Polymerization via Zwitterion. 11.[1] Alternating Cooligomerizations of 2-Phenyl-1,3,2-dioxaphospholane with Vinyl Monomers having Electron-Withdrawing Groups

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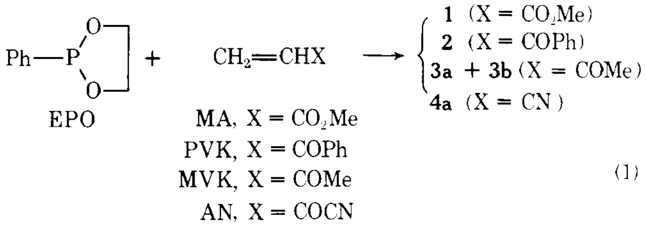
ABSTRACT: This paper describes novel alternating cooligomerizations of a nucleophilic monomer, 2-phenyl-1,3,2-dioxaphospholane (ethylene phenylphosphonite, EPO), with four electrophilic monomers (M_E). The M_E monomers examined were typical electron-deficient vinyl monomers such as methyl acrylate (MA), phenyl vinyl ketone (PVK), methyl vinyl ketone (MVK), and acrylonitrile (AN). All copolymerizations took place without added catalyst. Reactions at a 1:1 monomer feed ratio gave alternating cooligomers of the 1:1 EPO/M_E composition in EPO–MA, EPO–PVK, and EPO–MVK systems. The obtained phosphinate copolymers showed the structures **1**, **2**, and **3a–b**, respectively. In the combination of EPO–AN, AN was incorporated in excess into the copolymer, causing AN homosequences in the copolymer, e.g., the composition of EPO/AN of a copolymer was 18/82. In these cooligomerization a mechanism via zwitterion intermediate **7** was proposed, which was supported by the isolation of pentacovalent phosphoranes **8a** and **8b**. They were isolated from the equimolar reactions of EPO with MA and with PVK at lower temperatures. **8a** and **8b** were supposed to be in equilibrium with the corresponding zwitterion species of **7a** and **7b**. Heating the isolated **8a** and **8b** gave oligomers identical in structure with **1** and **2**, respectively. For the copolymerization with MVK zwitterions **7c-1** and **7c-2** may be involved, through which a hydrogen-transfer unit of **3b** was produced.

In a series of our studies on the "no-catalyst copolymerizations via zwitterion intermediates", we have hitherto found various combinations of nucleophilic (M_N) and electrophilic monomers (M_E) which gave rise to alternating cooligomers from M_N and M_E.[1-11] Among M_N monomers a phosphorus-containing monomer of 2-phenyl-1,3,2-dioxaphospholane (ethylene phenylphosphonite, EPO) has recently been explored.[11] EPO was copolymerized without any added catalyst with M_E monomers such as β-propiolactone, acrylic acid, and acrylamide to produce alternating copolymers, in which the hydrogen-transfer process was involved with acrylic acid and acrylamide to yield ester and amide units in the main chain of the copolymer. In the present study EPO was subjected to cooligomerization with vinyl monomers having electron-withdrawing groups. Electron-deficient vinyl monomers which were examined were methyl acrylate (MA), phenyl vinyl ketone (PVK), methyl vinyl ketone (MVK), and acrylonitrile (AN). Cooligomerization with MA, PVK, and MVK produced 1:1 alternating cooligomers. These results present the 1:1 alternating cooligomerization between a cyclic and a vinyl monomer.

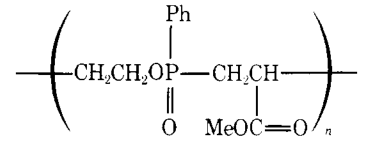


MA, X = CO_2Me
PVK, X = COPh
MVK, X = COMe
AN, X = COCN

(1)

