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Ring-Opening-Closing Alternating Copolymerization of Cyclic Phosphonites with Muconic Acid: Synthesis, Mechanism, and Kinetic Studies

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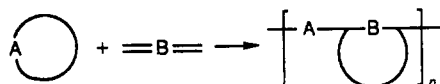
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ABSTRACT: A new type of alternating copolymerization between cyclic phosphonites (**1**) with *cis,trans*- and *cis,cis*-muconic acids (**2a** and **2b**) proceeds smoothly without any added catalyst to give copolymers **3a–c** having a repeating unit of the ring-opened structure of **1** and ring-closed structure of **2** (*ring-opening-closing alternating copolymerization* (ROCAC)). Cyclic phosphonites employed are 2-phenyl-1,3,2-dioxaphospholane (five-membered, **1a**), 2-phenyl-1,3,2-dioxaphosphorinane (six-membered, **1b**), and 2-phenyl-1,3,2-dioxaphosphepane (seven-membered, **1c**). A mechanism which involves a zwitterion intermediate is proposed for the copolymerization. The apparent values of the monomer reactivity ratio were determined as $r_{1a} = 0.06$ and $r_{2a} = 0.00$ in DMF at 100 °C. The kinetic study using ^1H NMR spectroscopy revealed that the rate constant of the Michael-type addition of **1a** to **2a** is much larger than that of **1a** to **2b**.

Introduction

The *ring-opening-closing alternating copolymerization* (ROCAC)^{1–4} provides us with a novel concept which combines ring-opening polymerization of a cyclic monomer (A)⁵ and cyclo (ring-closing) polymerization of a linear, bifunctional monomer (B).⁶ The combination of mono-

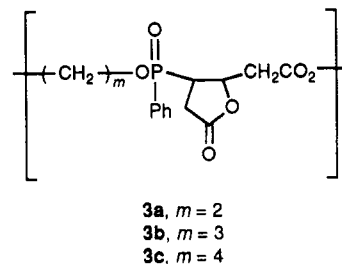
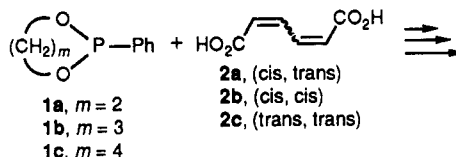


mers A and B induces the copolymerization without added catalyst to form an alternating copolymer having a repeating unit of a ring-opened and ring-closed structure.

In the previous paper we have reported the first example of ROCAC using 2-phenyl-1,3,2-dioxaphospholane (five-membered, **1a**) and *cis,trans*-muconic acid (**2a**).¹ The copolymerization proceeded via ring opening of **1a** and ring closing of **2a** alternatively. The present paper describes comprehensive results on the ROCAC of three cyclic phosphonites (**1a–c**) with *cis,trans*-muconic acid (**2a**) and *cis,cis*-muconic acid (**2b**).

Results and Discussion

Copolymerization of 1 with 2a. All of the cyclic phosphonites **1a** (five-membered), **1b** (six-membered), and **1c** (seven-membered) were readily copolymerized with **2a** to produce alternating copolymers **3**³ (Table I). In all runs,



the copolymerization took place in *N,N*-dimethylformamide (DMF) without any added catalyst. The structures of these product copolymers **3a–c** were determined by ^1H , ^{13}C , and ^{31}P NMR as well as IR spectroscopies (Table II). By comparing the integral value of peaks due to phenyl protons with that due to other protons, the content of **1** and **2** in the copolymer was calculated to be 50%. These data support that the copolymerizations proceeded involving ring opening of **1** and ring closing of **2a** to produce the alternating copolymers **3a–c** having phosphinate-lactone-ester unit structures.⁷

The isolated copolymers probably contain the terminal groups of carboxylic acid and alcohol structures (**4**), the former coming from proton abstraction by the carboxylate

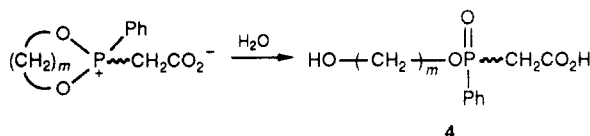
Table I
Ring-Opening-Closing Alternating Copolymerization of **1** with **2a**^a

entry	copolymerization			copolymer	
	cyclic phosphonite 1	temp (°C)	time (h)	yield ^b (%)	mol wt ^c
1	1a	35	786	68	1200
2	1a	100	9	54	1000
3	1a	100	17	57	3500
4 ^d	1a	100	40	50 ^e	3000 ^e
5	1b	100	6	54	1200
6	1c	50	70	60	1000
7	1c	100	70	51	1200

^a 1.0 mmol of each monomer in 1.5 mL of DMF. ^b Diethyl ether insoluble part. ^c Determined by GPC with CHCl₃ at 40 °C. ^d Solvent, CH₃CN. ^e The copolymer has the 3.0:1.0 (**1a**:**2a**) composition as shown in the text.

