Polymerization via Zwitterion. 9.[1] Alternating Copolymerizations of 2-Phenyl-1,3,2-dioxaphospholane with Electrophilic Monomers of Acrylic Acid, β-Propiolactone, and Acrylamide

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ABSTRACT: This paper describes the alternating copolymerizations of 2-phenyl-1,3,2-dioxaphospholane (ethylene phenyphosphonite, EPO) with three electrophilic monomers (M_E) of acrylic acid (AA), β-propiolactone (BPL), and acrylamide (AM). Copolymerization took place without any catalyst. Reactions of the 1:1 monomer feed ratio gave alternating copolymers of the 1:1 EPO/M_E compositions having the structures of the phosphinate-propionate **1a** (from EPO-BPL and EPO-AA) and of the phosphinate-amide **1b** (from EPO-AM). A mechanism of alternating copolymerization via zwitterion intermediate was proposed, which was supported by the isolation of crystalline materials having spiro-bicyclic pentacovalent phosphorus compounds, **4a** and **4b**, from equimolar amounts of EPO and M_E monomer. These pentacovalent compounds of **4a** and **4b** were supposed to be present in equilibrium with the corresponding zwitterion species of **5a** and **5b** which are probably the key intermediates for the alternating copolymerizations. Heating of **4a** and **4b** gave polymers of **1a** and **1b**, respectively.

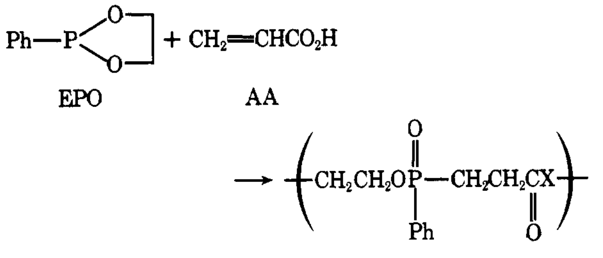
Recently, we have reported a series of new type copolymerizations which occur spontaneously without any added catalyst.[1-9] In these copolymerizations, a nucleophilic monomer (M_N) and an electrophilic monomer (M_E) react with each other to produce the key intermediate of zwitterion. In many cases, alternating copolymers are successfully produced. As the M_N component we have hitherto examined cyclic imino ethers,[2,7] 1,3,3-trimethylazetidine, and a Schiff base,[1] all of which contain nitrogen atoms as the site of the reaction with electrophilic monomers. In the present paper, we disclose a new series of alternating copolymerizations using a phosphorus containing monomer of 2-phenyl-1,3,2-dioxaphospholane (ethylene phenylphosphonite, EPO) as an M_N which is combined with three M_E monomers of acrylic acid (AA), β-propiolactone (BPL), and acrylamide (AM). Before this study, two papers reported the cationic ring-opening homopolymerization of EPO.[10,11] The copolymerization of EPO, however, has not been reported yet.

Results and Discussion

Alternating Copolymerization of EPO with AA. When an equimolar mixture of EPO and AA in a polar solvent was heated at a higher temperature than 100 °C, the system became viscous and turned to pale yellow. A usual work-up gave a yellowish, resinous polymer. It is soluble in polar solvents like DMF, CH_3CN, $CHCl_3$, and methanol, but insoluble in benzene, diethyl ether, and water. Some results are given in Table I (No. 1-3).

Figure 1 shows the ^{1}H NMR spectrum of the EPO-AA copolymer (sample No. 1). Three kinds of signals are observed. Peak A (δ 2.35) is reasonably assigned to two methylene protons (4 H) of $PCH_2CH_2CO_2$, B (δ 4.13) is due to two methylene protons (4 H) of $CO_2CH_2CH_2O$, and C is ascribed to phenyl protons (5 H). No olefinic signal is detected. From the integration ratio of peaks A and C the composition of EPO and AA was found to be 1:1. The ir spectrum of the copolymer (Figure 2a) shows characteristic absorptions of ester carbonyl $\nu_{C=O}$ at 1735 cm^{-1}, $\nu_{P=O}$ at 1230 cm^{-1}, and ν_{P-O-C} at 1050–1030 cm^{-1}. Any absorption due to carboxylic acid is not observed. Since the polymer is very hygroscopic, the result of the elemental analysis was in good agreement with the 1:1 composition taking the included water into account (see No. 1 of Table I).

