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Phosphorus-Containing Polystyrene Derivatives as Flame Resistance

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ABSTRACT: The synthesis of monomers containing phosphorus, their polymerization or copolymerization and the flame resistance of these polymers were investigated. It was found that diethyl-(*p*-vinylphenyl) phosphate (PO) and diethyl-(*p*-vinylphenyl) thiophosphate (PS) could be prepared readily from the sodium salt of *p*-vinylphenol. PO and PS underwent polymerization and copolymerization with methyl methacrylate (MMA), styrene (ST), methyl acrylate (MA), and maleic anhydride (Manh) to produce glassy and transparent solids, that are flame resistant. The copolymers of PO–Manh and PS–Manh were found to be alternating. The flame resistance was better with the polymers containing phosphorus–oxygen than phosphorus–sulfur. However, the flame resistance of the copolymers was not always higher than that of mixture of homopolymers. An aggregation state of phosphorus groups may effectuate high flame resistance of polymer mass.

KEY WORDS Diethyl-(*p*-vinylphenyl) Phosphate / Diethyl-(*p*-vinylphenyl) Thiophosphate / *p*-Trimethylsilyloxystyrene / Copolymerization / Monomer Reactivity Ratio / *Q–e* Value / Alternating Copolymerization / Phosphorus Containing Polymer / Flame Resistance /

The production of flame resistant materials is one of several important problems and there is very extensive literature on this subject.[1] The application of organophosphorus polymers, either by their simple addition to materials or as substances chemically linked to them, or absorbed on them, often offers a solution to this problem. It is well known that di-(2-chloroethyl)-vinyl phosphate[2,3] and the allyl or alkyl ester of the phoshorus acid[4-7] are generally utilized in copolymerization with the unsaturated polyester in order to obtain flame-proof polyester resins. These self-extinguishing characteristics are even retained in copolymers produced by copolymerization with other compatible monomers.[8,9] However, a comparison on the degree of flame resistance between the simple addition of phosphorus-containing polymers to the materials and the substances chemically linked to them is not well known.

The purpose of this study is to investigate the synthesis of the dialkylester of *p*-hydroxystyrene containing phosphorus-oxygen and phosphorus-sulfur, their polymerization and copolymerization characteristics, and then the difference in flame resistance between the blend of phosphorus-containing polymer to materials and the copolymers. *p*-Trimethylsilyloxystyrene was also synthesized.

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EXPERIMENTAL

Material

Toluene used as the solvent was purified in the usual manner. Styrene (ST), methyl methacrylate (MMA), and methyl acrylate (MA) were purified by distillation under a nitrogen atmosphere just before use. Maleic anhydride (Manh) was recrystallized from a chloroform solution. Azobisisobutyronitrile (AIBN) was used without further purification. BF_3OEt_2 was of reagent grade and used without further purification. *p*-Hydroxystyrene was recrystallized from a hexane solution, mp 71—72°C.[10]

Preparation of Monomers

Diethyl-(p-vinylphenyl) Phosphate. 30 g (0.25 mol) of *p*-hydroxystyrene in 100 ml of dry ether was added slowly with stirring to the suspension of sodium hydride 6.0 g (0.25 mol) in 150 ml of dry ether. The mixture was then stirred at room temperature for another 1 h. The suspension of sodium *p*-

vinylphenoxide so obtained was cooled to 0°C and a solution of diethyl phosphorochloridate 43.1 g (0.25 mol) in 50 ml of dry ether added slowly with stirring. The total content of the mixture was stirred for 5 h to ensure a complete reaction. Water was then added and the ether layer was washed successively with a 2% aqueous solution of sodium hydroxide, then with water, and dried over Na_2SO_4 and evaporated. The residue was distilled at 102—104°C (0.1 mmHg, giving diethyl-(*p*-vinylphenyl) phosphate (PO) 40.3 g (63.0% yield) as a colorless liquid, n_D^{20} 1.5028. (Found: C, 56.25%; H, 6.64%. Calcd: C, 55.98%; H, 6.33%.)