Results and Discussion

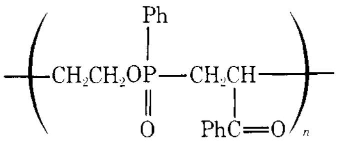
Alternating Cooligomerization of EPO with MA. When an equimolar mixture of EPO and MA in a polar solvent was heated at a higher temperature, the system gradually became viscous. Usual work-up gave a pale yellow gumlike polymer, which was very hygroscopic. It is soluble in polar solvents such as DMF, acetonitrile, chloroform, and methanol but insoluble in benzene, diethyl ether, and water. Some results are shown in Table I (No. 1 and 2). The structure of the cooligomer was established as **1** by NMR and IR spectroscopy (Table II), as well as elemental analysis (Table III). The result of the elemental analysis was in good agreement with the 1:1 composition, taking the included water into account. From all these findings the phosphinate structure **1** was established for the EPO–MA copolymer.



$$\left(-CH_2CH_2O\overset{Ph}{\underset{\overset{\|}{O}}{P}}-CH_2\underset{MeOC=O}{CH}-\right)_n$$

1

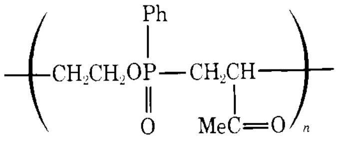
Alternating Cooligomerization of EPO with PVK. Without added catalyst the EPO–PVK system gave a 1:1 alternating cooligomer with the structure **2** (No. 3–6). The solubility of **2** was similar to that of **1**. The structure determination of **2** was carried out by spectroscopy (Table II) and elemental analysis (Table III), based on the fact that in the NMR the intensities of alkyl methylene protons ($C-CH_2-C$) and of $O-CH_2-$ were identical to each other. The results of IR spectrum and elemental analyses were also taken to support structure **2**.



$$\left(-CH_2CH_2O\overset{Ph}{\underset{\overset{\|}{O}}{P}}-CH_2\underset{PhC=O}{CH}-\right)_n$$

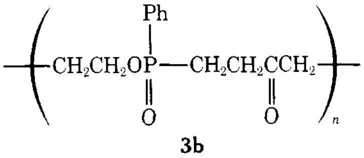
2

Alternating Cooligomerization of EPO with MVK. Cooligomerization of the EPO–MVK system took place at 150 °C to produce a 1:1 alternating cooligomer (No. 7). From spectroscopic analyses (Table II), the cooligomer consisted of units **3a** and **3b**. The unit ratio of **3a** to **3b** was calculated



$$\left(-CH_2CH_2O\overset{Ph}{\underset{\overset{\|}{O}}{P}}-CH_2\underset{MeC=O}{CH}-\right)_n$$

3a



$$\left(-CH_2CH_2O\overset{Ph}{\underset{\overset{\|}{O}}{P}}-CH_2CH_2\underset{\overset{\|}{O}}{C}CH_2-\right)_n$$

3b

Table I
Cooligomerization of EPO with Electron Deficient Vinyl Monomers (M_E[a])

No.	M_E[b]	Solvent (ml)	Temp, °C	Time, h	Copolymer yield, %	Copolymer structure (EPO/M_E molar ratio)	Mol wt[c]
1	MA	Benzonitrile (1.0)	130	100	48	1 (50/50)	1310
2	MA	DMF (1.0)	130	70	24	1 (50/50)	1260
3	PVK	Toluene (1.0)	130	100	19	2 (50/50)	780
4	PVK	Benzonitrile (0.5)	130	100	30	2 (50/50)	1560
5	PVK	Benzonitrile (1.0)	140	120	65	2 (50/50)	905
6	PVK	DMF (1.0)	130	70	53	2 (50/50)	737
7	MVK	DMF (1.0)	150	25	48	**3a** + **3b** (50/50) (36:64)	954
8	AN	Benzonitrile (1.0)	120	30	32	**4a** (18/82)	935

[a] EPO = M_E = 3 mmol. [b] MA = methyl acrylate, PVK = phenyl vinyl ketone, MVK = methyl vinyl ketone, AN = acrylonitrile. [c] Determined by vapor pressure osmometry.

