

Alternating Copolymerization of Vinylphosphonic Acid Monoethyl Ester with Cyclic Phosponites Involving Proton-Transfer

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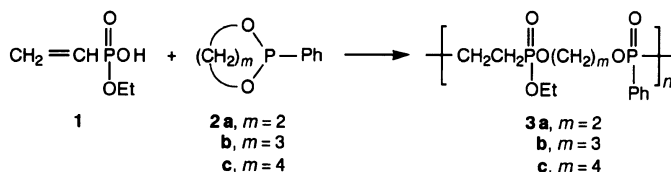
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ABSTRACT: This paper describes the alternating copolymerization of vinylphosphonic acid monoethyl ester **1** with five-, six-, and seven-membered cyclic phosponites (**2a**, **2b**, and **2c**). The copolymerization took place without any catalyst. Reaction of the 1:1 monomer feed ratio gave alternating copolymers having the phosphonite-phosphonate unit. During the copolymerization the proton-transfer in monomer **1** took place and the oxidation-reduction process is involved. The copolymerization is reasonably explained by a mechanism which involves zwitterion intermediates. The apparent monomer reactivity ratios determined in benzonitrile at 150°C are $r_1=0.00$ and $r_{2b}=0.16$. A kinetic study of the Michael-type addition in the initiation stage showed that **2b** was more reactive than **2a** or **2c**.

KEY WORDS Alternating Copolymerization / Vinylphosphonic Acid Monoethyl Ester / Cyclic Phosponite / Proton-Transfer / Zwitterion Mechanism /

A series of alternating copolymerizations involving a proton-transfer process have been studied extensively.¹ Very recently we have found an alternating copolymerization of vinylphosphonic acid monoethyl ester (**1**) with five-, six-, and seven-membered cyclic phospho-

nites (**2**) to produce an alternating copolymer (**3**).² The copolymerization took place without any catalyst. During the copolymerization, monomer **1** was reduced and monomer **2** was oxidized ("oxidation-reduction alternating copolymerization").³⁻⁶



The present paper reports comprehensive results including a kinetic study on the copolymerization of **1** with **2**.

EXPERIMENTAL

Materials

Monomers **2a—c** were synthesized according to the literatures.^{7,8} Solvents and other

reagents were purified in a usual manner. All operations were carried out under argon.

Synthesis of Vinylphosphonic Acid Monoethyl Ester (**1**)

When **1** was prepared according to the literatures^{9,10} in three step reactions, the overall yield of **1** was very low.

An alternative method for the synthesis of

1 was found as follows. To phosphorus pentachloride (20.9 g, 0.1 mol) was added diethylvinylphosphonate (16.4 g, 0.1 mol) with stirring at room temperature under argon. After stirring for 1 h, water (14.4 g, 0.8 mol) was added and the mixture was further stirred for 1 h. The reaction mixture was extracted with chloroform and the organic layer was dried over Na_2SO_4 . After evaporation of the solvent, the residue was subjected to distillation *in vacuo* to give 6.3 g of **1** (47% yield): bp 80–90°C (0.4 mmHg); ^1H NMR (CDCl_3) δ 1.28 (t, CH_3 , 3H), 4.00 (m, OCH_2 , 2H), 5.60–6.60 (m, $\text{CH}_2=\text{CH}$, 3H), 11.44 (s, OH, 1H); ^{31}P NMR (CDCl_3 with 85% H_3PO_4 external standard) δ +17.3.

Synthesis of Diethylphenylphosphonite (7)

Model compound **7** was synthesized in a similar manner to that of **2a–c** from dichlorophenylphosphine and ethanol in the presence of triethylamine in benzene and purified by distillation (70% yield): bp 62–64°C (1 mmHg); ^1H NMR (CDCl_3) δ 1.27 (t, CH_3 , 6H), 3.88 (m, OCH_2 , 4H), 7.42 (m, $\text{C}_6\text{H}_5\text{P}$, 5H); ^{31}P NMR (CDCl_3) δ +155.5.

