Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Kondo, Shuji , Muramatsu, Masataka and Tsuda, Kazuichi(1983) 'Photoinitiated Free Radical Polymerizations of Styrene and Methyl Methacrylate by Triphenylsulfonium Salts', Journal of Macromolecular Science, Part A, 19: 7, 999 — 1009

To link to this Article: DOI: 10.1080/00222338308081080

URL: http://dx.doi.org/10.1080/00222338308081080

J. MACROMOL. SCI.–CHEM., A19(7), pp. 999-1009 (1983).

Photoinitiated Free Radical Polymerizations of Styrene and Methyl Methacrylate by Triphenylsulfonium Salts

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ABSTRACT

Triphenylsulfonium salts with anions such as Cl^- (1), Br^- (2), I^- (3), and BF_4^- (4) were prepared, and the photoinitiation ability of these compounds was investigated. Compounds (1), (2), and (4) initiated the photopolymerization of styrene and methyl methacrylate. These polymerizations were inhibited by the addition of benzoquinone as a radical scavenger. The overall polymerization rate was proportional to the square root of the concentration of the sulfonium salt employed and first order to the monomer concentration. Further, copolymerization of styrene and methyl methacrylate by (2) showed a typical monomer reactivity ratio of free radical polymerization. The above results indicate that these photopolymerizations proceed through a free radical mechanism. In addition, the photoinitiation ability of these compounds increased in the order (2) > (1) > (4). This result suggested the possibility of initiation of radical polymerization by the phenyl radical which was generated from a one-electron transfer mechanism. On the other hand, Compound (3) did not initiate photopolymerization of styrene or methyl methacrylate.

0022-233X/83/1907-0999$3.50/0

INTRODUCTION

Recently, many papers concerning photosensitized cationic polymerization have been reported [1-13]. Crivello et al. [3] found that triarylsulfonium salts having nonnucleophilic anions such as BF_4^-, SbF_6^-, AsF_6^-, and PF_6^- photoinitiated cationic polymerization of vinyl or heterocyclic monomers by strong protonic acids generated from the photolysis of these sulfonium compounds.

Ledwith et al. [8-10] described that photocationic polymerization could be initiated by the cation which was generated from the oxidation of the free radical by metal complex initiator.

Previously we reported that benzyldiphenylsulfonium tetrafluoroborate photoinitiated the free radical polymerization of styrene and methyl methacrylate [14]. Further, tetraphenylphosphonium salts with such anions as BF_4^-, Cl^-, and Br^- were found to work as free radical initiators under photochemical conditions [15]. The remarkable difference of our results compared with Crivello's results [3] is very interesting. This may be considered due not only to the difference of cation center and substituent, but also to the nucleophilicity of counteranions except for onium salts with BF_4^-. On the other hand, it has been reported that photolysis of triphenylsulfonium halides gives the phenyl radical through homolysis of the carbon-sulfur bond of sulfonium salts [16, 17].

Because of the above results, triphenylsulfonium halides are expected to work as photoinitiators of free radical polymerization. Further, investigation of the effect of counterions in polymerization would give information about the polymerization mechanism. Therefore, we prepared triphenylsulfonium salts with such anions as BF_4^-, Cl^-, and Br^-, and investigated the polymerization mechanism of styrene and methyl methacrylate by these sulfonium compounds.

EXPERIMENTAL

Preparation of Triphenylsulfonium Bromide (2)

To a solution of diphenyl sulfoxide (2.83 g, 14 mmol) in benzene (100 mL), anhydrous aluminum chloride (12 g) was added. The solution soon turned violet. This mixture was refluxed for 20 h, cooled to room temperature, and then poured into 200 mL of ice-water containing 40 mL of conc hydrochloric acid. This mixture was warmed on a steam bath for a few minutes. After separation, the inorganic layer was washed with benzene twice. A solution of potassium bromide (40 g) in water was added to the mixture, extracted with chloroform, and dried with sodium sulfate. After evaporation of the solvent, the residue was dissolved in an acetone-chloroform (5:1 v/v) solution. The solution was poured into a large amount of ether and gave a white solid. The yield was 2.0 g (42%), mp 292°C (Ref. 18, 292.5°C).

Preparation of Triphenylsulfonium Iodide (3)

Triphenylsulfonium iodide was prepared by the same method as for triphenylsulfonium bromide by using potassium iodide instead of potassium bromide. The yield was 66%, mp 295°C (Ref. 19, 250°C).

