Preparations and Chelation Properties of Ethyl-(p-vinylphenyl)-phosphoric-Acid or Ethyl-(p-vinylphenyl)thiophosphoric-Acid Polymer and Copolymer

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ABSTRACT: Ethyl-(p-vinylphenyl) phosphorochloridate (POC1) and ethyl-(p-vinylphenyl) thiophosphorochloridate (PSC1) were readily synthesized from sodium p-vinylphenoxide and ethyl phosphorodichloridate or ethyl thiophosphorodichloridate. These were polymerized and copolymerized with MMA, ST or Manh to produce glassy and transparent polymers. The system of POC1-Manh and PSC1-Manh gave alternating copolymers. Ethyl-phenylphosphoric-acid and ethyl-phenylthiophosphoric-acid polymers were prepared by the alkaline hydrolysis of monochloridate polymer with a 2% sodium hydroxide solution at 70°C for 3 h. The binding ability of phosphoric acid polymers with heavy-metal ion such as Hg^{2+}, UO_2^{2+}, Cu^{2+}, Fe^{3+} or Ca^{2+} was evaluated by the equilibrium dialysis method. The order of the equilibrium constant of homopolymer (POH or PSH) was slightly greater than that of copolymers, due perhaps to the neighbouring effect of the carboxylic acid group in the copolymer.
    KEY WORDS   Ethyl-(p-vinylphenyl) Phosphorochloridate / Ethyl-(p-vinylphenyl) Thiophosphorochloridate / Phosphorochloridate Monomer / Radical Polymerization / Alternating Copolymerization / Hydrolysis of Phosphorochloridate Polymer / Polymer of Ethyl-phenylphosphoric Acid / Binding Ability of Polymer / Heavy-Metal Ion / Equilibrium Dialysis /

It is well known that organic phosphoric-acid derivatives are widely used as effective extracting agents[1-5] of metal ions. Much work has been done on monomeric chelates, but papers have also been published concerning the phosphoric-acid-type polymeric ligands, such as the phosphoric acid polymer prepared by the phosphorylation of the chloromethylated polystyrene[6] or of the chlorinated polyethylene.[7] Many of the workers in the field of polymeric chelating compounds are interested in the synthesis and the chelating ability of the resins by means of exchange capacity, but not by the equilibrium constant.

If a water-soluble polymer could be produced, it would be useful as a metal precipitant in a range of parts per billion of metal ions. The purpose of the present study is to develop a metal precipitant from these water-soluble polymers. This paper deals with

the synthesis of phosphorochloridate and thiophosphorochloridate monomers, and their polymerization and copolymerization characteristics, and the alkaline hydrolysis of monochloridate polymer to give the phosphoric-acid and thiophosphoric-acid polymer. Finally, the binding ability of phosphoric-acid polymers with heavy-metal ions such as Hg^{2+}, UO_2^{2+}, Fe^{3+} and Ca^{2+} was investigated.

EXPERIMENTAL

Ethyl-(p-vinylphenyl) Phosphorochloridate (POCl)
    30.0 g (0.25 mol) of p-hydroxystyrene, prepared from dehydrogenation of p-ethylphenol and then recrystallized from hexane (mp 71—72°C[8]), in 100 ml of dry ether, was added dropwise with stirring to the suspension of sodium hydride 6.0 g (0.25 mol) in 100 ml of dry ether. Then the mixture was stirred at room temperature for another 1 h. The suspension of sodium p-vinylphenoxide thus obtained was added slowly to a solution of ethyl phosphorodichlo-

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ridate 40.8 g (0.25 mol) in 150 ml of dry ether with stirring at 0°C. The total content of the mixture was stirred for 5 h at this temperature to ensure a complete reaction. The solution was then filtered, dried (Na$_2$SO$_4$), and the mixture was evapolated *in vacuo*. The residue was distilled at 88—91°C (0.01 mmHg, giving ethyl-(*p*-vinylphenyl) phosphorochloridate (POCl) 19.1 g (31.0% yield) as a colorless liquid. (Found: C, 48.68%; H, 4.87%. Calcd: C, 48.56%; H, 4.63%.) The IR spectrum of POCl (liquid film) is shown in Figure 1. It was found that