Table II
Spectroscopic Analyses of Alternating Copolymers **3a**–**c**

copolymer structure	¹ H, ¹³ C, and ³¹ P NMR and IR data
3a	¹ H NMR (CDCl ₃) δ 1.5–3.1 (br, CH ₂ C=O and PCH, 5 H), 4.2 (br, OCH ₂ and CHO, 5 H), 7.5 (br, C ₆ H ₅ P, 5 H) ¹³ C NMR (CDCl ₃) δ 20.4 and 37.2 (CH ₂ C=O), 26.8 (d, <i>J</i> _{CP} = 22.7 Hz, PCH), 62.2 and 63.5 (OCH ₂), 128.7–132.6 (C ₆ H ₅ P), 168.7–172.0 (C=O); (DMSO- <i>d</i> ₆) 75.6 (CHO) ³¹ P NMR (CDCl ₃) δ +50.0 IR (KBr) 1774 (ν _{C=O} of lactone), 1722 (ν _{C=O} of ester), 1208 (ν _{P=O}), 1026 cm ⁻¹ (ν _{P–O–C})
3b	¹ H NMR (CDCl ₃) δ 1.5–2.2 (br, CH ₂ CH ₂ CH ₂ , 2 H), 2.2–3.3 (br, CH ₂ C=O and PCH, 5 H), 4.2 (br, OCH ₂ and CHO, 5 H), 7.5 (br, C ₆ H ₅ P, 5 H) ¹³ C NMR (CDCl ₃) δ 23.5 and 37.6 (CH ₂ C=O), 28.7 (d, <i>J</i> _{CP} = 26.7 Hz, PCH), 29.6 (CH ₂ CH ₂ CH ₂), 61.3 and 62.2 (OCH ₂), 75.3 (CHO), 128.6–133.7 (C ₆ H ₅ P), 167.9–177.1 (C=O) ³¹ P NMR (CDCl ₃) δ +45.6 IR (KBr) 1785 (ν _{C=O} of lactone), 1727 (ν _{C=O} of ester), 1226 (ν _{P=O}), 1034 cm ⁻¹ (ν _{P–O–C})
3c	¹ H NMR (CDCl ₃) δ 1.9 (br, CH ₂ CH ₂ CH ₂ CH ₂ , 4 H), 2.4–3.5 (br, CH ₂ C=O and PCH, 5 H), 4.06 (br, OCH ₂ and CHO, 5 H), 7.5 (C ₆ H ₅ P, 5 H) ¹³ C NMR (CDCl ₃) δ 24.9 and 37.8 (CH ₂ C=O), 27.0 (CH ₂ CH ₂ CH ₂), 30.3 (d, <i>J</i> _{CP} = 20.7 Hz, PCH), 64.6 (OCH ₂), 75.3 (CHO), 128.6–133.7 (C ₆ H ₅ P), 162.8–173.0 (C=O) ³¹ P NMR (CDCl ₃) δ +41.6 IR (KBr) 1776 (ν _{C=O} of lactone), 1713 (ν _{C=O} of ester), 1206 (ν _{P=O}), 1027 cm ⁻¹ (ν _{P–O–C})



group and the latter due to hydrolysis of the phosphonium ring during the work-up procedures.¹

As shown in Figure 1, the monomer unit ratio in copolymer **3a** was ca. 0.5 at every stage of the copolymerization, indicating the alternating structure of **3a**.

When the copolymerization of **1a** with **2a** was carried out in acetonitrile, the product copolymer did not possess a 1:1 composition. The ratio of units **1a** and **2a** was 3.0:1.0 (entry 4 in Table I). The high **1a** unit content is due to the homosequence formation of **1a**. This may be explained by the heterogeneous reaction of **1a** with **2a** due to the low solubility of **2a** in acetonitrile.