The IR spectrum of PO (liquid film) is shown in Figure 1. It was found that there are an absorption due to vinyl group at 1615 cm^{-1}, two absorptions due to P–O–aryl at 1220, 1170 cm^{-1}, two absorptions due to P–O–alkyl at 1170, 1040, and an absorption due to P=O at 1310 cm^{-1}. The NMR spectrum ($CDCl_3$) of PO is illustrated in Figure 2, exhibiting a triplet signal due to six protons of the two methyl groups of $-O-CH_2-\underline{CH_3}$ at δ 1.36 ppm (J=7 Hz), a double quartet signal[11] due to four protons of the two methylene groups of $\underline{CH_2}CH_3$ at δ 4.20 ppm (J=7 Hz), three double doublet signal due to three protons of the vinyl group at δ 5.20 ppm (J=11 Hz), 5.63 (J=17.4 Hz), and 6.66 (J=11 Hz), respectively, and an AB quartet signal due to four protons of aromatic group at δ 7.30 ppm (J=8 Hz).

Diethyl-(p-vinylphenyl) Thiophosphate. Diethylthiophosphorochloridate, 47.1 g (0.25 mol) in 50 ml of dry ether was added slowly with stirring to the suspension of sodium *p*-vinylphenoxide prepared as described above from *p*-vinylphenol 30 g (0.25 mol) and sodium hydride 6.0 g (0.25 mol) in 150 ml of dry ether. The mixture was stirred at room temperature for another 5 h, and then was worked up as described for diethyl-(*p*-vinylphenyl) phosphate. The residual diethyl-(*p*-vinylphenyl) thiophosphate (PS) 39.5 g (58.0% yield) was distilled at 105—106°C (0.05 mmHg, as a colorless liquid, n_D^{20} 1.5297. (Found: C, 52.94%; H, 6.25%. Calcd: C, 52.38%; H, 6.24%.)

The IR spectrum of PS (liquid film) is shown in Figure 1. Similar spectral data were obtained for PS as detailed in PO, showing absorptions at 1610 (vinyl group), 1200, 1160, (P–O–aryl), 1160, 1015 (P–O–alkyl), 710 (P=S, weak) cm^{-1}. The NMR spectrum ($CDCl_3$) exhibited similar spectral data as detailed in PO, except for a little difference in chemical shift (Figure 2).

p-Trimethylsilyloxystyrene. Trimethylsilyl chloride 27.7 g (0.26 mol) was added slowly to the stirred solution of *p*-hydroxystyrene 30.6 g (0.26 mol) and dry pyridine 20.0 g (0.26 mol) in 200 ml of dry ether. The mixture was stirred at room temperature for another 5 h. Water was then added and the ether layer was washed with a 2% aqueous solution of sodium hydroxide, and then with water, and dried over Na_2SO_4 and evaporated. The residue was distilled at 47—48°C (0.08 mmHg), giving *p*-trimethylsilyloxystyrene (TS) 34.9 g (70.0% yield) as a colorless liquid. (Found: C, 68.72%; H, 8.33%. Calcd: C, 68.45%; H, 8.06%.)

The IR spectrum of TS (liquid film) is shown in Figure 1 and shows absorption due to a vinyl group at 1610 cm^{-1}, two absorptions due to $-Si(CH_3)_3$ at 1250, 840 cm^{-1}. The NMR spectrum ($CDCl_3$) of TS is illustrated in Figure 2 and exhibits a singlet signal due to nine protons of the three methyl groups of $-Si(\underline{CH_3})_3$ at δ 0.27 ppm, three double doublet signal due to three protons of the vinyl groups at δ 5.17 (J=11 Hz), 5.60 (J=17 Hz), and 6.75 ppm (J=11 Hz), respectively, and an AB quartet signal due to four protons of aromatic group at δ 7.07 ppm (J=9 Hz).

Polymerization

Some typical runs are described below.

