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CATIONIC PHOTOPOLYMERIZATION OF *p*-METHYLSTYRENE INITIATED BY PHOSPHONIUM AND ARSONIUM SALTS

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Abstract—Phenacyl benzyl phosphonium, and arsonium salts are useful photoinitiators for cationic polymerization of *p*-methylstryene (PMS); photosensitization of phenacyl triphenyl phosphonium salt by pyrene or *N*-methylphenothiazine enhances the rate of polymerization. Triphenylphosphine and triphenylarsine inhibits the polymerization of PMS. The effects of photolysis time, light intensity, initiator and sensitizer chemical structure on the rate of polymerization by salts of the above cations with hexafluoroantimonate (SbF_6^-) or hexafluorophosphate (PF_6^-) is presented.

INTRODUCTION

Onium salts such as diaryliodonium, triarylsulfonium bearing non-nucleophilic anions are powerful photoinitiators for the polymerization of a wide variety of vinyl and heterocyclic monomers. In photochemically initiated cationic polymerizations by triarylsulfonium salts, the primary process is generally assumed to be fragmentation of an appropriate excited state of the salt to produce the diarylsulfinium cation radical ($Ar_2S^{\cdot+}$) and an aryl radical. Crivello [1, 2], postulates that H-abstraction from solvent or monomer (R—H) yields the radical ($R^\cdot$) and protonated diaryl sulfide which could dissociate into Bronsted acid (H^+X^-) and initiate cationic polymerization as shown:

$$Ar_3S^+X^- \xrightarrow{h\nu} [Ar_3S^+X^-]^* \longrightarrow Ar_2S^{\cdot+}X^- + Ar^\cdot \quad (1)$$

$$Ar_2S^{\cdot+}X^- + R{-}H \longrightarrow Ar_2S^+{-}HX^- + R^\cdot \quad (2)$$

$$AR_2S^+{-}HX^- \longrightarrow Ar_2S + H^+X^- \quad (3)$$

The *p,p′*-bis [(triphenylphosphonio)methyl]benzophenone salts are reported to be useful photoinitiators for the cationic polymerization of cyclohexene oxide and free radical polymerization of styrene and methylmethacrylate monomers by selecting the proper excitation wavelength [3].

Recently we reported on the use of phenacyltriphenyl phosphonium salts (**1**) as photoinitiators for the cationic polymerization of cyclohexene oxide [4] and styrene [5].

PolyPMS has excellent potential for a broad range of applications in industrial products, for example reinforced plastic composites achieve higher thermal stability when PMS is substituted for styrene [6].

The reactivity of *para*-substituted styrene towards cationic polymerization depend on the type of substituent with the following order; $OCH_3 > CH_3 > H > Cl$ having been established.

Phase transfer catalyzed chlorination of polyPMS occurs by the action of commercial aqueous sodium hypochloride solution to produce the chloromethylated polystyrene which is considered a key intermediate in the preparation of anion exchange resins [7], and for lithographic evaluation [8, 9].

This paper reports on the use of phosphonium and arsonium salts (**1–7**) and ylid **8** as photoinitiators for cationic polymerization of PMS at 25° when irradiated with light from a Xenon arc lamp. The efficiency of these initiators depends on the type of the anion, the light intensity, the salt and photosensitizer structure.

EXPERIMENTAL PROCEDURES

Salt preparations and characterizations are as reported previously [4]. The bromide salts were converted to the required photoinitiator by adding 0.1 mol of each in 150 ml of water to a mole of the KPF_6 or $KSbF_6$ dissolved in 50 ml of water.

Para-methylstyrene, dichloromethane (Fluka) were dried over calcium hydride and distilled before use. Acetone (Fluka) "AnalaR" grade was used as received.

Spectroscopic measurements

Ultraviolet spectra were obtained on a Cary-2300 spectrophotometer. Infrared spectra were recorded on a Nicolet 50 × B FT-IR spectrophotometer. NMR spectra were taken in $CDCl_3$, on a XL-200 pulsed Fourier transform NMR spectrometer with tetramethylsilane as the internal standard.

Photopolymerization

The selected amounts of the monomer and initiator in CH_2Cl_2 were placed in a 12 mm dia Pyrex tube, the solution degassed under vacuum by conventional freeze thaw techniques and sealed off under vacuum. Irradiation was carried out using a Xenon ARC Lamp, IIC Model PS-150-8. The lamp was calibrated by comparison with the MSL reference Standard of spectral irradiance having calibration traceable to the National Bureau of Standards, U.S.A.

