Ring-Opening–Closing Alternating Copolymerization of Cyclic Phosphonites with Dialdehydes

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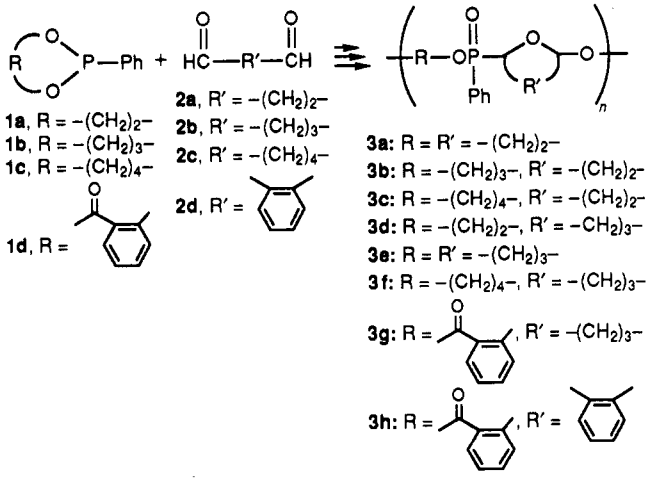
Received February 18, 1992; Revised Manuscript Received June 26, 1992

ABSTRACT: The present paper describes the *ring-opening–closing alternating copolymerization* (*ROCAC*) of four cyclic phosphonites (1) with four dialdehydes (2) including aliphatic and aromatic dialdehydes. The reaction of a 1:1 monomer feed ratio proceeded without any added catalyst to give an alternating copolymer 3 involving ring opening of 1 and ring closing of 2. The structure of copolymer 3 was determined by ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopies as well as elemental analysis. The copolymerization is reasonably explained by a mechanism of propagation via zwitterion intermediates. The electrophilic reactivity of a carbonyl carbon in **2a** and **2b** toward monomer **1a** was quantitatively examined.

Introduction

Ring-opening polymerization and cyclopolymerization belong to the methods used very frequently in the preparation of synthetic polymers. A completely novel mode of copolymerization has been developed, which combines these two modes of polymerization to lead to ring-opening–closing alternating copolymerization (ROCAC);[1-5] a ring-opening monomer (A) of cyclic structure provides a ring-opened structural unit and a ring-closing monomer (B) of noncyclic, bifunctional structure a ring-closed one in the resulting 1:1 alternating copolymer.[5]

In our recent paper,[2] we have reported a new scope of ROCAC using a cyclic phosphonite as the A monomer and a dialdehyde as the B monomer. The present paper describes the comprehensive results of such a new reaction of ROCAC. Monomers used as the A monomer are phosphorus(III) compounds of cyclic phosphonites: 2-phenyl-1,3,2-dioxaphospholane (**1a**), 2-phenyl-1,3,2-dioxaphosphorinane (**1b**), 2-phenyl-1,3,2-dioxaphosphepane (**1c**), and 2-phenyl-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane (**1d**); the latter two cyclic phosphonites are new A monomers. In turn the B monomers are the following dialdehydes: three aliphatic aldehydes of succinaldehyde (**2a**), glutaraldehyde (**2b**), and adipinaldehyde (**2c**) as well as an aromatic aldehyde of phthalaldehyde (**2d**).



Results and Discussion

Copolymerization of Cyclic Phosphonites (1a–d) with Aliphatic Dialdehydes (2a–c). The previous paper disclosed that reactions of five- and six-membered cyclic phosphonites **1a** and **1b** with succin- and glutaraldehydes **2a** and **2b** follow the novel type of ring-opening–closing alternating copolymerization (ROCAC).[2] This mode of copolymerization is not limited to the combinations of these monomers. Seven-membered cyclic phosphonite **1c** and aromatic-type cyclic phosphonite **1d** were also copolymerized with **2a** and **2b**.

As a typical run, monomers **1a** and **2a** were copolymerized in chloroform at 80 °C for 20 h under argon to give a copolymer in 72% yield. The molecular weight was determined as 3200 by gel permeation chromatography (GPC). The structure of the copolymer was determined by ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopies as well as elemental analysis.