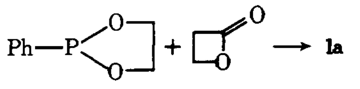
From these findings the alternating phosphinate–propionate structure **1a** was assigned to the EPO-AA copolymer. The derivation of the phosphinate unit in **1a** from EPO is similar to that of the cationic homopolymerization of EPO in which the Arbusov type reaction took place.[10,11] The formation of the propionate unit from AA is rather unusual, which was recently found by us. It involves a hydrogen-transfer process.[1,4,6,8,12]


EPO AA

1a, X = O
b, X = NH

(1)

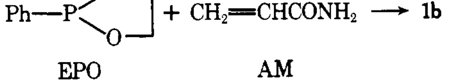
Alternating Copolymerization of EPO with BPL. Without added catalyst the EPO-BPL system gives the alternating copolymer having the same structure as that of the EPO-AA system (Table I, No. 4 and 5).


EPO BPL

(2)

The production of the propionate unit ($-CH_2CH_2CO_2-$) from AA as well as BPL was already found in the no catalyst copolymerizations via zwitterion intermediates using 2-oxazoline[4] and 2-benzyliminotetrahydrofuran[6] as an M_N component.

Alternating Copolymerization of EPO with AM. Copolymerization of EPO with AM took place at 150 °C to produce the 1:1 alternating copolymer **1b** (Table I, No. 6).


EPO AM

(3)

The alternating phosphinate–amide structure of the copolymer was established by ^{1}H NMR and ir spectroscopy as well as an alkaline hydrolysis of the copolymer. Peak A at δ 2.4 is ascribed to two methylene protons (4 H) of $-PCH_2CH_2CO_2-$. A broad peak B (δ 3.3–4.3) is due to two methylene protons (4 H) of $-OCH_2CH_2N-$. A signal C (δ 7.48) is assigned to phenyl protons and one amide proton (total 6 H) (Figure 3). The ir spectrum (Figure 2b) shows characteristic absorptions of ν_{N-H} at 3400 cm^{-1}, and $\nu_{C=O}$ at 1670 cm^{-1}

Table I
Alternating Copolymerization of EPO with Three M_E Monomers[a]

No.	M_E	Solvent (ml)	Temp, °C	Time, h	Copolymer yield, %	Copolymer structure	Mol wt[b]
1	AA	DMF (0.5)	150	10	82	**1a**	1750[c]
2	AA	DMF (0.5)	150	14	75	**1a**	
3	AA	PhCN (0.5)	140	60	46	**1a**	4370
4	BPL	CH_3CN (1.0)	120	16	29	**1a**	
5	BPL	PhCN (0.5)	130	20	35	**1a**	1320
6	AM	DMF (1.0)	150	40	85	**1b**	780

[a] EPO = M_E = 3 mmol. [b] Determined by vapor pressure osmometry. [c] Anal. Calcd for the 1:1 composition for $C_{11}H_{13}PO_4 \cdot 0.53(H_2O)$: C, 52.89; H, 5.68; P, 12.40. Found: C, 52.93; H, 5.94; P, 12.13.

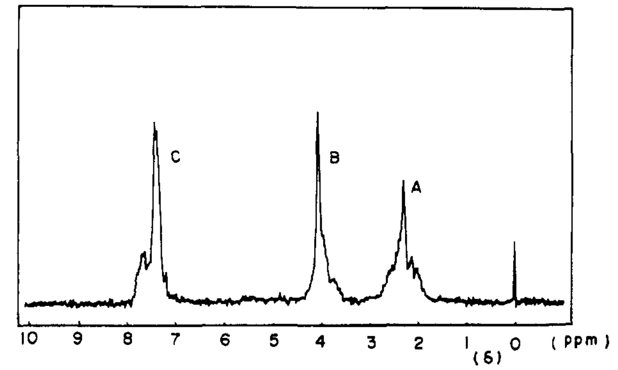
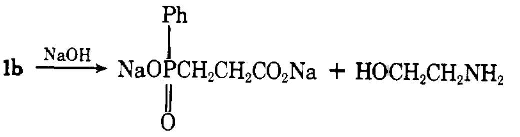


Figure 1. ^1H NMR spectrum of the EPO-AA copolymer (**1a**) in $CDCl_3$.

