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Photosensitized Polymerizations of Styrene and Methyl Methacrylate by Tetraphenylphosphonium Salts

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ABSTRACT

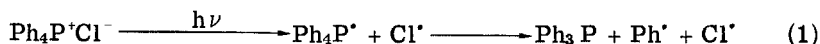
Tetraphenylphosphonium salts with anions such as Cl^- , Br^- , and BF_4^- have been shown to be photoinitiators of styrene (St) and methyl methacrylate (MMA). These polymerizations were inhibited by the addition of benzoquinone as a radical scavenger. Copolymerization of St and MMA by tetraphenylphosphonium tetrafluoroborate showed typical monomer reactivity ratios of a free-radical mechanism. Further, photodecomposition of tetraphenylphosphonium bromide in cyclohexene produced phenylcyclohexane and bicyclohexenyl. These results indicate that photolysis of these phosphonium salts gave the phenyl radical, which initiated the free-radical polymerizations of St and MMA. On the other hand, tetraphenylphosphonium iodide did not initiate the photopolymerization of vinyl monomers.

INTRODUCTION

There have been many papers and patents concerned with ionic polymerizations by onium salts under thermal conditions. Crivello et al. [1] have recently reported that triarylsulfonium and triarylselenium salts work as photoinitiators of cationic polymerization.

On the other hand, Furukawa et al. [2] previously reported that the binary mixture of dimethylaniline and benzyl chloride initiated the radical polymerization of methyl methacrylate at 70°C. The initiation mechanism was clarified by Otsu et al. [3] that the phenyl or methyl radical produced through redox interaction of anilinium chloride derived from the Menshutkin reaction initiated the free-radical polymerization. Redox interaction with counterions has also been considered in many cases of photolysis and thermal reactions of onium salts [4-10]. Therefore, the difference between triaryl-sulfonium salts and the anilinium salt on initiation mechanism is very interesting.

Though phosphine as well as nitrogen belong to the V group, there has been no report on free-radical polymerization by phosphonium salts. Griffin et al. [8] found that photolysis of tetraphenylphosphonium chloride in a solution of benzene and ethanol gave biphenyl, triphenylphosphine, and chlorobenzene. From these products, they explained that this reaction proceeded through a one-electron transfer mechanism:



The above mechanism was supported by the study on the effect of counterions of carbethoxytriphenylphosphonium salts in photolysis; that is, compounds which have easily oxidizable anions were shown to be reactive under photochemical conditions [5].

These results seem to indicate that phosphonium salts have the photoinitiation ability of vinyl monomers by a free radical mechanism in contrast to triarylsulfonium salts [1]. From these standpoints we first studied the photopolymerization of St and MMA by tetraphenylphosphonium salts with anions such as Cl⁻, Br⁻, I⁻, and BF₄⁻. Next, in order to clarify the initiation species of the polymerization, photolysis of tetraphenylphosphonium bromide in cyclohexene as a model of vinyl monomers was investigated.

EXPERIMENTAL

Preparation of Tetraphenylphosphonium Bromide (2)

A filtered solution of phenylmagnesium bromide which was prepared from 9.56 g of bromobenzene was added to 4 g of triphenylphosphine; the total volume of solution was 75 mL. Dry oxygen was passed over the surface of a vigorously stirred solution for 2 h, and a solid soon started to form. Then a solution of hydrobromic acid (9.5 mL of 45% hydrobromic acid and 20.5 mL of water) was added. After separation of the reaction mixture, the inorganic layer was washed with ether and extracted with chloroform. Then the chloroform was removed in vacuum and the ether was added to give a white solid.

The yield of tetraphenylphosphonium bromide was 3.2 g (50%), mp 286°C (Ref. 11, 287°C).

Preparation of Tetraphenylphosphonium Iodide (3)

Tetraphenylphosphonium iodide was prepared by the same method as tetraphenylphosphonium bromide by using hydroiodic acid instead of hydrobromic acid. The yield was 32%, mp 336-338°C (Ref. 12, 337°C).