there are absorptions due to vinyl group at 1610 cm^{-1}, two absorptions due to P–O–aryl at 1210, 1150 cm^{-1}, two absorptions due to P–O–alkyl at 1150, 1035 cm^{-1}, and an absorption due to P=O at 1280 cm^{-1}. The NMR spectrum (CDCl$_3$) of POCl is illustrated in Figure 2 and exhibited triplet signal due to three protons of the methyl group of –O–CH$_2$CH$_3$ at δ 1.40 ppm ($J=7$ Hz), a double quartet signal[9] due to two protons of the methylene group of –O–CH$_2$CH$_3$ at δ 4.3 ppm ($J=7$ Hz), three double doublet signals due to three protons of the vinyl group at
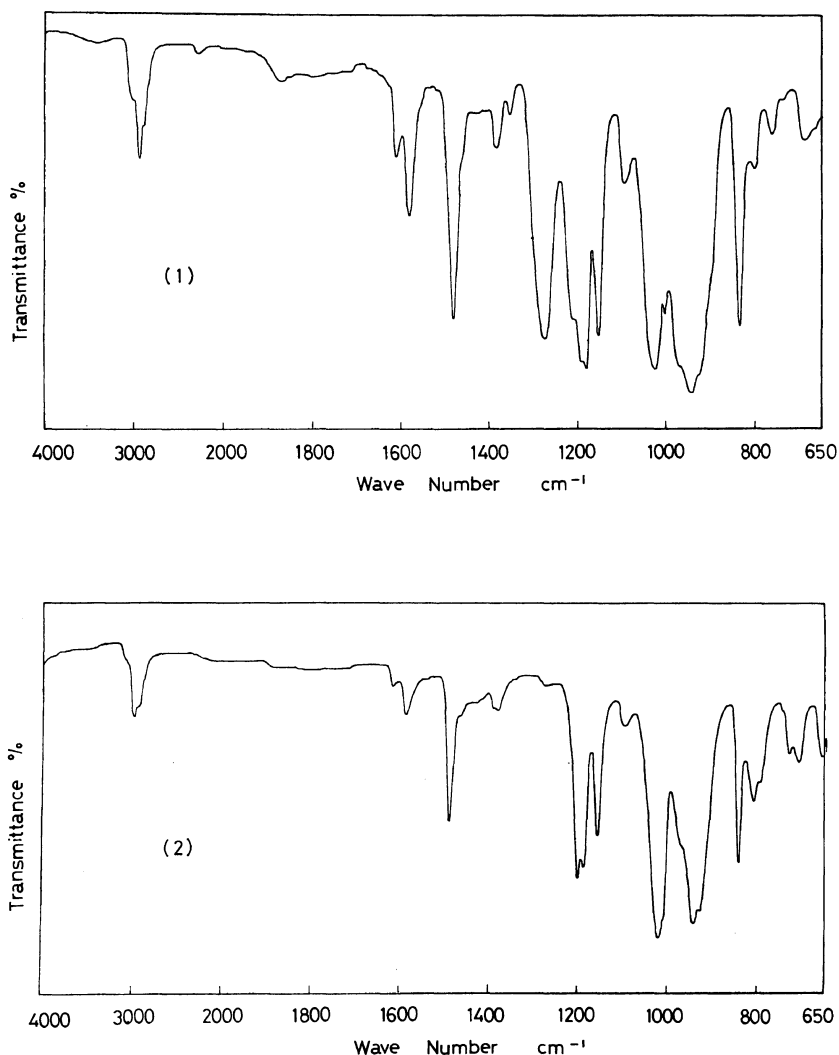

Figure 1. Infrared spectra of monomer: (1), ethyl-(*p*-vinylphenyl) phosphorochloridate (POCl); (2), ethyl-(*p*-vinylphenyl) thiophosphorochloridate (PSCl).
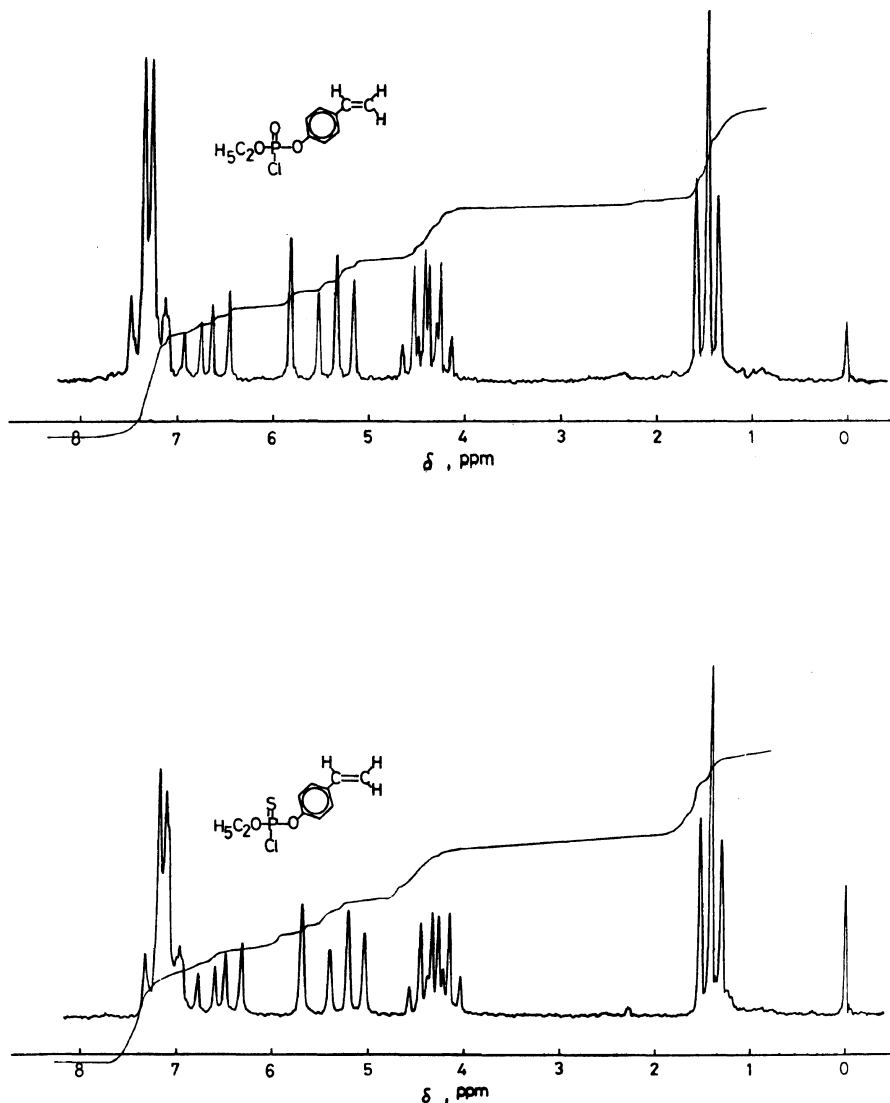
Figure 2. NMR spectra of monomer in CDCl$_3$.

