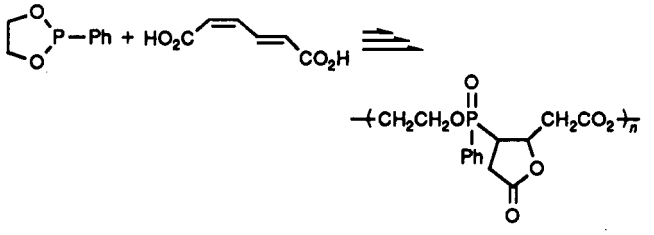
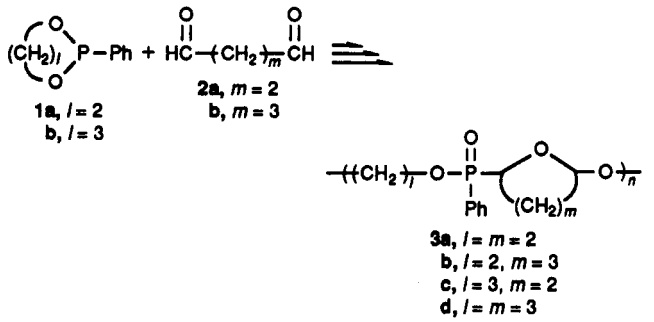
Ring-Opening–Closing Alternating Copolymerization of a Cyclic Phosphonite with a Dialdehyde

Ring-opening–closing alternating copolymerization is a novel concept in polymerization chemistry, in which one monomer provides a ring-opened structural unit and the other monomer a ring-closed one in the resulting 1:1 alternating copolymer. In a previous paper, we have shown the first example of this type of reaction, which takes place between 2-phenyl-1,3,2-dioxaphospholane and muconic acid.[1]



This paper reports a new scope for the concept by the reaction of 2-phenyl-1,3,2-dioxaphospholane (**1a**) or -di-



oxaphosphorinane (**1b**) with succinaldehyde (**2a**) or glutaraldehyde (**2b**) to produce an alternating copolymer (**3**) with ring-opening–closing.

The reaction of the 1:1 monomer feed ratio proceeded without any added initiator to give an alternating copolymer **3**, whose repeating unit consists of one part formed by the ring-opening of monomer **1** and the other part by the ring-closing of monomer **2** in an alternating arrangement. This pathway involves the oxidation of the trivalent phosphorus atom in **1** to a pentavalent form in the copolymer **3** and the reduction of the carbonyl groups of **2** into the ring-closed ether unit of **3** ("oxidation–reduction alternating copolymerization").[2,3]

In a typical copolymerization (entry 3), a dried polymerization tube was charged with **1a** (0.17 g, 1.0 mmol), **2b** (0.10 g, 1.0 mmol), and 0.3 mL of $CHCl_3$ under argon. The tube was sealed and kept at 80 °C for 1 h. The resulting material was precipitated in 20 mL of diethyl ether. After standing 24 h, the supernatant was decanted and the residue was washed twice with diethyl ether and dried for 2 h under vacuum (35 °C) prior to analysis.

The structure of the copolymer was determined by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopies as well as elemental analysis. Figure 1a shows the ^1H NMR spectrum of copolymer **3b**. Peaks at δ 7.3–8.0 are due to phenyl protons (5 H), a broad multiplet at δ 4.5–5.3 is assigned to the methine proton of OCHO (1 H), and a broad peak at δ 4.0 is ascribed to methylene protons of $-OCH_2-$ (4 H), the peak being overlapped with a doublet centered at δ 3.9 (J_{HCP} = 18 Hz) of the methine proton of –PCH– (1 H). A

