Polymerization via Zwitterion. 13.[1] Alternating Copolymerization of 3-Hydroxy-1-propanesulfonic Acid Sultone with Cyclic Phosphorous Compounds

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ABSTRACT: Ring-opening copolymerizations of 3-hydroxy-1-propanesulfonic acid sultone (PS) with two cyclic phosphorous compounds, i.e., 2-phenyl-1,3,2-dioxaphospholane (ethylene phenylphosphonite; EPO) and 2-phenoxy-1,3,2-dioxaphospholane (ethylene phenyl phosphite; EPI), have been studied. The copolymerizations took place without any added initiator to produce 1:1 alternating copolymers of PS–EPO and PS–EPI, respectively. The structures of the copolymers were established by IR and NMR spectroscopy, elemental analysis, as well as the identification of the alkaline hydrolysis products. The reaction scheme of the copolymerization via zwitterion mechanism (eq 4–6) was proposed.

Several combinations of nucleophilic monomers (M_N) and electrophilic ones (M_E) to produce alternating copolymers have been reported so far.[1-13] The copolymer from PS and 2-methyl-2-oxazoline, a cyclic imino ether, gave the amide–sulfonate structure.[11]

In the present study, ethylene phenylphosphonite (EPO) and ethylene phenylphosphite (EPI) were employed as M_N and 3-hydroxy-1-propanesulfonic acid sultone (PS) served as M_E. The present reaction is an extention of our studies on the alternating copolymerization of PS as M_E monomer.[11] The copolymers from EPO and EPI are interesting polymers having phosphorus atoms in the main chain.

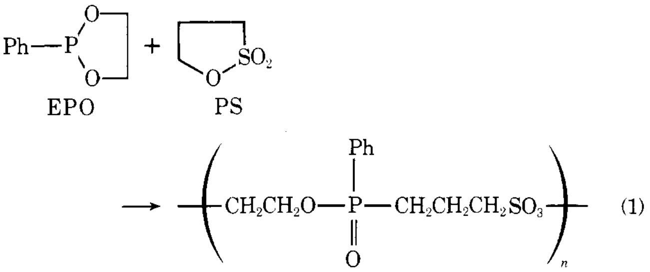
Results and Discussion

Copolymerization of PS with EPO. An equimolar mixture of PS and EPO (5 mmol each) in 1.5 ml of acetonitrile was kept at 80 °C. With the progress of the reaction the mixture became highly viscous. After 55 h the mixture was poured into a large amount of benzene to precipitate the copolymer. The copolymer was dried in vacuo to give 0.95 g (66% yield) of a glassy, white, and hygroscopic solid (Table I).

The structure of the copolymer was determined by IR, NMR spectroscopy, elemental analysis and the identification of the alkaline hydrolysis product. The IR spectrum of the copolymer (Figure 1) shows strong absorption bands at 1220 cm^{-1} due to P=O and at 1350 and 1170 cm^{-1} due to the SO_2 group.

The NMR spectrum of the copolymer (Figure 2) shows broad signals at δ 8.1–7.1 (5 H), 4.7–3.8 (4 H), 3.6–3.0 (2 H), and 2.6–1.8 (4 H). They are assigned respectively to protons of C_6H_5, $-OCH_2CH_2O-$, CH_2S, and $P-CH_2CH_2$.

These spectral data strongly indicate that the copolymer is composed of the phosphinate–sulfonate structure **1**, which has an alternating unit.



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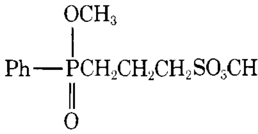
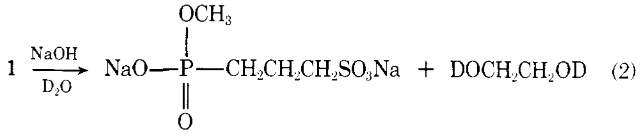
The elemental analysis of the copolymer further supported the 1:1 composition of EPO and PS (see Experimental Section).

The alkaline hydrolysis of the copolymer was carried out to confirm the copolymer structure. To 50 mg of the copolymer was added 0.5 ml of a 10% solution of NaOH in D_2O. The reaction of the hydrolysis mixture at 90 °C for 5 h gave an equimolar mixture of disodium salt of 3-(phenylphosphono)-propanesulfonic acid, **2**, and ethylene glycol (Figure 3a). The authentic sample of disodium salt of **2** was generated in an aqueous NaOH solution from methyl 3-(phenyl methoxyphosphono)propanesulfonate, **3**. The NMR spectrum of the reaction mixture was almost identical with that of a 1:1 mixture (Figure 3b) of the authentic samples, **3** and ethylene glycol, in D_2O containing NaOH. All the above findings strongly support the phosphinate–sulfonate structure **1**.