Figure 1a shows the ^{1}H NMR spectrum of the copolymer from **1a** and **2a** in $CDCl_3$. A broad peak at δ 1.5–2.5 is due to methylene protons of $-CCH_2C-$ (4 H) in the ring. A peak at δ 3.5–4.8 is ascribed to methylene protons of $-OCH_2-$ (4 H) and a methine proton of –PCH– (1 H). A broad multiplet at δ 5.0–5.5 is assigned to a methine proton of –OCHO– (1 H). Peaks at δ 7.3–8.0 are due to phenyl protons (5 H). By comparison of the integral value of the phenyl protons and the methylene protons in the ring, the content of monomers **1a** and **2a** in the copolymer was calculated to be 50%. The ^{13}C NMR spectrum (Figure 1b) of the copolymer in $CDCl_3$ shows peaks at δ 24.0–33.0 due to the two carbons of $-C\mathit{C}H_2\mathit{C}H_2C-$ in the ring, peaks at δ 61.9–63.9 ascribed to two $-OCH_2-$ carbons in the main chain, a doublet peak centered at δ 67.0 (J_{CP} = 27.0 Hz) assigned to the –PCO– carbon, peaks at δ 100.7 and 104.3 due to the –OCO– carbon, and peaks at δ 128.6–132.7 due to aromatic carbons. The ^{31}P NMR spectrum of the copolymer ($CDCl_3$) showed one peak at δ 38.2 (relative to H_3PO_4 as an external standard) ascribable to a phosphinate unit.

The IR spectrum of the copolymer is shown in Figure 2. Strong absorptions are found at 1214 cm^{-1} due to the P=O bond and at 1021 cm^{-1} for the POC stretching vibration. These spectroscopic data support that the copolymer obtained from **1a** and **2a** has the structure **3a**.

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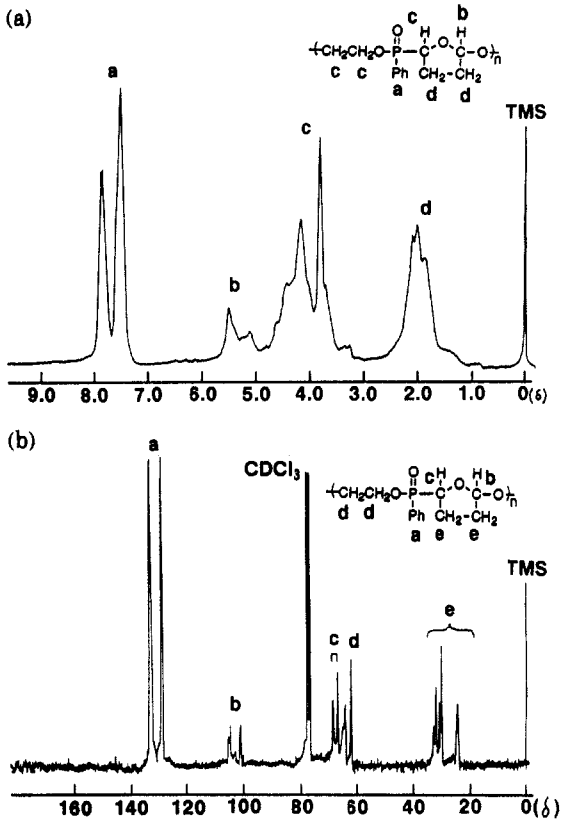


Figure 1. ^1H (250-MHz) (a) and ^{13}C (62.8-MHz) (b) NMR spectra of copolymer **3a** (entry 3 in Table I) in $CDCl_3$.

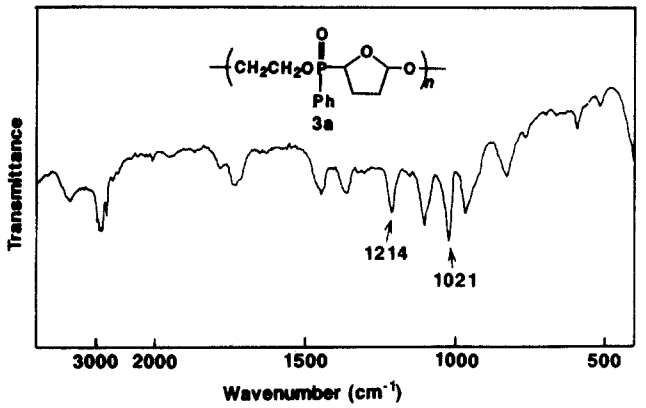


Figure 2. IR spectrum of the copolymer **3a** (entry 3 in Table I).