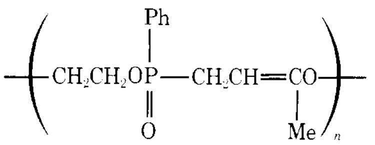
Table II
NMR and Ir Spectroscopic Data of Four Cooligomers

Cooligomer structure (appearance)	NMR and IR Data
1 (pale yellow gum)	NMR ($CDCl_3$) δ 1.5–3.0 (broad m, P–CH_2–CH–CH_2–, 4 H), 3.25 (m, CH–CH_2, 1 H), 3.63 (d, O–CH_3, 3 H), 4.00 (m, O–CH_2–, 2 H), 7.48 (m, C_6H_5–P, 5 H) IR (KBr) 2960, 1735 (ester), 1440, 1130, 1220 (P=O), 1050 (P–O–C), 960 cm^{-1}
2 (yellow gum)	NMR ($CDCl_3$) δ 1.5–2.8 (broad m, P–CH_2–CH–CH_2–, 4 H), 3.3 (m, CH–C(=O)–, 1 H), 3.9 (m, O–CH_2–, 2 H), 7.3 (m, C_6H_5–P, 5 H) IR (KBr) 3030, 2950, 1685 (aromatic ketone), 1438, 1220 (P=O), 1030 (P–O–C), 960 cm^{-1}
3a + **3b** (brown gum)	NMR ($CDCl_3$) δ 1.2–3.2 (broad m, P–CH_2–CH–CH_2– for **3a** and P–CH_2CH_2–C(=O)–CH_2–CH_2–C for **3b**), 2.1 (s, CH_3–C(=O)– for **3a**), 3.5 (m, CH–C(=O)– for **3a**), 4.0 (m, O–CH_2– for **3a** and **3b**, 2 H); 7.5 (m, C_6H_5–P, 5 H) IR (KBr) 3030, 2970, 1720 (ketone), 1665, 1440, 1400, 1230 (P=O), 1050 (P–O–C), 960 cm^{-1}
4a (pale yellow gum)	NMR ($(CD_3)_2S \rightarrow O$) δ 1.5–2.9 (broad m, P–CH_2–CH–CH_2– and –CH_2CH– of AN homounit), 3.3 (m, CH–CN of AN homounit), 3.95 (m, O–CH_2– of AN homounit), 7.5 (m, C_6H_5–P) IR (KBr) 2955, 2220 (C≡N), 1436, 1210 (P=O) 1123, 1030 (P–O–C), 958 cm^{-1}

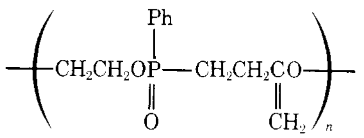
Table III
Analytical Data of Four Cooligomers

Sample No.	Formula	Calcd for 1:1 cooligomer C	H	N	P	Found C	H	N	P
2	$C_{12}H_{15}O_4P(H_2O)_{0.41}$	55.01	5.78		11.84	54.79	5.87		11.70
4	$C_{17}H_{17}O_3P(H_2O)_{0.90}$	64.51	5.99		9.79	64.58	5.83		9.99
7	$C_{12}H_{15}O_3P(H_2O)_{0.88}$	56.72	6.64		12.19	56.72	6.62		12.00
8	$C_{11}H_{12}NO_2P$	59.73	5.43	6.33	14.00	61.27	5.76	15.75	5.91

as 36/64 based on the peak's area of the methyl or methyne signal vs. the methylene signal at δ 1.2–3.2. The absence of other conceivable enolate structures such as **3c** and **3d** was shown by NMR.

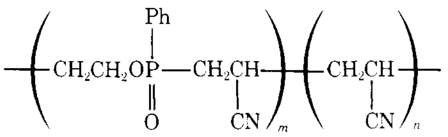

$$\left(-CH_2CH_2O\overset{Ph}{\underset{O}{P}}-CH_2CH=\underset{Me}{C}O-\right)_n$$

3c

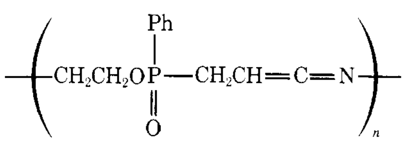

$$\left(-CH_2CH_2O\overset{Ph}{\underset{O}{P}}-CH_2CH_2\underset{CH_2}{C}O-\right)_n$$