δ 5.13 ($J=11$ Hz), 5.63 ($J=17.5$ Hz), and 6.7 ppm ($J=11$ Hz), respectively, and an AB quartet signal due to four protons of aromatic group at δ 7.2 ppm ($J=8$ Hz).

Ethyl-(p-vinylphenyl) Thiophosphorochloridate (PSCl)

The suspension of sodium p-vinylphenoxide prepared as described above from p-vinylphenol 30.0 g (0.25 mol) and sodium hydride 6.0 g (0.25 mol) in 150 ml of dry ether was added slowly with stirring to

44.7 g (0.25 mol) of ethyl thiophosphorodichloridate in 100 ml of dry ether at 0°C. The mixture was stirred at room temperature for another 5 h, then worked up as described for POCl. The residue was distilled at 93—94°C (0.01 mmHg), giving ethyl-(p-vinylphenyl) thiophosphorochloridate (PSCl) 27.6 g (42.0% yield) as a colorless liquid. (Found: C, 45.72%; H, 4.75%. Calcd: C, 45.30%; H, 4.23%.) The IR spectrum of PSCl (liquid film) is shown in Figure 1. Similar spectral data as detailed in POCl were obtained for PSCl, and showed absorptions at 1610 (vinyl group),

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1190, 1160 (–P–O–aryl), 710 (P=S), 840 (aromatic ring), 1160, and 1020, (P–O–alkyl) cm^{-1}. The NMR spectrum (CDCl$_3$) exhibited similar spectral data to those described in POCl except for a small difference in chemical shift (Figure 2).

Materials

Toluene, used as the solvent, was purified in the usual manner. Styrene (ST) and methyl methacrylate (MMA) were purified by distillation under a nitrogen atmosphere just before use. Maleic anhydride (Manh) was used without further purification.

Homopolymerization

Most of the results of polymerization are summarized in Tables. Some typical runs are described below. 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 1.18 g (4.8 mmol) of POCl and 1.5 ml of toluene were introduced into it. The glass ampoule was dipped into a bath cooled at −78°C, and was then sealed. Polymerization was carried out at 60°C. After 5 h, the ampoule was taken out, cooled, and opened. The content of the ampoule was poured into a large excess of ethyl ether. The coagulated polymer was washed with a large amount of ethyl ether or hexane, dried *in vacuo* and then weighed. Yield 0.53 g (45.0%) (see Table I).

Copolymerization

1.18 g (4.8 mmol) of POCl, 0.50 g (4.8 mmol) of styrene (ST), 2.0 ml of toluene, and 10 mg of AIBN were put into an ampoule under an atmosphere of pure nitrogen. The ampoule was sealed. Polymerization and the isolation of polymer were carried out by a procedure similar to that for homopolymerization. Yield 0.77 g (45.8%) (see Table II).

Hydrolysis of Polymer

The polymers and copolymers containing phosphoric acid diester were prepared by the hydrolysis of phosphorochloridate polymers and copolymers at 70°C for 3 h in a sealed test tube

Table I. Polymerization of POCl or PSCl at 60°C

Monomer		Initiator based on monomer	Solvent	Polymerization time	Polymer yield	$[\eta]_{30°C}^{DMF}$
mmol		wt%	ml	h	%	dl g^{-1}
POCl	4.8	AIBN 0.8	Toluene, 1.5	5	45.0	0.32
POCl	4.8	AIBN 0.8	None	3	53.0	0.26
PSCl	4.8	AIBN 0.8	Toluene, 1.5	5	32.0	0.25
PSCl	4.8	AIBN 0.8	None	3	62.0	0.21

Table II. Copolymerization of POCl or PSCl with MMA, ST or Manh at 60°C[a]

Monomer[b] molar ratio	AIBN based on monomer	Polymerization time	Polymer yield	$[\eta]_{30°C}^{DMF}$
	wt%	h	%	dl g^{-1}
POCl/MMA = 1	0.6	5	61.9	0.30
POCl/ST = 1	0.6	5	45.8	0.27
POCl/Manh = 1	0.3	0.2	49.7	2.38
PSCl/MMA = 1	0.6	5	32.3	0.33
PSCl/ST = 1	0.6	5	50.3	0.21
PSCl/Manh = 1	0.6	0.5	38.0	2.16

[a] Solvent, toluene 2 ml.
[b] Total monomer, 9.6 mmol.

containing about 0.5 g of polymer, 10 ml of tetrahydrofuran (THF), and 10 ml of a 2% aqueous sodium hydroxide solution under a nitrogen atmosphere. In the preparation of POH–Manh or PSH–Manh, hydrolysis was carried out in a 2% aqueous sodium hydroxide solution without THF. Abbreviations for the polymers are given as follows (Scheme I).