Free Radical Polymerization. 10 mg (0.06 mmol) of initiator (AIBN) was put into a dry glass ampoule, evacuated and flushed with a pure nitrogen gas, and subsequently 1.36 g (5.3 mmol) of PO and 2.0 ml of toluene were introduced into this under an atmosphere of nitrogen. The glass ampoule was dipped in a bath cooled at −78°C, and then sealed. Polymerization was carried out at 60°C (see Table I). After 7 h, the ampoule was taken out, cooled, and then opened. The content of the ampoule was poured into a large excess of methanol. The coagulated polymer was washed with a large amount of methanol, dried *in vacuo* and then weighed. Yield 0.5 g (37.0%).

Cationic Polymerization. 1.36 g (5.3 mmol) of PO and 10 ml of toluene were put into a dry 10 ml flask, which was evacuated and flushed with a pure nitrogen gas, and then dipped into a bath cooled at −30°C. 1.0 ml of the toluene solution containing 0.4 g (2.7 mmol)/100 ml of boron trifluoride etherate was injected through the three-way cock into the flask, and the mixture was allowed to stand for 1 h at

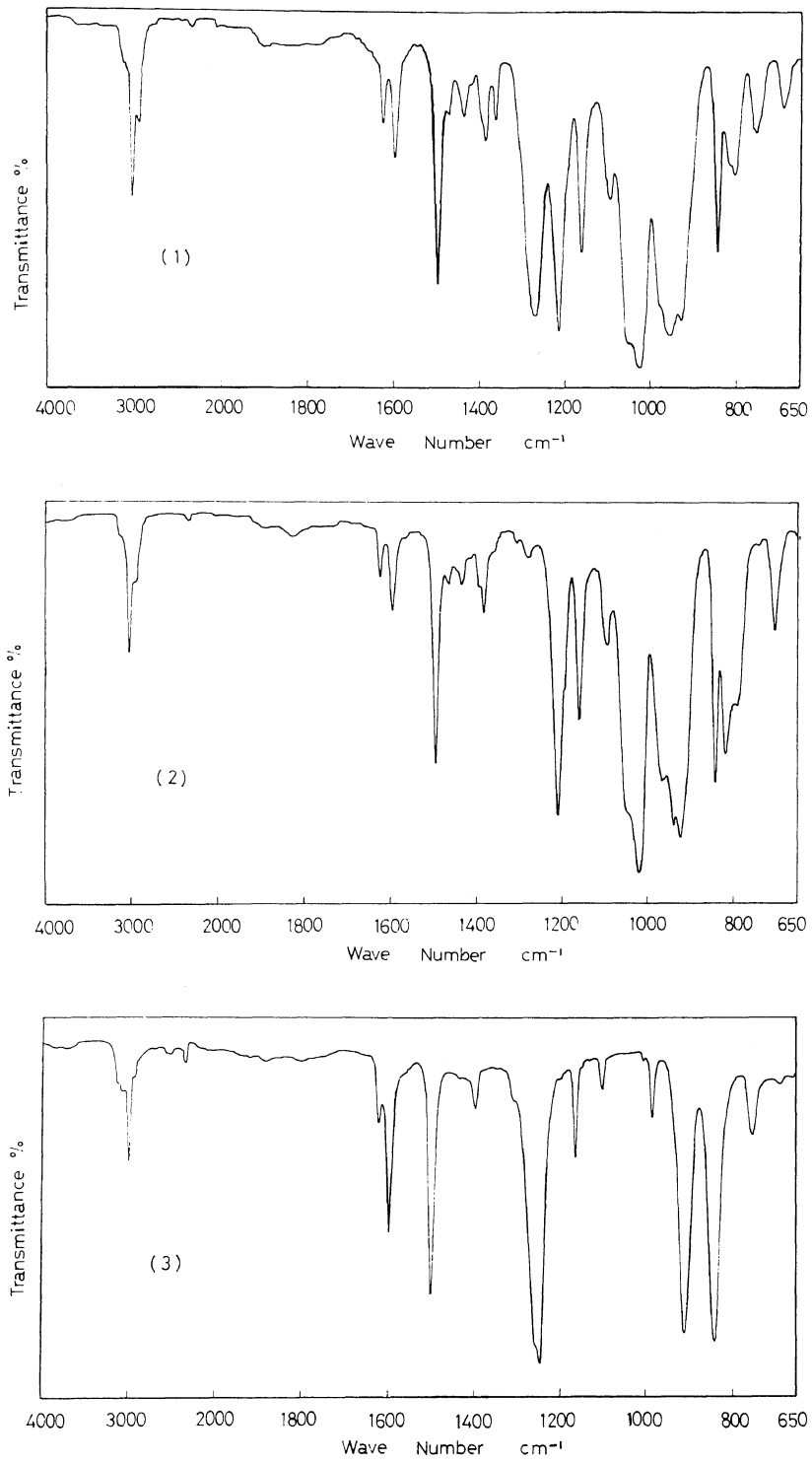


Figure 1. Infrared spectra of Monomer: (1), diethyl-(*p*-vinylphenyl) phosphate (PO); (2), diethyl-(*p*-vinylphenyl) thiophosphate (PS); (3), *p*-trimethylsilyloxystyrene (TS).

