this work through Grants-in-Aid for Scientific Research (No. 59550625) and for Energy Research (No. 59040068).

Registry No. **1a**, 99632-61-8; **1a** (homopolymer), 99632-63-0; **1b**, 99632-62-9; **1b** (homopolymer), 99632-64-1; **2a** (SRU), 99632-66-3; **2b** (SRU), 99632-67-4; **3a**, 99642-59-8; **3b**, 99642-60-1; **3c**, 99642-61-2; **3d**, 99642-62-3; **3e**, 99642-63-4; **10**, 78869-65-5; **11**, 84515-78-6; $PhPCl_2$, 644-97-3; $HS(CH_2)_3Cl$, 17481-19-5; $HS(CH_2)_4Cl$, 98019-02-4; $(COCl)_2$, 79-37-8; $HgCl_2$, 7487-94-7; $PdCl_2$, 7647-10-1; $CuSO_4$, 7758-98-7; MeI, 74-88-4; $PhCH_2Br$, 100-39-0; MeOTf, 333-27-7; BF_3OEt_2, 109-63-7.

References and Notes

(1) Kobayashi, S.; Suzuki, M.; Saegusa, T. *Polym. Bull.* (*Berlin*) **1981**, *4*, 315.

(2) Kobayashi, S.; Suzuki, M.; Saegusa, T. *Polym. Bull.* (*Berlin*) **1982**, *8*, 417.

(3) Kobayashi, S.; Suzuki, M.; Saegusa, T. *Macromolecules*, **1984**, *17*, 107.

(4) Kobayashi, S.; Suzuki, M.; Saegusa, T. *Macromolecules*, **1983**, *16*, 1010.

(5) Kobayashi, S.; Suzuki, M.; Saegusa, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2153.

(6) For a comprehensive review up to date, see: Kobayashi, S.; Saegusa, T. in "Alternating Copolymers"; Cowie, J. M. G., Ed.; Plenum Press: New York, 1985; pp 189–238.

(7) Kobayashi, S.; Suzuki, M.; Saegusa, T., unpublished data.

(8) Kobayashi, S.; Okawa, M.; Saegusa, T., unpublished data.

(9) Elliott, D. E.; Banks, C. V. *Anal. Chim. Acta* **1965**, *33*, 273.

(10) Sandell, E. B. "Colorimetric Determination of Traces of Metals", 3rd ed; Interscience: New York, London, 1959; p 629.

(11) (a) Reference 10, p 711. (b) Cheng, K. L. *Anal. Chem.* **1954**, *26*, 1984.

(12) (a) Reference 10, p 443. (b) Horiuchi, Y.; Nishida, H. *Bunseki Kagaku* **1969**, *18*, 694.

(13) (a) Savvin, S. B. *Talanta* **1961**, *8*, 673. (b) Ohnishi, H.; Toida, Y. *Bunseki Kagaku* **1965**, *14*, 1141.

Cationic Ring-Opening Polymerization of 2-Phenyl-1,3,2-dioxaphosphepane, a Seven-Membered Cyclic Phosphonite

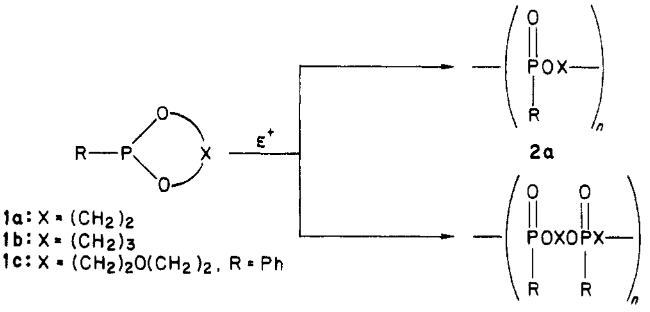
Shiro Kobayashi,* Masazumi Tokunoh, and Takeo Saegusa*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan.
Received April 22, 1985

ABSTRACT: Cationic ring-opening polymerization of 2-phenyl-1,3,2-dioxaphosphepane (a seven-membered cyclic phosphonite, **5**) has been investigated. The polymerization of **5** with MeI initiator produced polyphosphinate consisting exclusively of "normal" unit **6**. A Lewis acid and an oxonium initiator gave polyphosphinate consisting of both unit **6** and "isomerized" unit **7**. $MeOSO_2CF_3$ initiator yielded polyphosphinate of low molecular weights and an isomerized product **10** from **5**. The kinetic analysis of the polymerization of **5** with MeI has successfully been carried out. The stable propagating species were of covalent alkyl iodide type (**16**, **17**, and **19**). The rate constant of propagation (k_p) and kinetic parameters have been obtained. The polymerization kinetics of a six-membered cyclic phosphonite **13** has also been performed, and the polymerization reactivity of **5** is compared with that of **13**.

