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Ring-Opening–Closing Alternating Copolymerization of Cyclic Phosphonites with Methacrylic and Acrylic Anhydrides

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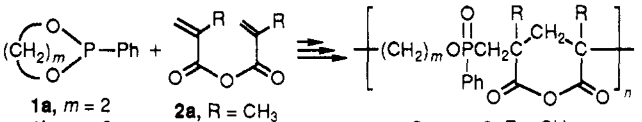
ABSTRACT: Copolymerization of cyclic phosphonites (**1a–c**) with methacrylic and acrylic anhydrides (**2a** and **2b**, respectively) has been investigated. The results show that a 1:1 mixture of monomers produces an alternating copolymer with one part of the repeating unit coming from the ring opening of monomer **1** and the other part from the ring closing of **2** (*ring-opening–closing alternating copolymerization* (*ROCAC*)). In the copolymerization of **1** with **2a** under some conditions, the quantitative cyclization of **2a** took place to form an alternating copolymer **3a**, whereas a small amount of pendant unsaturation has been observed in the copolymerization of **1** with **2b**; the cyclization of **2b** was not quantitative. A zwitterion mechanism is proposed to explain the course of the present copolymerization.

Introduction

In previous papers of this series we have developed a novel, general approach to the synthesis of new alternating copolymers, having the structure of a ring-opened unit from a cyclic monomer (A) and a ring-closed unit from a noncyclic, bifunctional monomer (B) (*ring-opening–closing alternating copolymerization, ROCAC*).[1-6] In this content, the extension of the scope of B-type monomers other than muconic acid[1,5] and dialdehydes[2,6] implies great synthetic relevance. The present paper reports a detailed study on the ROCAC between cyclic phosphonites (**1**) as A-type (ring-opening) monomers and methacrylic and acrylic anhydrides (**2**) as novel B-type (ring-closing) monomers. The resulting copolymers (**3**) have phosphinate–cyclic anhydride structures as ring-opened and ring-closed units, respectively.



1a, $m = 2$
1b, $m = 3$
1c, $m = 4$

2a, R = CH_3
2b, R = H

3a, $m = 2$, R = CH_3
3b, $m = 3$, R = CH_3
3c, $m = 4$, R = CH_3
3d, $m = 2$, R = H
3e, $m = 3$, R = H
3f, $m = 4$, R = H

Results and Discussion

Copolymerization of Cyclic Phosphonite (1) with Methacrylic Anhydride (2a). In a typical copolymerization, a 1:1 monomer mixture of 2-phenyl-1,3,2-dioxaphospholane (five-membered cyclic phosphonite, **1a**) and **2a** was dissolved in chloroform and kept at 35 °C for 43 h (entry 2 in Table I). After the copolymerization, the reaction mixture was poured into a large amount of *n*-hexane to precipitate polymeric materials. The copolymer was separated by decantation and dried under vacuum to give a solid white hygroscopic material in 66% yield, whose molecular weight was 1100 as determined by gel permeation chromatography (GPC) with $CHCl_3$ as eluent at 40 °C with polystyrene standards.

The structure of copolymer **3a** was determined by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopies as well as elemental analysis. Figure 1 shows the ^1H NMR spectrum of copolymer **3a** in $CDCl_3$. A peak at δ 1.28 is due to methyl protons (6 H). Broad peaks at δ 1.5–3.0 are ascribable to CCH_2C and PCH_2 (6 H). A peak at δ 4.19 is assignable to OCH_2 (2 H). Large multiplet peaks at δ 7.1–8.5 are due to phenyl protons (5 H). In addition, peaks at δ 3.69 and 7.00 are assigned to the terminal methylene and alcohol groups ($HOCH_2$), respectively. By comparison of the integral value of the phenyl protons and the OCH_2 protons, the content of monomers **1a** and **2a** in copolymer **3a** was calculated to be 50%. Assuming the signal at δ 3.69 to be due to a termianl CH_2OH group, the molecular weight was calculated from the signal integral values to be 1400, which is close to that obtained by GPC. Figure 2 shows the ^{13}C NMR spectrum of copolymer **3a** in $CDCl_3$. Peaks at δ 18.2 and 18.7 are due to methyl carbons. A doublet peak at δ 23.2 (J_{CP} = 73.4 Hz) is assignable to PCH_2. Peaks at δ 31–34 are ascribable to $C\mathit{CH_2}C$. Small peaks at δ 43.5 and 45.8 are due to quaternary carbons in the ring. Peaks at δ 62–63 are due to OCH_2. Multiplet peaks at δ 126–135 are assignable to aromatic carbons. A peak at δ 174.8 is ascribable to the carbonyl carbon. A peak at δ 58.9 is due to the terminal methylene group CH_2OH. The ^{31}P NMR spectrum of the copolymer showed one peak at δ 45.0, which is reasonably assigned to the phosphinate unit of copolymer **3a**.