3d

Cooligomerization of EPO with AN. In this system the cooligomerization also took place without added catalyst (No. 8). The cooligomer from an equimolar feed, however, was not of 1:1 composition. It was soluble in DMF, DMSO, and chloroform, but insoluble in nonpolar solvents. The AN units were incorporated in excess, which means that a considerable amount of a homosequence of AN was produced in the cooligomer. Spectroscopic analyses showed a structure of **4a**. The unit ratio of EPO/AN was calculated as 23/77 from NMR and as 18/82 from the elemental analysis. Both methods of analysis gave similar values. No indication of another conceivable unit of **4b** was detected by IR spectroscopy.


$$\left(-CH_2CH_2O\overset{Ph}{\underset{O}{P}}-CH_2\underset{CN}{CH}-\right)_m\left(-CH_2\underset{CN}{CH}-\right)_n$$

4a

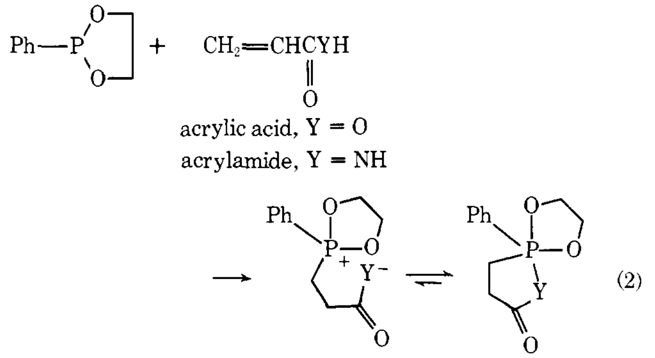

$$\left(-CH_2CH_2O\overset{Ph}{\underset{O}{P}}-CH_2CH=C=N-\right)_n$$

4b

Table IV
Oligomerization of Pentacovalent Compounds 8a and 8b

No.	Phosphorane[a]	Solvent (ml)	Temp, °C	Time, h	Polymer yield, %	Mol wt[b]	Polymer structure
9	**8a**	DMF (0.5)	130	100	12	901	**1**
10	**8a**		200	5	57	1430	**1**
11	**8a**		130	70	62	1350	**1**
12	**8b**		130	200	11	1200	**2**

[a] 2.0 mmol. [b] Determined by vapor pressure osmometry.

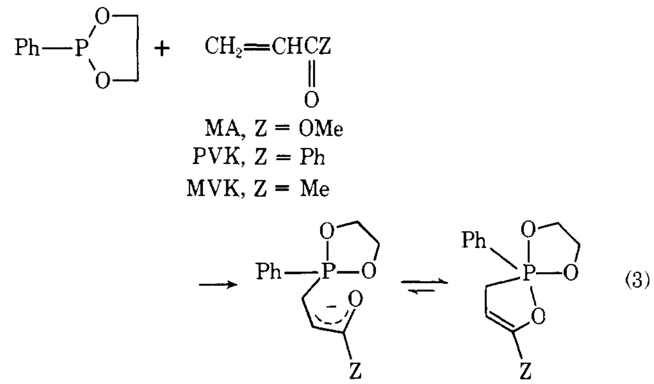

acrylic acid, Y = O
acrylamide, Y = NH

(2)

5a, Y = O **6a**, Y = O
b, Y = NH **b**, Y = NH

Isolation of 1:1 Reaction Products from EPO-MA and EPO-PVK. In the cooligomerization of EPO previously described,[11] pentacovalent phosphorane intermediates such as **6a** and **6b** were successfully isolated by the reaction of EPO with comonomer acrylic acid and with acrylamide. Similarly, the isolation of intermediates was attempted in the present study. In the EPO-MA system, an equimolar mixture of both monomers afforded 7-methoxy-5-phenyl-1,4,6-trioxa-5-phospha(5-P^V)spiro[4,4]nona-7-ene (**8a**). **8a** could even be distilled under high vacuum (107–111 °C (0.04 mm)), although the yield was not so high (18%) due to the formation of polymer on heating. The yield of **8a** was greatly improved when isolated by precipitation (56%) (see Experimental Section).