Preparation of Triphenylsulfonium Chloride (1)

To a solution of triphenylsulfonium bromide (3.0 g, 8 mmol) in water (100 mL), silver oxide (10 g, 48 mmol) was added, and stirred overnight. After filtration of the reaction mixture, the solid was washed with water. Then this solution was acidified with hydrochloric acid to pH 2-3. This solution was extracted with chloroform and dried with sodium sulfate. After evaporation of the solvent, the residue was reprecipitated with chloroform-acetone-ether. The yield was 0.95 g (62%), mp 286°C (Ref. 18, 297-298°C).

Preparation of Triphenylsulfonium Tetrafluoroborate (4)

A solution of triphenylsulfonium bromide (2 g, 5.83 mmol) in methylene chloride (10 mL) was added to a solution of silver tetrafluoroborate (1.7 g, 9 mmol) in methylene chloride (6 mL) and stirred for 5 min at room temperature. After the precipitated silver bromide was filtered off, the solvent was evaporated and gave a white solid. This solid was purified by reprecipitation with methylene chloride and ether. The yield was 1.6 g (79%), mp 186°C (Ref. 18, 190-191°C).

Other Reagents

Styrene, methyl methacrylate, and cyclohexene oxide were purified by ordinary methods and distilled under nitrogen before use. The other reagents and solvents were used after purification.

Polymerizations of Styrene and Methyl Methacrylate by Triphenylsulfonium Salts

The required amounts of monomer, triphenylsulfonium salts, and additive were charged into a tube. The tube was degassed under vacuum by the conventional freeze and thaw technique, and sealed off under vacuum. All polymerizations were carried out with shaking, and irradiation by a Riko 100 W high pressure mercury lamp was performed at 10 cm light length at room temperature. After a given time the tube was opened and its content was poured into a large amount of methanol to precipitate polymer. The resulting polymer was then purified by reprecipitation.

In the case of copolymerization, the composition of the copolymers was determined from elementary analysis of carbon and hydrogen. The monomer reactivity ratio was determined by the Fineman-Ross method.

Instruments

UV spectra were measured by a Hitachi-124 spectrometer. IR spectra were recorded on a Jasco IRA-2 spectrometer. NMR spectra were recorded in $CDCl_3$ on a 60-MHz Hitachi R-20B spectrometer with tetramethylsilane as the internal standard.

RESULTS AND DISCUSSION

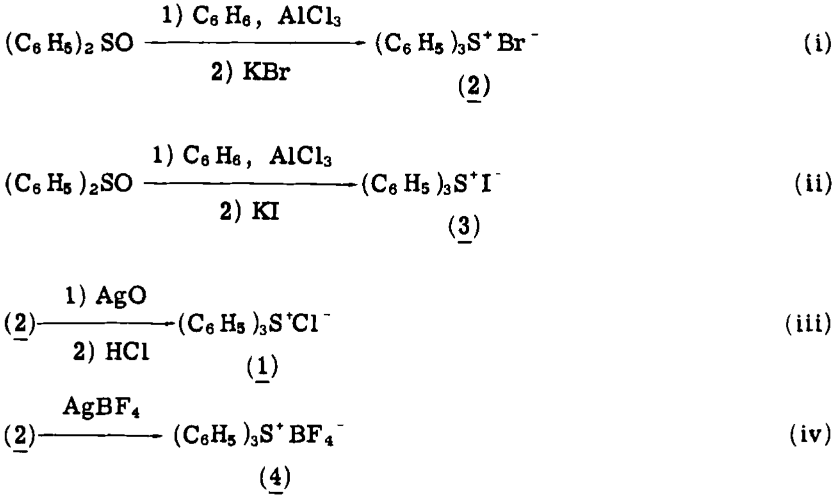
Although triphenylsulfonium halides have been prepared by the use of the Grignard reagent [18, 19], we found that triphenylsulfonium bromide (2) can easily be obtained by the reaction of diphenyl sulfoxide with benzene in the presence of anhydrous aluminum chloride, followed by reaction with potassium bromide. Triphenylsulfonium iodide (3) was prepared by the same method as (2) by the use of potassium iodide instead of potassium bromide. Other triphenylsulfonium compounds with such anions as Cl^-(1) and BF_4^-(4) were prepared by anion exchange reaction with (2), as shown in Scheme 1.

Photoinitiated polymerization of St and MMA by these sulfonium compounds was attempted by the use of a high pressure mercury lamp as the light source. Since these sulfonium compounds are insoluble in St and MMA, acetonitrile was employed as solvent. As can be seen from Table 1, Compounds (1), (2), and (4) initiate the photopolymerization of these vinyl monomers, but Compound (3) does not have the initiation ability required for photopolymerization. Further, the initiation ability increases with a change of anions in the order of $Br^- > Cl^- > BF_4^-$. The same result was obtained by photopolymerization of St and MMA by tetraphenylphosphonium salts [15].