Introduction

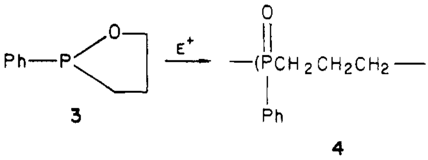
The following cyclic trivalent phosphorus monomers are known to have undergone cationic ring-opening polymerization: phospholanes[1-8] and deoxophostones[9,10] (five membered), phosphorinanes (six membered),[3,5,11] and a phosphocane (eight membered).[12] Cyclic phosphonite monomers (**1**) produced polyphosphinates (**2**). In most cases the polymers consist of a "normal" unit (**2a**) as well as an "isomerized" unit (**2b**).[1-8] In contrast, the polymerization of a deoxophostone (**3**) did not involve the isomerization and produced poly(phosphine oxide) (**4**) consisting exclusively of a "normal" unit.[9] The polymerization of **3** was so clean that it was possible to carry out the kinetic studies.[10] The present paper describes cationic ring-opening polymerization of 2-phenyl-1,3,2-dioxaphosphepane, a seven-membered cyclic phosphonite (**5**), which is a new compound. The polymerization of **5** by MeI initiator gave polyphosphinate composed only of "normal" unit **6**, an isomerized unit being not involved.



1a: X = $(CH_2)_2$
1b: X = $(CH_2)_3$
1c: X = $(CH_2)_2O(CH_2)_2$, R = Ph

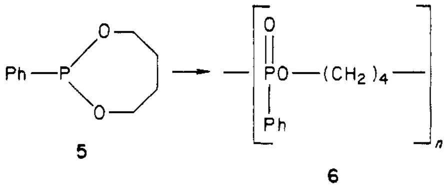
2a

2b



3

4



5

6

Results and Discussion

Polymerization of Monomer 5. Polymerization of **5** was carried out with cationic initiators of MeI, $MeOSO_2CF_3$, $Et_3O^+BF_4^-$, and BF_3OEt_2. Results are given in Table I. MeI initiator produced polymer **6** of higher molecular weights, whereas $MeOSO_2CF_3$ gave polymer of a low molecular weight in a lower yield. The oxonium and

0024-9297/86/2219-0466$01.50/0 © 1986 American Chemical Society

Table I
Cationic Ring-Opening Polymerization of 5[a]

no.	initiator (mol %)	solvent	temp, °C	time, h	polymer	
					yield, %	mol wt[b]
1	MeI (2.0)	PhCN	120	22	84	8000
2	MeI (2.0)	PhCN	100	20	81	6500
3	MeI (2.0)	bulk	100	20	71	12000
4	$MeOSO_2CF_3$ (9.7)	$CHCl_3$	100	2	38	800
5	$Et_3O^+BF_4^-$ (1.2)	PhCN	100	7	36	5000
6	$Et_3O^+BF_4^-$ (2.8)	PhCN	120	2	54	3000
7	BF_3OEt_2 (2.3)	PhCN	120	2	55	4000

[a] 5 = 10.0 mmol in 5.0 mL of solvent under nitrogen. [b] Determined by GPC with correlation to polystyrene standard.

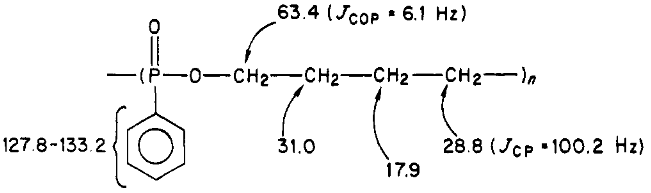
Table II
Alkaline Hydrolysis of Polymer Samples

sample	1,4-butanediol, %[a]	sample	1,4-butanediol, %[a]
1	0	5	28
2	trace	6	32
3	trace	7	28

[a] One molecule of 1,4-butadienediol corresponds to two phosphinate units.