The temperature of the tubes was maintained at 25°. Reaction tubes were irradiated at a distance of 65 cm from the light source. The polymer was precipitated by addition

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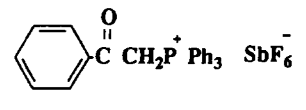

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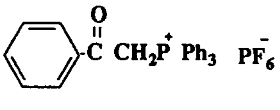

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$CH_3-\overset{O}{\overset{\|}{C}}CH_2\overset{+}{P}Ph_3\ SbF_6^-$

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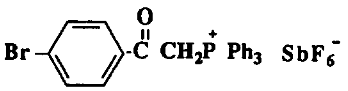

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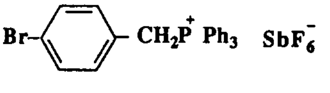

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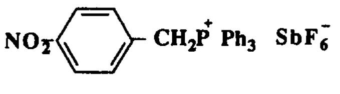

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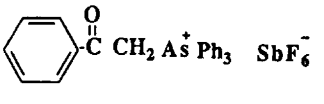

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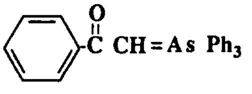


8

of methanol, filtered, dried and weighed. From the polymer masses the rate of polymerization was determined.

RESULTS AND DISCUSSION

The lamp was used at two different current values of 8 and 12 A. Lamp outputs are given in Table 1. Figure 1 shows the u.v. spectrum of PMS in dichloromethane has a double maximum at 267 and 237 nm in dichloromethane.

Figure 2(a) shows the u.v. absorption spectra of salts (**3**, **5** and **6**). Also Fig. 2(b) shows the u.v. absorption spectra of salts (**4** and **7**); a comparison between salt **7** and its ylid **8** in dichloromethane is clear in this figure.

Figure 3 shows photopolymerization yields of PMS by salt **1**–**4** under the same experimental conditions. The rates of polymerization with these salts fall in the following sequence: salt **1** $\approx$ salt **4** $>$ salt **3** $\gg$ salt **2**; clearly the effect of the counter ion is shown by salts **1** and **2**. This could be due to the termination of the growing polymer chain by the counter ion, and salts having the PF_6^- counterion are less reactive due to the greater stability of the counterion SbF_6^- as shown in equations (4)–(7).

$$H^+SbF_6^- \longrightarrow \text{stable anion } (SbF_6^-) + H^+ \quad (4)$$

$$PF_6^- \longrightarrow F^- + PF_5 \quad (5)$$

$$PF_5 + \text{monomer} \longrightarrow \text{polymer chain} \quad (6)$$

$$F^- + \text{propagated chain} \longrightarrow \text{dead polymer} \quad (7)$$

The physical and spectroscopic parameters of the phosphonium and arsonium (**1**–**7**) are shown in Table 2.

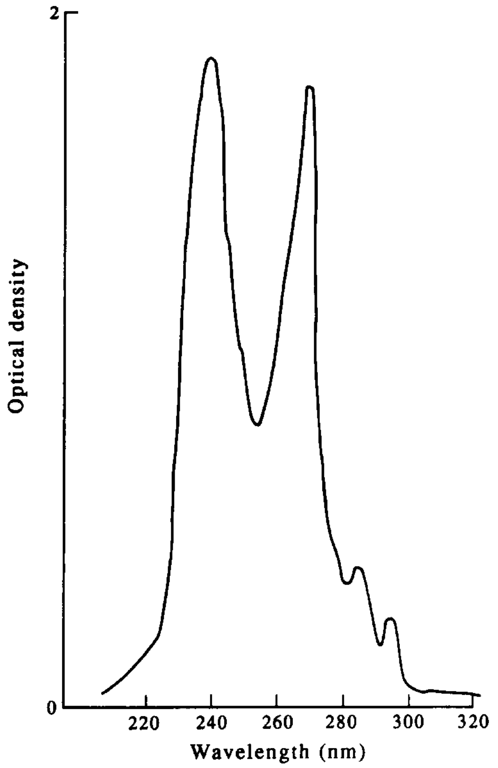


Fig. 1. Ultraviolet absorption spectrum of PMS in dichloromethane.