Figure 3a shows the IR spectrum of copolymer **3a**. Two characteristic absorptions at 1800 and 1725 cm^{-1} due to the C═O group of a cyclic anhydride are observed. This carbonyl absorption pattern is very similar to that of glutaric anhydride at 1802 and 1751 cm^{-1} (Figure 3b). In contrast, the IR spectrum of succinic anhydride (Figure 3c) exhibits two carbonyl absorptions in different positions from those of copolymer **3a**. In addition, the IR spectrum of copolymer **3a** should be compared with that of the polymers obtained by radical polymerization of **2a** and **2b**;[7-9] the similar pattern of the carbonyl absorptions (1800–1810 and 1740–1765 cm^{-1}) was observed in the spectrum of the homopolymer of **2** having a six-membered cyclic anhydride structure, whereas the homopolymer of **2** with a five-membered cyclic anhydride ring showed the carbonyl absorptions at 1860 and 1780 cm^{-1}. These IR data strongly support the six-membered cyclic anhydride structure for copolymer **3a**. Other characteristic absorptions at 1216 and 1033 cm^{-1} are due to P═O and POC stretching vibrations, respectively, supporting the phosphinate unit of copolymer **3a**. Anal. Calcd for $((C_{18}H_{23}O_5P(H_2O)_{0.3})_n$: C, 60.78; H, 6.64. Found: C, 60.75; H, 7.10. All the above spectroscopic as well as elemental analysis data indicate that the copolymerization of **1a** with **2a** under these conditions proceeded involving ring opening

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

	copolymerization				copolymer			
entry	cyclic phosphonite	solv	temp (°C)	time (h)	yield[b] (%)	structure	extent of cyclization (%)[c]	mol wt[d]
1[e]	**1a**	$CHCl_3$	−20	43	34	**3a**	100	1000
2[e]	**1a**	$CHCl_3$	35	43	66	**3a**	100	1100
3	**1a**	toluene	100	20	51	**3a**	98	1500
4	**1a**	$CHCl_3$	100	20	43	**3a**	98	2400
5[e]	**1a**	$CHCl_3$	100	43	44	**3a**	100	1200
6	**1a**	CH_3CN	100	20	45	**3a**	99	1200
7	**1b**	toluene	100	20	38	**3b** + **4b**	95	3100
8	**1b**	$CHCl_3$	100	20	35	**3b** + **4b**	91	1500
9	**1b**	CH_3CN	100	20	32	**3b** + **4b**	92	3100
10	**1c**	CH_2Cl_2	−20	16.5	64	**3c** + **4c**	47	1700
11	**1c**	CH_2Cl_2	20	16.5	65	**3c** + **4c**	58	1900
12	**1c**	CH_2Cl_2	50	16.5	70	**3c** + **4c**	53	2000
13	**1c**	toluene	100	20	45	**3c** + **4c**	84	3100
14	**1c**	$CHCl_3$	100	20	41	**3c** + **4c**	87	4500
15	**1c**	DMF	100	20	53	**3c** + **4c**	87	6500
16	**1c**	CH_3CN	100	20	46	**3c** + **4c**	84	6300
17	**1c**	CH_2Cl_2	150	16.5		cross-linking		

[a] A mixture of 1.0 mmol of each monomer in 1.0 mL of solvent. [b] Isolated yield of *n*-hexane insoluble part. [c] Determined by ^1H NMR. [d] Determined by GPC with $CHCl_3$ at 40 °C. [e] A mixture of 1.0 mmol of each monomer in 5 mL of solvent.