All spectroscopic data of copolymers from **1a–c** and **2a** and **2b** indicated patterns similar to the above data and supported that all these copolymerizations of **1a–c** with **2a** and **2b** proceeded involving ring opening of **1a–c** and ring closing of **2a** and **2b** to produce the alternating copolymers **3a–f**.

The elemental analyses of the copolymers also support the copolymer structure of **3a–f**. Anal. Calcd for $(C_{13}H_{17}O_4P(H_2O)_{1.0})_n$ (copolymer **3b**, entry 7 in Table I): C, 54.55; H, 6.64. Found: C, 55.10; H, 6.72.

The spectroscopic data of the copolymer (**3g**) from **1d** and **2b** were as follows. The ^1H NMR spectrum ($CDCl_3$) showed a broad peak at δ 1.0–2.5 due to the methylene protons of $-CCH_2C-$ (6 H) in the ring, a small peak at δ 3.5–5.5 due to methine protons of –OCHO– and –PCH– (2 H), and peaks at δ 7.0–8.0 due to phenyl protons (5 H). When the integral value of the phenyl peaks was compared with that of the methylene peak in the ring, the content of **1d** and **2b** in the copolymer was calculated to be 50%. The ^{13}C NMR spectrum ($CDCl_3$) of **3g** showed three groups of peaks at δ 21.0, 23.5, and 29.2 due to three carbons of $-CCH_2CH_2CH_2C-$ in the ring, a doublet peak at δ 43.2 (J_{CP} = 13.5 Hz) due to the –PCO– carbon, peaks at δ 117.1 and 118.7 due to the –OCO– carbon, peaks at δ 128.1–161.8 due to aromatic carbons, and a peak at δ 168.1 (ester carbonyl) and a small peak at δ 172.5 (carboxylic acid carbonyl). The ^{31}P NMR spectrum of **3g** ($CDCl_3$) showed one peak at δ 32.4. The peak is reasonably assigned to the phosphinate unit of the copolymer. The IR spectrum of copolymer **3g** exhibited two strong absorptions at 1716 cm^{-1} due to the C=O bond and at 1206 cm^{-1} due to the P=O bond. Anal. Calcd for $(C_{27}H_{21}O_5P)_n$ (entry 27 in Table I): C, 71.05; H, 4.61. Found: C, 70.94; H, 4.42. All these data can be taken to support that the new type of cyclic phosphonite **1d** as the A monomer was copolymerized with **2b** to produce the ring-opening–closing copolymer **3g**.

Experimental results of the copolymerizations between **1a–d** and **2a–c** are summarized in Table I. Examination of the data shows that ROCAC takes place at various temperatures, giving white hygroscopic materials in high to relatively high yields. The molecular weight values of the copolymer **3a–f** in the reaction of **1a–c** with **2a,b**, as determined by GPC, were in the range 1000–3200 at elevated reaction temperatures and less than 1000 at lower temperatures, i.e. < 40 °C. It is to be noted that ROCAC took place between **1d** and **2b** even at a lower temperature of 0 °C. A relatively lower polar solvent like chloroform and toluene gives higher molecular weight materials in higher yields compared with reactions in a higher polar solvent like acetonitrile and DMF. An extended reaction time (entry 13 in Table I) resulted in a higher yield as well as increased molecular weight in the copolymerization of **1a** with **2b**. However, the copolymer molecular weight did not go higher than 3200 under the reaction conditions examined. This is probably because the reactivity of a genetic zwitterion species is lowered due to its stabilization by forming a spirophosphorane intermediate (vide infra). In all the reactions, a clean ROCAC was achieved; i.e., both the ring-opening and ring-closing steps took place quantitatively.

Although the copolymerization of **1a** with **2c** was carried out, all investigated reaction conditions gave cross-linked materials (entries 33 and 34 in Table I), probably due to the unfavorable seven-membered ring formation during the ring-closing step of the reaction.

Copolymerization of Cyclic Phosphonite 1d with an Aromatic Dialdehyde (2d). ROCAC using a dialdehyde is not limited to aliphatic dialdehyde. An aromatic dialdehyde of phthalaldehyde (**2d**) was employed to copolymerize with cyclic phosphonites. In the reaction of **2d** with a cyclic phosphonite, however, the reaction path changed depending on the cyclic phosphonite employed, i.e., an attack of the phosphorus atom either at the oxygen atom or at the carbon atom of the carbonyl group. The nucleophilic attack of the phosphorus atom in the cyclic phosphonite at the carbon atom of the carbonyl group in the dialdehyde followed by an Arbuzov-type reaction will give a phosphinate-type product, whereas the attack at the oxygen atom of the carbonyl group will produce a phosphonate-type product.

