Table II
Triad Molar Fractions Calculated with the Best Values of K_1 and K_2 Compared with the Experimental Data

		A-centered triad			B-centered triad		
		F_{AAA}	$F_{\overline{AAB}}$	F_{BAB}	F_{ABA}	$F_{\overline{BBA}}$	F_{ABA}
$F_A = 0.60, K_1 = 6, K_2 = 6^a$	calcd	0.353	0.222	0.025	0.055	0.162	0.183
	exptl	0.32	0.22	0.06	0.08	0.17	0.15
$F_A = 0.75, K_1 = 8, K_2 = 0.2^b$	calcd	0.398	0.326	0.026	0.165	0.050	0.035
	exptl	0.42	0.28	0.05	0.15	0.07	0.03

[a] Acidic hydrolysis. [b] Basic hydrolysis.

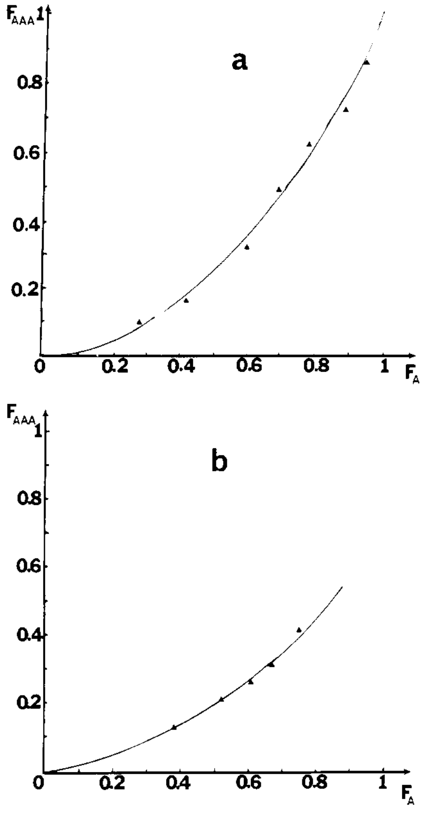


Figure 2. Curve-fitting procedure for determination of the relative rate constants K_1 and K_2 of hydrolysis. (a) Reaction in concentrated H_2SO_4: (▲) experimental points; (—) theoretical probabilities of triad AAA taking $K_1 = K_2 = 6$ (calculated with the SEQDIST program). (b) Reaction in 2-propanol/water/KOH mixture: (▲) experimental points; (—) theoretical probabilities of triad AAA taking $K_1 = 8$ and $K_2 = 0.2$ (calculated with the SEQDIST program).

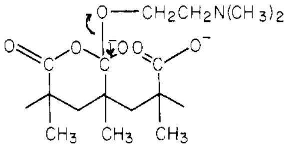
probabilities are shown in Table I (Figure 2). The theoretical values of the alternating character θ are also between 0.5 and 1.

The differences observed in the constants are due to the following:

(1) The conditions of the reactions were not chosen for a kinetic study. The purpose of these reactions was to prepare polyampholytes with different sequence distributions. In acidic medium as in basic medium, the reaction was first heterogeneous and then became homogeneous. This can modify the rate constants. The temperature was not kept absolutely constant.

(2) Klesper's procedure (modified) requires the B-centered triad data, which are less accurate due to the poorer resolution of the ^{13}C NMR pattern of the ester carbon. Table II gives an example for each kind of hydrolysis (acidic and basic) of the triad molar fractions calculated with the best values of K_1 and K_2 (from Table I), using the program SEQDIST, compared with the experimental data. The agreement is quite satisfactory, taking into account the errors due to the deconvolution method.

Scheme I



In conclusion, the activating effect of the neighboring carboxylic units is confirmed in acidic as well in basic media, as was determined in the past by kinetic studies of the hydrolysis of poly(MMA).[13] However, in the case of basic hydrolysis, the presence of two neighboring acid units (triad ABA) seems to slow down the hydrolysis of the ester unit, probably because the formation of the six-membered cyclic intermediate, as Morawetz et al.[14] have suggested, is more difficult due to the negative potential of the second ionized acid unit (Scheme I).