$$\mathrm{Ph{-}}\overset{\displaystyle OCH_3}{\underset{\displaystyle \| \atop O}{P}}\mathrm{CH_2CH_2CH_2SO_3CH_3}$$

3



$$1 \xrightarrow[D_2O]{NaOH} \mathrm{NaO{-}}\overset{\displaystyle OCH_3}{\underset{\displaystyle \| \atop O}{P}}\mathrm{{-}CH_2CH_2CH_2SO_3Na + DOCH_2CH_2OD} \quad (2)$$

diNa salt of **2**

Copolymerization of PS with EPI. In a similar way an equimolar mixture of PS and EPI (5 mmol each) in 1.5 ml of benzonitrile was kept at 140 °C. With the proceeding of the reaction the mixture became viscous. After 70 h the mixture was poured into a large amount of benzene to precipitate the

Table I.
Copolymerization of PS with EPO and EPI

M_N	Solvent	Temp, °C	Time, h	Copolymer[a] Yield, %	Mol wt[b]
EPO	CH_3CN	80	55	66	1710
EPO	C_6H_5CN	140	42	84	2230
EPO	C_6H_5Cl	120	75	79	3240
EPO	$C_6H_6 + Et_2O$	25	168	35	730
EPI	C_6H_5CN	140	70	75	1720
EPI	CH_3CN	90	66	59	1120

[a] M_N/M_E ratios of the copolymers were in all cases 1.0:1.0 determined by the S content and by NMR spectroscopy. [b] The molecular weights were determined by vapor pressure osmometry in DMF at 55 °C.

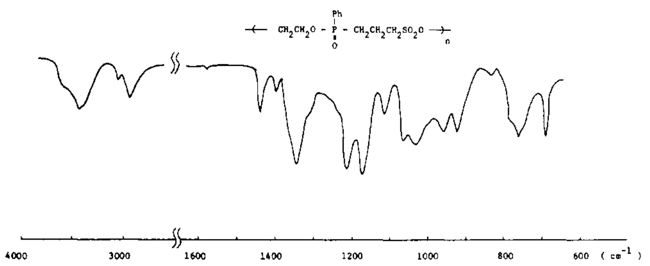


Figure 1. IR spectrum of the EPO–PS polymer (neat).

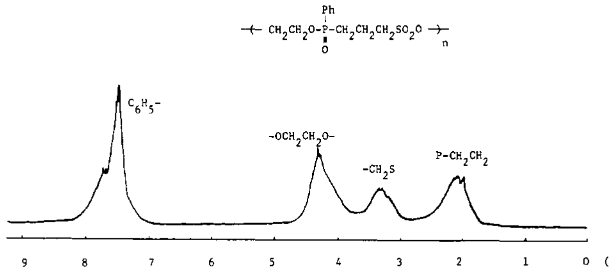
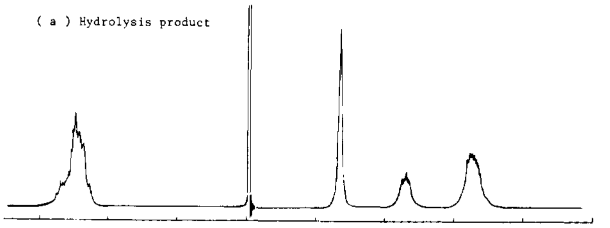


Figure 2. NMR spectrum of the EPO–PS copolymer ($CDCl_3$).



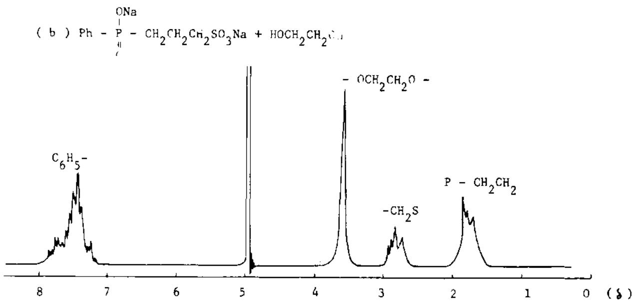
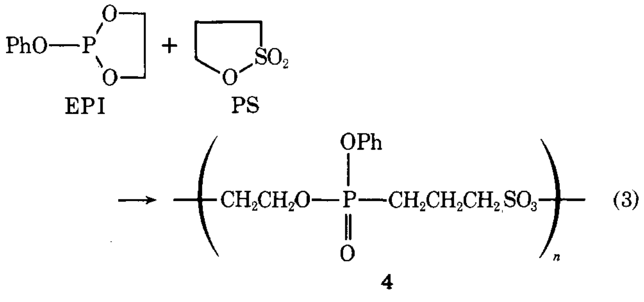


Figure 3. NMR spectra of (a) the alkaline hydrolysis product of the EPO–PS copolymer and (b) a mixture of Na salt of 2 and ethylene glycol in D_2O.