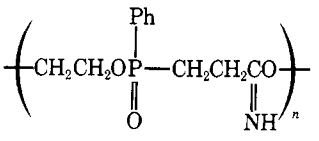
due to the secondary amide, $\nu_{P=O}$ at 1210 cm^{-1}, and ν_{P-O-C} at 1040 cm^{-1}. These data are quite compatible with the structure **1b.**

An alkaline hydrolysis of **1b** should give an equimolar mixture of a phosphinate derivative **2** and 2-aminoethanol (eq 4). As a possible alternative for **1b**, a phosphinate-imidate structure of **3** is conceivable. An alkaline hydrolysis of **3** is



$$\mathbf{1b} \xrightarrow{NaOH} NaO\overset{\overset{Ph}{|}}{\underset{\underset{O}{\|}}{P}}CH_2CH_2CO_2Na + HOCH_2CH_2NH_2 \quad (4)$$

2



3

$$\xrightarrow{NaOH} \mathbf{2} + HOCH_2CH_2OH + NH_3 \quad (5)$$

expected to give **2** and ethylene glycol (eq 5). The ^1H NMR spectrum of the hydrolysis mixture of the copolymer showed the production of 2-aminoethanol, i.e., two triplets at δ 2.96 due to NCH_2 and at δ 3.83 due to OCH_2 in the relative intensity of 1:1. Furthermore, the 1:1 mixture of the authentic **2** and 2-aminoethanol in the alkaline solution showed an identical ^1H NMR spectrum with that of the hydrolysis mixture. These results indicate that the copolymer consisted exclusively of **1b**, the possibility of **3** being ruled out.

Isolation of 1:1 Reaction Products from EPO-AA and EPO-AM. In order to obtain information concerning the copolymerization mechanism, an attempt was made to isolate intermediates of the copolymerization. An equimolar mixture of EPO and AA in diethyl ether gave a crystalline material

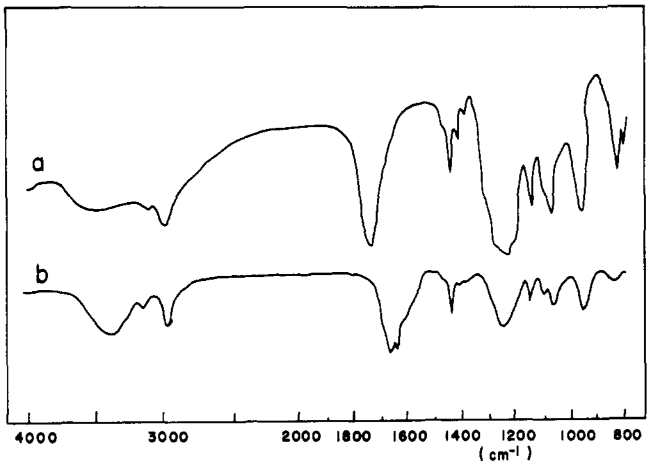


Figure 2. Ir spectra of (a) the EPO-AA copolymer (**1a**) and (b) the EPO-AM copolymer (**1b**) (KBr).

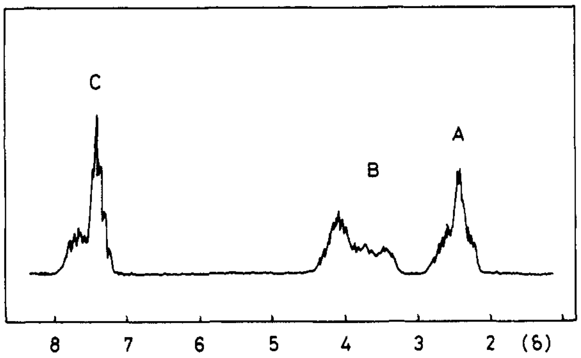
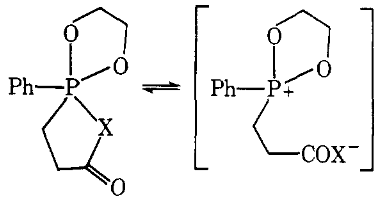


Figure 3. ^1H NMR spectrum of the EPO-AM copolymer (**1b**) in $CDCl_3$.