Copolymerization of **1** with **2**

A typical run was as follows. An equimolar mixture of **1** and **2b** (1.0 mmol) in 0.3 ml of benzonitrile was kept under argon at 150°C for 24 h. After 24 h the mixture was poured into a large amount of diethyl ether to precipitate the polymeric product. The product was isolated by decantation and was dried *in vacuo* to give 0.11 g (36% yield) of **3b**.

Hydrolysis of Copolymer

To 0.18 g of the copolymer **3b** (entry 11) in 0.3 ml of acetonitrile, 0.3 ml of 6 M hydrochloric acid was added at room temperature. The mixture was kept at 150°C for 112 h. Products were identified by HPLC analysis compared with the authentic samples. Then, 5 ml of water was added to the reaction mixture

and the solution was poured into a large amount of acetonitrile to precipitate the solid material. The material was isolated by decantation and dried *in vacuo* to give hydrolysis product **4**. The supernatant was concentrated by evaporation to give trimethylene glycol **5**.

Model Reaction

Diethylphenylphosphonite **7** was reacted with an equimolar of **1** (3.0 mmol) in 1.0 ml of PhCN under argon at 150°C for 51 h. After removing the solvent, the residue was dried *in vacuo* to produce 0.68 g (68% yield) of **8**: ^1H NMR (CDCl_3) δ 1.28 (t, CH_3 , 9H), 2.00 (br, CH_2P , 4H), 4.04 (m, CH_2O , 6H), and 7.48 (m, $\text{C}_6\text{H}_5\text{P}$, 5H); ^{13}C NMR (CDCl_3) δ 16.5 (m, CH_3C), 18.2 (dd, $J_{\text{cp}}=144.5$ Hz, $J_{\text{ccp}}=4.0$ Hz, CH_2P), 23.1 (dd, $J_{\text{cp}}=101.6$ Hz, $J_{\text{ccp}}=6.6$ Hz, CH_2P), 61.5 (d, $J_{\text{cop}}=6.6$ Hz, CH_2O), 127.6–132.7 (m, $\text{C}_6\text{H}_5\text{P}$); ^{31}P NMR (CDCl_3) δ +41.5 and +30.4.

Measurements

^1H NMR spectra were recorded on 60 MHz Hitachi R-24A, 60 MHz JEOL FX-60Q, and 250 MHz Bruker AC-250T NMR spectrometers. ^{13}C NMR spectra were recorded on 15 MHz FX-60Q and 62.6 MHz Bruker AC-250T NMR spectrometers. ^{31}P NMR spectra were recorded on 36.4 MHz JEOL FX-90Q and 100 MHz Bruker AC-250T spectrometers. IR spectra were recorded on a Shimadzu IR-27G spectrometer. Gel permeation chromatographic (GPC) and high pressure liquid chromatographic (HPLC) analyses were performed by using Hitachi 665 A with RI detector under the following conditions: GPC analysis, TSKgel G2500H_{XL} column with DMF eluent at a flow rate of 0.5 ml min⁻¹ with poly(ethylene glycol) standards; HPLC analysis, Gelpack W-520 column with water eluent at a flow rate of 1.0 ml min⁻¹.

RESULTS AND DISCUSSION

Copolymerization of 1 with 2

As reported in a previous paper,² **1** was readily copolymerized with **2a–c** to produce **3a–c**. The results are shown in Table I.

In all cases, the copolymerization took place in a solvent without any added catalyst. The structure of copolymers **3a–c** were confirmed

by ³¹P, ¹H, and ¹³C NMR as well as IR spectroscopy (Table II). From ¹H NMR analysis, an equimolar ratio of two monomers **1** and **2** was also confirmed from the ratio of integrated area of methyl protons derived from **1** and phenyl protons derived from **2**. Figure 1 shows the ¹³C NMR spectrum of the copolymer **3b** (entry 5). A doublet at δ 14.8 ($J_{\text{cop}} = 5.1$ Hz) is assigned to methyl carbon of