After the reaction, the solution was passaged repeatedly through a column containing the cation-exchange resin (Amberlite IR-120B H type). The

Poly(POCl): X = O   POH: X = O
Poly(PSCl): X = S   PSH: X = S

Poly(POCl–Manh): X = O   POH–Manh: X = O
Poly(PSCl–Manh): X = S   PSH–Manh: X = S

Poly(POCl–MMA): X = O   POH–MMA: X = O
Poly(PSCl–MMA): X = S   PSH–MMA: X = S

Poly(POCl–ST): X = O   POH–ST: X = O
Poly(PSCl–ST): X = S   PSH–ST: X = S
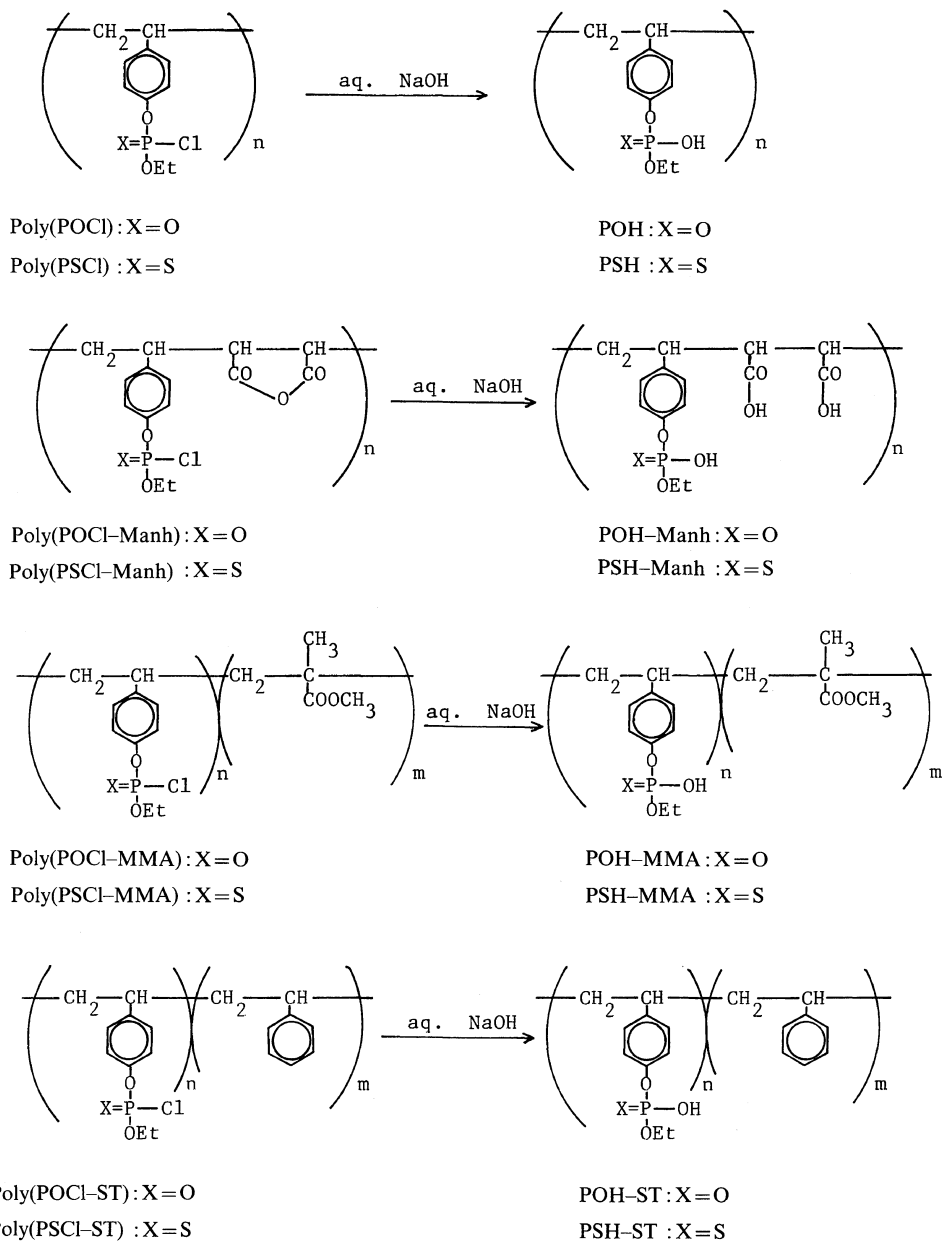
Scheme I

hydrolyzed products were precipitated by the addition of a large excess of a methanol–ethyl ether (1 : 3) mixture. The polymer precipitated was coagulated, washed with ethyl ether and then dried under reduced pressure at room temperature. The extent of hydrolysis was determined on the basis of elementary analysis of the product.

Characterization of the Polymers

The composition of the polymers was determined by elementary analysis and NMR spectra. The NMR spectrum was obtained by a 60 MHz JNM-PMX60 NMR spectrometer. The IR spectra were recorded on a HITACHI-EPI-S2-type spectrometer in a KBr disk form. The potentiometric titration of the polymers or copolymers solution was carried out by a TOA-pH meter model HM-5B, titrating the aqueous sodium hydroxide solution containing polymer with 0.01 N aqueous hydrogen chloride solution. The intrinsic viscosity of polymer was measured in a dimethylformamide solution by an Ubbelohde-type viscometer at $30 \pm 0.05°C$.