Preparation of Tetraphenylphosphonium Tetrafluoroborate (4)

One gram of tetraphenylphosphonium bromide was dissolved in a hot solution of 5 mL of acetone and 8 mL of water. To this solution a solution of 0.46 g of silver tetrafluoroborate in 10 mL of water was added and stirred for 3 h. Then the silver bromide produced was filtered off, and the filtrate was cooled to precipitate a white solid. This solid was reprecipitated from water and acetone. The yield of tetraphenylphosphonium tetrafluoroborate was 0.81 g (79%), mp 345°C (Ref. 12, 350.5°C).

Preparation of Tetraphenylphosphonium Chloride (1)

A solution of 2.3 g of tetraphenylphosphonium tetrafluoroborate in 50 mL of ethanol was added to equimolecular potassium chloride in 10 mL of water with stirring. After stirring for 10 h at room temperature, the reaction mixture was filtered. The filtrate was reduced to give a sirupy residue. Then ether was added to the solution of this residue in chloroform to give a solid. The solid was recrystallized from chloroform and ether. The yield of tetraphenylphosphonium chloride was 1.1 g (52%), mp 65-66°C (Ref. 12, 67-68°C).

Other Reagents

Styrene (St) and methyl methacrylate (MMA) were purified by ordinary methods and used just after distillation. Benzoquinone was recrystallized from methanol.

Polymerizations of Styrene or Methyl Methacrylate by Tetraphenylphosphonium Salts

The required amounts of monomer, tetraphenylphosphonium salts, and additive were charged into a test tube. This 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 done at 10 cm distance at room temperature. After a given time the tube was opened and its content 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 ratios were estimated by the Fineman-Ross method.

Photolysis of Tetraphenylphosphonium Bromide (2)

Four grams of tetraphenylphosphonium bromide, 10 mL of cyclohexene, and 10 mL of acetonitrile were charged into a Pyrex tube. The tube was degassed and sealed under vacuum. Photolysis was carried out under the irradiation of a 500-W high pressure mercury lamp [USHIO] from a distance of 10 cm for 20 h at room temperature. The reaction mixture was poured into a large amount of ether, and 2.73 g of starting material was precipitated. From the filtrated solution, 5.1% of bromobenzene, 12.7% of bromocyclohexane, 1.9% of bicyclohexenyl, and 6.8% of cyclohexylbenzene were isolated by gas chromatography (Carbowax 20 M, 10%), and a further 21% of triphenylphosphine and two unknown compounds were also obtained by column chromatography (silica gel). The products were identified by comparison with authentic samples by the use of NMR and IR spectrometry.

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

Photopolymerizations of MMA and St by tetraphenylphosphonium compounds with anions such as Cl^- (1), Br^- (2), I^- (3), and BF_4^- (4) were attempted by the use of a high pressure mercury lamp as the light source. As can be seen from Table 1, Compounds (1), (2), and (4) initiate photopolymerization of these vinyl monomers, but Compound (3) does not have the initiation ability of photopolymerization. Furthermore, the initiation ability increased with the change of anions in the

TABLE 1. Photopolymerization of MMA and St by Tetraphenylphosphonium Salts

Monomer (mL)	Initiator (10^2 M)	BQ ^a (10^2 M)	Conversion (%)
MMA	5		1.3
	5	Ph ₄ P ⁺ I ⁻ 1	0
	5	" 1	1
	5	Ph ₄ P ⁺ Br ⁻ 1	7.2
	5	" 1	1
	5	Ph ₄ P ⁺ Cl ⁻ 1	3.1
	5	" 1	1
	5	Ph ₄ P ⁺ BF ₄ ⁻ 1	2.2
	5	" 1	1
St	5		0.8
	5	Ph ₄ P ⁺ I ⁻ 1	0
	5	" 1	1
	5	Ph ₄ P ⁺ Br ⁻ 1	2.6
	5	" 1	1
	5	Ph ₄ P ⁺ Cl ⁻ 1	2.0
	5	" 1	1
	5	Ph ₄ P ⁺ BF ₄ ⁻ 1	1.5
	5	" 1	1

^aBQ: benzoquinone (25°C, 8 h).

order Br⁻ > Cl⁻ > BF₄⁻. The same result was also obtained in the case of photopolymerization of St. This order coincides with the ease of photooxidation of anions [14].