Table I. Copolymerization of vinylphosphonic acid monoethyl ester **1** with cyclic phosphonites **2**

| Entry | Cyclic phosphonite 2 | Solvent | Temp. | Time | Yield ^a | M_w^b | M_w/M_n^b |
|-------|-----------------------------|--------------------|-------|------|--------------------|---------------------------|-------------|
| | | | °C | h | % | | |
| 1 | 2a | PhCN | 150 | 90 | 78 | 4000 | 2.5 |
| 2 | 2a | DMF | 150 | 20 | 100 | 1300 | 1.3 |
| 3 | 2b | CH ₃ CN | 25 | 8 | 9 | 870 | 1.5 |
| 4 | 2b | CH ₃ CN | 100 | 45 | 68 | 640 ^c 750 | 1.3 |
| 5 | 2b | CH ₃ CN | 150 | 24 | 44 | 810 ^c 1100 | 1.2 |
| 6 | 2b | PhCN | 25 | 8 | 11 | 900 ^c 800 | 1.4 |
| 7 | 2b | PhCN | 100 | 45 | 63 | 640 ^c 1500 | 1.3 |
| 8 | 2b | PhCN | 150 | 1 | 34 | 1690 ^c 750 | |
| 9 | 2b | PhCN | 150 | 24 | 36 | 2300 | |
| 10 | 2b | PhCN | 150 | 90 | 52 | 2070 ^c 2700 | 1.9 |
| 11 | 2b | DMF | 150 | 20 | 95 | 1900 | 1.3 |
| 12 | 2c | PhCN | 150 | 90 | 61 | 3000 | 3.9 |
| 13 | 2c | DMF | 150 | 20 | 90 | 1300 | 1.2 |

^a Isolated yield.

^b Determined by GPC with DMF eluent at 60°C.

^c Determined by ³¹P NMR.

Table II. ¹H NMR and IR spectroscopic data of copolymers **3a–c**

| | 3a (entry 1) | 3b (entry 9) | 3c (entry 12) |
|--|--|--|--|
| ¹ H NMR (CD ₃ OD) | δ 1.2 (t, CH ₃ C, 3H) 2.0 (br, CH ₂ P, 4H) 4.1 (br, CH ₂ O, 6H) 7.4 (br, C ₆ H ₅ P, 5H) | δ 1.2 (t, CH ₃ C, 3H) 1.8 (br, CCH ₂ C, 2H) 2.0 (br, CH ₂ P, 4H) 4.0 (br, CH ₂ O, 6H) 7.5 (br, C ₆ H ₅ P, 5H) | δ 1.2 (t, CH ₃ C, 3H) 1.6 (br, CCH ₂ C, 4H) 2.0 (br, CH ₂ P, 4H) 3.9 (br, CH ₂ O, 6H) 7.5 (br, C ₆ H ₅ P, 5H) |
| IR (neat) | 1225 cm ⁻¹ ($\nu_{\text{P=O}}$) 1025 cm ⁻¹ ($\nu_{\text{P-O-C}}$) | 1215 cm ⁻¹ ($\nu_{\text{P=O}}$) 1030 cm ⁻¹ ($\nu_{\text{P-O-C}}$) | 1210 cm ⁻¹ ($\nu_{\text{P=O}}$) 1010 cm ⁻¹ ($\nu_{\text{P-O-C}}$) |

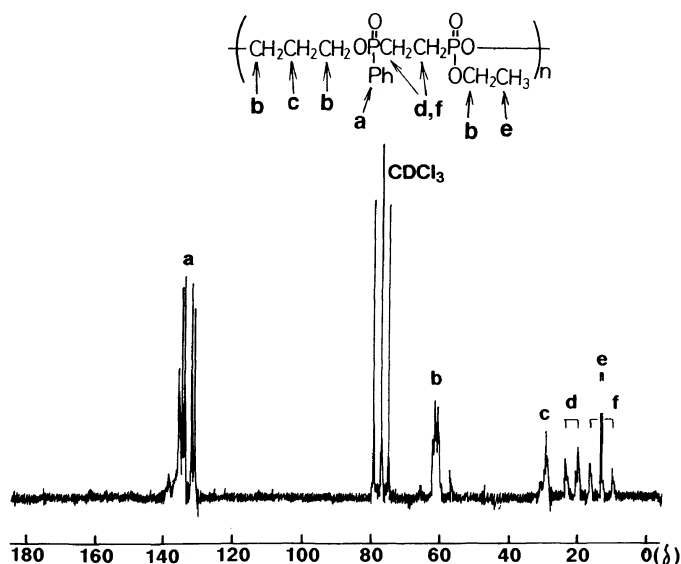


Figure 1. ^{13}C NMR (15 MHz) spectrum of copolymer **3b** (entry 5) in CDCl_3 .