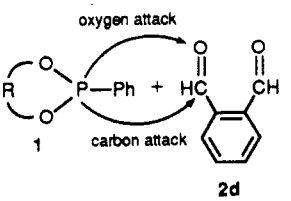


Table I
Ring-Opening–Closing Alternating Copolymerization of 1a–d with 2a–c under Various Reaction Conditions[a]

	copolymerization					copolymer		
	monomer							
entry	1	2	solv	temp (°C)	time (h)	yield[b] (%)	structure	mol wt[c]
1	**1a**	**2a**	$CHCl_3$	40	5	51	**3a**	700
2	**1a**	**2a**	$CHCl_3$	40	24	58	**3a**	800
3	**1a**	**2a**	$CHCl_3$	80	5	66	**3a**	1500
4	**1a**	**2a**	$CHCl_3$	80	20	72	**3a**	3200
5	**1a**	**2a**	$CHCl_3$	120	5	71	**3a**	1400
6	**1a**	**2a**	toluene	100	4	51	**3a**	1100
7	**1b**	**2a**	toluene	100	4	42	**3b**	1500
8	**1c**	**2a**	toluene	100	4	30	**3c**	1600
9	**1c**	**2a**	CH_3CN	100	4	35	**3c**	1000
10	**1c**	**2a**	DMF	100	4	37	**3c**	1000
11	**1a**	**2b**	$CDCl_3$	80	0.5	10	**3d**	1200
12	**1a**	**2b**	$CHCl_3$	80	5	47	**3d**	1200
13	**1a**	**2b**	$CHCl_3$	80	20[d]	75	**3d**	2600
14	**1a**	**2b**	CH_3CN	100	4	52	**3d**	1000
15	**1a**	**2b**	toluene	100	4	79	**3d**	1200
16	**1a**	**2b**	$CDCl_3/CD_3CN$	120	0.75	20	**3d**	1300
17	**1a**	**2b**	$CDCl_3/CD_3CN$	150	0.5	17	**3d**	2200
18	**1a**	**2b**	$CDCl_3/CD_3CN$	180	0.5	30	**3d**	1400
19	**1a**	**2b**	bulk	150	48	81	**3d**	1500
20	**1b**	**2b**	bulk	150	48	77	**3e**	1500
21	**1b**	**2b**	CH_3CN	100	4	36	**3e**	1200
22	**1b**	**2b**	DMF	100	4	16	**3e**	1000
23	**1b**	**2b**	toluene	100	4	57	**3e**	2000
24	**1c**	**2b**	CH_3CN	100	4	45	**3f**	1500
25	**1c**	**2b**	DMF	100	4	16	**3f**	1000
26	**1c**	**2b**	toluene	100	4	59	**3f**	1300
27	**1d**	**2b**	$CHCl_3$	0	9	48	**3g**	1200
28	**1d**	**2b**	$CHCl_3$	rt	28	53	**3g**	900
29	**1d**	**2b**	$CHCl_3$	50	45	30	**3g**	1100
30	**1d**	**2b**	$CHCl_3$	80	46	34	**3g**	800
31	**1d**	**2b**	$CHCl_3$	100	21	68	**3g**	900
32	**1d**	**2b**	PhCN	50	45	24	**3g**	1100
33	**1a**	**2c**	$CHCl_3$	80	15		cross-linking	
34	**1a**	**2c**	$CHCl_3$	50	8		cross-linking	

[a] A mixture of 1.0 mmol of each monomer in 0.3 mL of solvent. [b] Isolated yield of the diethyl ether insoluble part. [c] Determined by gel permeation chromatography. [d] Days.

Table II
Reaction of 1a–d with 2d[a]

					attacking site (%)[b]	
entry	monomer	solv	temp (°C)	time (h)	at carbon	at oxygen
1	**1a**	$CDCl_3$	100	19	30	70
2	**1b**	$CDCl_3$	100	43	10	90
3	**1c**	$CDCl_3$	100	40	21	79
4	**1d**	$CDCl_3$	*c*	66	100	0

[a] A mixture of 1.0 mmol of each monomer in 0.3 mL of solvent. [b] Determined by ^{31}P NMR. [c] The reaction was carried out at temperatures at 0 °C, rt, 90 °C, and 100 °C.