All polymerizations were inhibited by the addition of benzoquinone as a radical scavenger. This fact indicates that these polymerizations proceeded through a free-radical mechanism.

The time-conversion of the photopolymerization of MMA by (4) is shown in Fig. 1. From this figure the overall rate (R_p) was calculated as 9.7×10^{-6} mol/L's, and the induction period of polymerization was not found.

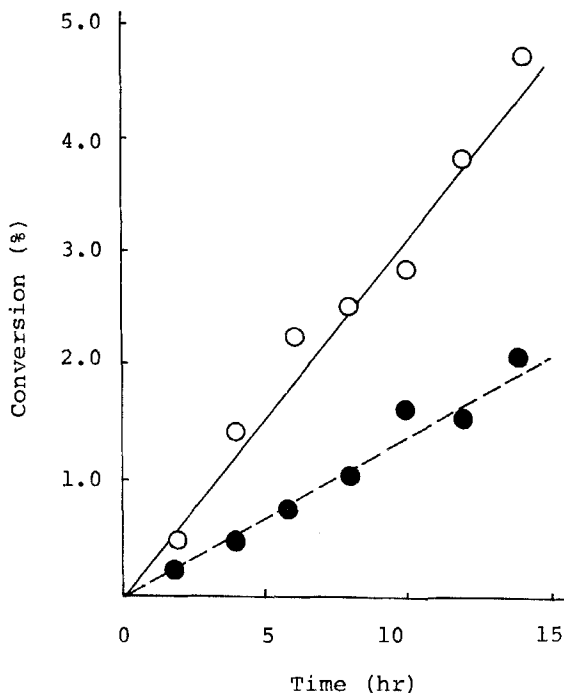


FIG. 1. Time-conversion of photopolymerization of MMA by $\text{Ph}_4\text{P}^+\text{BF}_4^-$. (—) 1×10^{-2} mol/L of $\text{Ph}_4\text{P}^+\text{BF}_4^-$. (- -) No initiator added.

Figure 2 shows plots of R_p against the initial concentration of the initiator (4). R_p was found to be proportional to the square root of the concentration of (4). The correlation between R_p and MMA concentration is shown in Fig. 3; R_p was directly proportional to the monomer concentration. Accordingly, the equation for R_p in the polymerization of MMA by (4) was formulated as

$$R_p = k[\text{MMA}][\text{phosphonium salt}]^{1/2}$$

This rate equation also indicates that (4) initiates radical polymerization of MMA.

In order to confirm the radical mechanism, copolymerization of St and MMA was carried out by using Compound (4) as the photoinitiator.

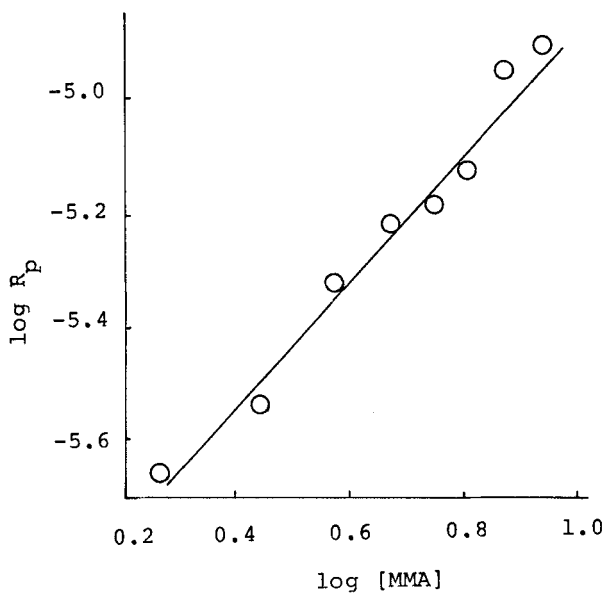


FIG. 2. Relationship between R_p and MMA concentration.