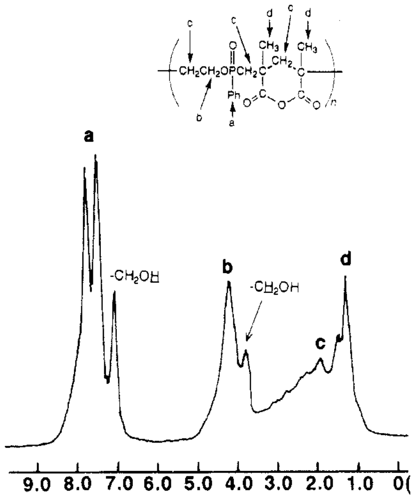


Figure 1. ^1H (250-MHz) NMR spectrum of copolymer **3a** (entry 2 in Table I) in $CDCl_3$.

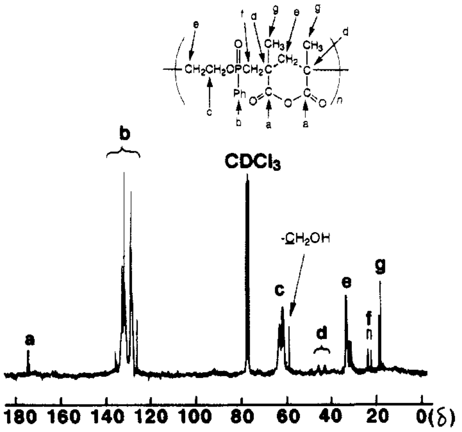


Figure 2. ^{13}C (62.8-MHz) NMR spectrum of copolymer **3a** (entry 2 in Table I) in $CDCl_3$.

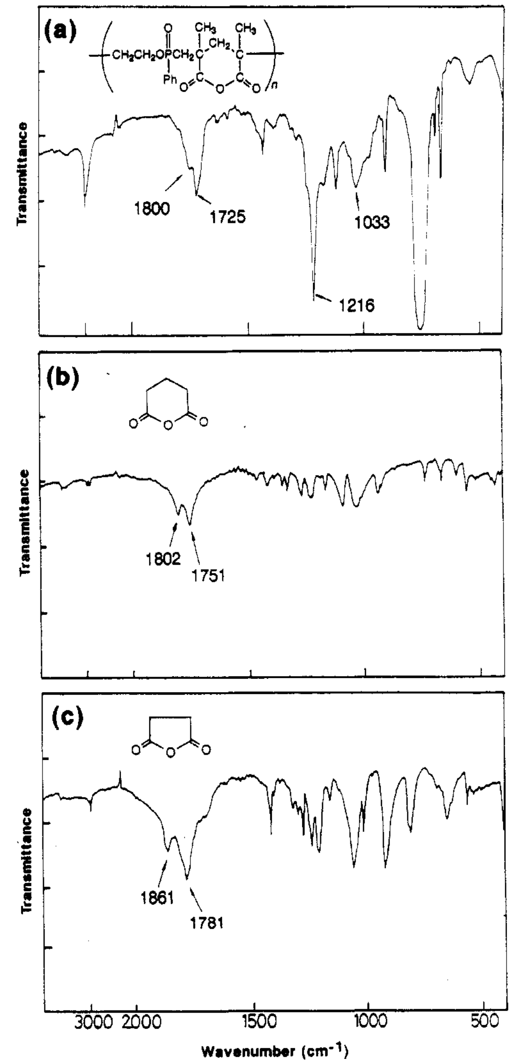


Figure 3. IR spectra of copolymer **3a** (a), glutaric anhydride (b), and succinic anhydride (c).

of **1a** and ring closing of **2a** to produce the alternating copolymer **3a**.

In the copolymerization of **1b** or **1c** with **2a**, however, the ^1H NMR spectra of some isolated copolymers showed peaks at δ 1.95 and 5.5–6.2 due to methyl protons and vinyl protons of the $CH_2{=}C(CH_3)C{=}O$ group, respectively, as shown in Figure 4 (entry 12 in Table I). These data indicate that the ring closing of **2a** was not quantitative in the copolymerization under some reaction conditions. In this case, the structure of the product can be assigned as a random copolymer possessing two alternating units **3** and **4** having the pendant methacrylate group as