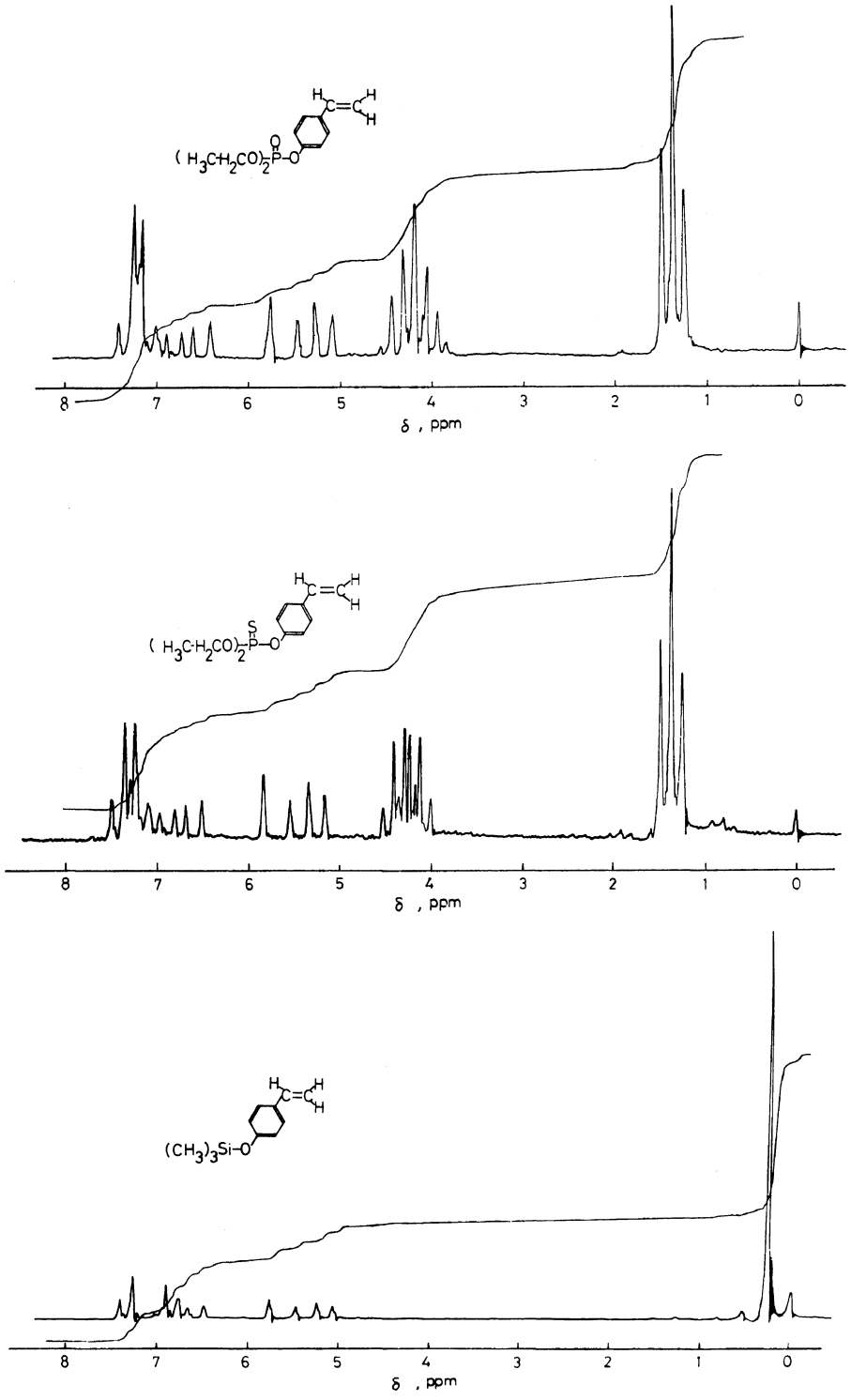


Figure 2. NMR spectra of monomer.

Table I. Polymerization of PO, PS, and TS

Monomer		Initiator based on monomer		Solvent	Polymerization time	Polymerization time	Polymer yiled	T_m	$M_n \times 10^{-3}$
mmol		wt%		ml	h	°C	%	°C	
PS	3.5	AIBN	1.1	Toluene 2	20	60	74	97—100	5.7
PS	3.5	〃	1.1	None	15	60	83	100—105	4.8
PO	5.3	〃	0.7	Toluene 2	7	60	37	73—82	4.2
PO	5.3	〃	0.7	None	4	60	53	76—85	3.8
TS	5.5	〃	0.5	Toluene 2	12	60	28	113—116	1.8
TS	5.5	〃	0.5	None	18	60	72	112—115	3.3
PS	3.5	BF_3OEt_2	0.8[c]	Toluene 10	1	25	69	80—83	2.7
PO	5.3	〃	0.5[c]	Toluene 10	1	25	26	Viscous oil	—
TS	5.5	〃	0.5[c]	Toluene 10	1	25	70[a]	220—225	0.45[b]
TS	5.5	〃	0.1[c]	Toluene 10	1	25	40	135—138	3.0

[a] Poly(hydroxystyrene).
[b] $[\eta]$, dl g^{-1} at 30°C in DMF ($[\eta]^{\text{acetone}}_{30°C}$=0.50 dl g^{-1}). Refer to M. Kato, *J. Polym. Sci., A-1*, **7**, 2405 (1969).[12]
[c] mol% based on monomer.