Monomer reactivity ratios between **1a** and **2a** were determined. Copolymerization was carried out in DMF at 100 °C for 0.5 h, which resulted in a low conversion. The

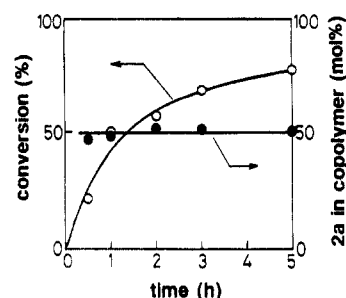


Figure 1. Time-conversion curves and copolymer compositions in the copolymerization of **1a** with **2a** at 100 °C in DMF; [**1a**]₀ = [**2a**]₀ = 0.1 mmol in 0.15 mL of DMF.

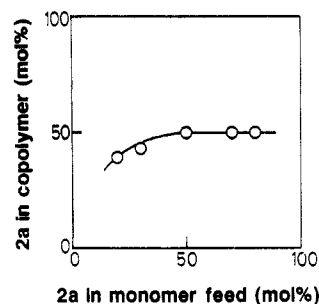
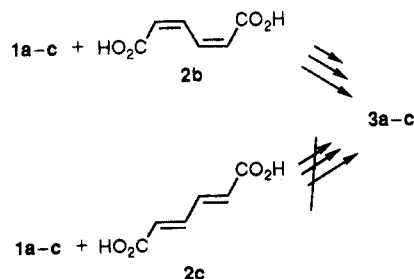


Figure 2. Copolymerization of **1a** with **2a** at 100 °C in DMF for 0.5 h. Polymer compositions at various comonomer feeds: [**1a**] + [**2a**] = 0.2 mmol in 0.15 mL of DMF.

copolymer **3a** was isolated, and the copolymer composition was determined by ¹H NMR analysis. Figure 2 shows a copolymer composition curve with varying the monomer feed ratio. In the region where the feed amount of **2a** is more than 50 mol %, alternating propagation takes place. When the feed amount of **2a** is less than 50 mol %, the copolymer containing less than 50 mol % of the unit ratio from **2a** was obtained. This indicates that both the alternating propagations as well as the homopropagations of **1a** occur. The apparent copolymerization parameters were determined as *r*_{1a} = 0.06 and *r*_{2a} = 0.00.⁸ Although the copolymerization mechanism of the present reaction is different from that of the usual radical copolymerization, these values are informative to see the alternating tendency of the arrangement of copolymer units.

Copolymerization of 1 with 2b and 2c. The copolymerization of geometrical isomers of **2a**, *cis,cis*- and *trans,trans*-muconic acids (**2b** and **2c**, respectively), with



1 was examined. The *cis,cis* isomer **2b** was copolymerized with **1a**–**c** to produce copolymers **3a**–**c**, respectively. The spectral data of these product copolymers **3a**–**c** from **2b** were found identical with those of the corresponding copolymers from **2a**. Polymerization results are summarized in Table III. The use of acetonitrile as solvent afforded the copolymer having a higher content of units from **1a** (3.2:1.0, entry 4 in Table III). This is again due to the low solubility of **2b** toward acetonitrile.

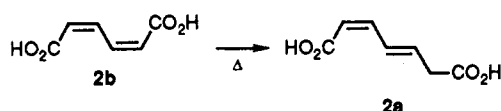
When the copolymerization of **1** with **2b** was monitored by ¹H NMR, peaks due to **2a** were observed. It has already

Table III
Ring-Opening-Closing Alternating Copolymerization of 1
with 2b^a

entry	copolymerization			copolymer	
	cyclic phosphonite 1	temp (°C)	time (h)	yield ^b (%)	mol wt ^c
1	1a	35	960	68	1200
2	1a	100	9	80	2300
3	1a	100	62	60	2800
4 ^d	1a	100	47	60 ^e	4200 ^e
5	1b	50	62	77	1100
6	1b	100	6	85	2100
7	1c	50	70	58	1000
8	1c	100	44	39	1400

^a 1.0 mmol of each monomer in 1.5 mL of DMF. ^b Diethyl ether insoluble part. ^c Determined by GPC with CHCl₃ at 40 °C. ^d Solvent, CH₃CN. ^e The copolymer has the 3.2:1.0 (1a:2b) composition as shown in the text.