All polymerizations were inhibited by the addition of benzoquinone as a radical scavenger.

The time conversion of the photopolymerization of MMA by (2) is shown in Fig. 1. From this figure the overall rate (R_p) was calculated to be 2.05×10^{-5} mol/L·s and no induction period was seen. This value is similar to that obtained by benzyldiphenylsulfonium tetrafluoroborate [14].

In Fig. 2 the rate of photopolymerization of MMA by (2) is plotted



$$(C_6H_5)_2SO \xrightarrow[\text{2) KBr}]{\text{1) } C_6H_6,\ AlCl_3} \underset{(\underline{2})}{(C_6H_5)_3S^+Br^-} \qquad \text{(i)}$$

$$(C_6H_5)_2SO \xrightarrow[\text{2) KI}]{\text{1) } C_6H_6,\ AlCl_3} \underset{(\underline{3})}{(C_6H_5)_3S^+I^-} \qquad \text{(ii)}$$

$$(\underline{2}) \xrightarrow[\text{2) HCl}]{\text{1) AgO}} \underset{(\underline{1})}{(C_6H_5)_3S^+Cl^-} \qquad \text{(iii)}$$

$$(\underline{2}) \xrightarrow{AgBF_4} \underset{(\underline{4})}{(C_6H_5)_3S^+BF_4^-} \qquad \text{(iv)}$$

SCHEME 1.

logarithmically against the initiator concentration, and a straight line having a slope of 0.45 is found. The correlation between R_p and MMA concentration is shown in Fig. 3; R_p is proportional in the 0.92 order to the monomer concentration. Accordingly, the equation for R_p in this polymerization is

$$R_p = k[\text{MMA}]^{0.92}[\text{Ph}_3\text{S}^+\text{Br}^-]^{0.45}$$

This equation also seems to indicate that ($\underline{4}$) initiates the radical polymerization of MMA.

Further, in order to confirm the mechanism of this photopolymerization, copolymerization of St and MMA was carried out. Figure 4 shows the monomer-copolymer composition curve. This curve is a typical free radical polymerization curve. From this composition curve, monomer reactivity ratios were calculated as $r_{\text{MMA}} = 0.49$ and $r_{\text{St}} = 0.50$. These values are very similar to the value of ordinary radical polymerization; that is, $r_{\text{MMA}} = 0.46\text{-}0.50$, and $r_{\text{St}} = 0.51\text{-}0.54$ [21-24].

From these results, photoinitiated polymerizations of St and MMA by triphenylsulfonium salts obviously proceed through a free radical mechanism.

On the other hand, Crivello et al. [2] reported that Compound ($\underline{4}$) works as an effective photoinitiator in cationic polymerization.

TABLE 1. Photopolymerization of MMA and St by Triphenylsulfonium Salts[a]

Monomer (mL)		Initiator (10^2 M)		BQ (10^2 M)	Conversion (%)
MMA	5				4.5
	5	$PH_3S^+I^-$	1		0
	5		1	1	0
	5	$Ph_3S^+Br^-$	1		18.9
	5		1	1	0
	5	$Ph_3S^+Cl^-$	1		14.9
	5			1	0
	5	$Ph_3S^+BF_4^-$	1		11.6
	5		1	1	0
St	5				0.9
	5	$Ph_3S^+I^-$	1		0
	5		1	1	0
	5	$Ph_3S^+Br^-$	1		7.8
	5		1	1	0
	5	$Ph_3S^+Cl^-$	1		2.1
	5		1	1	0
	5	$Ph_3S^+BF_4^-$	1		2.3
	5		1	1	0

[a] BQ = benzoquinone. Polymerization: 25°C, 12 h.

Cyclohexene oxide is known as a monomer which is readily polymerized by cationic initiators. However, this monomer was not polymerized by (2) or (4) under our irradiation conditions. This fact was further confirmed by the competitive polymerization of cyclohexene oxide and MMA as shown in Table 2. That is, when a mixture of MMA and cyclohexene oxide was irradiated in the presence of (2) or (4), the only polymer obtained was polyMMA.