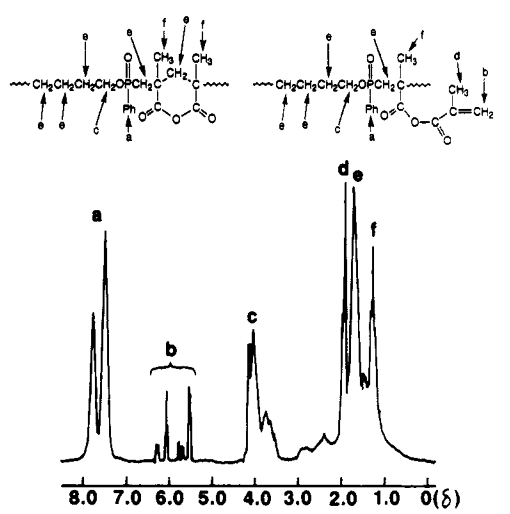
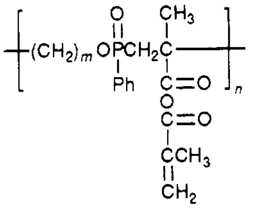


Figure 4. ^1H (250-MHz) NMR spectrum of a copolymer composed of mixed units of **3c** and **4c** (entry 12 in Table I) in $CDCl_3$.

shown below. In the same monomer concentration, the reaction of **1a** with **2a** gave a trace amount (<2%) of an uncyclized unit (entries 3, 4, and 6 in Table I).

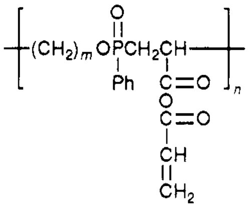

$$\left[(CH_2)_mO\overset{O}{\overset{\|}{\underset{Ph}{P}}}CH_2\overset{CH_3}{\underset{C(=O)OC(=O)C(CH_3)=CH_2}{C}}\right]_n$$

4b, *m* = 3
4c, *m* = 4

Copolymerizations of **1a–c** with **2a** were carried out under various conditions (Table I). Although the monomer conversions were always quantitative, isolated copolymer yields were not quantitative. This indicates that the relatively lower molecular weight part was lost during a reprecipitation procedure. The extent of the cyclization was calculated based on the integral ratio of the ^1H NMR peaks due to vinyl protons and phenyl protons. The copolymerization of **1a** with **2a** gave quantitatively (>98%) cyclized copolymer **3a**, whereas the cyclization was not quantitative in the copolymerization of **1b** or **1c** with **2a**. At a temperature below 50 °C, the extent of the cyclization was quite low in the copolymerization of **1c** with **2a** (entries 10–12). The molecular weight of the copolymer obtained from **1c** and **2a** was relatively higher than that of the copolymers obtained from **1a** or **1b** with **2a**. The highest molecular weight of 6500 was obtained in the copolymerization of **1c** with **2a** in *N,N*-dimethylformamide (DMF) at 100 °C (entry 15). The reaction temperature of 150 °C gave a cross-linked material (entry 17), probably because a thermal or radical polymerization of the pendant methacrylate group in the unit **4c** occurred.

Copolymerization of Cyclic Phosphonite (1) with Acrylic Anhydride (2b). Similarly, copolymerizations of cyclic phosphonites **1a–c** with acrylic anhydride (**2b**) were carried out (Table II). The product copolymer was isolated by precipitation of the polymeric materials with pouring the reaction mixture into diethyl ether.

Figure 5 shows the ^1H NMR spectrum of the isolated copolymer obtained from **1a** and **2b**. Broad peaks at δ 2.0–3.3 are due to CCH_2C and $CCH(C{=}O)C$. A peak at δ 4.26 is ascribable to OCH_2. Large peaks at δ 7.2–8.3 are assignable to phenyl protons. Peaks at δ 3.75 and 6.80 can be ascribable to the terminal $HOCH_2$ group. In addition, multiplet peaks at δ 5.8–6.4 due to vinyl protons are observed, indicating the existence of the unit **4d** having the pendant acrylate group. By comparison of the integral value of peaks due to phenyl protons and OCH_2 protons, the content of monomers **1a** and **2b** in the copolymer was calculated to be 50%. The ^{31}P NMR shows only one peak at δ 46.8 assignable to the phosphinate unit. The IR spectrum of the copolymer showed 1795, 1720, 1216, and 1041 cm^{-1}, which are patterns similar to that of copolymer **3a**, and supports that the copolymer obtained from **1a** with **2b** has six-membered cyclic anhydride and phosphinate structures. In addition, a small absorption at 1631 cm^{-1} due to the pendant vinyl group was observed. Anal. Calcd for $(C_{16}H_{19}O_5P(H_2O)_{0.7})_n$: C, 57.38; H, 6.10. Found: C, 57.49; H, 6.19. On the basis of the above data, the structure of the copolymer obtained from **1a** and **2b** was found to be composed of mixed units of **3d** and **4d**. The copolymerization of **1b** or **1c** with **2b** also proceeded involving the cyclization of **2b** to produce the copolymer having two units **3** and **4**.