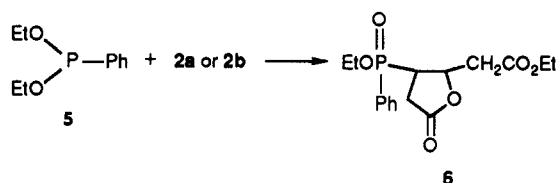
been reported that 2b is easily isomerized to 2a upon heating.⁹ During the copolymerization, both 2a and 2b



coexisted due to the isomerization of 2b to 2a. Therefore, 1 probably reacts with both 2a and 2b concurrently to produce 3 in the copolymerization.

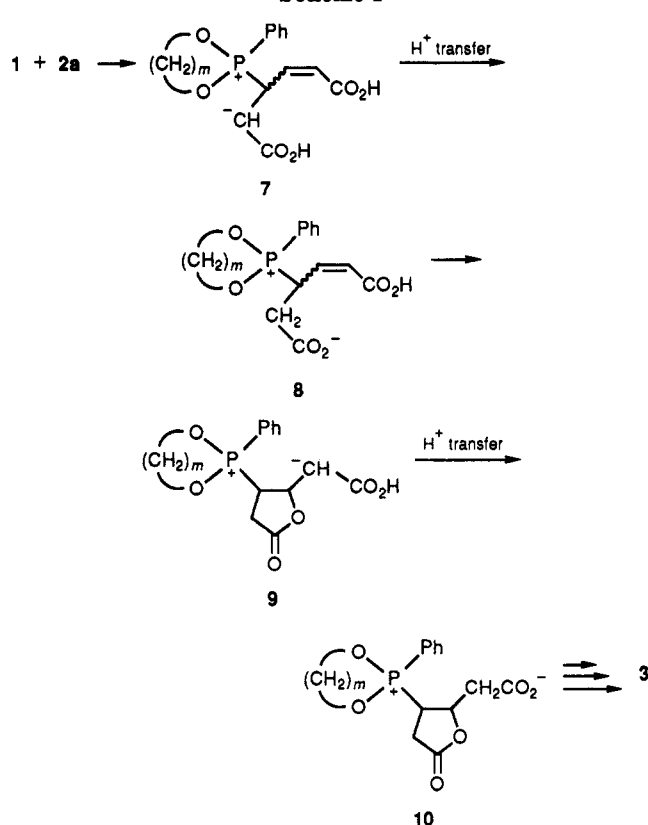
The copolymerization of 1 with 2c did not occur under similar polymerization conditions probably due to the poor solubility of 2c in common organic solvents.

Model Reaction. In order to confirm the structure of the copolymer 3, the following model reaction was carried out using diethyl phenylphosphonite (5) as a noncyclic model compound for monomer 1.

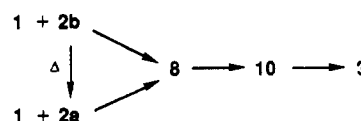


An equimolar mixture of 5 and 2a or 2b in DMF-*d*₇ was heated at 100 °C for 24 h in an NMR tube. The ¹H and ³¹P spectra of the mixture indicated a quantitative formation of the adduct 6. The ¹H NMR spectrum (DMF-*d*₇) showed a multiplet peak at δ 1.34 due to CH₃ (6 H), a broad multiplet peak at δ 2.39–3.05 ascribable to CCH₂C (4 H), a broad peak at δ 3.22–3.30 due to PCH (1 H), a multiplet peak at δ 3.64 due to CHO (1 H), a broad multiplet peak at δ 3.77–4.21 ascribable to OCH₂ (4 H), and multiplet peaks at δ 7.65 and 7.79 due to C₆H₅ (5 H). In the ³¹P NMR spectrum (DMF-*d*₇) only one peak at δ +44.6 was observed. Although the ¹³C NMR spectrum was also measured in situ, the peaks due to CCH₂C were overlapping with peaks due to CD₃ of DMF-*d*₇. In order to confirm further the structure of 6 by ¹³C NMR, reaction of 5 and 2 in CDCl₃ was carried out. After heating at 100 °C for 24 h, the ¹³C NMR spectrum in situ showed peaks at δ 14.1 and 17.0 due to methyl carbons, a peak at δ 17.7 (*d*, *J*_{CCP} = 18.2 Hz) assignable to methylene carbon of lactone, a peak at δ 31.1 (*d*, *J*_{CP} = 32.9 Hz) due to methine carbon of PCH, a peak at δ 39.0 due to α -carbon of ester, peaks at δ 61.0 and 62.0 (*d*, *J*_{COF} = 3.6 Hz) due to OCH₂ of ester and phosphinate, respectively, a peak at δ 75.3 (*d*, *J*_{CCP} = 4.2 Hz) assignable to methine carbon of CHO, peaks at δ 128.1–141.3 due to aromatic carbons, and peaks at δ 169.1

Scheme I



Scheme II



and 173.6 assignable to carbonyl carbons. These spectral data can be taken to identify the structure of 6. The quantitative formation of 6 by the model reaction clearly supports the copolymer structure 3 by the ROCAC.