(6)

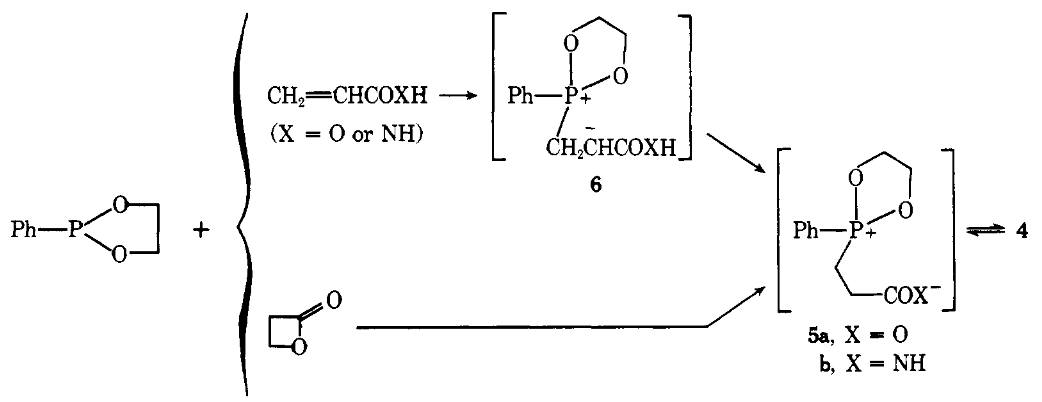
4a, X = O
b, X = NH

5a, X = O
b, X = NH

after standing overnight at room temperature (92% yield, mp 80 °C from chlorobenzene). The product was a 1:1 reaction product of EPO and AA. The structure of a pentacovalent phosphorous compound, 7-oxo-5-phenyl-1,4,6-trioxa-5-phospha(5-P^v)spiro[4,4]nonane (**4a**)[13] was established: ^1H NMR (CD_3OD) δ 2.59 (m, $PCH_2CH_2CO_2$, 4 H), 3.88 (m, OCH_2CH_2O, 4 H), 7.80 (m, C_6H_5P, 5 H); ir (KBr) $\nu_{C=O}$ at 1735 cm^{-1}, ν_{P-O-C} at 1025 cm^{-1}, and no $\nu_{P=O}$ at 1250 cm^{-1}. Anal. Calcd for $C_{11}H_{13}PO_4$: C, 55.01; H, 5.46; P, 12.90. Found: C, 54.55; H, 5.59; P, 12.45.

The ^{31}P NMR spectrum of **4a** in DMF showed a large peak at +2.9 ppm relative to H_3PO_4 external standard. The peak is reasonably assigned to the pentacovalent phosphorane **4a**.[14d] In addition, a very small peak appeared at −43.5 ppm. The peak's assignment has not been finished yet. It is considered at present, however, that the peak is due to zwitterion **5a** or to a phosphinate which is a hydrolysis product of **4a** due to a trace amount of water present as impurity in DMF.

The reaction of EPO with BPL also produced **4a** in a 31%

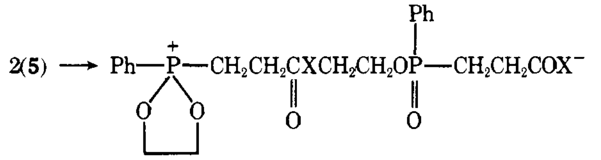


(7)

yield at a higher temperature of 50 °C for 10 h.

An equimolar mixture of EPO with AM in acetonitrile was allowed to react at 50 °C for 25 h to give a white crystal (71% yield), mp 158 °C (from acetonitrile, hygroscopic), whose structure was determined as 7-oxo-5-phenyl-1,4-dioxa-6-aza-5-phospha(5-P^V)spiro[4,4]nonane (**4b**): ^{1}H NMR (CD_3OD-D_2O) δ 2.56 (m, PCH_2CH_2CO, 4 H), 3.88 (m, OCH_2CH_2O, 4 H), 7.64 (m, C_6H_5P, 5 H); ir (KBr) ν_{N-H} at 3400 and 3175 cm^{-1}, $\nu_{C=O}$ at 1680 cm^{-1}, ν_{P-O-C} at 1065 cm^{-1}, and no $\nu_{P=O}$ at 1250 cm^{-1}. Anal. Calcd for $C_{11}H_{14}NO_3P$: C, 55.23; H, 5.90; N, 5.86; P, 12.95. Found: C, 54.73; H, 5.92; N, 5.86; P, 12.69. The pentacovalent phosphorus compounds **4a** and **4b** may probably be present in equilibrium with their zwitterion forms of **5a** and **5b**, respectively.[13]