$$\left[(CH_2)_mO\overset{O}{\overset{\|}{\underset{Ph}{P}}}CH_2\underset{C(=O)OC(=O)CH=CH_2}{CH}\right]_n$$

4d, *m* = 2
4e, *m* = 3
4f, *m* = 4

In all coolymerizations (Table II), the extent of the cyclization calculated by the integral ratio of the ^1H NMR peaks due to phenyl protons and vinyl protons was not quantitative. The extent is increased at higher temperatures, being at most 95% (entry 2). The polymerization results indicate that higher molecular weights (>5000) require reaction temperatures as high as 100 °C. Similarly to the copolymerization of **1** with **2a**, a further increase in temperature up to 150 °C resulted in a cross-linked material (entries 6, 12, and 16).

Copolymerization Mechanism. By combining the results obtained by spectroscopic analyses, the following mechanism involving zwitterion intermediates is suggested to explain the course of the present copolymerization of the cyclic phosphonite with acrylic and methacrylic anhydrides (Scheme I). Monomers **1** and **2** form a Michael-type intermediate **5** followed by an intramolecular cyclization (ring closing) via Michael addition to give zwitterion **6**. Then, an Arbuzov-type reaction occurs between two molecules of **6**, i.e., the reaction of the oxygen anionic site of the zwitterion **6** with the carbon adjacent to the OP^+ group of **6** to form a dimeric zwitterion **7**. The subsequent propagations are the reaction between a phosphonium site and an oxygen anion site of zwitterions **6** and **7** and/or macrozwitterions. Depending upon the polymerization conditions, the Arbuzov-type propagation of the zwitterion **5** also took place to give the alternating unit **4**. The cyclization of **5** to **6** and the propagation from **5** to uncyclized unit **4** are competitive, and, therefore, the lower monomer concentration is expected to favor the formation of intramolecular ring-closed zwitterion **6** rather than the intermolecular propagation leading to **4**. Actually, the extent of cyclization was perfect at a lower monomer concentration (entries 1, 2, and 5 in Table I), whereas the extent was not perfect at a higher one (entries 3, 4, and 6 in Table I) in the copolymerization of **1a** with **2a**.

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

	copolymerization				copolymer			
entry	cyclic phosphonite	solv	temp (°C)	time (h)	yield[b] (%)	structure	extent of cyclization (%)[c]	mol wt[d]
1	**1a**	CH_2Cl_2	20	24	40	**3d** + **4d**	56	1300
2	**1a**	toluene	100	18	38	**3d** + **4d**	95	1300
3	**1a**	$CHCl_3$	100	18	92	**3d** + **4d**	94	2100
4	**1a**	DMF	100	18	100	**3d** + **4d**	85	2000
5	**1a**	CH_3CN	100	18	79	**3d** + **4d**	94	2700
6	**1a**	$CHCl_3$	150	24		cross-linking		
7	**1b**	CH_2Cl_2	−20	24	54	**3e** + **4e**	58	1700
8	**1b**	toluene	100	18	33	**3e** + **4e**	86	3600
9	**1b**	$CHCl_3$	100	18	92	**3e** + **4e**	76	4000
10	**1b**	DMF	100	18	100	**3e** + **4e**	72	5900
11	**1b**	CH_3CN	100	18	72	**3e** + **4e**	89	8900
12	**1b**	$CHCl_3$	150	24		cross-linking		
13	**1c**	CH_2Cl_2	−20	24	55	**3f** + **4f**	80	2500
14	**1c**	toluene	100	18	36	**3f** + **4f**	80	3600
15	**1c**	$CHCl_3$	100	18	100	**3f** + **4f**	83	5800
16	**1c**	$CHCl_3$	150	24		cross-linking		

[a] A mixture of 1.0 mmol of each monomer in 1.0 mL of solvent. [b] Isolated yield of diethyl ether insoluble part. [c] Determined by ^1H NMR. [d] Determined by GPC with $CHCl_3$ at 40 °C.