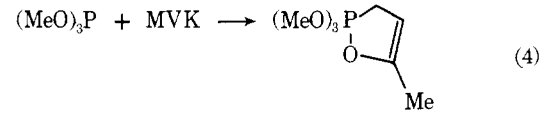
A crystalline material, 5,7-diphenyl-1,4,6-trioxa-5-phospha(5-P^V)spiro[4,4]nona-7-ene, **8b**, was prepared analogously from EPO-PVK. Isolation and purification of **8b** was carried out by recrystallization from ether (mp 131 °C).


MA, Z = OMe
PVK, Z = Ph
MVK, Z = Me

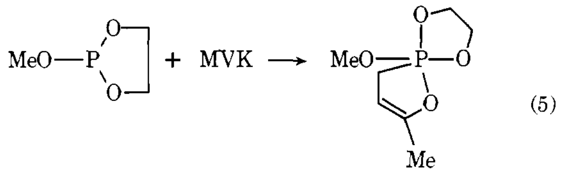
(3)

7a, Z = OMe **8a**, Z = OMe
b, Z = Ph **b**, Z = Ph
c-1, Z = Me **c-1**, Z = Me

Related reactions of MVK have been reported previously.[12,13] MVK reacted with trimethyl phosphite (eq 4)[12] and with cyclic phosphite (eq 5)[13] to form pentacovalent phosphorus compounds **9a** and **9b**, respectively. **9b** was isolated at a lower temperature.

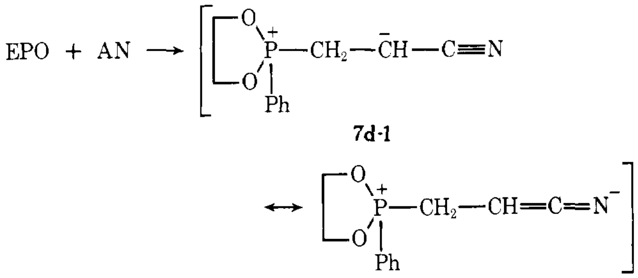

(4)

9a


(5)

9b

On the contrary, a pentacovalent compound could not be isolated in the EPO-AN combination. It is well-known[14] that a phosphorane is usually stabilized by a five-membered ring and by an electron-withdrawing group attached to the phosphorus atom. AN, even if it could form a Michael-type adduct of **7d-1** with EPO, cannot give a five-membered ring, because the -CH=C=N group of **7d-2** is linear.

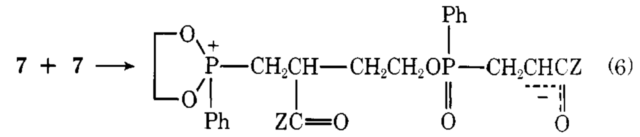

7d-1

7d-2

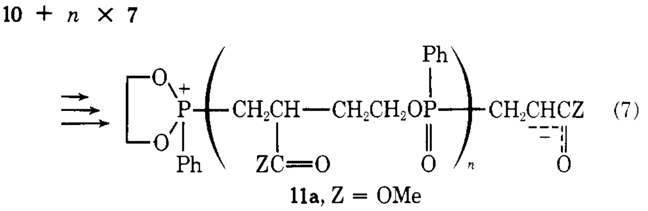
8a and **8b** thus obtained could readily be polymerized when heated as a "monomer" with or without solvent. The results of the polymerizations are shown in Table IV. The structures of oligomers from **8a** and **8b** were identical with those of **1** and **2**, respectively. The bulk oligomerization of **8a** was more efficient than the solution polymerization. The oligomerization of **8b** was very slow probably because of its enhanced stability.

Mechanism of Alternating Cooligomerization. All the above findings are best represented by the following scheme of cooligomerization via zwitterion intermediates as proposed in the series of no-catalyst copolymerizations.[1–11] At the beginning, a Michael-type addition between monomers takes place and a zwitterion **7** is first formed according to eq 3. **7a–c** can then be isomerized to the more stabilized phosphorane species **8a–c**. At lower temperatures **8a** and **8b** could be successfully isolated in the cases of MA and PVK. Being different from the systems EPO-acrylic acid and EPO-acrylamide, a hydrogen-transfer step is not involved in the formation of phosphoranes **8a–c**. Under the reaction conditions at higher temperatures in polar solvents a bond scission between the phosphorus atom and the enol group of **8** occurs to generate **7**, which plays an important role for both initiation and propagation. The reaction of two molecules of **7** produces dimeric zwitterion **10** which then propagates to macrozwitterion