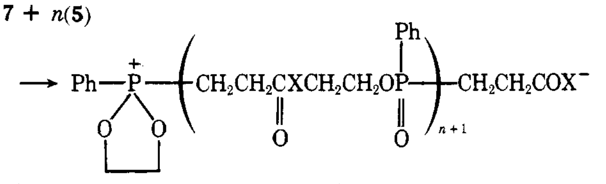
Mechanism of Alternating Copolymerizations. All the above findings are best represented by the following scheme of copolymerization via zwitterion intermediate as proposed in a series of our studies of copolymerizations.[1-9] At the beginning of the copolymerization of EPO with AA or with AM, an adduct **6** is first formed, followed by a hydrogen transfer to yield zwitterion **5**. In the copolymerization of EPO with BPL **5a** is directly produced. Zwitterion **5** is in equilibration with pentacovalent species **4**. Under the conditions of lower temperature in a less polar solvent, **4** could be isolated as a crystalline material. Under the copolymerization conditions of higher temperatures in polar solvents, **5** will begin to play an important role for both initiation and propagation (eq 8 and 9), in which the Arbusov reaction of EPO occurred to yield a phosphinate unit in **7** and **8**.



(8)

7a, X = O
b, X = NH

7 + *n*(5)

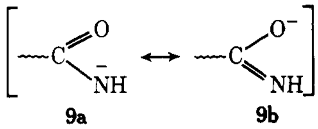


(9)

8a, X = O
b, X = NH

The importance of **4** and/or **5** in the alternating copolymerization is demonstrated by the polymerization using the isolated **4** as a "monomer" (Table II). Polymerizations of **4a** and **4b** proceeded readily to produce polymers quantitatively in all runs. The structure of polymer from **4a** monomer was identical with **1a** and that from **4b** monomer was identical with **1b**. Bulk polymerizations of **4a** and **4b** without solvent (No. 8, 9, 11, and 12) gave higher molecular weight polymers than solution polymerizations (No. 7 and 10).

In the copolymerization of EPO with AM, amide anions in **5b**, **7b**, and **8b** are of an ambident nature having an anionic site at nitrogen (**9a**) and at oxygen (**9b**). The copolymerization took place exclusively through **9a** to give an amide unit **1b** in a regiospecific manner. This should be compared with the reaction mode in the alternating copolymerization of cyclic imino ethers with AM, in which the reaction proceeded exclusively via the form of **9b** to produce an imidate structure.[5]



9a **9b**

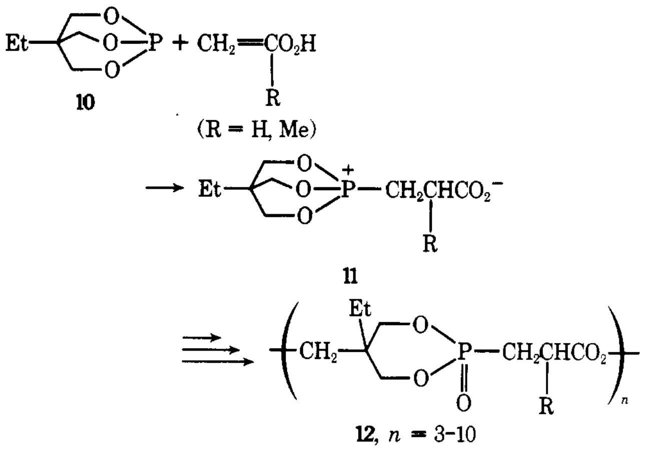
As is shown in Tables I and II, the molecular weights of the product polymers are generally low. According to the general scheme of the new copolymerization between Mn and Me monomers,[9] the molecular weights of the copolymers of the present study will be increased only at a stage of very high conversion.