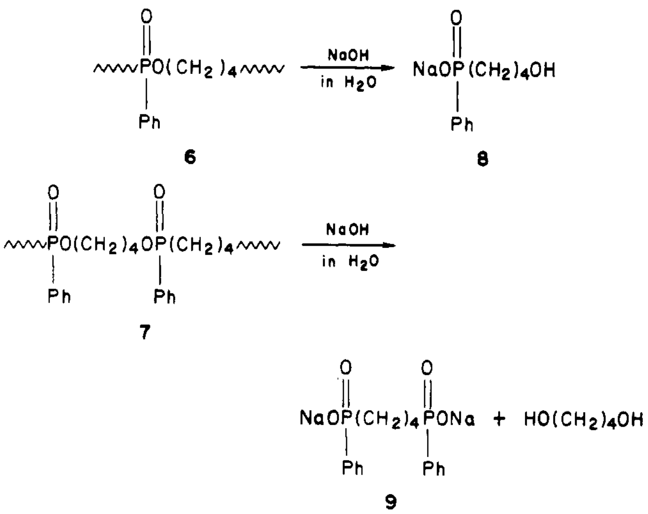
BF_3 catalysts were also effective. Anionic and radical initiators did not induce the polymerization of 5.

Polymer Structure. All polymers were waxy materials soluble in polar organic solvents such as $CHCl_3$ but insoluble in less polar solvents like diethyl ether and hexane. The phosphinate structure 6 was determined on the basis of the following data: The ^1H NMR spectrum of polymer (sample no. 1) in $CDCl_3$ showed three signals, a signal at δ 1.3–2.0 ascribable to $PCH_2CH_2CH_2$ (6 H), a triplet-like signal at δ 3.3–4.0 due to CH_2O (2 H), and a signal at δ 7.2–7.9 assignable to aromatic protons (5 H). The ^{31}P NMR of the polymer showed only a single peak at +44.9 ppm (the lower magnetic field relative to external H_3PO_4) ascribable to a phosphinate unit. The assignment of ^{13}C NMR signals in $CDCl_3$ is shown below.



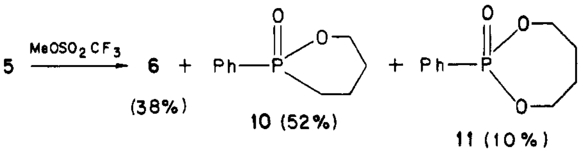
The IR spectrum of the polymer showed characteristic strong peaks at 1220 cm^{-1} ($\nu_{P=O}$) and 1020 cm^{-1} ($\nu_{P-O-alkyl}$). Anal. Calcd for $[C_{10}H_{13}O_2P(H_2O)_{0.5}]_n$: C, 58.54; H, 6.88; P, 15.09. Found: C, 58.57; H, 6.86; P, 14.93. All these data supported the structure of 6.

However, the above data are not sufficient to exclude the presence of "isomerized" unit 7 if any, as observed for the case of polymerization of a phosphocane.[12] So, the alkaline hydrolysis of polymer samples was undertaken. The "normal" unit 6 should produce a phosphinic acid 8, whereas the "isomerized" unit is expected to give a bis(phosphinic acid) 9 and 1,4-butanediol. The alkaline hydrolysis mixture of polymer sample no. 1 exhibited a single ^{31}P NMR peak at +34.8 ppm assignable to 8. The GLC analysis of the mother liquid of the alkaline hydrolysis mixture showed essentially the absence of 1,4-butanediol (Table II). These results of alkaline hydrolysis experiments are taken to indicate that MeI initiator produced a polyphosphinate consisting exclusively of unit 6, whereas the oxonium and BF_3·OEt_2 initiators gave a polyphosphinate consisting of both unit 6 (major) and unit 7 (minor, 28%–32%).