Therefore, the ratio of the carbon attack and the oxygen attack in the reaction of **2d** with various cyclic phosphonites was determined by ^{31}P NMR analysis, in which the chemical shift of the phosphinate (δ 30–40) in the ^{31}P NMR is different from that of the phosphonate (δ 15–20). The results are shown in Table II. In the reaction of **1d** with **2d**, **1d** attacked exclusively at the carbon at four different temperatures examined. On the other hand, in the reactions of **1a–c** with **2d**, both the carbon and oxygen attacks were observed at various reaction temperatures. For instance, at 100 °C the ratios of the carbon attack using **1a–c** were 30%, 10%, and 21%, respectively (Table II). Therefore, only **1d** could be employed as the A monomer for the clear ROCAC in combination with **2d**. The structures of the products from **1a–c** and **2d** were very complicated and are now under further investigation.

The copolymerization of **1d** with **2d** is much faster than that in combinations with an aliphatic dialdehyde and is exothermic even at room temperature to produce powdery materials. The structure of the resulting copolymer was determined by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopies as well as elemental analysis.

The ^1H NMR spectrum of the copolymer (entry 2 in Table III) ($CDCl_3$) showed a broad peak at δ 4.5–6.5 due to methine protons (2 H) and a large peak centered at δ 7.31 due to aromatic protons (13 H). By comparison of the integral value of these peaks, the content of **1d** and **2d** in the copolymer was calculated to be 50%. The ^{13}C NMR spectrum of the copolymer ($CDCl_3$) showed a peak at δ 112.8 due to the –OCO– carbon, a doublet peak centered at δ 118.0 (J_{CP} = 25.3 Hz) due to the –PCO– carbon, peaks at δ 122.7–161.8 due to aromatic carbons, and a peak at δ 168.4 (ester carbonyl) and a small peak at δ 172.5 (carboxylic acid carbonyl). The ^{31}P NMR spectrum of the copolymer in $CDCl_3$ showed one peak at δ 34.0 ascribable to a phosphinate unit. The IR spectrum of the copolymer showed strong absorption bands at 1713 cm^{-1} due to a C=O bond and 1201 cm^{-1} due to a P=O bond. Anal. Calcd for $(C_{21}H_{15}O_5P(H_2O)_{1.0})_n$: C, 63.64; H, 4.29. Found: C, 63.82; H, 4.51. These spectroscopic as well as elemental analysis data strongly support the copolymer structure **3h**. The copolymerization of **1d** with **2d** was performed under various reaction conditions (Table III). The molecular weight (4000) and the yield of the copolymer (63%) were highest when the reaction was carried out in $CDCl_3$ at room temperature for 48 h.

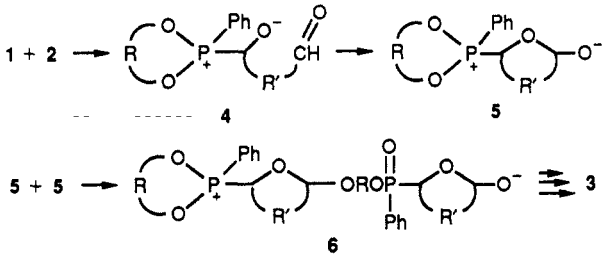
Copolymerization Mechanism. On the basis of the above data, the copolymerization of 1 with 2 can be

Table III
Ring-Opening–Closing Alternating Copolymerization of 1d with 2d[a]

entry	solv	temp (°C)	time (h)	yield[b] (%)	mol wt[c]
1	$CDCl_3$	0	4	15	600
2	$CDCl_3$	rt	48	63	4000
3	$CDCl_3$	90	40	41	1400
4	$CDCl_3$	100	21	37	2000
5	CD_3CN	35	25	37	1400

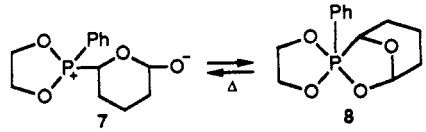
[a] A mixture of 1.0 mmol of each monomer in 0.3 mL of solvent. [b] Isolated yield of the diethyl ether insoluble part. [c] Determined by gel permeation chromatography.