Binding of Heavy-Metal Ions with Polymers

The equilibrium dialysis method was employed to evaluate the binding ability of the heavy-metal ion with the polymer. Polymers used were initially purified by dialysis through distilled water for 3 days. A visking cellulose tube (21 mm in the diameter) was thoroughly washed with distilled water for 24 h. Commercial G.R. grade mercuric chloride, cupric nitrate, calcium chloride, ferric chloride, and uranyl nitrate were used as heavy-metal ions, and potassium chloride and sodium nitrate as supporting electrolytes. The cellulose tube containing 5 ml of buffer solution of polymer $(3 \times 10^{-3} \, mol \, l^{-1})$ was placed in a glass vessel containing 25 ml of buffer solution of heavy-metal ion. The glass vessel was maintained at 20°C for 7 days with occasional agitation. Seven days were sufficient to attain equilibrium. After this, the dialysis tube was removed from the glass vessel, and then the total concentration of heavy-metal ion inside the tube and in the glass vessel was determined by the following methods using a JAPAN SPECTROSCOPIC-UVIDEC-505 UV spectrophotometer.

Mercury   dithizone–carbon   tetrachloride   at 490 nm

Copper   oxine–chloroform at 410 nm

Iron   oxine-chloroform at 470 nm

Uranyl   arsonaso III at 655 nm

The concentration of calcium ion was determined by titration with 0.01 N aqueous EDTA solution using 2-hydroxyl-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid (NN) as the indicator.

RESULTS AND DISCUSSION

Preparation of Monomers

Ethyl-(p-vinylphenyl)   phosphorochloridate (POCl) or ethyl-(p-vinylphenyl) thiophosphorochloridate (PSCl) was prepared by the addition of ethyl phosphorodichloridate or ethyl thiophosphorodichloridate to sodium p-vinylphenoxide in dry ether. The crude yields were relatively high, although isolated yields were considerably lower as described in the experimental part, because of losses incured during the distillation necessary to obtain a pure product (Scheme **II**).

Polymerization and Copolymerization

The polymerization conditions and the results are listed in Table I. Glassy and colorless polymers were obtained. The purification of polymers were carried out in dry ether or hexane to avoid solvolysis of poly(POCl) or poly(PSCl). The molecular weight of the POCl or PSCl polymer seems relatively lower. This may be due to the purification method used for the monomers, which might have contained a trace of p-vinylphenol not removable by distillation. The polymer obtained was soluble in common organic solvents, such as benzene and chloroform, and softened at temperatures below the range, 87—103°C. The IR and NMR spectra of polymers were broader than those of monomers and disappeared the absorptions due to the vinyl group.

Table II shows the copolymerization conditions and the results of POCl or PSCl with MMA, ST or Manh. The molecular weight was rather low. The resulting copolymer was soluble in $CHCl_3$, acetone, and in common organic solvents.

The copolymerization for POCl or PSCl with Manh appeared to be significantly faster than that for POCl or PSCl with MMA or ST. The molecular weight of POCl–Manh or PSCl–Manh copolymer was fairly high. From these results, it was found that POCl and PSCl have the high copolymerizability.

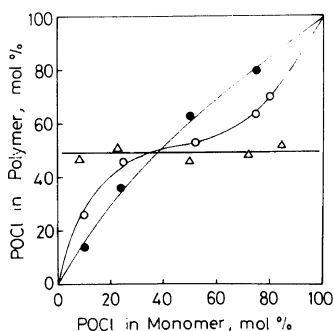Figures 3 and 4 illustrate the copolymer com-
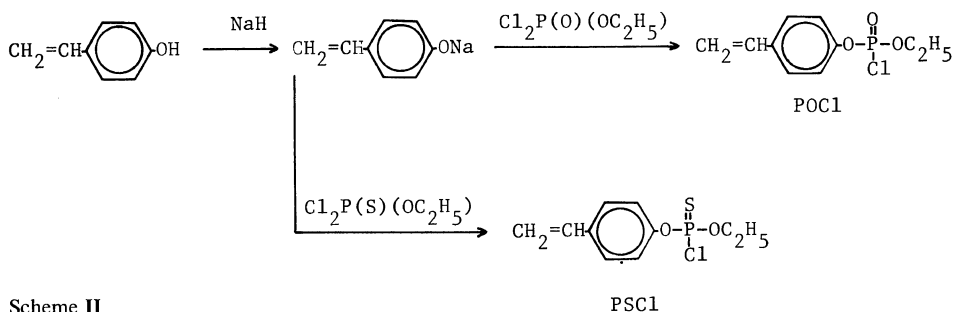
Scheme II

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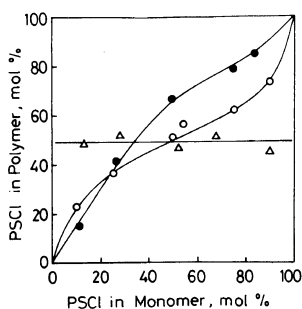

Figure 4. Copolymer composition of PSCl in relation to monomer composition at 60°C: ○, PSCl–MMA; ●, PSCl–ST; △, PSCl–Manh; total feed monomer, 1 mmol ml^{-1} in toluene; AIBN, 0.1 mol% with respect to feed monomers.

position curve in toluene at 60°C in which the ratio of maleic anhydride, MMA or ST to POCl or PSCl varied from 10/90 to 90/10 (mol/mol). The copolymer yield was below 10% in each case. The copolymer compositions were calculated from the results of the elementary analysis and NMR spectrum. The alternating tendency is thus greater in MMA than in ST, as expected. In the copolymerization of POCl or PSCl with Manh, the resulting copolymers contain both monomer components in equimolar portion, suggesting that the copolymers possess a highly alternating sequence.