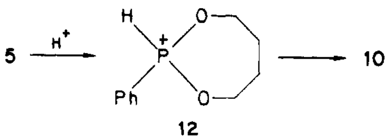


In accordance with the alkaline hydrolysis results, the ^{31}P NMR spectrum of the hydrolysis mixture in aqueous NaOH (sample no. 5) showed two peaks at +34.8 ppm (76%) and at +34.7 ppm (24%), suggesting the production of 8 and 9, respectively. In turn, the ^{31}P NMR of the product polymer (sample no. 5) in $CHCl_3$ also exhibited two peaks at +44.9 ppm (70%) and at +44.7 ppm (30), probably due to units 6 and 7, respectively. This result indicates that the content of 6 and 7 can be determined directly by ^{31}P NMR of the polymer.

Polymerization of 5 by $MeOSO_2CF_3$ (no. 4 in Table I) produced oligomeric 6 in low yield accompanied by low molecular weight byproducts 10 and 11. A cyclic phosphinate 10 is the main product. The byproducts of 10 and 11 were isolated as follows. The polymerization mixture was poured into a mixed solvent of Et_2O/hexane (10/3) to precipitate 6. The supernatant layer was concentrated and distilled in vacuo to give 10 and 11 (bp, 200 °C (0.3 torr), Kugelrohr). Byproducts 10 and 11 were obtained by preparative TLC (silica gel): (10) mp 86–86 °C; ^1H NMR ($CDCl_3$) δ 1.5–2.5 (P-$CH_2CH_2CH_2$, 6 H), 3.8–4.8 (OCH_2, 2 H), 7.0–8.0 (C_6H_5, 5 H); ^{31}P NMR ($CDCl_3$) +37.6 ppm. Anal. Calcd for $C_{10}H_{13}O_2P$: C, 61.22; H, 6.68; P, 15.79. Found: C, 61.36; H, 6.55; P, 15.54. (11) mp 75–76 °C; ^1H NMR ($CDCl_3$) δ 1.5–2.2 (CCH_2CH_2C, 4 H), 3.5–4.5 (OCH_2, 4 H), 7.0–8.0 (C_6H_5, 5 H); ^{31}P NMR ($CDCl_3$) +21.2 ppm. Anal. Calcd for $C_{10}H_{13}O_3P$: C, 56.61; H, 6.17; P, 14.60. Found: C, 56.77; H, 6.10; P, 14.45.



The production of 10 is due to the acid-catalyzed isomerization of 5 involving an intermediate like 12. In fact, the CF_3SO_3H-catalyzed reaction of 5 as a separate experiment produced 10 in high yield. Compound 11 is an oxidation product of monomer 5.



12

Relevant to the present investigation, we have investigated here the structure of polymer derived from a corresponding six-membered cyclic phosphonite, 2-phenyl-1,3,2-dioxaphosphorinane (13), by MeI initiator. The ^{31}P NMR of the resulting polymer showed only a single peak

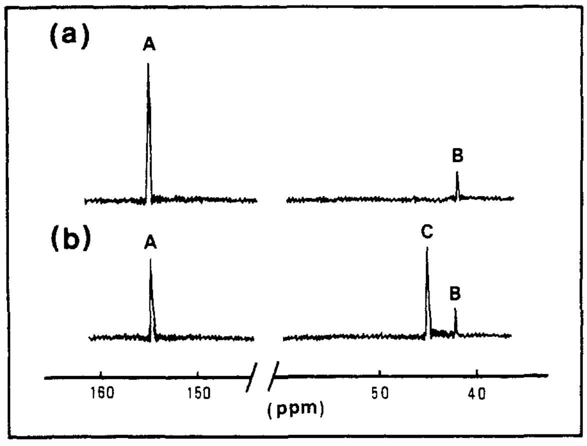
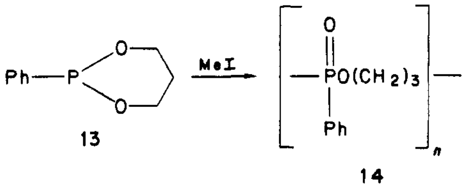


Figure 1. $^{31}P\{^{1}H\}$ NMR spectra of the polymerization system of 5 with MeI initiator in $CHCl_3$, [5] = 1.19 mol/L and [MeI] = 0.128 mol/L: (a) reaction time = 1 min at 95 °C; (b) reaction time = 40 min at 95 °C.

at +42.8 ppm. The alkaline hydrolysis mixture of the polymer exhibited a single ^{31}P NMR peak at +34.8 ppm. The GLC analysis of the mother liquid of the alkaline hydrolysis mixture showed the absence of 1,3-propanediol. These results clearly indicate that the MeI-initiated polymerization produced the polymer 14, consisting exclusively of a normal phosphinate unit, in the case of the six-membered phosphonite monomer also.