Finally, related copolymerizations of cyclic phosphorus compounds should be cited. A patent by Clovis and Sullivan discloses the production of alternating cooligomers **12** as flame retardants, which were prepared from a bicyclic phosphite **10** and AA or methacrylic acid in the presence of acetic anhydride.[15] A zwitterion **11** has been considered as a key intermediate, although the complicated reactions were suggested.

Table II
Polymerization of Pentacovalent Compounds, 4a and 4b[a]

No.	Monomer[b]	Solvent (ml)	Temp, °C	Time, h	Mol wt[c]	Softening point, °C	Structure of polymer
7	4a	DMF (0.2)	150	9	650		1a
8	4a		150	6	2090	45–55	1a
9	4a		160	5	3430		1a
10	4b	DMF (0.2)	150	31	530		1b
11	4b		150	3.5	1180[d]	85–90	1b
12	4b		160	3	1880		1b

[a] Polymer yield was quantitative in all cases. [b] 2.0 mmol. [c] Determined by vapor pressure osmometry. [d] Anal. Calcd for $C_{11}H_{14}O_3NP\cdot 0.50(H_2O)$: C, 53.22; H, 6.09; N, 5.64; P, 12.49. Found: C, 53.20; H, 5.92; N, 5.76; P, 12.09.

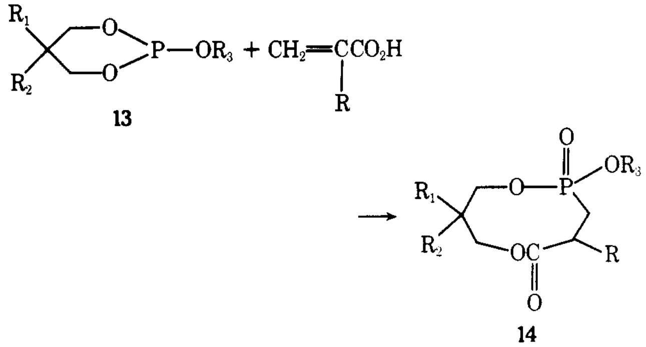


10

11

12, n = 3-10

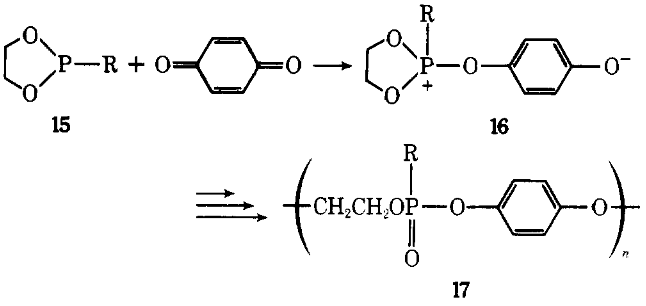
Another related study from the same authors has revealed the ring-enlargement reaction of a six-membered phosphite **13** with AA or methacrylic acid to produce a nine-membered phosphonate **14**.[16] The reaction was supposed to involve complicated pathways to produce **14**, and hence, it should be compared with the isolation of **4a** and the polymerization of **4a** to polymer **1a** in the present study.



13

14

A Japanese patent claims the alternating copolymerizations of cyclic phospholanes **15** with p-benzoquinone, in which a zwitterion **16** is probably involved.[17]



15

16

17

Experimental Section

Materials. Solvents of acetonitrile and DMF were purified as previously reported. Benzonitrile was purified by distillation over P_2O_5. AA and BPL were commercial reagents and purified by distillation under nitrogen before use. AM was also a commercial reagent by recrystallization from ethyl acetate (mp 84 °C) and it was stored under nitrogen in the dark.

EPO was prepared according to Mukaiyama et al.[10] from dichlorophenylphosphine (Aldrich Co.) and ethylene glycol in the presence of triethylamine in benzene and purified by fractional distillation: bp 58–59 °C (0.2 mm) (lit.[10] bp 79–80 °C (0.8 mm)); ^{1}H NMR ($CDCl_3$) δ 3.88 (m, OCH_2CH_2O, 4 H), 7.34 (m, C_6H_5-P, 5 H). EPO is readily polymerized at room temperature and hence it was stored in a refrigerator under nitrogen.