11 by the successive reaction of 7 with 10. The equilibrium of 7 ⇌ 8 is similar to the 5 ⇌ 6 equilibrium (eq 2) postulated in the copolymerizations of EPO with acrylic acid and with acrylamide.[11]

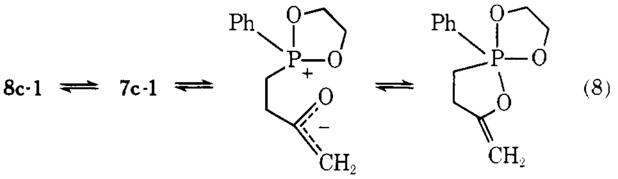


10a, Z = OMe
b, Z = Ph

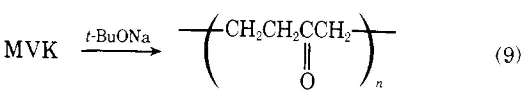


11a, Z = OMe
b, Z = Ph

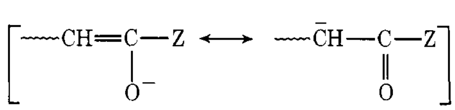
In the cooligomerization of EPO with MVK, an interconversion of **8c-1** to **8c-2** is probably involved (eq 8), in which a hydrogen shift in **7c-1** producing **7c-2** took place at a higher temperature. The propagation via **7c-2** will bring about the formation of cooligomer unit of **3b**. Concerning the production of the unit **3b** from MVK a similar anionic homopolymerization of MVK involving proton transfer has been reported using sodium *tert*-butoxide catalyst (eq 9).[15] Such isomerization does not occur in the PVK system, and thus, only cooligomer **2** was produced.



7c-2 **8c-2**



Through the above cooligomerizations alternating cooligomers **1**, **2**, and **3a–b** are produced. In the propagation steps (eq 6 and 7) Arbuzov-type reactions between phosphonium and enolate anion occurred to yield phosphinate units. Enolate anion **12** is of ambident nature having an anionic site at oxygen (**12a**) and at carbon (**12b**). It is notable that the above cooligomerization took place exclusively through **12b** in a regiospecific manner.



12a **12b**

In the cooligomerization of EPO with AN propagation did not proceed exclusively via **7d**, but instead, **10** attacks free AN to produce homosequences of AN, because **7d** cannot be stabilized in the form of phosphorane. It is assumed that the latter reaction is faster even at a low temperature and homopropagation of AN by the catalysis of EPO would occur.

In these cooligomerizations the molecular weight of products is not so high. This might be caused by the low stability (high reactivity) of the enolate anion. On this account, the 7 ⇌ 8 equilibrium tends toward 8 and the concentration of 7 becomes low, which results in a slow rate of polymerization. In the course of the reaction, the carbanion, having an enhanced reactivity, is likely to bring about side reactions, e.g., hydrogen abstraction. These reactions are kinds of termination and should prevent attainment of high molecular weight.

Finally, the present cooligomerization opens a new field of no-catalyst copolymerization via zwitterion intermediate from the viewpoint that the typical vinyl monomers can be used for M_E and that they can be copolymerized with a cyclic monomer to afford alternating unit.[16] Copolymerizations between cyclic and vinyl monomers had not often been reported.[16] Thus, electron deficient vinyl monomers in general were polymerized at the vinyl group with EPO in the present study, whereas acrylic monomers containing active hydrogens such as acrylic acid and acrylamide provided alternating copolymers with EPO involving a hydrogen-transfer process.[11]

Experimental Section

Materials. Solvents of acetonitrile, chloroform, DMF, and benzonitrile were purified as previously described.[11] Toluene and *n*-hexane were purified by distillation over sodium metal. EPO was prepared and purified according to Mukaiyama's method.[17] Monomers of MA, MVK, and AN were commercial reagents and were purified by distillation under nitrogen. PVK was prepared by the method of Allen et al.,[18] bp 110–111 °C (17 mm) (lit.[18] bp 115 °C (18 mm)), which was purified by fractional distillation and stored in a dry ice bath under nitrogen.