Scheme I

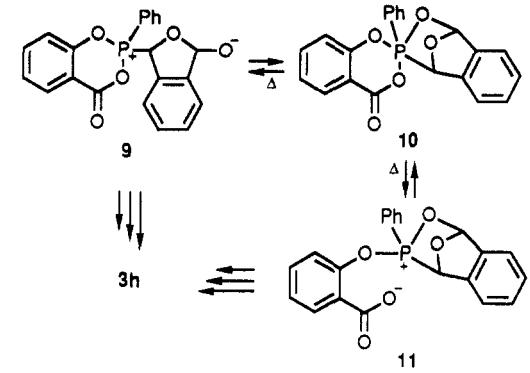


explained by the mechanism in Scheme I. The first step of the reaction involves the nucleophilic attack of the phosphorus(III) atom of 1 toward a carbon atom of a carbonyl group in 2 forming an intermediate 4. The second step is the fast intramolecular cyclization (ring-closing) reaction of 4 giving rise to a genetic zwitterion 5. The propagation is the reaction between two molecules of 5, i.e., the reaction of the oxygen anionic site of the zwitterion 5 with the carbon adjacent to the OP^+ group of 5 via an Arbuzov-type of ring-opening reaction to form a dimeric zwitterion 6. The subsequent propagations are the reactions between a phosphonium site and an oxygen anion site of zwitterions 5 and 6 and/or macrozwitterions. Thus, the repeating unit of 3 has one part which comes from the ring opening of monomer 1 and the other part which comes from the ring closing of monomer 2 (*ring-opening–closing alternating copolymerization*). From the other viewpoint, the present reaction provides additional "oxidation-reduction alternating copolymerization".[1,2,6]

The reaction was further studied by ^{31}P NMR in order to confirm the copolymerization mechanism. When a mixture of **1a** and **2b** in $CDCl_3$ was monitored in situ by ^{31}P NMR at a lower temperature (25 °C), it was found that immediately after mixing both monomers two peaks at δ −24.3 and +41.4 appeared, the former being reasonably assigned as a pentacovalent spirophosphorane and the latter as a phosphinate unit of the copolymer **3d**. The monomer peak due to **1a** at δ 162.0 decreased gradually with time, whereas the concentrations of the spiro compound and the copolymer increased at the same time and then remained almost constant for more than 2 h at 25 °C. When the reaction mixture was heated to 80 °C for 15 min, ^{31}P NMR showed the conversion of the spiro compound into the pentavalent phosphorus atom of the copolymer **3d**. At higher reaction temperatures (>80 °C), the peak due to **1a** disappeared almost completely after 5–10 min of reaction and one single new peak at δ 41.4 was observed. These observations suggest that at lower temperatures (<40 °C) 7 is in equilibrium with a spiro compound of a proposed structure 8. The formation of



Scheme II

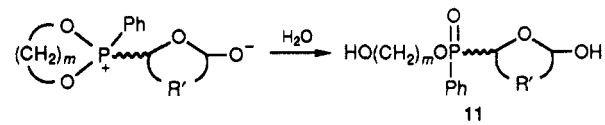


8 was observed by ^{31}P NMR at a temperature range from −20 to +25 °C, which can at elevated temperatures undergo a thermally induced ring-opening polymerization, giving rise to copolymer **3d**.

Although the reaction of **1b–d** with **2b** was followed by ^{31}P NMR under similar reaction conditions, the formation of a spiro compound was not observed, probably due to the highly unfavorable situation to form a spiro structure involving a six- or seven-membered ring from **2b–d**.

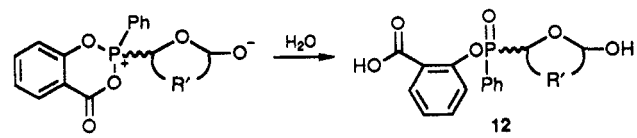
In the copolymerization of **1d** with **2d**, an analogous pathway from a genetic zwitterion 9 to copolymer **3h** is considered. In addition, however, the other pathway is conceivable; i.e., 9 is cyclized to give spirophosphorane 10, although it was not detected directly by ^{31}P NMR, and 10 is in equilibrium with zwitterion 11, leading eventually to copolymer **3h**. In the former case, the oxygen atom of P=O in **3h** is originated from monomer **1d**, whereas in the latter case it comes from monomer **2d**. At the present moment, it is difficult to distinguish these two pathways (Scheme II).