Methyl 3-(Methoxyphenylphosphono)propionate. A mixture of 3 mmol each of dimethoxyphenylphosphine and AA in 0.6 ml of chlorobenzene was kept at 120 °C for 5 h. Column chromatography was employed for the isolation of the product (silica gel, ethyl acetate eluent). The isolated material was colorless viscous oil (80% yield). Anal. Calcd for $C_{11}H_{15}O_4P$: H, 6.24; C, 54.56; P, 12.80. Found: H, 6.37; C, 54.60; P, 12.80. ^{1}H NMR ($CDCl_3$) δ 2.38 (m, $PCH_2CH_2CO_2$, 4 H), 3.65 (s, CO_2CH_3, 3 H), 3.70 (d, J_{P-H} = 11.0 Hz, P-OCH_3, 3 H), 7.50 (m, C_6H_5P, 5 H); ir (film) 1736, 1220, and 1040 cm^{-1}.

Na Salt of 3-(Phenylphosphono)propionic Acid (2). A mixture of the above propionate (87 mg, 0.36 mmol) and a 2 N NaOH solution (5 ml) was heated at 70 °C for 5 h. After neutrallization with 1 N HCl (phenolphthalein indicator) water was evaporated. The residue was extracted with 10 ml of ethanol. Evaporation of ethanol gave a white crystal of **2** in a 64% yield: ^{1}H NMR (D_2O) δ 2.25 (m, $PCH_2CH_2CO_2$, 4 H), 7.70 (m, C_6H_5P, 5 H).

Copolymerizations. In a typical solution polymerization, 3 mmol each of EPO and AA were mixed in 0.5 ml of DMF at room temperature. The mixture was allowed to react under nitrogen at 150 °C. After 10 h, the mixture was poured into a large amount of diethyl ether to precipitate the polymeric material. The product was isolated by decantation and purified by reprecipitation from a $CHCl_3$–diethyl ether system. The polymer isolated was dried in vacuo. These results are shown in Table I.

Polymerization of 4a and 4b. A typical example was as follows. **4a** (2 mmol) was heated at 150 °C without solvent under nitrogen. After 6 h, the polymeric material was dissolved in $CHCl_3$ and poured into a large amount of diethyl ether–pentane (50:50) mixed solvent. Polymer was isolated by filtration and dried in vacuo. Results are given in Table II.

Alkaline Hydrolysis of Copolymer 1a. To 50 mg of copolymer was added 0.5 ml of a 15% NaOH aqueous solution of D_2O. The mixture was kept at 100 °C for 20 h. The reaction product was directly subjected to NMR measurement: 2.25 (m, $PCH_2CH_2CO_2$, 4 H), 2.96 (t, N-CH_2, 2 H), 3.83 (t, OCH_2, 2 H), 7.70 (m, C_6H_5P, 5 H). These signals were also observed for the equimolar mixture of **2** and 2-aminoethanol.

Molecular Weight Determination. The molecular weight of the copolymer was measured by vapor pressure osmometry (Hitachi Perkin-Elmer Model 115) in DMF at 55 °C.

Acknowledgment. Thanks are due to Dr. Chokki (Takeda Pharmaceutical Co. Ltd., Osaka) for recording ^{31}P NMR spectra.

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(13) For more detailed characterizations of **4a** and **4b** including chemical reactions of both compounds and the **4** ⇌ **5** equilibrium, see T. Saegusa, S. Kobayashi, and Y. Kimura, to be reported elsewhere.
(14) It should be mentioned at present that **4a** is the first instance of isolation of a pentacovalent cyclic acylphosphorane, which has been strongly implicated as an intermediate in the acyl phosphate hydrolysis of biological importance, see: (a) S. J. Benkovic and K. J. Schray, *J. Am. Chem. Soc.*, **91**, 5653 (1969); (b) G. D. Smith, C. N. Caughlan, F. Ramirez, S. L. Glaser, and P. Steru, *ibid.*, **96**, 2698 (1974); (c) F. H. Westheimer, *Acc. Chem. Res.*, **1**, 70 (1968); (d) F. Ramirez, *Acc. Chem. Res.*, **1**, 168 (1968).
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