Cooligomerizations. A typical solution polymerization was performed as follows. In a sealed tube 3 mmol each of EPO and MA were mixed in 0.5 ml of DMF at room temperature. The mixture was then allowed to react under nitrogen at 130 °C. After 70 h the mixture was poured into a large amount of mixed solvent (diethyl ether–pentane (50–50)) to precipitate the oligomeric material. The product was isolated by decantation and purified further by reprecipitation from chloroform into the mixed solvent system used above. The obtained cooligomer was dried in vacuo and weighed. These results are shown in Table I.

Isolation of Pentacovalent Intermediate 8a. A mixture of 5 mmol each of EPO and MA in 2 ml of acetonitrile was kept at 50 °C for 10 h under nitrogen. After the solvent was evaporated, the residue was distilled under high vacuum to give **8a** as a colorless viscous oil in 18% yield. **8a:** bp 107–111 °C (0.04 mm); ^{1}H NMR (CD_3CN) δ 2.60 (m, P–CH_2–, 2 H), 3.67 (d, O–CH_3, 3 H), 3.85 (m, O–CH_2–CH_2–O, 4 H), 4.10 (m, –CH=C, 1 H), 7.21 (m, C_6H_5–P, 5 H); IR (film) 1620 ($\nu_{C=C}$), 1050 cm^{-1} (ν_{P-O-C}). Anal. Calcd for $C_{12}H_{15}O_4P(H_2O)_{0.50}$: C, 54.76; H, 6.13; P, 11.70. Found: C, 54.84; H, 6.29; P, 11.43. The isolated material was very hygroscopic, and moisture readily led to the decomposition.

An alternative method for the isolation of **8a** was found as follows. When 5 mmol each of EPO and MA were reacted in 3 ml of *n*-hexane at 50 °C for 15 h as above, the colorless liquid product was separated from the solution. The upper *n*-hexane layer was then removed and the residue (94% yield) was washed twice with small portions of diethyl ether. The material was further purified by reprecipitation with a chloroform–*n*-hexane system and dried in vacuo. All the above operations were performed under nitrogen. The isolated yield of **8a** was 56%. **8a** thus isolated was identical with the distilled sample by NMR and IR. Anal. Calcd for $C_{12}H_{15}O_4P(H_2O)_{0.50}$: C, 54.76; H, 6.12; P, 11.70. Found: C, 54.62; H, 6.10; P, 11.30.

Isolation of a Pentacovalent Intermediate of 8b. A mixture of 5 mmol each of EPO and MA was allowed to react in 10 ml of diethyl ether under nitrogen. While standing at room temperature for 5 h white crystalline material was precipitated. It was isolated by filtration and washed with diethyl ether (65% yield). **8b:** mp 131 °C (from ether); ^{1}H NMR ($CDCl_3$) δ 3:10 (m, P–CH_2–, 2 H), 3.72 (m, O–CH_2–CH_2–O, 4 H) 5.29 (m, –CH=C, 1 H), 7.31 (m, C_6H_5–P and C_6H_5–C, 10 H); IR (KBr) 1629 ($\nu_{C=C}$), 1045 cm^{-1} (ν_{P-O-C}). Anal. Calcd for $C_{17}H_{17}O_3P$: C, 68.00; H, 5.71; P, 10.31. Found: C, 67.99; H, 5.71; P, 9.97.

Oligomerization of 8a and 8b. A typical example was as follows. **8a** (2 mmol) was heated at 200 °C without solvent under nitrogen. After 5 h, the oligomeric material was dissolved in $CHCl_3$ and poured into a large amount of diethyl ether–pentane (50–50). Oligomer was isolated by decantation and dried in vacuo. Results are given in Table IV.

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.