ethyl group. Two doublets at δ 14.8 ($J_{\text{cp}} = 91.0$ Hz) and 21.2 ($J_{\text{cp}} = 53.0$ Hz) are due to two methylene carbons of PCH_2 . Signals at δ 21.2 and 60.5 are ascribed to methylene carbons of CCH_2C and OCH_2 , respectively. Multiplet peaks at δ 126.9–136.5 are due to aromatic carbons.

The ^{31}P spectrum of **3** in CD_3OD showed two main peaks at $\delta +35.5$ and $+51.2$ (relative to 85% H_3PO_4 external standard), which are assignable to two kinds of phosphorus atom of phosphinate unit and phosphonate unit, respectively. Besides these peaks a small peak at $\delta +23.3$ due to the terminal phosphorus atom of phosphonate type.

The molecular weight of the resulting copolymer **3** was determined by gel-permeation chromatography (GPC) with *N,N*-dimethylformamide (DMF) eluent.¹¹ It depends mainly upon the reaction temperature, the solvent, and the reaction time. The copolymer of higher molecular weight was obtained when the reaction was carried out at 150°C in benzonitrile and DMF. Even though the copolymerization proceeded at 25°C , the molecular weight

was very low (entry 3 and 6). Acetonitrile solvent was not suitable for the copolymerization; the copolymerization at 150°C in acetonitrile gave the copolymer of lower molecular weight (entry 5). The longer the reaction time, the higher the molecular weight of **3** (entry 8–10). The solubility of **3** was dependent on the molecular weight; **3** of relatively higher molecular weight is soluble in higher polar solvents such as DMF, methanol, and water. The copolymers of lower molecular weight (<1000) are soluble not only in these solvents but also in chloroform.

As shown in Figure 2, monomer **1** was consumed in the early stage of the copolymerization and the composition ratio of **1** in the copolymer was almost 50% at every stage of the reaction. These results support that the copolymerization proceeds alternately.

Figure 3 indicates a copolymer composition curve with varying monomer feed ratios. In the region where **1** is more than 50 mol% in the feed, alternating propagation took place. In the area where **1** is less than 50 mol%, however, both the alternating as well as homopropagation of **2b** occurred. The apparent

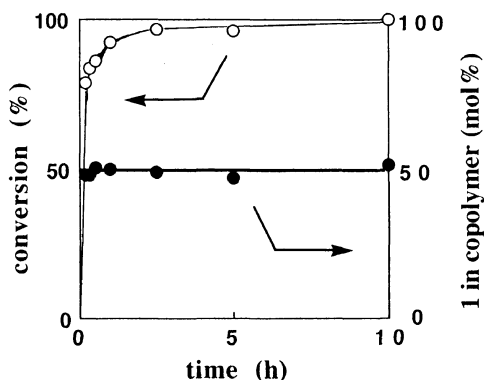


Figure 2. Time conversion curve of **1** in the copolymerization of **1** with **2b** and the composition ratio of **1** in the copolymer. Copolymerization was carried out with the 1 : 1 feed ratio in PhCN at 150°C.

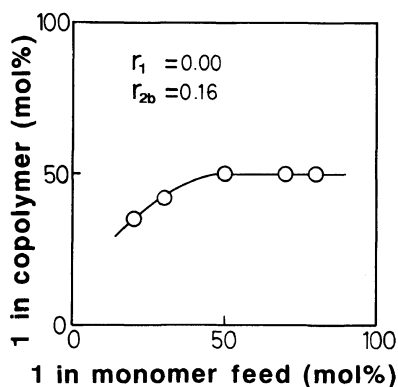


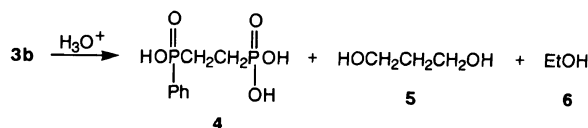
Figure 3. Copolymer composition curves of the copolymerization of **1** with **2b** at 150°C in PhCN: $[1] + [2b] = 2.0$ mmol in 0.3 ml of PhCN.