copolymer. The copolymer was dried in vacuo to give 1.15 g (75% yield) of a white, hygroscopic solid (Table I). The structure of the copolymer was determined by IR and NMR spectroscopy, and elemental analysis of the copolymer. The IR spectrum of the copolymer (Figure 4) shows strong absorption bands at 1210 cm^{-1} due to $\nu_{P=O}$ and at 1350 and 1170 cm^{-1} due to ν_{SO_2}. The NMR spectrum of the copolymer (Figure 5) shows the broad signals at δ 7.4–6.7 (C_6H_5, 5 H), 4.6–3.7 ($-OCH_2CH_2O-$, 4 H), 3.5–2.9 (CH_2S, 2 H), and 2.5–1.7 (PCH_2CH_2-, 4 H). These spectral data are quite compatible with the phosphonate–sulfonate structure, **4**, of the copolymer. The elemental analysis of the copolymer further supported the 1:1 composition of EPI and PS (see Experimental Section).



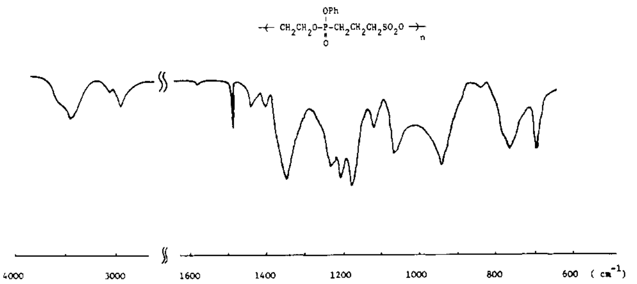


Figure 4. IR spectrum of the EPI–PS copolymer (neat).

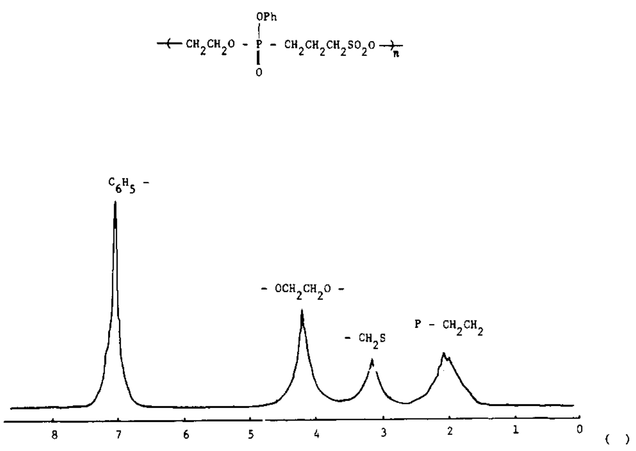
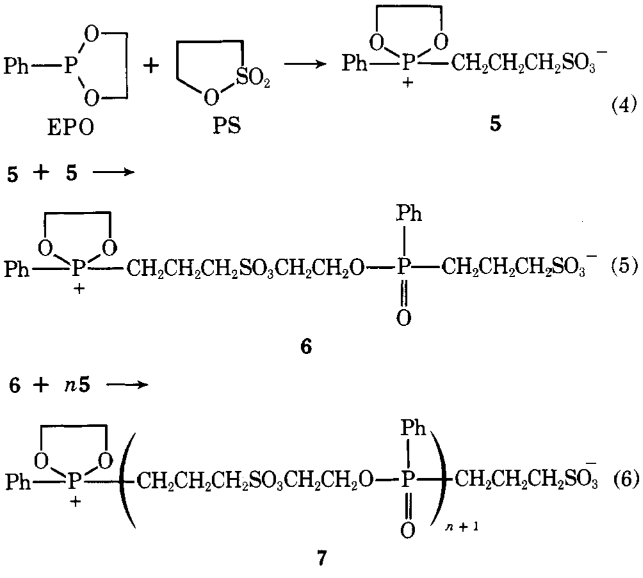


Figure 5. NMR spectrum of the EPI–PS copolymer ($CDCl_3$).

Similarly a 1:1 alternating copolymer was obtained in acetonitrile at 90 °C. Copolymers derived from EPI are soluble in chloroform, methanol, acetonitrile, and DMF, whereas insoluble in water, benzene, ether, chlorobenzene, and other common organic solvents.

Copolymerization Mechanism. On the basis of the above data, a reaction scheme of eq 4–6 is proposed to explain the copolymerization of EPO with PS, which involves zwitterion intermediates, **5**, **6**, and **7**.

The first step is the reaction of EPO with PS to give the genetic zwitterion **5**, which is an important key intermediate in both the initiation and propagation. The reaction of 2 mol



6 + 6, 6 + 7, 7 + 7 ⟶ higher zwitterions (7)

of **5** gives dimeric zwitterion **6**. The subsequent steps of the propagation involve the attack of **5** to **6** to yield a macrozwitterion **7**.