Kinetics and Mechanism of Polymerization. Since the cationic ring-opening polymerization of 5 with MeI initiator proceeded via the Arbuzov-type reaction without producing an "isomerized" unit, it is worthwhile to carry out the kinetic study of the polymerization. The study was performed by using ^{31}P NMR. Figure 1a shows the first ^{31}P NMR spectrum of the kinetic run. The initiation was very fast and already finished at this stage to give the first propagating species 16, as shown by a new peak B (+42.2 ppm) in addition to peak A (+154.7 ppm) of 5. A cyclic phosphonium species 15 was not detected at all, which was expected to appear at around +80 ppm. So, 15 was not stable enough under the reaction conditions to convert via the Arbuzov-type reaction to 16. The reaction proceeded further, and an additional new peak, C (44.9 ppm), appeared. Peak C was ascribed to phosphinate species like 17 and 19. Again, any peak due to cyclic phosphonium species like 18 was not found. Thus, the stable propagating species were of alkyl iodide type (16, 17, and 19). It should be added that a stable phosphonium species 20 was produced by the reaction of 5 with $MeOSO_2CF_3$. The ^{31}P NMR signal of 20 appeared at +83.8 ppm in $CHCl_3$. However, subsequent polymerization reactions from 20 were not clean, as mentioned above.

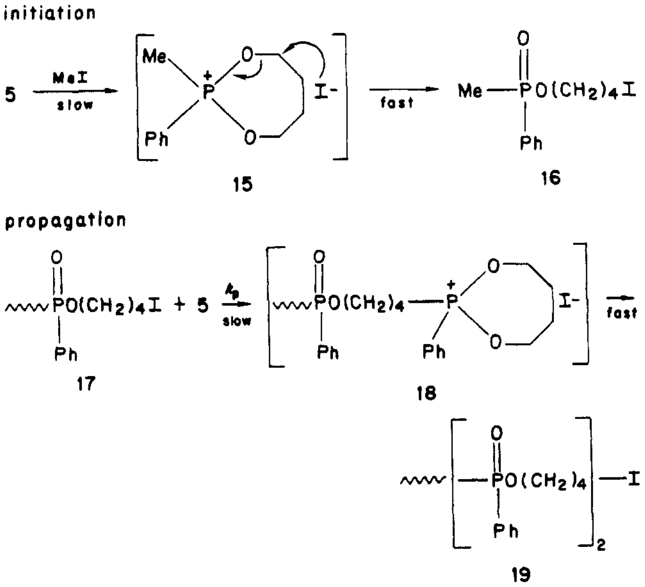
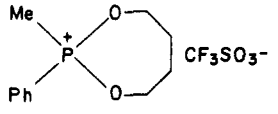


Table III
Kinetic Data of Polymerization of 5 by MeI in $CHCl_3$

$k_p \times 10^3$, L/(mol·s)	0.39 (72 °C) 1.16 (84 °C) 2.48 (95 °C) 4.26 (103 °C) 9.60 (120 °C)
E_a, kJ/mol	82.6
A, L/(mol·s)	1.37×10^9
$\Delta H^{\ddagger}$ at 95 °C, kJ/mol	79.5
$\Delta S^{\ddagger}$ at 95 °C, J/(K·mol)	-61.6



20

According to the above observations the propagation rate constant (k_p) was obtained by the equation

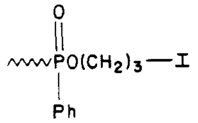
$$-\frac{d[M]}{dt} = k_p[P^*][M]$$

where [P*] and [M] are the concentrations of propagating species and of monomer, respectively. The polymerization system consisted of fast initiation and propagation, and hence [P*] = [MeI]. The integrated form of the above equation is

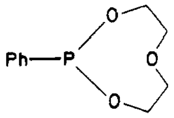
$$\ln \frac{[M]_1}{[M]_2} = k_p[MeI](t_2 - t_1)$$

Actually, plots of this equation gave a straight line passing through the origin whose slope led to a k_p value. Results of the kinetic analysis are given in Table III. Activation parameters are also included.

