	60	PMPSi (2.10 ⁻⁵)	-	16.4
CL-960	1.10	60	PMPSi (2.10 ⁻⁵)	EMP ⁺ (1.10 ⁻²)	20.46
CL-960	1.10	3 [*]	PMPSi (2.10 ⁻⁵)	-	79.81
CL-960	1.10	3 [*]	PMPSi (2.10 ⁻⁵)	EMP ⁺ (1.10 ⁻²)	69.9

* The experiments were carried out in the presence of oxygen.

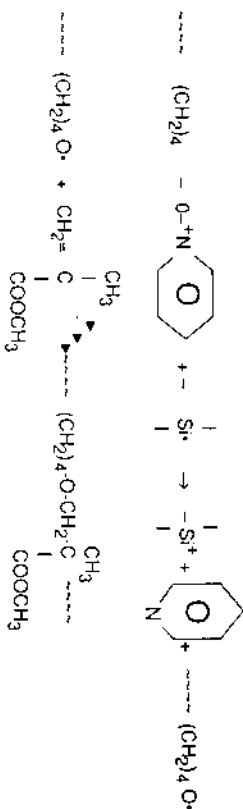
In the presence of the pyridinium salt, ethoxy radicals, which are produced from EMP⁺ induce the polymerization while silyl radicals are converted to the corresponding cation.



The effect on photopolymerization at high monomer concentrations is less pronounced due to high quantum yield of photolysis of polysilanes and some of the silyl radicals formed may add to the monomer. Notably, the

polymerization is much more accelerated with the more reactive monomer CL-960. The reduced rate of polymerization in the presence of EMP⁺ in oxygen saturated systems also support the diversion effect of the salt. Polysilane photoinitiator systems are reported to be insensitive to oxygen inhibition and ethoxy radicals formed are expected to react with oxygen.

Further evidence for the validity of diverting effect of the cationic salt was obtained from the HPLC analysis of the solution of THF containing PMPSi (1.10⁻⁵ g/l) EMP⁺ (1.10⁻² mol/l) after irradiation at 350 nm for 3 hours. Both 2-picolone and ethanol derived from the photodecomposition of EMP⁺ and from ethoxy radical by hydrogen abstraction is detected. The initiation of polymerization of MMA with the aid of pyridinium ion terminated polytetrahydrofuran provided more convincing evidence. Irradiation of MMA containing PMPSi (1.10⁻⁵ g/l) and pyridinium ion terminated polytetrahydrofuran (Mn = 8500) after 3 hours produced polymer with a higher molecular weight (Mn = 17000). In this successful polymerization, the initiating radicals are obtained from the fragmentation of polymenic salt.



As a very simple demonstration of the possible value of photoinitiated free radical polymerization by polysilane in the presence of a cationic salt in UV curing applications, several experiments were performed using a monomer mixture containing tripropylene glycol dimethylacrylate. Because of the presence of two acrylate groups, this monomer ultimately forms intermolecular crosslinked gels. Here, we will consider only the results (listed in Table 3) in which gelation times in the presence and absence of EMP⁺ are compared. It is interesting to note that shorter gelation times were required in the presence of the salt, regardless of the structure of the polysilane and cationic salt.

Irradiations of monomer systems containing both Ph₂I⁺PF₆⁻ and PPBPSi were performed at 385 nm in order to prevent the direct absorption of the iodonium salt which has a tail absorption at 350 nm. In this case, phenyl radicals formed from the reduction of the iodonium salt initiates the polymerization.

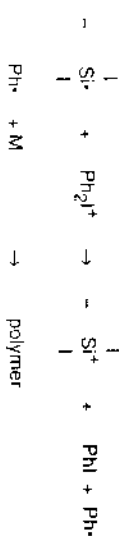


Table 3. Photoinitiated Gel Formation of Acrylate System*

Photoinitiator	Gel Time (min)
MPSI	19
PMPS/EMP+	6.5
PPGSI	7.34
PPBPS/Ph ₂ I ⁺	5.13

* TPGD/AMMA/CH₂Cl₂ (w/w/w) = 50/20/30

In this connection, it is interesting to point out the work of Baumann and Timpe [9] who showed that the rate of photopolymerization of monomers such as MMA and acrylamide initiated by nucleophilic radical precursors increases when onium salts were added. The main effect on photopolymerization is caused by oxidation of the inhibiting nucleophilic radicals by onium salts to give reactive arene radicals. Similarly, the use of phenylazo triphenylmethane, which decomposes thermally and photochemically, as a free radical initiator is restricted by its property to terminate growing chains. In our laboratory, we have shown that the use of Ph₂I⁺ ions converts terminating triphenylmethyl radicals to the corresponding cations and thus improves the efficiency of phenylazotriphenylmethane as a free radical initiator.

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