According to the Fineman–Ross method, the monomer reactivity ratiors r_1 and r_2, of MMA or ST and POCl were calculated to be 0.25 and 1.30, 0.20, and 0.75, respectively. Similarly, r_1 and r_2 of MMA or ST and PSCl were 0.20 and 1.1, 0.30, and 0.65, respectively.

Hydrolysis of Polymers

The preparation of poly[ethyl-(p-vinylphenyl)-phosphoric acid] (POH), poly[ethyl-(p-vinylphenyl)phosphorothioic acid] (PSH), copolymers POH–Manh or PSH–Manh, PSH–MMA or PSH–ST was carried out by alkaline hydrolysis. The degree of hydrolysis was found to be about 85—95% under the condition that the copolymers are treated with a 2% aqueous sodium hydroxide solution at 70°C for 3 h. The extent of hydrolysis is estimated from the molar ratio of carbon, nitrogen, and chlorine. The alkaline hydrolysis under conditions (10% aqueous NaOH soln) more severe than the above is unfavorable since hydroxide ions also attack POH or PSH at phosphorus atoms, producing poly-(hydroxystyrene). The infrared spectra of POH or PSH show the characteristic absorption band assignable to –P–OH of phosphoric acid at 2000—2800 cm^{-1}. Similarly, the absorption due to –P–OH of the copolymer POH–MMA or PSH–MMA, PSH–ST, PSH–Manh show broad absorption at 2000—2800 cm^{-1} (Figure 5). The hydrolyzed polymer or copolymer was soluble in DMSO or aqueous sodium hydroxide solution for a short time. How-
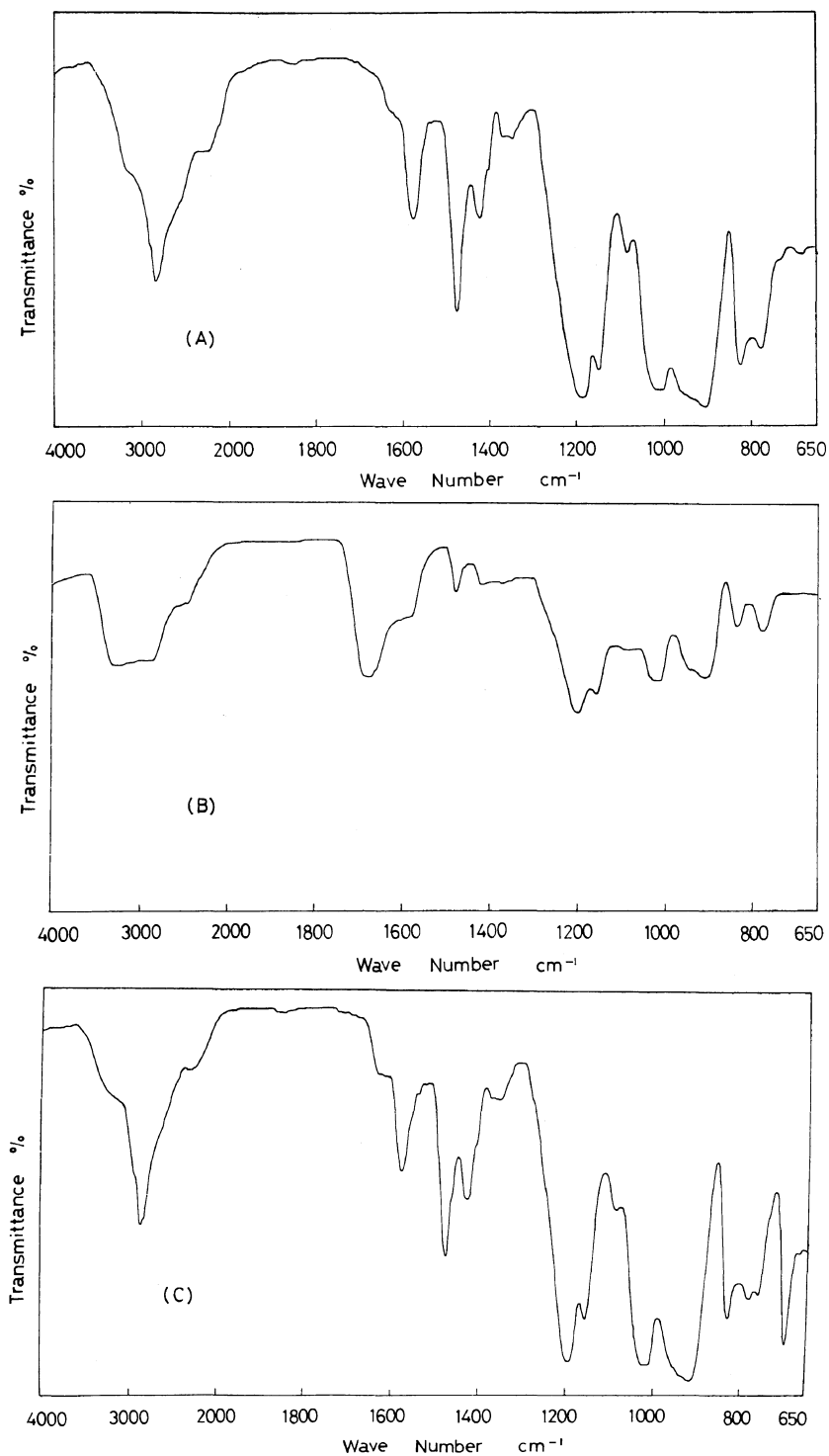
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Figure 5. Infrared spectra of hydrolyzed polymer: (A), PSH; (B), PSH–Manh; (C), PSH–ST. Hydrolysis products prepared by hydrolysis of monochloridate polymer in a 2% aqueous sodium hydroxide solution at 70°C for 3 h.

ever, after standing to dryness *in vacuo*, these gradually becoming insoluble even in an aqueous hydroxide solution. These results show that perhaps gellation is achieved by condensing the phosphoric acid.