monomer reactivity ratio are thus obtained as $r_1 = 0.00$ and $r_{2b} = 0.16$.¹²

Hydrolysis of Copolymer

In order to confirm further the structure of

copolymer **3**, the hydrolysis of the copolymer **3b** was carried out. The copolymer **3b** in acetonitrile was treated with 6*N* hydrochloric acid at 150°C for 112 h. An acid hydrolysis of **3b** is expected to give **4**, trimethylene glycol **5**, and ethyl alcohol **6**.

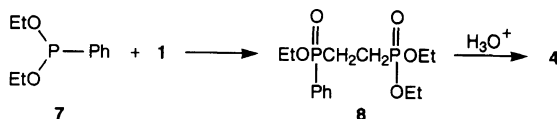


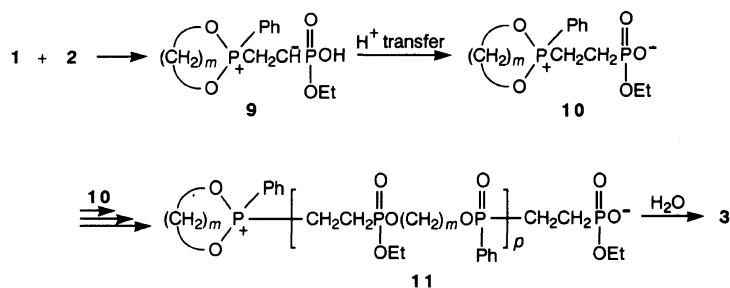
The hydrolysis products **4**—**6** were identified by high pressure liquid chromatographic (HPLC) analysis of the reaction mixture compared with the authentic samples. Furthermore **4** and **5** were isolated as follows. Water was added to the reaction mixture and the solution was poured into a large amount of acetonitrile to precipitate the solid material. From the ¹H NMR analysis, the main product of this crude solid was found to be **4**; the multiplet peak at δ 1.5—2.0 is due to the methylene protons (4H) and the peak at δ 7.7 is assignable to the phenyl protons (5H). The ³¹P NMR also supported the structure of **4**; a signal at δ +34.7 is ascribed to

$\text{HOP}(=\text{O})(\text{Ph})\text{CH}_2$ and a signal at δ +25.9 is due to $\text{CH}_2\text{P}(=\text{O})(\text{OH})_2$. The supernatant solution was evaporated and dried *in vacuo* to give the viscous liquid. From the ¹H NMR analysis, the product is trimethylene glycol **5**; the multiplet peak at δ 1.80 due to CCH_2C (2H) and the triplet peak at δ 3.69 due to OCH_2 (4H). Ethyl alcohol **6** of the hydrolysis product may be removed by drying the hydrolysis product.

Model Reaction

In order to confirm further the structure of the copolymer **3**, the following model reaction was carried out.





Scheme 1.

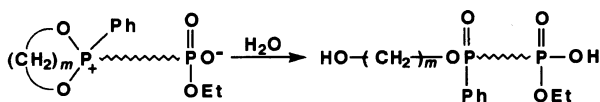
An equimolar mixture of **1** and diethylphenylphosphonite (**7**), a model of cyclic monomers **2**, in benzonitrile was heated at 150°C for 51 h to give **8**. The structure of **8** was confirmed by ^1H , ^{13}C , and ^{31}P NMR spectroscopy. The hydrolysis of **8** was carried out in a similar manner as described above to give the product **4**.