Table 1. Irradiation used at different output currents

Current (A)	Total irradiance ($\mu W/cm^2$)	Photon irradiance (photons/sec cm^2)	Illuminance [Lux(lm/m^2)]
8	2.238×10^5	7.084×10^{17}	4.979×10^5
12	3.554×10^5	1.124×10^{18}	7.958×10^5

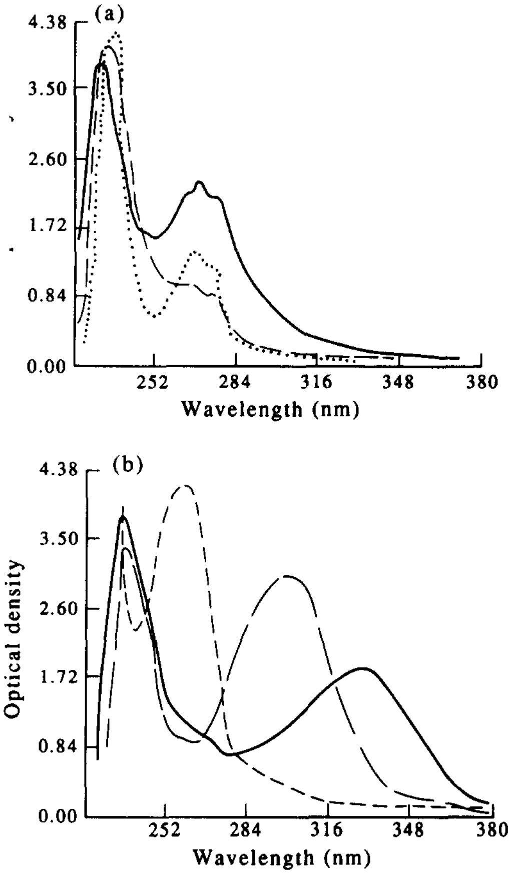


Fig. 2. (a) Ultraviolet absorption spectra of salts **3**, **5**, **6**. Salt **3** · · · · ; salt **5** — —; salt **6** ——. (b) Ultraviolet absorption spectra of salts **4**, **7**, **8**. Salt **4** — —; salt **7** - - -; salt **8** ——.

The result of polymerization of PMS by salt **7** is reported in Fig. 4 where a comparison between salts **7** and **1** indicate that salt **7** is more reactive; this figure also shows that the polymerization of PMS without initiator (in CH_2Cl_2, 50/50 by volume) gives about 5% conversion to polymer in 12 hr. The results indicate that salt **7** is more reactive than salt **1**, and the polymerization rates increase as the light intensity increases.

Figure 5 compares the efficiency of salts **5** and **6**; the results show 5% conversion to polymer was obtained after 3 hr with salt **5**, on the other hand salt **6** gives 25% conversion under the same conditions. Also the light intensity can affect the polymerization rate in this case as <15% yield was obtained when using salt **6** at light output 8 A.

Table 2. Physical and spectroscopic parameters of the Onium salts (1–7)

No.	m.p. (°C)	ν C=O cm^{-1}	δ Ch$_2$ (nm)	λ_{max}	ϵ^*_{max} $\times 10^{-4}$
1	144–146	1687	5.6	257	3.23
2	170–172	1682	5.3	257	2.6
3	154–155	1700	4.7	275	8.70
				268	8.80
				257	2.2
4	166–168	1677	5.3	275	4.1
				257	2.2
5	155–159	—	4.8	276	0.39
				268	0.47
6	173–175	—	4.8	275	3.0
				268	3.5
				264	3.3
7	120–122	1660–1672	5.35	258	2.15

*Molar absorptivity, l mol^{-1} cm^{-1}, in CH_2Cl_2.

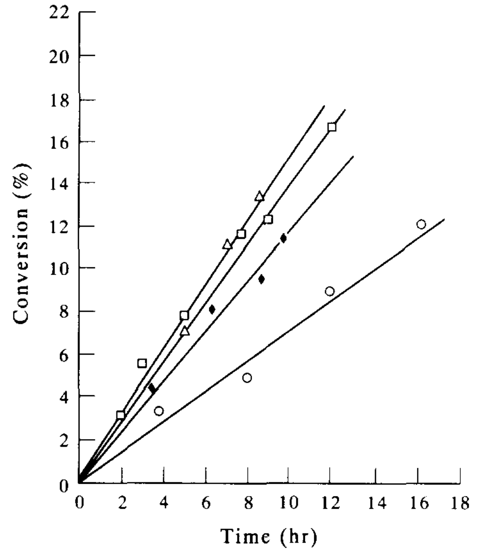


Fig. 3. Photopolymerization of PMS by salts (**1**–**4**). □, Salt **1**; ○, salt **2**; ■, salt **3**; △, salt **4**.