UV spectra of these sulfonium compounds were measured in ethanol and chloroform. As can be seen from Fig. 5, all sulfonium salts in ethanol have the same spectrum in the range of wavelengths longer than 240 nm. Since all anions employed here have absorption

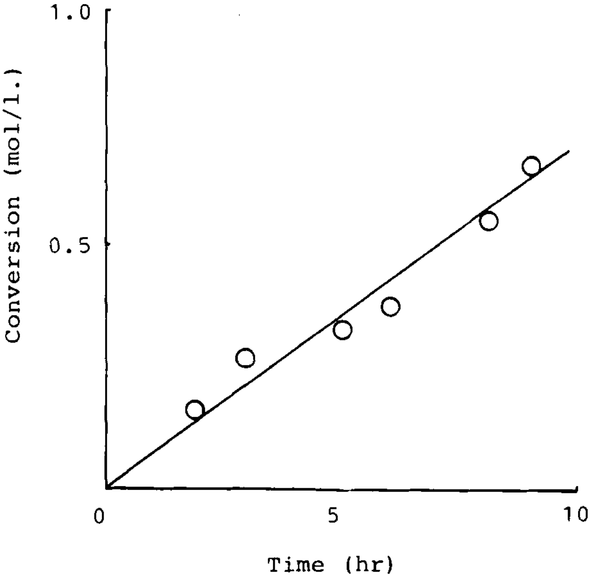


FIG. 1. Time conversion of photopolymerization of MMA by $Ph_3S^+Br^-$ (2). [Initiator] = 1 × 10^{-2} mol/L.

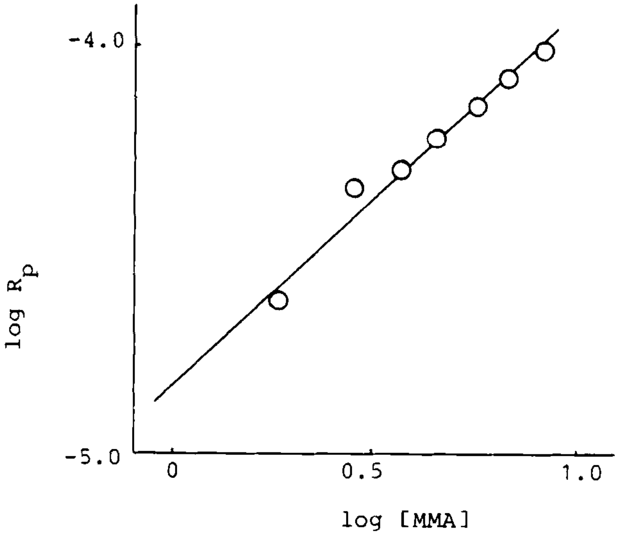


FIG. 2. Relationship between R_p and MMA concentration in the photopolymerization of MMA by (2).

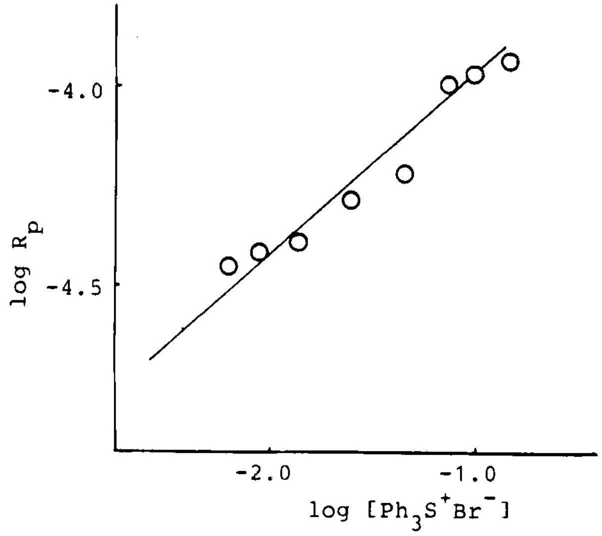


FIG. 3. Relationship between R_p and $Ph_3S^+Br^-$ (2) concentration in the photopolymerization of MMA.

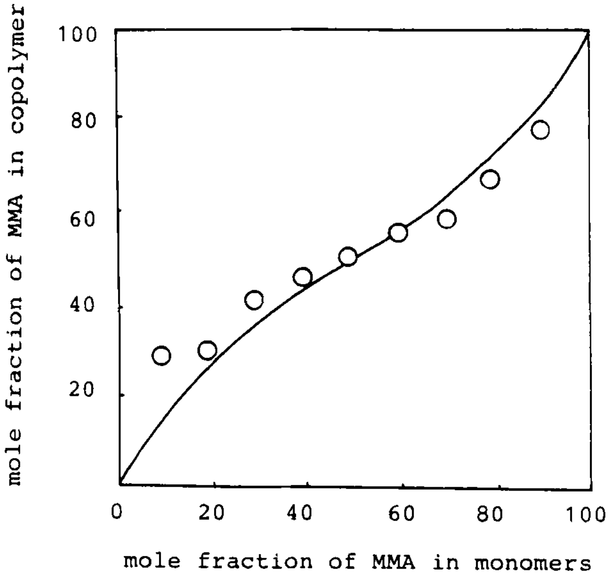


FIG. 4. Monomer-copolymer composition curve of MMA and St by (2).