25°C under an atmosphere of nitrogen. The contents were treated in almost the same way as in the free radical polymerization. Yield 0.35 g (26.0%).

Copolymerization. 1.36 g (5.3 mmol) of PO, 0.55 g (5.3 mmol) of styrene (ST), 4.0 ml of toluene and 20.0 mg of AIBN were put into an ampoule under an atmosphere of nitrogen (see Table II). The ampoule was sealed according to the procedure employed in the free radical polymerization. Copolymerization

Table II. Copolymerization of PS, PO, and TS with MMA, ST, Manh and MA at 60°C[a]

Monomer molar ratio	AIBN based on monomer	Polymerization time	Polymer yield	T_m	$M_n \times 10^{-3}$
	wt%	h	%	°C	
PS/MMA=1[b]	1.5	15	97	112—115	1.2
PS/ST=1[b]	1.5	15	97	110—115	5.2
PS/Manh=1[b]	0.4	3	48	168—175	0.68[e]
PS/MA=1[b]	0.4	10	76	87—93	1.8
PO/MMA=1[c]	1.1	8	73	110—115	1.2
PO/ST=1[c]	1.1	8	62	115—118	3.2
PO/Manh=1[c]	0.5	3	57	163—172	0.52[e]
PO/MA=1[c]	0.6	10	42	96—110	2.2
TS/MMA=1[d]	0.3	17	46	158—162	2.0
TS/ST=1[d]	0.3	50	25	145—150	4.0