Binding of Heavy Metal Ions with Phosphoric Acid Polymers

The equilibrium constant can be determined precisely.[10,11] Here, the authors estimated the equilibrium constant K by the equation,

$$K = [\text{metal ion}]_{\text{bound}} / [\text{metal ion}]_{\text{outside}} [P]^n_{\text{free}}$$

where $[P]_{\text{free}}$ is the concentration of non-bounded polymer with metal ion, n means the number of monomeric units bounded with one metal ion. The $[P]^n_{\text{free}}$ is a function of the following equation.

$$[P]_{\text{free}} = [P] - [\text{metal ion}]_{\text{bound}} / n$$

The $[P]$ is the initial concentration of the monomeric unit of the polymer in mol l^{-1}. The number of n is one for Hg^{2+} and UO_2^{2+}. However, the K-values summarized in Table III are calculated to be $n = 2$. In the case of Fe^{3+} at pH 3—5, Fe^{3+} may change to a hydroxo-complex, suggesting uncertainty of the K-value. The equilibrium constants thus calculated are summarized in Table III. The order of the equilibrium constant of polymers was somewhat smaller than that of the low-molecular dialkyl-phosphoric acid or dialkyl-phosphorothioic acid.[5,12]

The dialkyl-phosphorothioic acid exhibits tautomeric equilibrium, *i.e.*, thiono form and thiol one.[6] The reaction of phosphorothioic acid with a metal ion of high electron-affinity is expected to produce complexes by a coordination through sulfur, and accordingly differs greatly from phosphoric acid.[5,13] However, no great difference could be observed in the present system. The stability constant of PSH for Hg^{2+} was a little greater than that of POH. The reverse tendency was observed for Cu^{2+}. These results might be explained by the softness of metal and ligand.

Table III also shows the neighbouring effect on the chelation. Previously, the authors found that the complex formation between carboxylic acid and copper (II) is promoted by a neighbouring substituted group such as the ether group or the thioether group on the main chain.[14] This fact suggests that perhaps the stabilization of the complex is due to the chelation of the neighbouring

Table III. Equilibrium constant of metal ion with diester of phosphoric-acid polymer at 20°C

Metal ion	pH	Supporting electrolyte	Equilibrium constant, K^a mol l^{-1}					
			POH	PSH	POH–Manh	PSH–Manh	PSH–MMA	PSH–ST
Hg^{2+}	4	1 M KCl	5×10^5	7×10^6	4×10^5	2×10^6	1×10^6	2×10^7
	7		5×10^5	2×10^6	3×10^5			
	9		6×10^5	3×10^6	4×10^5			
UO_2^+	3	1 M NaNO$_3$	5×10^7	2×10^8	6×10^6	3×10^6	2×10^6	7×10^6
	5.5		8×10^7	3×10^8	7×10^6			
Cu^{2+}	4	1 M KCl	7×10^5	4×10^4	5×10^5	4×10^5	1×10^5	4×10^5
Fe^{3+}	3	1 M KCl	8×10^8	3×10^8		2×10^8		
Ca^{2+}	4	1 M KCl	2×10^5	3×10^4				
	9		1×10^5	1×10^4				

^{a} The equilibrium constants K were calculated as the number of monomeric units which can be complexed with one metal ion is approximately 2 for polymer. The polymer and metal concentration were 3×10^{-3} and $(3-8) \times 10^{-3}$ mol l^{-1}, respectively.

group. However, the order of the equilibrium constant of homopolymers was slightly greater than that of copolymer for all metals employed except for Cu^{2+}, implying that there is no great effect on the chelation although the phosphoric-acid sequence is intercepted with MMA or ST. In the UO_2^{2+}, the constant of POH–Manh or PSH–Manh copolymer was 10^1—10^2 smaller than that of POH or PSH homopolymer. The reason for this phenomenon is not clear.

The maximum binding number of metals with the polymer was estimated from the limiting value of $\bar{\gamma}$ obtained at the highest concentration. This number was markedly influenced by the metal employed. The value $\bar{\gamma}$ of copper(II) with polymers was estimated to be about 0.5 with respect to the monomeric unit. The fact means that the number of phosphoric acid groups utilized for the complex formation with the metal ion may be limited to two with respect to the monomeric unit of polymers. The number of binding sites of copper(II) is limited to two. On the other hand, the value of Hg^{2+} with polymers was estimated to be about 1.0 with respect to the monomeric unit. This fact means that the number of phosphoric-acid groups utilized for a complex formation with the Hg^{2+} ion may be limited to one with respect to the monomeric unit of the polymers. A similar tendency was also observed for UO_2^{2+}. The following equation was reported for Zn^{2+} and dialkyl-phosphorothioic acid $(2HR + Zn^{2+} \rightleftharpoons ZnR_2 + 2H^+)$.[13] The reason why this phenomenon is

peculiar to Hg^{2+} or UO_2^{2+} with present system is not clear at the present. The authors can not say much about the structure of the complex of the polymer ligand and metal ions.