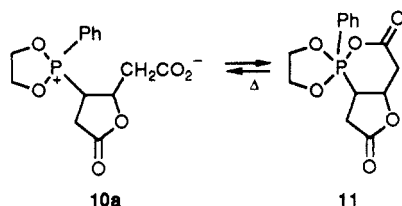
Copolymerization Mechanism. On the basis of the above data, the mechanism in Scheme I is proposed for the ROCAC of 1 with 2a.

The first step of the reaction is an intermolecular Michael-type addition of 1 to 2a to form a phosphonium-carbanion intermediate 7, followed by a hydrogen transfer to give a transient zwitterion 8. Then, 8 is converted into a key species of genetic zwitterion 10 via a ring-closing process by an intramolecular Michael-type addition and a hydrogen-transfer process in a phosphonium-carbanion intermediate 9. In the next step, the phosphonium ring of 10 is opened by a nucleophilic attack of the anion from another molecule 10 according to an Arbuzov-type reaction. The propagation proceeds via successive combination among genetic and dimeric zwitterions to lead to alternating copolymer 3 of a zwitterion structure.¹⁰

On the other hand, the mechanism of the copolymerization of 1 with 2b is explained in Scheme II.

Due to the isomerization of 2b to 2a, two routes are possible to form the zwitterion 8. One is a Michael-type addition of 1 to 2b and the other the Michael-type addition of 1 to 2a. Then, 8 is converted into the zwitterion 10 which leads to the alternating copolymer 3.

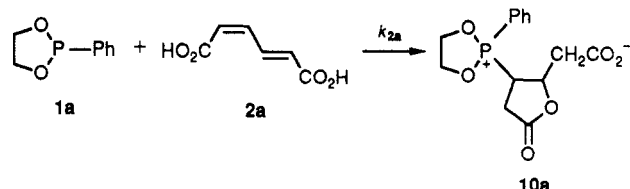
In the ³¹P NMR in situ spectrum of the copolymerization of 1a with 2a or 2b, small signals at δ +0.7 and -14.9 ascribable to a zwitterion 10a and a pentacoordinate spiro phosphorus compound 11, respectively, appeared in addition to the main signal due to the copolymer. This result



implies the existence of equilibrium between 10a and 11. However, the spiro compound has not been observed in the copolymerization of 1b and 1c with 2 in the ^{31}P NMR spectra. These findings suggest that the spiro compound is involved only in the copolymerization of 1a with 2.

Kinetic Study. Kinetic analysis was carried out by monitoring the copolymerization system by ^1H NMR spectroscopy, in which the disappearance of olefinic protons of monomer 2 was followed to obtain the conversion of 2. Figure 3 shows the time-conversion curves for the monomers in the copolymerization of 1a with 2a and with 2b at 60 °C (a) and 35 °C (b). At a high temperature (60 °C), the conversion of 1a using 2a as comonomer was higher than that in the copolymerization with 2b (Figure 3a). At 35 °C, the time-conversion curves of both monomers show almost identical patterns.

In order to examine these phenomena in more detail, a kinetic analysis of the copolymerization was carried out by using ^1H NMR spectroscopy. In the ^1H NMR spectra in situ during the copolymerization of 1a with 2a, the peaks due to olefinic protons of only monomer 2a were detected; no peak due to olefinic protons of the zwitterion 7 or 8 was observed. Therefore, it can be assumed that the intramolecular Michael-type addition and the hydrogen-transfer process are much faster than the intermolecular Michael-type addition; the Michael-type addition of 1a to 2a is the rate-determining step in the formation of zwitterion 10a. Therefore, the rate equation for the zwitterion formation in the copolymerization of 1a and 2a is given by eq 1 based on the scheme