Copolymerization Mechanism

On the basis of the above data, we propose the following copolymerization mechanism (Scheme 1). The first step is the formation of zwitterion **9** by the Michael-type addition of **2** onto **1** followed by a proton-transfer process to give a genetic zwitterion **10**. Then, the reaction between two molecules of **10** occurs,

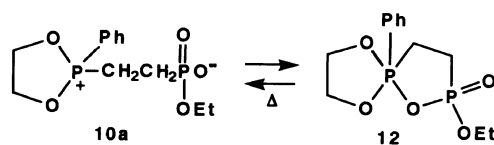
in which the phosphonium ring of one molecule **10** is opened by nucleophilic attack of the anion of the other molecule **10** according to the mode of the Arbuzov reaction involving an oxidation-reduction. The propagation proceeds *via* the reactions between a phosphonium site and a phosphonate anion site of genetic, dimeric, and/or oligomeric zwitterions **10/11** ($p=1, 2, \dots$) to form macrozwitterion **11** ($p=n$) of the copolymer **3**.

The terminal groups of the isolated copolymer are probably of alcohol and phosphonic acid structures; the former due to the hydrolysis of phosphonium ring and the latter coming from proton abstraction by the phosphonate anion group during the isolation process as the following scheme.



The small signal at δ 3.7 in the ^1H NMR spectrum may be assigned to the terminal methylene group (HOCH_2). The small absorption at 3200–3400 cm^{-1} in the IR spectrum may be due to the terminal hydroxyl group.

The ^{31}P NMR spectrum of the copolymerization between **1** and **2a** *in situ* in CD_3CN showed a signal at δ -13.7 assignable to a spiro compound **12** besides the main peaks due to the copolymer. The zwitterion **10a** is assumed to be in equilibrium with **12**.



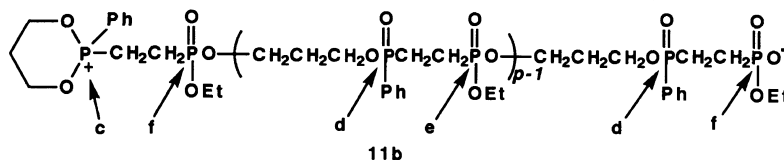
However, the spiro compound was not observed in the copolymerization of **1** with **2b** or **2c**.

^{31}P NMR Analysis of the Copolymerization System

The copolymerization of **1** with **2b** in

benzonitrile was monitored by using ^{31}P NMR spectroscopy. Figure 4(a) shows ^{31}P NMR spectrum of the copolymerization system immediately after mixing **1** and **2b**. Peak a at $\delta +156.5$ is due to the phosphorus atom of monomer **2b** and peak b at $\delta +20.5$ is

assigned to that of **1**. In the spectrum of the mixture after 8 h at 25°C , new peaks c—f appeared; peak f is overlapping with peak b (Figure 4(b)). The assignment of the peaks is made as follows on the basis of the above and following observations.

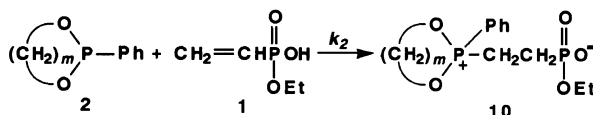


When the monomers **1** and **2b** were completely consumed in the copolymerization system at 25°C , the integrated ratio of the three peaks f, c, and d, was almost 2 : 1 : 1 and the peak e was very small, which implied that the reaction mixture produced mainly a dimeric zwitterion species. This result indicates that the Arbuzov-type reaction between two molecules of the zwitterion **10** proceeded immediately even at 25°C to produce the dimeric zwitterion, but the reaction of the dimeric species hardly proceeded at 25°C . In addition, the molecular weight of the isolated copolymer at 25°C was 800 by gel permeation chromatographic (GPC) analysis (entry 6), which agreed well with the calculated one of the dimeric species (mol. wt. = 640). Figure 4(c) shows the ^{31}P NMR spectrum of the copolymerization mixture *in situ* after 45 h at 100°C . The monomer peak a disappeared and the intensity of the peaks c and e increased. After further heating at 150°C for 24 h, the intensity of the peaks c and f due to

the phosphorus atoms of the terminal groups decreased (Figure 4(d)). These spectra indicate that the copolymerization proceeded by heating at the higher temperature. By the isolation of the copolymer, the peak c disappeared by the hydrolysis of the terminal groups during the work-up process (Figure 4(e)). The molecular weight, calculated from the integrated area of the peak e and the peak f, was 2070 (entry 9), which agreed well that obtained by GPC (mol. wt. = 2300). The molecular weight values of some isolated copolymers were calculated by ^{31}P NMR analysis and found to be closed to those by GPC (Table I).