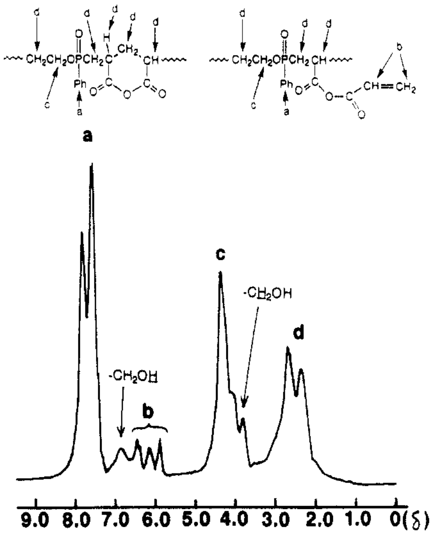
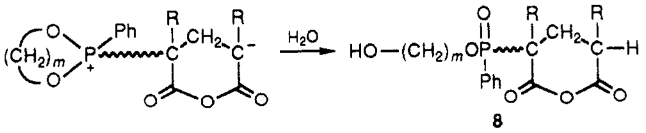


Figure 5. ^1H (250-MHz) NMR spectrum of a copolymer composed of mixed units of **3d** and **4d** (entry 5 in Table II) in $CDCl_3$.

The terminal groups of the isolated copolymer are probably of OH and methine or methylene groups coming from proton abstraction by the carbanion group and hydrolysis of the phosphonium ring during the isolation process as given by **8**.



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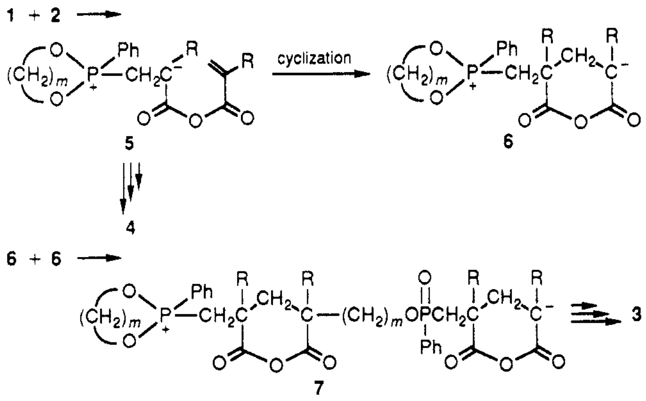
Conclusion

We have reported herein a novel synthesis of a 1:1 alternating copolymer with one part of the repeating unit coming from the ring opening of one monomer and the other part from the ring closing of the other monomer. The copolymerization of cyclic phosphonite **1** with methacrylic anhydride **2a** and with acrylic anhydride **2b** led readily to a 1:1 alternating copolymer. The reaction follows the new type of *ring-opening–closing alternating copolymerization (ROCAC)*.

Scheme I



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 from the reaction between diol and dichlorophenylphosphine in the presence of triethylamine in a benzene solution[10,11] and distilled under reduced pressure immediately prior to use. Acrylic anhydride (**2b**) was prepared by the reaction between acrylic acid and thionyl chloride.[12] Methacrylic anhydride (**2a**) was a commercial reagent and purified by distillation under reduced pressure. Toluene, dichloromethane, and chloroform were purified by distillation. Acetonitrile was dried over anhydrous potassium carbonate and distilled over P_2O_5. DMF was stirred over CaH_2 and distilled in vacuo.

Copolymerization. In a typical copolymerization, a dried polymerization tube was charged with **1a** (0.168 g, 1.0 mmol), **2a** (0.154 g, 1.0 mmol), and 5.0 mL of $CHCl_3$ under argon. The tube was sealed and kept at 35 °C for 43 h. The reaction mixture was poured into a large amount of *n*-hexane to precipitate the polymeric material. The copolymer was separated by decantation and dried in vacuo to give 0.213 g (66% yield) of **3a**.

Measurements. ^1H NMR spectra were recorded on a 250-MHz Bruker AC250T NMR spectrometer. ^{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 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.

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Registry No. **1a**, 1006-83-3; **1b**, 7526-32-1; **1c**, 7526-37-6; **2a**, 2051-76-5; **2b**, 760-93-0; (**1a**)(**2a**) (alternating copolymer), 143309-61-9; (**1a**)(**2b**) (alternating copolymer), 143329-64-0; (**1b**)(**2a**) (alternating copolymer), 143309-62-0; (**1b**)(**2b**) (alternating copolymer), 143309-64-2; (**1c**)(**2a**) (alternating copolymer), 143309-63-1; (**1c**)(**2b**) (alternating copolymer), 143309-65-3.