$$d[10a]/dt = k_{2a}[1a][2a] \quad (1)$$

where [1a], [2a], and [10a] are the concentrations of monomers 1a, 2a, and zwitterion 10a, respectively. In the copolymerization of 1a is always equal to that of 2a because the consumption rates of both monomers are the same. In addition, the formation rate of 10a is equal to the consumption rate of 2a. Therefore, the relationship of eq 2 will be valid. Equation 1 is then expressed as eq 3. The

$$d[10a]/dt = -d[2a]/dt \quad (2)$$

$$-d[2a]/dt = k_{2a}[2a]^2 \quad (3)$$

integrated form of eq 3 is given as

$$1/[2a] - 1/[2a]_0 = k_{2a}t + A \quad (4)$$

where [2a] and [2a]₀ are the instantaneous and initial concentrations of 2a, respectively. Plots of $1/[2a] - 1/[2a]_0$ against t showed a linear relationship, indicating that the

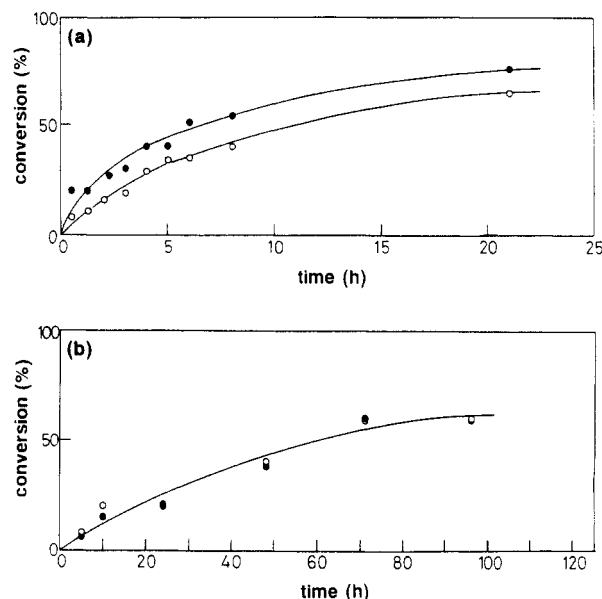


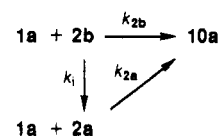
Figure 3. Time-conversion curves of the copolymerization of 1a with 2a (●) and with 2b (○): (a) at 60 °C, (b) at 35 °C; [1a]₀ = [2a]₀ = [2b]₀ = 0.943 mol/L.

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

temp (°C)	$k_{2a} \times 10^4$ [L/(mol·s)]		$k_i \times 10^4$ (s ⁻¹)
	in the copolymn of 1a with 2a	in the copolymn of 1a with 2b	
35	0.0694	0.0754	0.337
60	0.500	0.613	2.08
80	2.26	2.50	4.86
100	7.20	8.84	12.8
ΔH^\ddagger (60 °C), kJ/mol	63.2	64.4	47.2
ΔS^\ddagger (60 °C), J/(K·mol)	-166	-161	-204

rate for the Michael-type addition obeys second-order kinetics. Results of k_{2a} values in DMF- d_7 are given in Table IV.

On the other hand, the following scheme will explain the course of the formation of the zwitterion 10 in the copolymerization of 1a with 2b, in which both the isomerization of 2b to 2a and the formation of zwitterion 10a take place concurrently.



Now, the following kinetics equations are given on the basis of the above scheme

$$-d[2b]/dt = k_i[2b] + k_{2b}[2b][1a] \quad (5)$$

$$-d[1a]/dt = k_{2a}[2a][1a] + k_{2b}[2b][1a] \quad (6)$$

where [1a], [2a], and [2b] are the concentration of the monomers 1a, 2a, and 2b, respectively, and k_i denotes the isomerization rate constant of 2b to 2a. Then eq 5 becomes

$$-d[2b]/dt = (k_i + k_{2b}[1a])[2b] \quad (7)$$

Integration of eq 7 gives

$$\ln \frac{[2b]_0}{[2b]} = k_i \int_0^t dt + k_{2b} \int_0^t [1a] dt \quad (8)$$

Therefore

$$\frac{1}{t} \ln \frac{[2b]_0}{[2b]} = k_i + k_{2b} \frac{\int_0^t [1a] dt}{t} \quad (9)$$

The integrated value of [1a] was obtained by graphical integration of the [1a]–time curve, in which [1a] can be calculated from the conversion of 1a. Plots of $(1/t) \ln ([2b]_0/[2b])$ vs $\int_0^t [1a] dt/t$ showed a linear relationship, whose slope gives a k_{2b} value, which was nearly equal to zero ($k_{2b} \sim 1.0 \times 10^{-8}$) at four temperatures examined. The k_i values were determined from the intercept and are given in Table IV. Therefore, these data indicate that the Michael-type addition of 1a to 2b is much slower than that of 1a to 2a and than the isomerization of 2b to 2a.