The terminal groups of the isolated copolymers **3a–f** are probably of OH groups coming from proton abstraction by the alkoxy anion group from water and hydrolysis of the phosphonium ring during the isolation process as given by 11. The absorption at 3300–3400 cm^{-1} in the IR



spectrum of the copolymers is assigned to the terminal OH groups.

On the other hand, the isolated copolymers **3g** and **3h** showed a small peak at δ 172.5 in the ^{13}C NMR spectra in addition to an ester carbonyl group (δ 168) and the absorption at 3300–3400 cm^{-1} in the IR spectra which can be assigned to the terminal carboxylic acid and OH groups as shown by 12. Furthermore, the weak absorption at



around 1730 cm^{-1} in the IR spectra of the some isolated copolymers may be due to the terminal aldehyde groups as given by 13, if any.

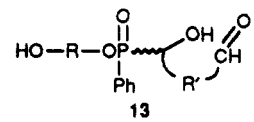
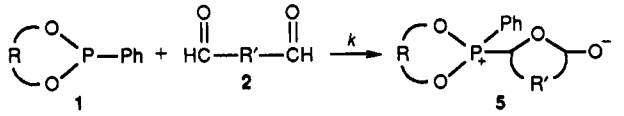


Table IV
Rate Constants in the Copolymerization of 1a with 2a and 2b

entry	monomer 1	monomer 2	temp (°C)	$k \times 10^3$ [L/(mol·s)]	kinetic param
1	1a	2a	80	0.75	
2	1a	2b	25	0.25	$\Delta H^{\ddagger}$ = 25.6 (kJ/
3	1a	2b	35	0.42	mol); $\Delta S^{\ddagger}$ =
4	1a	2b	80	1.17	−263.9 [J/(K·mol)]
5	1a	2b	120	5.00	at 80 °C

Kinetic Studies. The rate equation for the formation of the first genetic zwitterion in the copolymerization of 1 with 2 is given by eq 1, which is based on the scheme



$$d[5]/dt = k[1][2] \quad (1)$$

where [1], [2], and [5] are the concentrations of the monomers 1 and 2 and the zwitterion 5, respectively. The copolymer composition was equal to the composition of the monomer feed (1:1) in all cases, and the consumption rate of 1 and 2 is the same throughout the course of the polymerization, i.e., [1] = [2] = c. In addition, the formation rate of 5 is equal to the consumption rate of 2

$$d[5]/dt = -d[2]/dt \quad (2)$$

Equation 1 can then be expressed as

$$-d[c]/dt = k[c]^2 \quad (3)$$

Integration of eq 1 gives

$$1/[c] - 1/[c]_0 = kt + A \quad (4)$$

where $[c]_0$ and A denote the initial concentration of monomer and the constant. The instantaneous monomer concentration [c] was determined by the integration ratio between the peak due to the phenyl protons of 1 and the peak due to the aldehyde protons of 2 in the ^{1}H NMR spectrum. Plots of $1/[c] - 1/[c]_0$ vs t showed a linear relationship; thus the formation of the genetic zwitterion obeyed second-order kinetics. The rate constants for the reaction of 1a with 2a and with 2b are listed in Table IV. These rate constants are a direct measure of the reactivity (electrophilicity) of the carbonyl carbon in 2 toward the phosphorus atom in 1 based on the assumption that the intramolecular ring-closing step (4 → 5) in the formation of the genetic zwitterion is much faster than the intermolecular step (1 + 2 → 4). From Table IV, the rate constants for the reaction between 1a and 2a are slightly lower at 80 °C compared with the reaction between 1a and 2b. Therefore, the electrophilicity of the carbonyl carbon in 2b is higher than that in 2a. From the kinetic parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values), the reaction of 1a with 2b is a very entropically unfavorable one as normally observed for a dipole–dipole S_N2 type reaction.

Conclusion

It has been found that the copolymerization of a cyclic phosphonite 1 with a dialdehyde 2 undergoes the *ring-opening–closing alternating copolymerization* (*ROCAC*) without added initiator to give an alternating copolymer 3. ROCAC belongs to a new concept in the polymerization chemistry. The ROCAC reaction controls the sequence as well as the repeating unit structure of copolymers, where one part of the repeating unit is derived from ring opening of 1 and the other part from ring closing of 2 in an alternating manner.