The K value summarized in Table III indicates the magnitude of the chelating capacity. However, the K value may be influenced by a competitive inhibition in the presence of different kinds of heavy-metal ions. The competitive inhibition was evaluated by the distribution ratio of a metal ion between the solution and the polymer as follows.

$$D = \frac{\text{Amount of metal on the polymer (mol l}^{-1})}{\text{Amount of metal in the solution (mol l}^{-1})}$$

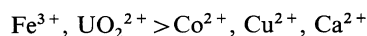The D value is summarized in Table IV.

In the mixture of Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, and UO_2^{2+} at pH 3, the order of the metal binding ability is as follows.

PSH–Manh copolymer,

$$Cu^{2+} > UO_2^{2+} > Ca^{2+}, Co^{2+} > Fe^{3+}$$

PSH polymer,

$$Fe^{3+}, UO_2^{2+} > Co^{2+}, Cu^{2+}, Ca^{2+}$$
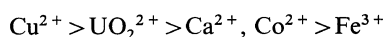
On the other hand, in the mixture of Ca^{2+}, Co^{2+}, Fe^{3+}, Cu^{2+}, and Hg^{2+} at pH 3, the order is as follows.

PSH–Manh copolymer,

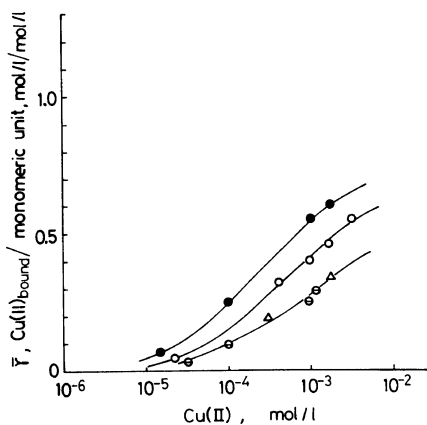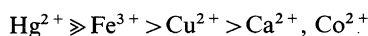$$Hg^{2+} \gg Fe^{3+} > Cu^{2+} > Ca^{2+}, Co^{2+}$$

Figure 6. Copper binding to the polymer measured by equilibrium dialysis at pH 5 and 25°C: ●, PSH; ○, PSH–Manh; ⊖, PSH–MMA; △, POH; polymer concentration, $(3.0—4.0) \times 10^{-3}$ mol l^{-1}; supporting electrolyte, 1 M NaNO$_3$.
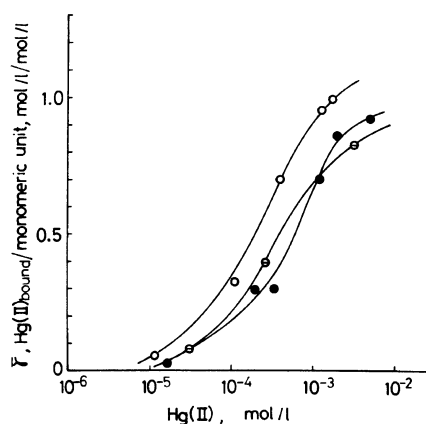
Figure 7. Mercury binding to the polymer measured by equilibrium dialysis at pH 5 and 25°C: ●, PSH; ○, PSH–Manh; ⊖, PSH–MMA; polymer concentration, $(3.0—4.0) \times 10^{-3}$ mol l^{-1}; supporting electrolyte, 1 M KCl.

Table IV. Distribution ratios of metal ions between an aqueous solution
and polymer at 20°C[a]

	Distribution ratios of metal ions D					
	PSH–Manh			PSH		
M^+	pH 3^b	pH 5^b	pH 3^c	pH 3^b	pH 3^b	pH 3^c
Ca^{2+}	1.1	0	0.8	0	5.0	5.8
Co^{2+}	0.9	0.3	0.5	0	5.2	4.3
Cu^{2+}	10.7	6.1	1.6	0	6.5	3.7
Fe^{3+}	0.3	0	2.9	4.0	—	3.5
UO_2^{2+}	6.0	2.0		3.4	2.0	
Hg^{2+}			33.0			22.0

[a] Values were determined by dialysis method for 25 ml of 1 M KCl solution containing about $(1—5) \times 10^{-4}$ mol l^{-1} of total metals. Polymer concentration was 3×10^{-3} mol l^{-1} determined by titration. The amount of metals bounded with polymer was determined by atomic absorption method except UO_2^{2+} measured by colorimetry.
[b] Equimolar mixture of metals Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, and UO_2^{2+} was used.
[c] Equimolar mixture of metals Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, and Hg^{2+} was used.

PSH polymer,

$$Hg^{2+} \gg Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}$$

The selectivity of PSH–Manh copolymer for Hg^{2+}, Cu^{2+}, and UO_2^{2+}, and that of PSH polymer for Hg^{2+}, Fe^{3+}, and UO_2^{2+} are predominant. Consequently, the PSH–Manh copolymer exhibited a high selectivity for Hg^{2+}. On the other hand, the D values at pH 3 and 5 show complicated phenomena and do not suggest a definite conclusion.

Finally, the ion Hg^{2+} or UO_2^{2+} in parts per billion concentration was dialyzed by the PSH–Manh copolymer solution $(3 \times 10^{-3}$ mol $l^{-1})$ at pH 5. However, on decreasing the concentration of metal ion, the amount of metal binding also decreased and 10% or 30% of the metal ion was chelated, respectively, indicating the insufficient chelating capacity of the present system and the slight difference between the low molecular weight of phosphoric-acid derivatives[12] and the phosphoric-acid group bound to polymer in regard to the capacity for chelating.

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