From the above results, $k_{2b}[2b][1a]$ can be neglected, and then eq 6 is converted into

$$-d[1a]/dt = k_{2a}[2a][1a] \quad (10)$$

Then eq 10 becomes

$$-d[1a]/[1a] = k_{2a}[2a] dt \quad (11)$$

Integration of eq 11 gives

$$\ln \frac{[1a]_0}{[1a]} = k_{2a} \int_0^t [2a] dt \quad (12)$$

By comparison of the integral value of peaks in the 1H NMR spectra, [2a] was determined. Therefore, the integrated value of [2a] was obtained by graphical integration on the [2a]–time curve. The rate constants k_{2a} were determined from the slope of the linear plots of eq 12, which are also given in Table IV. These values are very close to the k_{2a} values determined in the copolymerization of 1a with 2a. The activation parameters were obtained from the Arrhenius plots of these calculated rate constants (Table IV).

Then, eq 12 can be changed to

$$[1a] = \exp(\ln [1a]_0 - k_{2a} \int_0^t [2a] dt) \quad (13)$$

Therefore, the conversion of 1a is given as

extent of reaction =

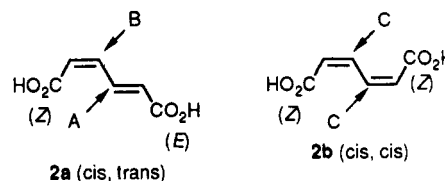
$$\frac{[1a]_0 - \exp(\ln [1a]_0 - k_{2a} \int_0^t [2a] dt)}{[1a]_0} \quad (14)$$

At 35 °C, the k_i value is much higher than the k_{2a} value in the copolymerization of 1a with 2b. Therefore, 2b is mainly isomerized to 2a at the early stage of the copolymerization before the isomerized 2a was consumed. In this case, the concentration of 2a in the copolymerization of 1a with 2b is almost equal to that in the copolymerization of 1a with 2a. From eq 14, the time–conversion curve in the copolymerization of 1a with 2b is identical with that in the copolymerization of 1a with 2a at 35 °C as observed in Figure 3b.

On the other hand, at a higher temperature, as 60 °C, 2a formed by the isomerization of 2b reacts with 1a before the complete isomerization of 2b to 2a, indicating that the concentration of 2a in the copolymerization of 1a with 2b is lower than that in the copolymerization of 1a with 2a. From eq 14, therefore, it is evident that the consumption of 1a in the copolymerization of 1a with 2b is slower in rate than that in the copolymerization of 1a with 2a.

The difference in reactivity between 2a and 2b toward 1a may be understood as follows. The olefinic carbon A in 2a is sterically more hindered by the (E)-carboxylic acid group than the olefinic carbon B which may be

hindered by the (Z)-carboxylic acid. The steric hindrance of carbon C in 2b is very similar to that of A. Therefore, the nucleophilic attack of 1a occurs most readily at carbon B in 2a, explaining the higher reactivity of monomer 2a than monomer 2b. The electronic factors may also affect the reactivity of these carbons.¹¹



Conclusion

The reaction of a cyclic phosphonite 1 with muconic acid 2 led readily to a 1:1 alternating copolymer 3, which has a structure with a ring-opened unit from 1 and a ring-closed unit from 2 in an alternating arrangement. This reaction provides a new category of reaction in the polymerization chemistry, i.e., *ring-opening-closing alternating copolymerization (ROCAC)*.