[a] Solvent, toluene, 4 ml.
[b] Total monomer, 7.0 mmol.
[c] Total monomer, 10.6 mmol.
[d] Total monomer, 11.0 mmol.
[e] $[\eta]$, dl g^{-1} at 30°C in DMF.

and isolation of copolymer were carried out by a procedure similar to that of free radical polymerization. Yield 1.18 g (62.0%).

Measurements

The NMR spectrum was measured by a 60 MHz JNM-PMX60 NMR spectrometer at 35°C. The IR spectrum was taken with a HITACHI-EPI-S2 type spectrometer. Molecular weights were determined on a Hitachi Perkin-Elmer 115 vapor pressure osmometer. The intrinsic viscosity of the polymer was measured in a dimethylformamide solution by an Ubbelohde-type viscometer at 30 ± 0.05°C.

Flame Resistance

The flame resistance was evaluated by a modification of JIS K6705-1972. Test polymer pieces (10 mm × 10 mm × 10 mm) were prepared by casting of molten polymers followed by cooling. It was pierced with a hole of 1.6 mm in diameter at the center of the face. An electric wire of 1.4 mm in diameter was passed through the hole, and was maintained horizontally. An electric current was turned on, and the electric power of consumption was maintained at 70 W per 100 mm length and continued for ten minutes, and then stopped. After the electric current was turned on, the time until the polymer was ignited and the flame-continuing time after stopping the current were measured.

RESULTS AND DISCUSSION

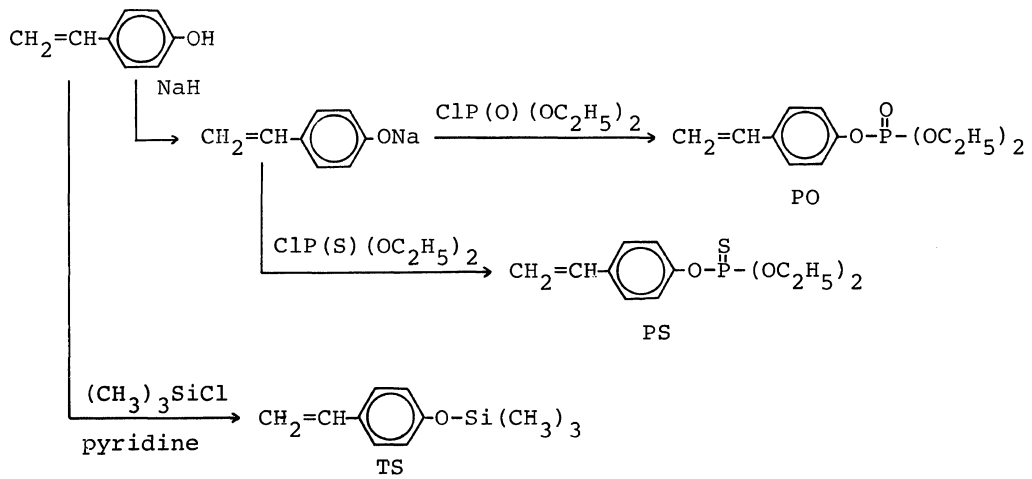
Synthesis of Monomers

Monomers were synthesized by the following steps (Scheme **I**).

Dry conditions were necessary, because *p*-vinylphenol is reactive to give poly(hydroxystyrene) with a trace of acid. The Crude yield was essentially quantitative by the NMR method, although the isolated yield was sometimes considerably low as described in the experimental part because of losses incured during the distillation necessary for obtaining a pure product.