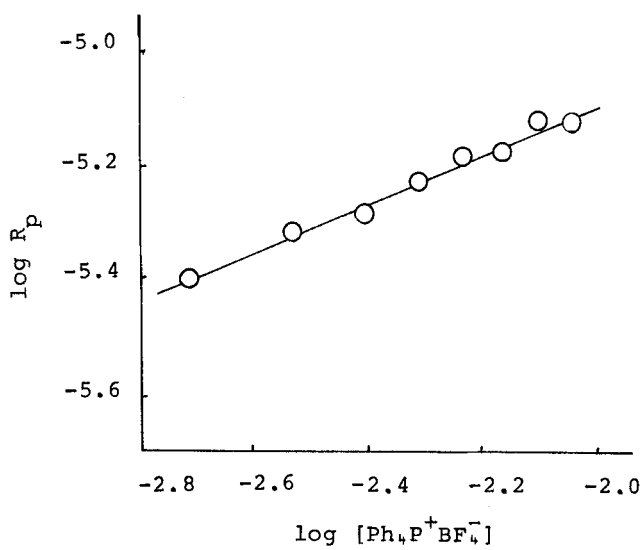


FIG. 3. Relationship between R_p and $\text{Ph}_4\text{P}^+\text{BF}_4^-$ concentration.

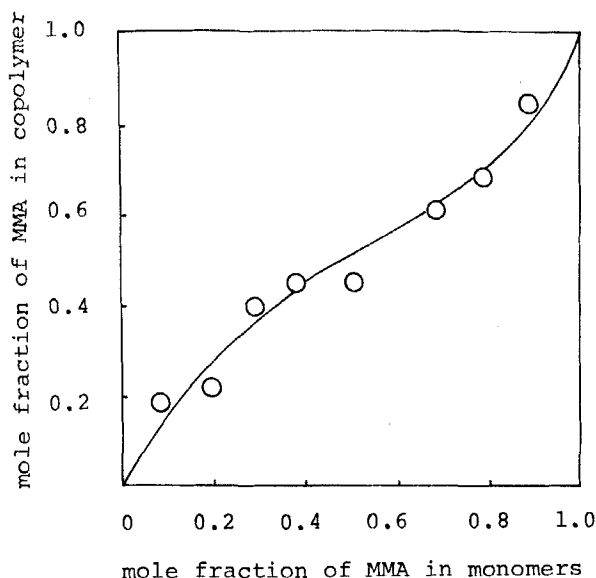


FIG. 4. Monomer polymer composition curve of MMA with St.

As can be seen in Fig. 4, the composition curve is a typical radical copolymerization curve, and monomer reactivity ratios were computed as $r_{\text{St}} = 0.48$, $r_{\text{MMA}} = 0.43$. This result is in good agreement with the data [15] which were reported for the radical polymerization of MMA and St.

The effect of radical scavenger and the kinetic study clarified that photopolymerization of St and MMA by tetraphenylphosphonium salts proceeded by a free-radical mechanism.

The absorption spectra of these phosphonium salts were measured in ethanol and chloroform. As can be seen from Fig. 5, all tetraphenylphosphonium salts show the same spectra in wave lengths longer than 240 nm. However, when Compound (3) was irradiated for 2 h in chloroform, new absorption bands appeared at 290 and 360 nm. It is known that these absorption bands are characteristic for triiodide ion (I_3^-) [10]. This fact gives a plausible explanation to the result that Compound (3) did not work as a photoinitiator; namely, Compound (3) was irradiated to give iodine, which inhibited the radical polymerization of St and MMA.