Acknowledgment. We cordially thank Mr. Alain Dupommier for rewriting Bauer's program into Basic and Professor Michel Thellier of the Université de Haute-Normandie for the use of the HP 9835 A computer.

Registry No. Poly(DMAEM), 25154-86-3.

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Preparation of Poly(styrene-*g*-phenyltrimethylenephosphine oxide) and Its Chelating Properties

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Received September 29, 1982

We recently reported that a five-membered deoxophostone (1) was polymerized by a cationic initiator via ring

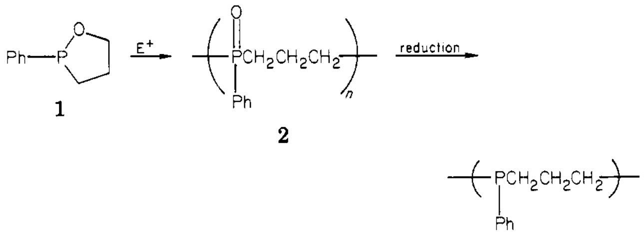
0024-9297/83/2216-1010$01.50/0

Table I
Graft Copolymerization of Deoxophostone 1 onto Halomethylated Polystyrene 4[a]

no.	X of 4	[1]/[-CH_2X]	solvent	temp, °C	time, h	conversion of 1, %	graft efficiency, %	length of graft chain (*n*)
1	Cl	24.1	none	130	31	74	23	4.1
2	Cl	24.3	PhCN	130	120	63	54	8.3
3	Cl	19.9	PhCl	*b*	*b*	65	72	9.4
4	Cl	19.4	toluene	*c*	*c*	83	65	10.5
5	Cl	7.6	xylene	150	120	94	90	6.5
6	I	25.0	$CHCl_3$	80	65	93	36	8.3

[a] Cross-linked with 3 molar % divinylbenzene; degree of halomethylation = 58.7%. [b] At 130 °C for 48 h and at 140 °C for 65 h. [c] At 130 °C for 63 h and at 140 °C for 62 h.

opening to give poly(phenyltrimethylenephosphine oxide) (2).[1] The reduction of 2 to poly(phenyltrimethylenephosphine) (3) has also been reported.[1,2] In the course

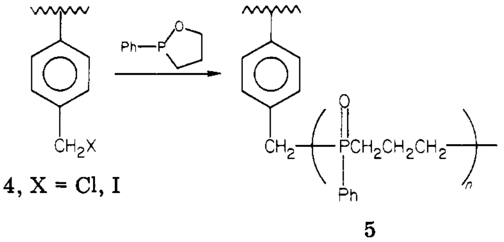


1

2

3

of studies on the cationic ring-opening polymerization of 1, it was found that benzyl chloride was an effective initiator.[3] These results suggest that chloro- or iodomethylated polystyrene (4) initiates the polymerization of 1 to give a graft copolymer (5). The present paper reports the synthesis of 5 and its chelating properties.



4, X = Cl, I

5

Results and Discussion

Graft Copolymerization. Macroporous-type cross-linked halomethylated polystyrene 4 was used to induce the polymerization of monomer 1 (Table I). The bulk reaction (no. 1) showed lower graft efficiency, giving rise to the homopolymer of 1 due to chain-transfer reactions. In the reactions using a solvent (no. 2–5) less polar solvents such as chlorobenzene, toluene, and xylene showed better results, i.e., a higher conversion of 1 and a higher graft efficiency. The graft copolymerization using iodomethylated polystyrene in chloroform at a lower temperature of 80 °C (no. 6) gave the copolymer in a lower yield.

The product copolymer of poly(styrene-*g*-phenyltrimethylenephosphine oxide) (5) is a white beadlike resin showing an IR band at 1145 cm^{-1} due to $\nu_{P=O}$ (KBr).