Kinetic Study

In order to evaluate the reaction rate of the Michael-type addition in the copolymerization system, a kinetic study in the following scheme was performed. The reaction was carried out in the equimolar feed ratio between **1** and **2a—c**.



The rate equation for the formation of the zwitterion **10** is expressed as follows;

$$\frac{d[\mathbf{10}]}{dt} = k_2[\mathbf{1}][\mathbf{2}] \quad (1)$$

where $[\mathbf{1}]$, $[\mathbf{2}]$, and $[\mathbf{10}]$ are the concentrations of the monomer **1**, **2**, and the zwitterion **10**, respectively. The reaction is stoichiometric, and hence, the concentration of **1** was always the same as that of **2**. The formation rate of the

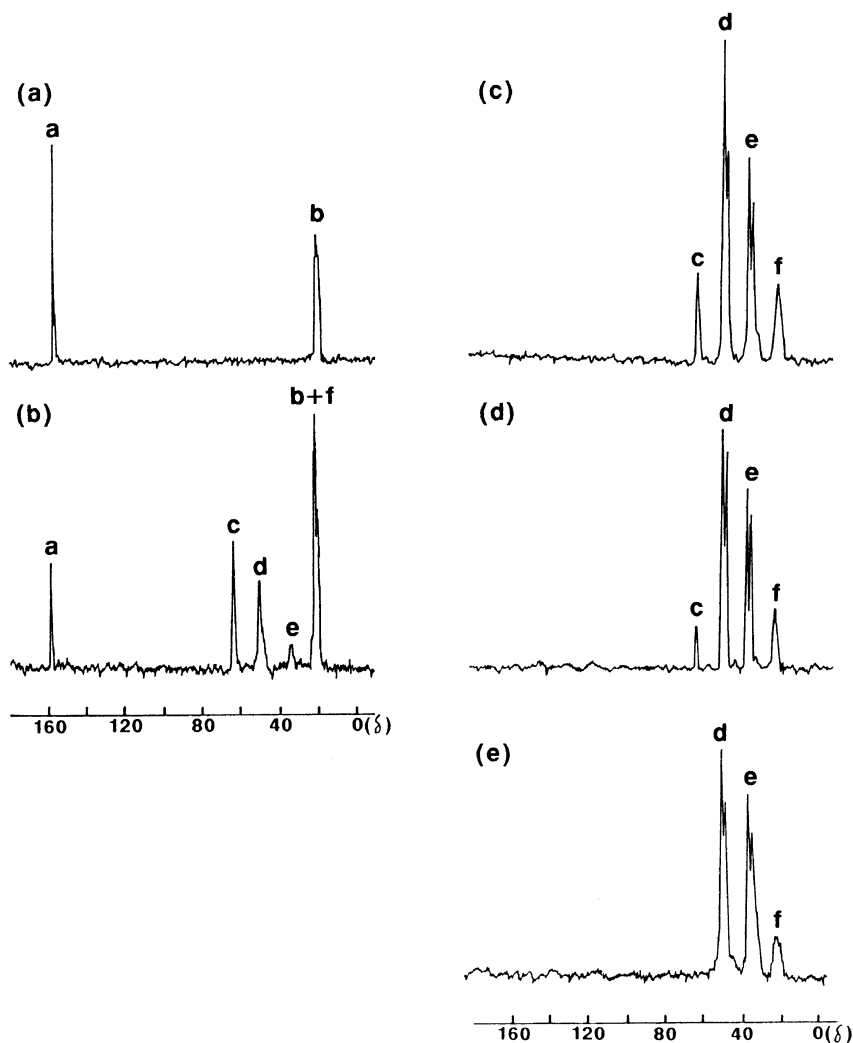


Figure 4. ^{31}P NMR spectra of copolymerization system of **1** with **2b** in PhCN; (a) for 0 h, (b) at 25°C for 8 h, (c) at 100°C for 45 h, (d) at 150°C for 24 h, (e) isolated copolymer **3b**. Copolymerization in the equimolar feed ratio of both monomers was carried out in PhCN under argon.