Next, to clarify the initiation species of this radical polymerization, the photolysis of (2) was investigated. Irradiation of (2) in cyclohexene as a model compound of vinyl monomers afforded bromobenzene, bromocyclohexane, bicyclohexenyl, cyclohexylbenzene,

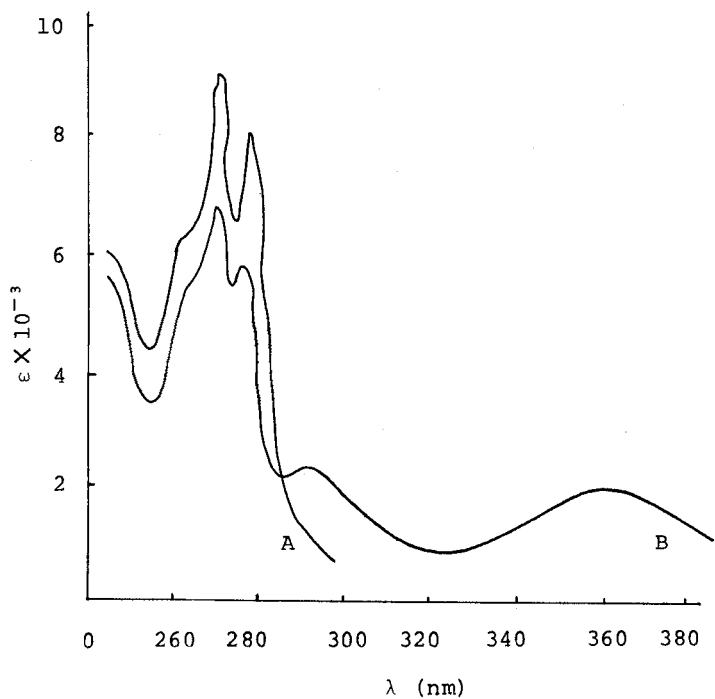
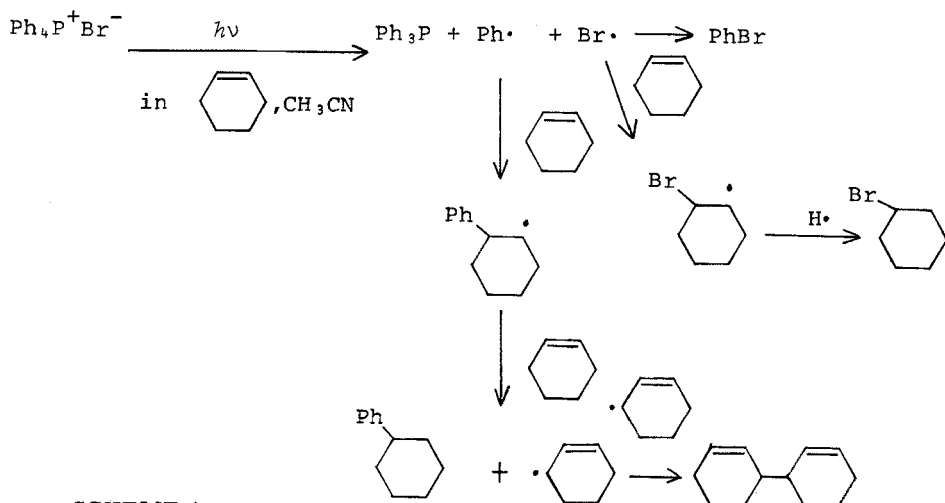


FIG. 5. UV spectra of tetraphenylphosphonium salts. A: $\text{Ph}_4\text{P}^+\text{X}^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{BF}_4$) in $\text{C}_2\text{H}_5\text{OH}$. B: $\text{Ph}_4\text{P}^+\text{I}^-$ in CHCl_3 (after 2 h irradiation).



triphenylphosphine, two unknown compounds, and polymeric material. These products indicate that the reaction proceeds by a radical mechanism as shown in Scheme 1.

The production of bromine atom is suggested from Scheme 1, but it has not yet been reported in the literature that halogen atoms participate in the initiation of radical polymerization. Therefore, the initiation species may be the phenyl radical. This consideration would be supported by the result that a tetraphenylphosphonium salt carrying the tetrafluoroborate anion has initiation ability for the polymerization of St and MMA.

Further, it was shown that the initiation ability of these phosphonium salts was increased in the order (2) > (1) > (4). This result might be explained by the assumption that one electron transfer from anion to phosphonium ion occurred under photochemical conditions as reported by Griffin et al. [8].

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