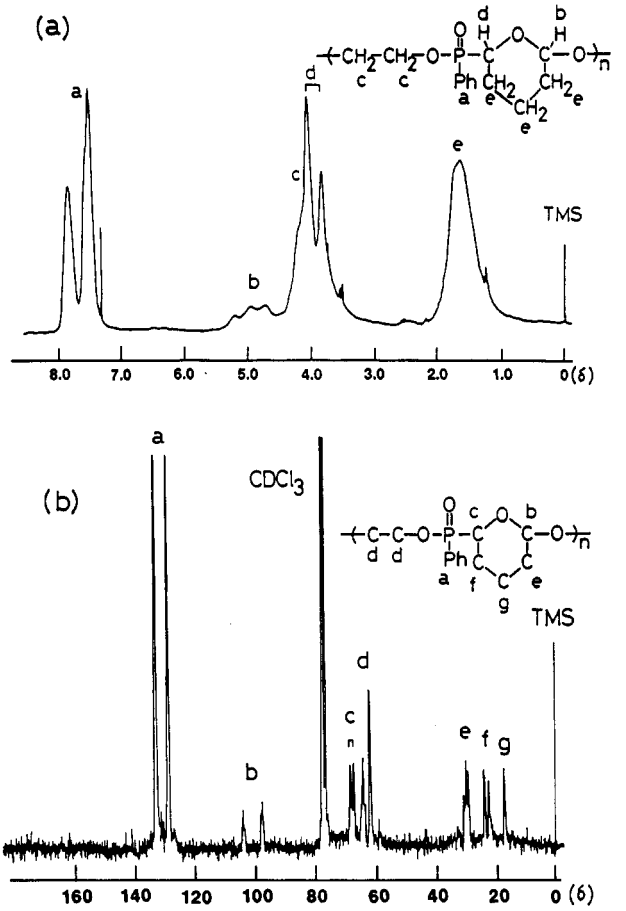


Figure 1. ^1H (250-MHz) (a) and ^{13}C (62.8-MHz) (b) NMR spectra of copolymer **3** (entry 2) in $CDCl_3$.

broad peak at δ 1.0–2.0 is due to the methylene protons of $-CCH_2C-$ (6 H) in the ring. By comparison of the integral value of the phenyl protons and the methylene protons of the ring, the content of monomers **1a** and **2b** in the copolymer **3b** was calculated to be 50%. The ^{13}C NMR spectrum (Figure 1b) of **3b** showed one peak at δ 17.3, two peaks at δ 22.3 and 23.9, and a broad peak at δ 29.8 due to the three carbons of $CCH_2CH_2CH_2C$ in the ring, peaks at δ 61.9 and 63.9 ascribed to two OCH_2 carbons of the main chain, peaks at δ 97.2 and 102.5 due to the –OCO– carbon, peaks at δ 128.5–132.7 due to aromatic carbons, and a doublet peak centered at δ 67.0 (J_{CP} = 22.6 Hz) assigned to the PCO carbon.

The ^{31}P NMR spectrum of the copolymer **3b** in $CDCl_3$ showed one peak at δ +38.1 (relative to H_3PO_4 as an external standard) ascribable to a phosphinate unit. The IR spectrum of the copolymer exhibited two strong absorptions at 1205 cm^{-1} due to the P=O bond and at 1026 cm^{-1} due to the P–O–C stretching vibration and weak absorptions at 3365 and 1715 cm^{-1} assignable to terminal OH and aldehyde groups of copolymer **3b**, respectively. Anal. Calcd for $(C_{13}H_{17}O_4P(H_2O)_{1.50})_n$ (entry 2): C, 53.15; H, 6.35. Found: C, 53.11; H, 6.38.

In all copolymerization runs between **1** and **2** ring-opening–closing alternating copolymers **3a–3d** have been obtained in relatively high to moderately high isolated yields (Table I).

It can be seen that reaction temperatures around 100 °C and relatively short reaction times (4–5 h) favor the copolymer formation. There is no significant change in the molecular weight of **3** using different cyclic phosphonites, **1a** or **1b**. However, **2b** gave a higher molecular weight

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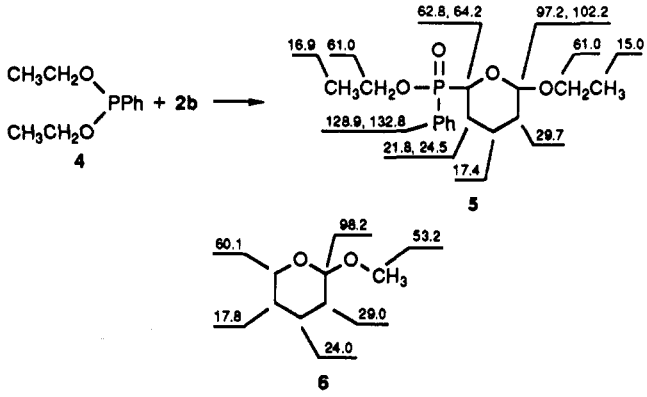
Table I
Ring-Opening–Closing Alternating Copolymerization of 1 with 2[a]

copolymerization							copolymer	
	monomer							
entry	1	2	solv	temp, °C	time, h	yield,[b] %	structure	mol wt[c]
1	1a	2a	$CHCl_3$	80	5	66	3a	1500
2	1a	2b	toluene	100	1	79	3b	1200
3	1a	2b	$CHCl_3$	80	1	62	3b	1200
4	1b	2a	$CHCl_3$	80	5	47	3c	1200
5	1b	2a	toluene	100	4	30	3c	1400
6	1b	2b	toluene	100	4	57	3d	1900

[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 by using Gelpack GL-A130 column with chloroform eluent at a flow rate of 1.0 mL/min at 40 °C. The calibration curves were obtained by using polystyrene standards.