As described above, the MeI-initiated polymerization of a corresponding six-membered phosphonite 13 is a clean system involving no isomerization. Therefore, a kinetic study on the polymerization of 13 has been carried out by ^{31}P NMR spectroscopy to compare the reactivity of 5 with that of 13. The ^{31}P NMR spectrum of the polymerization mixture of 13 is very similar to that of 5 (Figure 1). Stable propagating species are of alkyl iodide type 21 under reaction conditions. A k_p value obtained is 1.34×10^{-3} L/(mol·s) at 95 °C in $CHCl_3$. These results show that 5 (seven membered) is slightly (1.9 times) more reactive in kinetic polymerizability than 13 (a six-membered analogue). The cationic polymerization rate of 5 is much higher than that of an eight-membered cyclic phosphonite 22[12] and seems comparable to that of a five-membered deoxophostone 3.[10]



21



22

In conclusion, the present study provides the first clear-cut example of the cationic ring-opening polymerization of cyclic phosphonites to give a polyphosphinate having a definite repeating structure **6** by MeI initiator. Therefore, the polymerization allowed us to perform a kinetic study and to compare the polymerization reactivity of **5** with that of **13**.

Spontaneous copolymerizations using **5** as a nucleophilic monomer with electrophilic monomers such as α,β-unsaturated carboxylic acids or α-keto acids will be reported later.

Experimental Section

Materials. Monomer **5** was prepared in a similar manner to that of the other trivalent phosphonite compounds as follows.[12] To a cooled mixture of 1,4-butanediol (16.3 mL, 0.184 mol) in 200 mL of benzene and triethylamine (52.0 mL, 0.184 mol) was added a benzene solution of dichlorophenylphosphine (25.0 mL, 0.184 mol) dropwise at about 5 °C under nitrogen for 2 h. The reaction mixture was then stirred at 60 °C for 30 h. The resulting ammonium salt was removed by filtration. The filtrate was concentrated, and the vacuum distillation gave 18.1 g (50% yield) of monomer **5**: bp 80 °C (0.3 torr), ^{31}P NMR (neat) 154.7 ppm (singlet). Anal. Calcd for $C_{10}H_{13}O_2P$: C, 61.22; H, 6.68; P, 15.79. Found: C, 61.33; H, 6.82; P, 15.97.

Monomer **13** was obtained by reaction of dichlorophenylphosphine with 1,3-propanediol: bp 78–80 °C (1.0 torr); ^{31}P NMR signal at +151.6 ppm.[13]

Benzonitrile, $CHCl_3$, MeI, and BF_3OEt_2 were purified by distillation under nitrogen. $MeOSO_2CF_3$ was prepared from CF_3SO_3H and dimethyl sulfate. $Et_3O^+BF_4^-$ was prepared from BF_3OEt_2, diethyl ether, and epichlorohydrin.

Products **10** and **11** were isolated from the precipitation supernatant (Et_2O:hexane = 10:3). The supernatant was concentrated and distilled in vacuo to give a mixture of **10** and **11** bp about 200 °C (0.3 torr, Kugelrohr). Compounds **10** and **11** were then separated by column chromatography employing columns packed with silica gel using a developing solvent of acetone:ethyl acetate = 2:1 (v/v). R_f values of **10** and **11** in TLC analysis were 0.5 and 0.7, respectively.

Polymerization. A typical run (no. 1) was as follows. In a tube 9.28 mmol of monomer **5** and 0.16 mmol of MeI were placed in 5 mL of dry benzonitrile under nitrogen. The tube was sealed and kept at 120 °C for 22 h. The mixture was then poured into a large amount of dry diethyl ether. The supernatant layer was decanted, and the precipitated waxy polymer in the bottom of the flask was washed with several milliliters of dry diethyl ether. This reprecipitation procedure was repeated three times, and the polymer was dried in vacuo. The yield of **6** was 1.53 g (84%).