Chelating Properties of Graft Copolymer 5. One possible application of copolymer 5 is utilization as a chelating resin, probably for "bed-type" use. Five heavy-metal ions were examined for the adsorption with 5 (sample polymer no. 5) under various conditions (Table II). The contact period was established as 72 h in Table II, which was determined on the basis of the following observations. Under similar conditions for the 3 N HNO_3 system, adsorption of UO_2^{2+} was 77% for 4 h, 85% for 8 h, 98% for 48 h, and 98% for 72 h, suggesting that 72 h is a sufficient period to adsorb the metal ions. Under strong and slightly acidic conditions, UO_2^{2+} and Th^{4+} were adsorbed very efficiently with 5. Hg^{2+} and Cu^{2+} were adsorbed more in less acidic or in weak basic conditions. With Pd^{2+} systems, Pd^{2+} was soluble in solutions of 3 N HNO_3, pH 1 and pH 8, but insoluble at pH 4 and pH 6 and was adsorbed more under acidic conditions.

Table II
Adsorption of Heavy-Metal Ions with Copolymer 5[a]

	amt of adsorbed metal ions,[c] %				
conditions[b]	UO_2^{2+}	Th^{4+}	Hg^{2+}	Pd^{2+}	Cu^{2+}
3 N HNO_3	93	98	45	~100	~0
pH 1	92	21[d]	~100	~100	~0
pH 4	97	99	98		10
pH 6	98 (88)[e]	66	95		34
pH 8	55	8	98	53	84

[a] 50 mg of copolymer 5 (sample no. 5) containing 2.5 × 10^{-4} mol of phosphine oxide unit in 1 mL of a metal ion aqueous solution (1 × 10^{-4} mol/L). The period of the contact was 72 h at room temperature, with occasional shaking. Metal ions were from metal salts of $UO_2(OAc)_2$, $Th(NO_3)_4$, $HgCl_2$, $PdCl_2$, and $CuSO_4$. [b] pH values were adjusted by the following systems: pH 1, HCl-KCl buffer; pH 4, potassium hydrogen phthalate-NaOH buffer; pH 6, potassium hydrogen phthalate-NaOH buffer (sodium tartrate was added and its concentration adjusted to 1 × 10^{-3} mol/L in the case of Th^{4+}); pH 8, H_3BO_3, KCl-NaOH, Na_2CO_3 buffer ([CO_3^{2-}] = 2 × 10^{-3} mol/L) for UO_2^{2+}, H_3BO_3, KCl-NaOH buffer ([sodium tartrate] adjusted to 1 × 10^{-2} mol/L) for Th^{4+}, H_3BO_3, KCl-NaOH buffer for Hg^{2+}, and NH_4Cl-NH_4OH buffer for Pd^{2+} and Cu^{2+}. [c] Determined by light absorption analysis. [d] When the system was adjusted by $NaNO_3$ to [NO_3^-] = 1 mol/L, Th^{4+} was adsorbed in 98%. [e] The experiment was performed with 50 mg of copolymer 5 (sample no. 5) in 100 mL of $UO_2(OAc)_2$ aqueous solution at a concentration of 1 × 10^{-6} mol/L. pH of the solution = 5.7. The solution was not a buffer system but contained 3.0 mol/L $NaNO_3$.

The desorption of the adsorbed metal ions was examined. Adsorbed UO_2^{2+} was readily and quantitatively recovered by treating the metal-adsorbed resin with 10% aqueous Na_2CO_3. Treatment of the Th^{4+}-adsorbed resin with a 1:1 mixed aqueous solution of 10% sodium tartrate and 0.2 N NaOH gave 91% adsorbed Th^{4+}. Hg^{2+} and Cu^{2+} were recovered in 44% and 92% yields by treating the resins adsorbing these ions with 3 N HNO_3. Treatment of the Pd^{2+}-adsorbed resin with aqueous 0.1 N NH_4OH liberated the metal ion in 40% yield.