Free Radical and Cationic Homopolymerization

The polymerization conditions and the results of the polymerization are summarized in Table I. The polymerization of PO, PS or TS was carried out in solution or in bulk. Glassy and transparent polymers were obtained. The molecular weight of polymer was independent of the polymerization conditions and was not so high in either the free radical or the cationic polymerization. This was due perhaps to the presence of inhibiting groups such as a trace of *p*-vinylphenol or sulfur group in the monomer. It is well known that some sulfur-containing compounds inhibit a peroxide-catalyzed polymerization. However, the molecular weight of polymers derived from radical polymerization was a little high in comparison with that of polymers cationically polymerized.



Scheme **I**

In the cationic polymerization of TS, the product was varied with the concentration of BF_3OEt_2. At a high catalyst concentration, poly(hydroxystyrene) was produced by the hydrolysis of oxygen–silicon bond with acid. By using less than 0.1 mol% of BF_3OEt_2 based on TS, poly(TS) was obtained.

Copolymerization

Copolymerization conditions and the results of the polymerization are listed in Table II. Copolymerizations of PS, PO or TS with MMA, ST, Manh or MA were carried out using AIBN as an initiator. Transparent and colorless copolymers were produced in each case. Also, the molecular weights were not so high. However, the melting points of the copolymers were somewhat higher than those of homopolymers. The rate of copolymerization for PO or PS with Manh appeared significantly faster than that for PO or PS with MMA, ST or MA. The molecular weight of PO–Manh or PS–Manh copolymer was fairly high. From these results, it was found that PO or PS have high copolymerizability.

The relationship between the monomer and copolymer composition is indicated in Figures 3—5. The copolymer yield was kept below 10% in each case. The copolymer compositions were calculated from the results of NMR spectrum and the elementary analysis. Alternating copolymers were obtained in the copolymerization of PO or PS with Manh. The alternating tendency of PO or PS is greater in copolymerization with MMA than in that with ST, as expected. The monomer reactivity ratios evaluated by the Fineman–Ross method and Q-e values proposed by Alfrey and Price are shown in Table III.

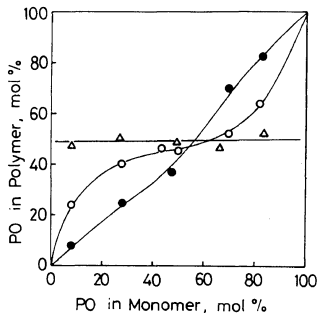


Figure 3. Copolymer compositions of PO in relation to monomer composition at 60°C: ○, PO–MMA; ●, PO–ST; △, PO–Manh; total feed monomer, 1 mmol ml^{-1} in toluene; AIBN, 0.1 mol% with respect to feed monomers.

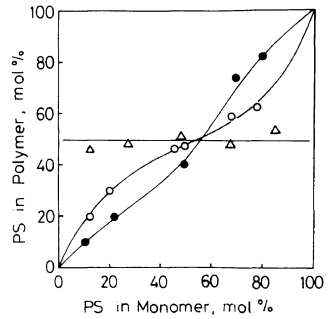


Figure 4. Copolymer compositions of PS in relation to monomer composition at 60°C: ○, PS–MMA; ●, PS–ST; △, PS–Manh; total feed monomer; 1 mmol ml^{-1} in toluene; AIBN, 0.1 mol% with respect to feed monomers.

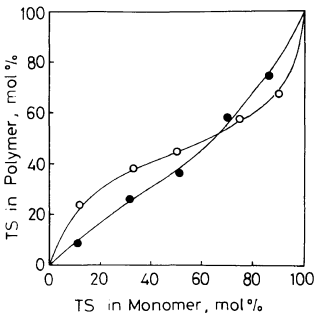


Figure 5. Copolymer compositions of TS in relation to monomer composition at 60°C: ○, TS–MMA; ●, TS–ST; total feed monomer, 1 mmol ml^{-1} in toluene; AIBN, 0.1 mol% with respect to feed monomers.