TABLE 2. Competitive Photopolymerization of Cyclohexene Oxide and MMA by (2) or (4)[a]

Cyclohexene oxide (mL)	MMA (mL)	Initiator (10^2 M)	Conversion (%)
5	-	(2) 1	0
5	5	1	25 (PolyMMA)
5	-	(4) 1	0
5	5	1	19 (PolyMMA)

[a] Conditions: 12 h, 100 W high pressure mercury lamp.

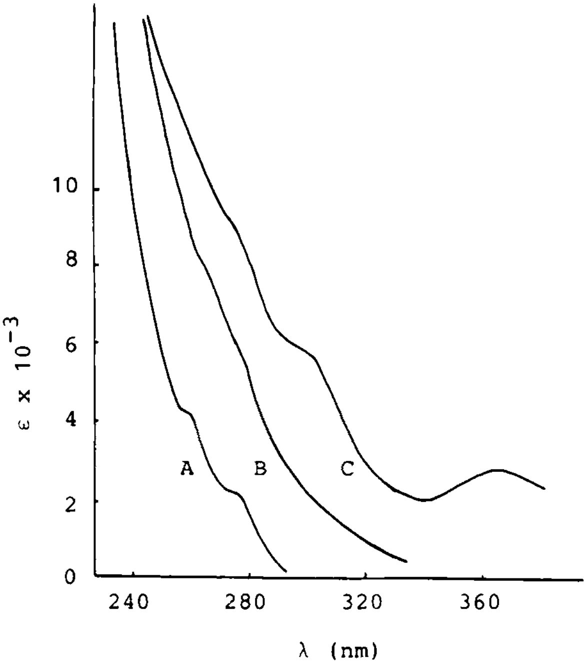


FIG. 5. UV spectra of triphenylsulfonium salts. A: $Ph_3S^+X^-$ (X = Cl, Br, I, BF_4) in C_2H_5OH. B: $Ph_3S^+I^-$ in $CHCl_3$. C: $Ph_3S^+I^-$ in $CHCl_3$ (after 2 h irradiation).

bands lower than 200 nm, this spectrum may be a characteristic band of the triphenylsulfonium cation. Triphenylsulfonium iodide (3) has a different absorption band from other sulfonium compounds in chloroform. This spectrum was found to be a charge transfer absorption band by Kampmeier et al. [17]. When a chloroform solution of (3) was irradiated for 2 h, new absorption bands appeared at 360 and 290 nm due to the triiodide ion [17]. This fact explains the inhibition of polymerization by iodide produced from the photolysis of (3).

McEven et al. [16] reported that triarylsulfonium salts photolyzed in alcohol to give aryl radicals, and the generation mechanism of these radicals was assumed to be Equation (A) or (B):

$$Ar_3S^+ \xrightleftharpoons{h\nu} (Ar_2S^{+\cdot}\ \cdot Ar) \longrightarrow Ar_2S^{+\cdot} + Ar\cdot \qquad (A)$$

$$Ar_3S^+ + X^- \xrightleftharpoons{h\nu} Ar_3S{-}X \rightleftharpoons (Ar_3S\cdot\ \cdot X) \longrightarrow Ar_3S\cdot + X\cdot$$

$$Ar_3S\cdot \rightleftharpoons Ar_2S + Ar\cdot \qquad (B)$$

Since Path A is not predicted by a change of anion, this mechanism is not reasonable from our study of polymerization. On the other hand, Path B involves direct charge transfer by irradiation. As mentioned above, initiation ability increased in the order (2) > (1) > (4). This order coincides with the ease of photooxidation of counteranions [25]. Therefore, the initiation mechanism of these sulfonium salts might be explained by a charge transfer mechanism as well as by phosphonium salts [15]. However, the electron releasing ability of BF_4^- is very low, and Path A cannot be ruled out in the case of triphenylsulfonium tetrafluoroborate [4].

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Accepted by editor October 5, 1982
Received for publication November 5, 1982