Experimental Section

Reagents. EPO and EPI were prepared by the reactions of ethylene glycol with phenyldichlorophosphine and with phenyl dichlorophosphite in the presence of triethylamine, respectively.[14,15] PS was a commercial reagent, which was dried on molecular sieves 4A and distilled, bp 130–131.5 °C (4 mm). Methyl 3-(phenylmethoxyphosphino)propanesulfonate (**3**) was prepared by the reaction of dimethoxyphenylphosphine with an excess amount of PS at 120 °C for 10 h and was purified by thin-layer chromatography. All solvents were purified by distillation in the usual manner.

Polymerization Procedure and Copolymer Analysis. To 1.5 mol of solvent in a test tube, EPO (or EPI) and PS, 5.0 mmol each, were added at room temperature under nitrogen and the tube was sealed. Then, the mixture was kept at a desired temperature. After the reaction, the reaction mixture was poured into a large amount of benzene to precipitate the copolymer. White glassy material was obtained after drying in vacuo.

Both copolymers of EPO–PS and EPI–PS were very hydroscopic. The calculation of elemental analysis was made on the basis of the formula having occluded water. EPO–PS copolymer: Anal. Calcd for $C_{11}H_{15}O_5PS \cdot 0.21(H_2O)$: C, 44.93; H, 5.29; P, 10.53. Found: C, 44.64; H, 5.27; P, 10.30. EPI–PS copolymer: Anal. Calcd for $C_{11}H_{15}O_6PS \cdot 0.27(H_2O)$: C, 42.42; H, 5.50; P, 9.94. Found: C, 42.03; H, 5.46; P, 9.66.

Hydrolysis of Copolymer. To 0.05 g of copolymer was added 0.5 ml of 10% D_2O solution of NaOH at room temperature and the mixture was heated at 90 °C for 5 h. Then the reaction mixture was subjected to NMR measurement.

Methyl 3-(phenylmethoxyphosphono)propanesulfonate (3). **3** was prepared by the reaction of dimethoxyphenylphosphine with PS in chlorobenzene solvent at 120 °C for 14 h. After the reaction, **3** was purified by TLC: a pale yellow, viscous liquid; ir (neat) 1220 ($\nu_{P=O}$), 1360 and 1170 cm^{-1} (ν_{SO_2}); NMR ($CDCl_3$) δ 8.0–7.3 (m, C_6H_5, 5 H), 3.9 (s, $-SO_3CH_3$, 3 H), 3.70 (d, $P-OCH_3$, 3 H, J_{P-H} = 11 Hz), 3.4–3.1 (m, CH_2S, 2 H), 2.5–1.8 (m, $P-CH_2CH_2$, 4 H). Anal. Calcd for $C_{11}H_{17}O_5PS$: C, 57.87; H, 7.51; P, 13.57. Found: C, 57.11; H, 7.65; P, 13.39.

References and Notes

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Matrix Polymerization of Ionene–Styrene Sulfonate Complexes. An Interpretation in Terms of "Counterion Condensation"

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ABSTRACT: Simple polyelectrolyte theory is applied to the data on the kinetic of polymerization of polystyrenesulfonic acid on templates constituted by ionenes with varying linear charge. It is shown that this model, based on the assumption of a local concentration of "mobile condensed counterions", provides a satisfactory explanation of a number of experiments including the effect of the degree of filling and the influence of added salt.

Much interest has been devoted in the recent years to the matrix polymerization of ionic monomers on polyelectrolyte templates. The fact that the first experiments of Kabanov[1] involving the polymerization of vinylpyridine on polyacids specifically required the formation of a pyridinium salt, as well as some stereospecific effects detected in other systems,[2] has favored the discussion of the experiments in terms of a filling process followed by a nearest neighbor polymerization process. Much attention is then paid to the distance between monomers along the template and to the break in the monomer sequence resulting from a competition with other counterions.

Following a series of investigations by one of us[3] of the polymerization of *p*-styrenesulfonic (pSSA) acid on ionenes with an average charge separation *b* varying from 4.5 to 11.5 Å (Figure 1), it has been shown that the initial rate is a linear function of the linear charge density, which becomes equal to zero for an average distance of 23 Å. This seems to indicate that the concept of stoichiometric site binding of immobilized monomers may be misleading. We have therefore tried to apply to these experiments the general concepts of polyelectrolytes theory.

Experimental Section

The details of the experimental procedures being already published elsewhere,[3] we just recall their principal features. Ionene bromides have been synthesized according to general techniques described by Rembaum.[4] They are converted into hydroxide using an excess of freshly precipitated silver hydroxide and neutralized by freshly purified pSSA, for the stoichiometric complex, $r = 1$, or, for other degrees

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