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Polymerization via Zwitterion. 12.[1] Novel 1:1:1 Alternating Terpolymerizations of 2-Phenyl-1,3,2-dioxaphospholane, Electron Deficient Vinyl Monomers of Acrylonitrile and Acrylate, and Carbon Dioxide

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ABSTRACT: This paper reports novel 1:1:1 alternating terpolymerizations of two systems composed of three monomers, i.e., 2-phenyl-1,3,2-dioxaphospholane (ethylene phenylphosphonite, EPO)–acrylonitrile (AN)–carbon dioxide (CO_2) and EPO–methyl acrylate (MA)–CO_2. The terpolymerizations took place without catalyst. Into an equimolar mixture of EPO–AN and EPO–MA, CO_2 was introduced under atmospheric or high pressure. A reaction occurred at a wide range of temperatures (room temperature–150 °C) to produce 1:1:1 alternating terpolymers having the structures of **7a** and **7b**, respectively. The structures of terpolymers **7a** and **7b** was established by NMR and ir spectroscopy and the elemental analyses as well as an alkaline hydrolysis experiment. A mechanism via zwitterion **18** was proposed for the terpolymerization. It is considered that **18** is formed by the reaction of a zwitterion **17** with CO_2, which was supported by the findings that analogous terpolymer **7b** was obtained from the reaction of phosphorane **16** with CO_2.

A series of our studies on the no-catalyst copolymerizations via zwitterion intermediate have revealed the importance of combination between a nucleophilic monomer (M_N) and an electrophilic one (M_E) in order to achieve alternating copolymerizations.[1-12] The M_N monomers which have hitherto been studied are 2-oxazolines,[3-5,8,9] 5,6-dihydro-4*H*-1,3-oxazine,[8] 2-benzyliminotetrahydrofuran,[6] 1,3,3-trimethylazetidine,[7] Schiff base,[10] and 2-phenyl-1,3,2-dioxaphospholane.[1,11,12] The M_E monomers are β-propiolactones,[3-6] acrylic acid,[5-7] acrylamide,[8] acrylate,[1] vinyl ketone,[1] 3-hydroxypropanesulfonic acid sultone,[9] and ethylenesulfonamide.[12] In these copolymerizations two monomers react at first to produce a zwitterion **1**, which is a key intermediate responsible for initiation as well as for propagation.

$$M_N + M_E \longrightarrow \underset{\mathbf{1}}{{}^+M_N\text{-}M_E^-} \rightleftharpoons \underset{\mathbf{2}}{{}^+M_N\text{-}(M_EM_{N_N})_n\text{-}M_E^-} \quad (1)$$

It is to be noted that the polymerization occurs without added catalyst to yield a 1:1 alternating copolymer **2**. Up to now, we have explored seven kinds of M_N and eight kinds of M_E monomers.[1-12] As an extension of these studies, the possibility of 1:1:1 alternating terpolymerization via a zwitterion formed from three monomer components has been examined.

As for the way of this ternary zwitterion formation two types of combination are conceivable as formulated in eq 2 and 3, i.e., zwitterion **4a** from one M_N and two M_E (M_{E_1}, M_{E_2}) and **4b** from two M_N (M_{N_1}, M_{N_2}) and one M_E, respectively.

$$M_N \xrightarrow{M_{E_1}} \underset{\mathbf{3a}}{{}^+M_N\text{-}M_{E_1}^-} \xrightarrow{M_{E_2}} \underset{\mathbf{4a}}{{}^+M_N\text{-}M_{E_1}\text{-}M_{E_2}^-} \quad (2)$$

$$M_E \xrightarrow{M_{N_1}} \underset{\mathbf{3b}}{{}^+M_{N_1}\text{-}M_E^-} \xrightarrow{M_{N_2}} \underset{\mathbf{4b}}{{}^+M_{N_2}\text{-}M_{N_1}\text{-}M_E^-} \quad (3)$$

In the preceding paper of this series of copolymerizations, we have reported the novel no-catalyst copolymerizations between 2-phenyl-1,3,2-dioxaphospholane (ethylene phenylphosphonite, EPO) and four vinyl monomers having an electron-withdrawing group, methyl acrylate (MA), phenyl vinyl ketone (PVK), methyl vinyl ketone (MVK), and acrylonitrile (AN).[1] For each of these copolymerizations a zwitterion **5** was involved, through which 1:1 alternating copolymer was produced except for the AN system. It is then considered that **5** is expected to react with a third monomer of M_E. In the present paper we disclose novel 1:1:1 terpolymerizations (eq 4), in which carbon dioxide (CO_2) was employed