The polymerization of monomer **13** was carried out in the following manner. To the ice-cooled $CHCl_3$ solution (0.5 mL) of **13** (0.84 mmol), MeI (0.058 mmol) was added under nitrogen. The mixture was heated in a sealed tube at 82 °C for 24 h. Polymeric materials were isolated by pouring the mixture into a large amount of diethyl ether and dried in vacuo to give 0.102 g of **14** (67% yield) as waxy materials. The molecular weight of **14** was 3000 by vapor pressure osmometry.

Alkaline Hydrolysis of Polymer. A typical example is given. Polymer sample no. 5 (1.07 g, 5.46 mmol) was placed in 10 mL of water containing 50 mmol of NaOH and refluxed for 2.5 h. During the reaction the system became homogeneous. The solution was then neutralized by concentrated HCl aqueous solution. The GLC analysis (internal standard: pentamethylene glycol) of 1,4-butanediol in the solution revealed that the polymer contained the isomerized unit in 28% (Table II).

Kinetic Procedure. The kinetic analysis was carried out by using ^{31}P NMR spectroscopy. A typical run was as follows. In an NMR tube under nitrogen were placed 0.810 mmol of monomer **5** and 0.0546 mmol of MeI in 0.427 mL of a $CHCl_3$ solution ($[M]_0 = 1.19$ mol/L and $[MeI]_0 = 0.128$ mol/L). The NMR tube was sealed and kept at 95° C in the NMR probe insert. The polymerization was monitored, and the spectrum of the polymerization mixture was recorded at about an interval of 10 min.

Acknowledgment. S.K. acknowledges the partial support of this work by Grant-in-Aid for Scientific Research (No. 59550625), the Ministry of Education, Science, and Culture, Japan.

Registry No. **5**, 7526-37-6; **5** (homopolymer), 99632-65-2; **6** (SRU), 99632-68-5; **10**, 55549-39-8; **11**, 7191-20-0; **13**, 7526-32-1; **13** (homopolymer), 29153-60-4; **14** (SRU), 99632-69-6; BF_3OEt_2, 109-63-7; $MeOSO_2CF_3$, 333-27-7; $Et_3O^+BF_4^-$, 368-39-8; 1,4-butanediol, 110-63-4; dichlorophenylphosphine, 644-97-3; 1,3-propanediol, 504-63-2; MeI, 74-88-4.

References and Notes

(1) Petrov, K. A.; Nifantev, E. E.; Sopikova, I. I. *Vysokomol. Soedin.* **1960**, *2*, 685.
(2) Petrov, K. A.; Nifantev, E. E.; Khorkhoyanu, L. V.; Merkulova, M. I.; Voblikov, V. F. *Ibid.* **1962**, *4*, 246.
(3) Mukaiyama, T.; Fujisawa, T.; Tamura, Y.; Yokota, Y. *J. Org. Chem.* **1964**, *29*, 2572.
(4) Shimidzu, T.; Hakozaki, T.; Kagiya, T.; Fukui, K. *J. Polym. Sci., Part B* **1965**, *3*, 871.
(5) Harwood, H. J.; Patel, N. K *Macromolecules* **1968**, *1*, 233.
(6) Yamashita, Y. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 447.
(7) Vogt, W.; Ahmad, N. A. *Makromol. Chem.* **1977**, *178*, 1711.
(8) Kawakami, Y.; Miyata, K.; Yamashita, Y. *Polym. J. (Tokyo)* **1979**, *11*, 175.
(9) Kobayashi, S.; Suzuki, M.; Saegusa, T. *Polym. Bull. (Berlin)* **1981**, *4*, 315.
(10) Kobayashi, S.; Suzuki, M.; Saegusa, T. *Macromolecules* **1984**, *17*, 107.
(11) Singh, G. *J. Org. Chem.* **1979**, *44*, 1060.
(12) Kobayashi, S.; Huang, M. Y.; Saegusa, T. *Polym. Bull. (Berlin)* **1981**, *4*, 185.
(13) Kobayashi, S.; Chow, T. Y.; Saegusa, T. *Ibid.* **1983**, *9*, 588.