zwitterion **10** is equal to the consumption rate of the monomer **1**. Therefore, the eq 1 is changed to eq 2.

$$-\frac{d[\mathbf{1}]}{dt} = k_2[\mathbf{1}]^2 \quad (2)$$

Integration of eq 2 gives

$$\frac{1}{[\mathbf{1}]} - \frac{1}{[\mathbf{1}]_0} = k_2 t + A \quad (3)$$

where $[\mathbf{1}]_0$ and A denote the initial concentration of **1** and the constant. $[\mathbf{1}]$ was determined by monitoring the intensity of vinyl protons of **1** by ^1H NMR spectroscopy. In all cases, plots of the equation gave a straight line and a k_2 value was obtained from its slope. The k_2 values and kinetic parameters are summarized in Table III. Monomer **2b** (six-membered) is slightly more reactive in the Michael-type addition than **2c** (seven-membered). The k_2

Table III. Rate constants k_2 and kinetic parameters of Michael-type addition of **1** to **2** in CDCl_3

| Temp | $k_2 \times 10^5 / \text{l mol}^{-1} \cdot \text{s}^{-1}$ | | |
|---|---|-----------|-----------|
| °C | 2a | 2b | 2c |
| 35 | | 1.23 | 1.11 |
| 45 | | 1.39 | 1.33 |
| 55 | | 2.09 | 1.72 |
| 65 | 0.51 | 4.96 | 3.94 |
| 75 | 0.85 | | |
| 85 | 1.18 | | |
| 100 | 3.24 | | |
| ΔH^\ddagger (65°C) /kJ mol ⁻¹ | 51.2 | 36.5 | 32.0 |
| ΔS^\ddagger (65°C) /J(K·mol) ⁻¹ | -198 | -211 | -258 |

Table IV. Rate constants of Michael-type addition of **1** to **2b** at 25°C

| Solvent | $k_2 \times 10^5 / \text{l mol}^{-1} \cdot \text{s}^{-1}$ |
|------------------------|---|
| CDCl_3 | 0.611 ^a |
| CD_3CN | 2.61 |
| PhCN | 2.86 |

^a Extrapolated value at 25°C.

value of **2b** is much larger than that of **2a** (five-membered). From the results, the order of the reactivity of **2a—c** for the Michael-type addition is **2b** > **2c** >> **2a**. The reason of the difference in reactivity may be correlated as follows. The chemical shift values of the three cyclic phosphonites **2a**, **2b**, and **2c** in ³¹P NMR spectra are δ +160.3, +152.0, and +156.5, respectively. From these values the electron density of the phosphorus atoms decreases in the following order: **2b** > **2c** > **2a**. This order must be the same as the nucleophilic order, which agrees with that of the reactivity for the Michael-type addition. Table IV shows the values of k_2 in the reaction of **1** with **2b** in three solvents at 25°C. The values are dependent upon the polarity of the solvents. The k_2 value in a more polar solvent such as CD_3CN and PhCN was at least 4 times larger than that in a less polar solvent of CDCl_3 .

The present kinetic results give the reactivity of phosphorus monomers **1** for the first step of the Michael-type addition in the copolymerization to form genetic zwitterion intermediates **10**. The subsequent steps of propagation involve reactions of genetic and oligomeric zwitterions. However, the quantitative evaluation of the reactivity of these zwitterions requires further studies.

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- The phosphorus atom in monomer **2** is trivalent, whereas that in the polymer unit is changed to pentavalent. Thus, an oxidation of phosphorus atom takes place in the copolymerization. On the other hand, vinyl monomer **1** is reduced; the oxidation state of vinyl carbons is changed from -2 to -3. Therefore, the copolymerization is termed as "oxidation-reduction alternating copolymerization."
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- The molecular weight values obtained by GPC with DMF eluent were always smaller than those by GPC with water eluent [poly(ethylene glycol) standards] as described in our previous paper.² The difference was rather larger when the molecular weight became

higher. The difference is probably attributed to the high polarity of these copolymers; they are more highly solvated in water, therefore, elute faster in

GPC with water eluent than with DMF eluent.

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