Experimental Section

Materials. All solvents were purified by distillation. 2-Phenyl-1,3,2-dioxaphospholane (1a), 2-phenyl-1,3,2-dioxaphosphorinane (1b), and 2-phenyl-1,3,2-dioxaphosphepane (1c) were prepared from reactions between corresponding glycols and dichlorophenylphosphine in the presence of triethylamine in a benzene solution.[7,8] 2-Phenyl-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane (1d) was prepared in a similar manner to that of 1a–c from the reaction between salicylic acid and dichlorophenylphosphine.[9] Succinaldehyde (2a) was prepared by hydrolysis of 2,5-dimethoxytetrahydrofuran and distilled twice.[10] Glutaraldehyde (2b) was a commercial reagent of 40% solution in water, which was extracted with chloroform and purified by distillation under reduced pressure. Adipinaldehyde (2c) was prepared by the reaction of lead tetracetate with 1,2-cyclohexanediol.[11] Phthalaldehyde (2d) was recrystallized from ligroin and stored under argon before use for polymerization studies.

Copolymerization. A typical run was as follows (entry 4 in Table I). A dried polymerization tube was charged with 1a (0.168 g, 1.0 mmol), 2a (0.086 g, 1.0 mmol), and 0.3 mL of $CHCl_3$ under argon. The tube was sealed and kept at 80 °C for 20 h. The reaction mixture was poured into a large amount of diethyl ether to precipitate the polymeric material. After standing 24 h the interior was decanted and the residue washed twice with diethyl ether and dried for 4 h under vacuum (35 °C) to give 0.183 g (72% yield) of 3a.

Kinetic Procedure. The kinetic analysis was performed by determining the instantaneous concentrations of the monomers by using ^{1}H NMR spectroscopy. A typical run was as follows. In a NMR tube under argon were placed 1 mmol of 1 and 1 mmol of 2 in 0.3 mL of a $CDCl_3$ solution ($[M]_0$ = 3.33 mol/L). The NMR tube was sealed and kept at 80 °C in the NMR probe insert. The polymerization was monitored, and the spectrum of the copolymerization mixtures was recorded at about an interval of 10 min. The monomer concentrations were obtained directly from the integral intensity of the phenyl protons of 1 and aldehyde protons of 2 in the spectrum.

Measurements. ^{1}H NMR spectra were recorded on 60-MHz Hitachi R-24A and 250-MHz Bruker AC250T NMR spectrometers. ^{13}C NMR spectra were recorded on a 62.8-MHz Bruker AC250T NMR spectrometer. ^{31}P NMR spectra were recorded on a 36.4-MHz JEOL FX-90Q NMR spectrometer. IR spectra were recorded with polymer samples on KBr on a Shimadzu IR-27G spectrometer. Gel permeation chromatographic (GPC) analysis was performed by using a Tosoh 8010 apparatus with an RI detector under the following condition: Gelpack GL-A130 column with a chloroform eluent at a flow rate of 1.0 mL/min.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Area of "New Functional Materials Design, Preparation, and Control" from the Ministry of Education, Science and Culture, Japan (Nos. 02205010 and 03205009). We also acknowledge the partial support through International Joint Research Projects by Japan Society for the Promotion of Science (JSPS). S.L. gratefully acknowledges the receipt of a PYF scholarship from the Swedish Board for Technical Development (STU) and a scholarship from JSPS.

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Registry No. **1a**, 1006-83-3; **1b**, 7526-32-1; **1c**, 7526-37-6; **1d**, 66737-42-6; **2a**, 638-37-9; **2b**, 111-30-8; **2c**, 1072-21-5; **2d**, 643-79-8; (**1a**)(**2a**) (alternating copolymer), 143309-66-4; (**1a**)(**2b**) (alternating copolymer), 137111-57-0; (**1a**)(**2c**) (alternating copolymer), 143309-71-1; (**1a**)(**2d**) (alternating copolymer), 143309-72-2; (**1b**)(**2a**) (alternating copolymer), 137111-58-1; (**1b**)(**2b**) (alternating copolymer), 143309-68-6; (**1b**)(**2d**) (alternating copolymer), 143309-73-3; (**1c**)(**2a**) (alternating copolymer), 143309-67-5; (**1c**)(**2b**) (alternating copolymer), 143309-69-7; (**1c**)(**2d**) (alternating copolymer), 143309-74-4; (**1d**)(**2b**) (alternating copolymer), 143309-70-0; (**1d**)(**2d**) (alternating copolymer), 143309-75-5.