Concerning UO_2^{2+}, the above adsorption–desorption procedures could be performed repeatedly, at least four times, on resin 5 without reducing the adsorption and desorption efficiencies and without destroying the beadlike structure of the resin.

Experimental Section

Materials. PhCN, PhCl, and $CHCl_3$ solvents dried over P_2O_5 and toluene and xylene solvents dried on Na metal were distilled under nitrogen. Monomer 1 was prepared by reacting $PhPCl_2$

with 3-chloro-1-propanol followed by treatment with Li metal: bp 66–71 °C (0.2–0.4 mmHg); ^{31}P NMR ($CDCl_3$) +109 ppm (single peak).[3] Macroporous beads of chloromethylated polystyrene cross-linked with 3% divinylbenzene (supplied by Mitsubishi Chemical Industries Co.) were washed in refluxing 1,4-dioxane using a Soxhlet apparatus to remove acidic impurities and non-cross-linked polystyrene and then dried in vacuo. The degree of chloromethylation was calculated by the chlorine content of 15.6% to be 58.7% toward the styrene unit, which corresponded to 4.43 mmol/g of resin **4**. Iodomethylated polystyrene was obtained by the chlorine–iodine exchange reaction of the above chloromethylated polystyrene according to the reported procedure.[4] The exchange reaction was found to be quantitative by IR analysis. All other reagents used for preparing buffers and for metal ion analyses were commercially obtained and used without further purification.

Graft Copolymerization. A typical run (run no. 5 in Table I) was as follows. Under nitrogen, monomer **1** (1.4 g, 8.4 mmol) and cross-linked chloromethylated polystyrene (0.245 g) in 10 mL of xylene were placed in a test tube, and the tube was sealed and stirred at 150 °C. As the reaction progressed, the resin increased in volume. After 120 h, decantation of the mixture gave white polymer beads, which were washed in refluxing methanol with a Soxhlet apparatus to remove unreacted monomer and homopolymer and dried in vacuo to give 1.47 g of graft copolymer **5** (85% yield based on charged **1**); IR $\nu_{P=O}$ at 1145 cm^{-1} (KBr). Assuming that every chloromethyl group initiated the polymerization of **1**, the graft chain length was calculated as $n = 6.5$. The amounts of the unreacted monomer and the homopolymer were determined by ^{31}P NMR analysis of the combined solution of the soluble part of the polymerization mixture and the Soxhlet extracts.

Adsorption of Heavy-Metal Ions by Resin 5. A general procedure was as follows. An aqueous 1-mL solution of heavy-metal salt (1×10^{-4} mol/L) was occasionally shaken in the presence of 50 mg of resin **5** (sample no. 5) for 3 days. After filtration of the resin, the amount of the metal ion remaining in the filtrate was determined by light absorption analysis according to the procedures previously reported for UO_2^{2+},[5] Th^{4+},[6] Cu^{2+} and Hg^{2+},[7] and Pd^{2+}.[8]

Recovery of Heavy-Metal Ions Adsorbed on Resin 5. The resin that adsorbed metal ions was gently shaken for 2 days in an aqueous 1-mL solution to desorb the metal ions. For the desorption the following aqueous solutions were employed: 10% Na_2CO_3 for UO_2^{2+}, 10% sodium tartrate + 0.2 N NaOH (1:1) for Th^{4+}, 3 N HNO_3 for Hg^{2+} and Cu^{2+}, and 0.1 N NH_4OH for Pd^{2+}. The resin was separated by filtration, and the amount of the recovered metal ion in the filtrate was determined by light absorption analysis.

Acknowledgment. We acknowledge Mr. T. Mizutani for preparation of the cross-linked iodomethylated polystyrene.

Registry No. U, 7440-61-1; Th, 7440-29-1; Hg, 7439-97-6; Pd, 7440-05-3; Cu, 7440-50-8.

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