Photosensitization of PMS cationic polymerization was investigated using equimolar concentrations of the salt and the photosensitizers. Pyrene (triplet excitation energy = 48.1 kcal/mol and singlet = 76.9 kcal/mol), and phenothiazine (triplet excitation energy = 57 kcal/mol) were used [10]. Figure 6 shows that polymerization by salt **1** could be sensitized by pyrene to give rapid initiation; photosensitization by different concentrations of pyrene in the range 2.5×10^{-4}–2.5×10^{-3} M gives no significant increase in the amount of polymer obtained. The efficiency of

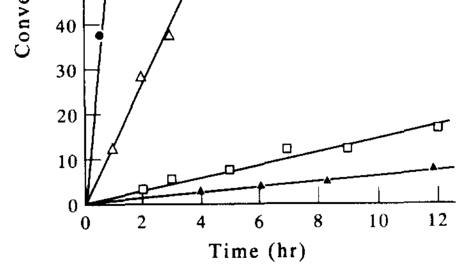


Fig. 4. Photopolymerization of PMS by salts (**1** and **7**), and PMS alone. □, Initiator **1** at 12 A output current; △, initiator **7** at 8 A output current; ●, initiator **7** at 12 A output current; ▲, PMS without initiator.

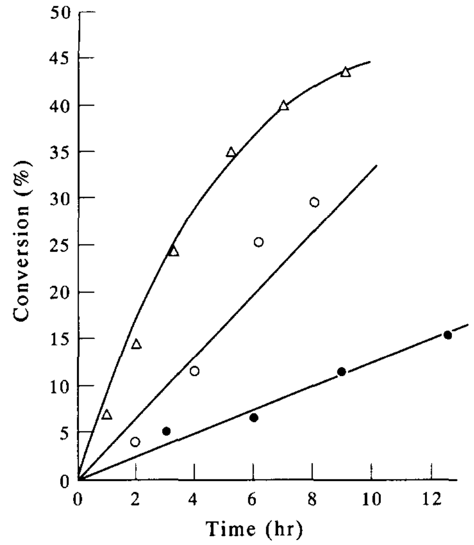


Fig. 5. Photopolymerization of PMS salts (**5** and **6**). ●, Initiator **5** at 12 A output current; ○, initiator **6** at 8 A output current; △, initiator **6** at 12 A output current.

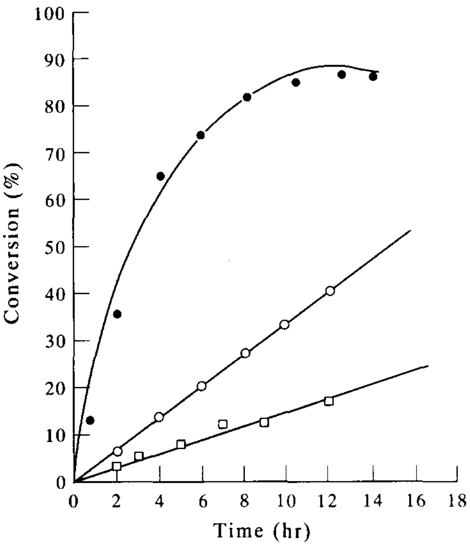


Fig. 6. Photopolymerization of PMS by salt **1**. □, Salt **1**; ○, initiator **1** + *N*-methylphenothiazine; ●, initiator **1** + pyrene.

these photosensitizers varies and depends on the nature of the reactive excited state. *N*-Methylphenothiazine photosensitizes salt **1** to a lesser extent as less polymer was obtained in the presence of phenothiazine compared to pyrene. The difference in the sensitization ability is due to the photochemical character of the reactive excited state species and their relation to formation of an active intermediate [10]. Photosensitization by electron transfer is supported by spectroscopic evidence for the formation of *N*-methylphenothiazine cation radical on irradiation of *N*-methylphenothiazine in the presence of salt **1** [4]. The use of *N*-methylphenothiazine cation radical to initiate the cationic polymerization of cyclohexene oxide has been reported [11, 12].