The e_1-value or the polarity factor of PO, PS or TS is more negative than it is for *p*-methoxystyrene (-1.11).[13] Among these values, the e_1-value for TS was rather close to that for *p*-methoxystyrene. It is generally accepted that styrene derivatives substituted with an electron-donating group in the *ortho* or *para* position have a more negative *e*-value than styrene itself and give an alternating copolymer with an electron-acceptor monomer such as Manh.

The resonance term Q_1 for PO or PS was higher than that for *p*-methoxystyrene (1.36). On the other hand, Q_1 for TS was somewhat smaller than that for *p*-methoxystyrene. However, the Q_1 value is influenced by the comonomer to a small extent.

Flame Resistance

Many polymers of organic phosphonates are of

Table III. Monomer reactivity ratios r_1, r_2, and Q–e values[a] for PS, PO, and TS at 60°C by AIBN in toluene

M_1	M_2	r_1	r_2	$r_1 \times r_2$	e_1	Q_1
PS	MMA	0.25	0.25	0.063	−1.26	1.50
	ST	1.15	1.10	1.27		
PO	MMA	0.20	0.20	0.04	−1.39	1.78
	ST	1.05	1.25	1.31		
TS	MMA	0.20	0.40	0.08	−1.19	0.98
	ST	0.55	1.50	0.83	−1.23	0.93

[a] ST, $e=0.80$, $Q=1.00$; MMA, $e=0.40$, $Q=0.74$. Refer to G. E. Ham, Ed., "Copolymerization," Interscience, New York, N.Y., 1964.

the self-extinguishing type. It has been assumed that this high flame resistance is due to the presence of the phosphorus atom. Table IV lists the flame resistance evaluated by the JIS K6705-1972 method for a simple mixture of PO or PS polymer and polyethylene or poly(methyl methacrylate), and copolymers of PO or PS with MMA, MA or ST, along with the calculated values for the phsophorus contents of polymers.

It is obvious from these data that flame resistance is more effective in the polymers containing phosphorus–oxygen than phosphorus–sulfur, while the flame was soon extinguished in the PS type copolymers and the flame was not widely extended by electrical reheating. Polymers containing phosphorus–oxygen were not burnt and were chared independent of such conditions as simple blend or copolymers. Also, there was no direct correlation-

Table IV. Flame resistance[a]

Sample[b]	Ignition delay time[c] / s	Flame-continuing[d] time / s	P / wt%
Poly(MMA)	20	120	0
Copoly(PS–MMA)	50	Soon extinguished	5
Copoly(PO–MMA)	No ignition	Charred	5
Poly(MA)	17	120	0
Copoly(PS–MA)	80	Soon extinguished	4
Copoly(PO–MA)	No ignition	Charred	4
Poly(ST)	48	120	0
Copoly(PS–ST)	80	Soon extinguished	4
Copoly(PS–ST)	No ignition	Charred	4
Poly(E)	30	150	0
Poly(PS)+Poly(E)	No ignition	Charred	1
Poly(PO)+Poly(E)	No ignition	Charred	1
Poly(PS)+Poly(MMA)	No ignition	Charred	1
Poly(PO)+Poly(MMA)	No ignition	Charred	1

[a] The flame resistance was evaluated by the modification of JIS K6705-1972.
[b] Poly(MMA), poly(methyl methacrylate); Poly(MA), poly(methyl acrylate); Poly(ST), polystyrene; Poly(E), polyethylene.
[c] The time until the polymer was ignited.
[d] The flame-continuing time after stopping the current.

ship between the phosphorus content and flame resistance as reported previously.[8,9] However, it is noteworthy that the flame resistance of simple blend of polyethylene or poly(methyl methacrylate) with homopolymer of PO or PS seems to be slightly higher than that of copolymers, indicating that an aggregate state of the phosphorus groups may induce a high flame resistance.

Consequently, mixtures of phosphorus-containing homopolymer and the flammable polymer are excellent from the point of flame resistance, but the phosphorus-containing copolymers have a miscibility with the flammable polymers and show superiority in processability for a polymer blend.

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