Experimental Section

Materials. 2-Phenyl-1,3,2-dioxaphospholane (1a), 2-phenyl-1,3,2-dioxaphosphorinane (1b), and 2-phenyl-1,3,2-dioxaphosphepane (1c) were prepared according to the literatures.^{13,14} *cis,cis*-Muconic acid (2b) was used as supplied from Mitsubishi Kasei Co., Tokyo (prisms, mp = 194–195 °C). *cis,trans*-Muconic acid (2a) was prepared according to the literature⁹ as follows: *cis,cis*-Muconic acid (2b) was heated in boiling water, and the resulting solution was cooled to room temperature. The precipitate was collected by filtration and dried in vacuo (needles, mp = 190–191 °C). Diethyl phenylphosphonite (5) was prepared by a similar method of 1a from dichlorophenylphosphine and ethanol in the presence of triethylamine in benzene and was purified by distillation, bp_{1.0} = 62–64 °C. DMF was purified by distillation over P₂O₅. DMF-*d*₇ and CDCl₃ for solvents of the model reaction and NMR analysis are commercial reagents which were dried by 4A molecular sieves.

Copolymerization. A typical procedure was as follows. A mixture of monomers 1a (0.168 g, 1.0 mmol) and 2a (0.142 g, 1.0 mmol) in 1.5 mL of DMF was heated at 100 °C under argon. After 17 h, the reaction mixture was poured into a large amount of diethyl ether to precipitate the polymeric products. The material was isolated by filtration and dried in vacuo to give 0.183 g of a hygroscopic powder (59% yield).

Model Reaction. To 0.142 g of 2 in 1.5 mL of DMF-*d*₇ or CDCl₃ was added 0.198 g of 5. The mixture was kept in a sealed tube at 100 °C for 24 h. The reaction product was directly subjected to NMR measurement.

Kinetic Procedures. The kinetic analysis was carried out by using 1H NMR spectroscopy. The disappearance of the olefinic protons of 2a (δ 5.9–7.2, 3 H, δ 8.2–8.8, 1 H, DMSO-*d*₆) and those of 2b (δ 5.6–5.9, 2 H, δ 7.4–7.7, 2 H, DMSO-*d*₆) was monitored. A typical run was as follows. In an NMR tube under argon was placed 0.2 mmol of each monomer 1a and 2 in 0.15 mL of a DMF-*d*₇ solution ($[1a]_0 = [2]_0 = 0.943$ mol/L). The NMR tube was kept at a desired temperature. The copolymerization was monitored, and the spectrum of the copolymerization mixture was recorded.

Measurements. 1H NMR spectra were recorded on 250-MHz Bruker AC250T and 60-MHz Hitachi R-24A NMR spectrometers. ^{13}C NMR spectra were recorded on a 62.8-MHz Bruker AC250T NMR spectrometer. ^{31}P NMR spectra were recorded on 100-MHz Bruker AC250T and 36.4-MHz JEOL FX-90Q NMR spectrometers. IR spectra were recorded on a Shimadzu IR-27G spectrometer. Gel permeation chromatographic (GPC) analysis was performed by using a Tosoh 8010 apparatus with a UV detector under the following condition: Gelpack GL-A130 column with a chloroform eluent at a flow rate of 1.0 mL/min. The calibration curves were obtained by using polystyrene standards.

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References and Notes

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- (10) The molecular weight of the copolymers was not so high, at most 3500. This is probably due to the lower reactivity of the anionic site of the zwitterion species. In the copolymerization of a cyclic phosphinite with acrylic acid, an alternating copolymer of low molecular weight was also produced, in which the structure of the anionic site in the zwitterion of the copolymerization is similar to that of the present copolymerization. Saegusa, T.; Kimura, Y.; Ishikawa, N.; Kobayashi, S. *Macromolecules* **1976**, *9*, 724.
- (11) The total electron density (TED) calculations by the PM3 method were performed with MOPAC Version 5.0. TED values of each of the carbons A-C in most stable conformations of **2a** and **2b** were 4.0691, 4.0381, and 4.0609, respectively. TED of carbon B was lower than that of another carbon A or C, suggesting the preference of nucleophilic attack of **1a** onto carbon B.
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Registry No. **1a**, 1006-83-3; **1b**, 7526-32-1; **1c**, 7526-37-6; **2a**, 1119-72-8; **2b**, 1119-73-9; (**1a**)(**2a**) (alternating copolymer), 137111-53-6; (**1a**)(**2b**) (alternating copolymer), 143309-90-4; (**1b**)(**2a**) (alternating copolymer), 137111-55-8; (**1b**)(**2b**) (alternating copolymer), 143309-91-5; (**1c**)(**2a**) (alternating copolymer), 143309-89-1; (**1c**)(**2b**) (alternating copolymer), 143330-01-2; **5**, 1638-86-4; **6**, 143309-92-6.