The photosensitizer cation radical ($PS^{\cdot +}$) may abstract a hydrogen atom and regenerate the sensitizer by releasing a proton

$$P \longrightarrow P^* \tag{8}$$

$$P^* + \text{salt} \longrightarrow P^{\cdot +}X^- + \text{ylid} \tag{9}$$

$$P^{\cdot +}X^- + nM \xrightarrow{h\nu} \text{polymer} \tag{10}$$

This mechanism is very similar to that proposed for the photosensitization of dialkylphenacyl sulfonium salt [13, 14].

The effect of pre-irradiation of salt **1** or **7** in dichloromethane solution followed by addition of PMS is shown in Table 3. We found when irradiating salt **7** for 60 min in dichloromethane and following with addition of PMS, no polymer was obtained when the reaction mixture was left for 10 hr. However, irradiation of salt **1** for 60 min followed by the monomer addition under otherwise similar conditions gives 90% conversion to polymer in 8 hr. These results suggest that for polymerization the excited state of salt **7** readily de-excites to the ground state and thus the excitation energy is removed as shown in equation (11).

$$\text{Salt } \mathbf{7} \underset{1\,\text{hr}}{\overset{h\nu}{\Leftrightarrow}} [\text{salt } \mathbf{7}]^* \xrightarrow[\text{dark, 10 hr}]{\text{PMS}} \text{No polymer} \tag{11}$$

$$\text{Salt } \mathbf{1} \underset{1\,\text{hr}}{\overset{h\nu}{\Rightarrow}} [\text{salt } \mathbf{1}]^* \xrightarrow[\text{dark, 10 hr}]{\text{PMS}} 90\% \text{ polymer} \tag{12}$$

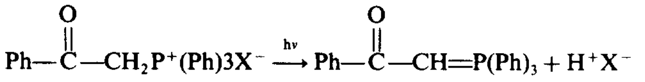
It was found also that when PMS was irradiated for 8 hr with triphenyl arsine (2×10^{-3} M) or triphenyl phosphine (2×10^{-3} M) only 2.3% polymer was obtained, while when the monomer was irradiated alone 4.7% polymer was obtained; this suggests that triphenyl phosphine and arsine can act as inhibiters in the cationic polymerization of PMS.

Table 3. Effect of irradiation of salts **1** and **7** on the rate of polymerization of PMS

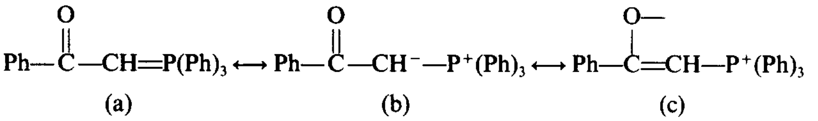
Initiator No.	Irradiation time of salt alone (min)	Total time after mixing (min)	Conversion
1	60	660	96
7	60	180	5.2
7	60	660	6.7

Suggested mechanism

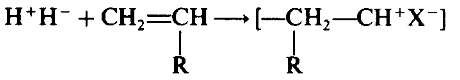
The suggested mechanism by which photopolymerization of PMS is initated by the use of onium salts is given in equations (13)–(16):



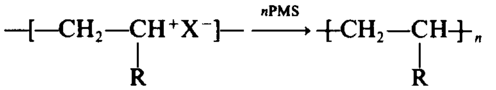
$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH_2P^+(Ph)3X^-} \xrightarrow{h\nu} \mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH{=}P(Ph)_3 + H^+X^-} \tag{13}$$



$$\underset{(a)}{\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH{=}P(Ph)_3}} \longleftrightarrow \underset{(b)}{\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}CH^-{-}P^+(Ph)_3}} \longleftrightarrow \underset{(c)}{\mathrm{Ph{-}\overset{\overset{O-}{|}}{C}{=}CH{-}P^+(Ph)_3}} \tag{14}$$



$$\mathrm{H^+H^- + CH_2{=}\underset{\underset{R}{|}}{C}H \longrightarrow [{-}CH_2{-}\underset{\underset{R}{|}}{C}H^+X^-]} \tag{15}$$



$$\mathrm{{-}[{-}CH_2{-}\underset{\underset{R}{|}}{C}H^+X^-]{-}} \xrightarrow{n\mathrm{PMS}} \mathrm{{+}CH_2{-}\underset{\underset{R}{|}}{C}H{+}_n} \tag{16}$$

$$R = (C6H4)p - CH_3$$

In equation (14) structure (a) shows the stabilized ylid and structures (b) and (c) represents charge-separated carbanion; the stabilization is provided by the carbonyl adjacent to the carbanion.

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