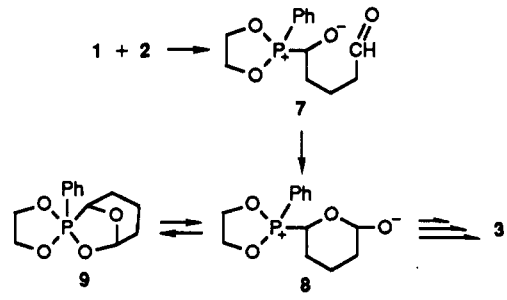
copolymer with the same cyclic phosphonite **1b** compared with **2a** (entries 5 and 6). It is important to note that all copolymers **3** have ring-closed structures, which is an indication of the complete cyclization of monomer **2a** or **2b** during the copolymerization.

In addition a model reaction of **2b** with diethyl phenylphosphonite (**4**) as a model of **1a** gave a cyclized product



5.[4] ^{13}C NMR chemical shifts and spectral assignments of the model reaction product **5** and compound **6** (2-methoxytetrahydropyran) for a model of the cyclized unit of **3** supported these structures, indicating that the ring-closing step is definitely involved in the copolymerization.

The reaction of **1** with **2** can be explained by the following mechanism. The first step of the reaction involves the



nucleophilic attack of the phosphorus(III) atom of **1** toward the carbonyl carbon atom in **2**, forming intermediate **7**. The second step is the fast intramolecular cyclization (ring-closing) reaction of **7**, giving rise to a genetic zwitterion **8**. The copolymers **3** are then produced by reacting the oxygen anionic site of **8** and/or macrozwitterions with the methylene carbon adjacent to the OP^+ group of **8** and/or macrozwitterions via an Arbuzov type reaction with ring-opening.

Thus, the repeating unit of **3** has one part that comes from the ring-opening of monomer **1** and the other part from the ring-closing of monomer **2** (ring-opening–closing alternating copolymerization). When a mixture of **1** and **2** in $CDCl_3$ was monitored in situ by ^{31}P NMR at 25 °C, immediately after mixing both monomers a peak at δ −24.3 and another one at δ +41.4 appeared, the former being reasonably assigned as a pentacovalent spirophosphorane **9** and the latter as a phosphonite unit of copolymer **3**.[5] An attempt has been made to isolate intermediate **9** from a reaction of **1** with **2** at a lower temperature. However, the reaction at −20 °C produced not only **9** but also copolymer **3**; the propagation still took place at this temperature. Thus, the isolation of **9** was not successful, but it has been found that **9** was relatively stable at a temperature of −20 °C.[6]

In conclusion, the reaction of cyclic phosphonite **1** with dialdehyde **2** led readily to a 1:1 alternating copolymer with the proposed structure **3**. This reaction provides a new example of the novel concept of the ring-opening–closing alternating copolymerization. A more detailed study including different cyclic phosphonites and dialdehydes is now in progress.

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References and Notes

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(4) When a mixture of diethyl phenylphosphonite (**4**) and **2b** in $CHCl_3$ was heated at 100 °C for 24 h, adduct **5** was formed (yield 76%), whose structure has been verified by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopies.

(5) The peak due to **2** at δ +162.0 disappeared completely after 5 min of reaction, whereas the concentration of **9** and **3** remained almost constant for more than 2 h at 25 °C. When the reaction

mixture then was heated to 80 °C for 15 min, ^{31}P NMR showed the complete conversion of **9** to **3**.

(6) Into 20 mL of diethyl ether containing 3.0 mmol of **1** was added 3.0 mmol of **2** at 0 °C under argon, and then the mixture was allowed to react at 0 °C for 5 h. The mixture was further kept in a refrigerator (−20 °C) for 14 days, and a precipitation was observed. The diethyl ether solution was decanted, and the ^{31}P NMR spectrum was taken on the separated white precipitate. Two peaks were observed; one at δ +39.0 due to **3** and another at δ −29.7 due to **9**, the latter being in 35% of the total concentration.

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