neous agreement with experimental data of dimensions (see preceding paper[13]) and hydrodynamic properties, reproducing the respective ratios g, h, and g'. The influence of intramolecular interactions is higher for the ratio g, since radii of gyration are more sensitive than hydrodynamic properties to the location of the inner segments of the chain, for which repulsive effect are important.

The remaining discrepancies with the data can be attributed to the model poor description of interactions in the very compact central part of the star chains, discussed previously,[13] and in the possible deficiencies still present in the treatment of hydrodynamic interactions represented by the Oseen tensor, neglecting the possible coupling between these interactions and flexibility,[9,10] finite-size effects not eliminated in the extrapolations to high N, etc. Nevertheless, the results here described allow us to think that the general assumptions implicit in this work are sufficient to give a first coherent simultaneous explanation of all these properties for both linear and star polymers at their unperturbed state. Further refinements may have to take in consideration the particular chemical structure of the chains.

Very recent work by Zimm[23,24] on wormlike star molecules is also based in his method of Monte Carlo simulation over rigid conformations and gives results in the flexible chain limit that are similar to those obtained by us for the Gaussian model.[8] However, Zimm's results are restricted to $F \leq 6$; i.e., they correspond to stars in which discrepancies between the preaveraged theory and the data are not very remarkable. At any rate, these results show that only null or small stiffness in the arms can reproduce the experimental ratios. We believe that, in comparison with stiffness, the mutual repulsion of the chain elements close to the central part of the chain, described in our present model with intramolecular interactions, is a significantly more important effect. In fact, the Zimm calculations also take into account this effect in a first approximation by placing in a symmetric way the units surrounding the center of the chain.

Acknowledgment. This work was supported in part by a grant from the Comisión Asesora de Investigación Científica y Técnica (Grant 1409/82).

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Ring-Opening Polymerization of Deoxothiolphostones: Synthesis of Poly(phosphine sulfides)

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ABSTRACT: Ring-opening polymerization of new cyclic monomers of five- and six-membered deoxothiolphostones (**1a** and **1b**) is described. The polymerization of monomer **1a** is induced by a cationic initiator or thermally. Monomer **1b** is only polymerized with a cationic initiator. The polymerization of **1a** and **1b** produces poly(phosphine sulfides) **2a** and **2b**, respectively. The reaction mechanism of cationic as well as thermal polymerizations is discussed. These polymerizations involve a new mechanism of the C—S bond cleavage via an Arbuzov-type reaction to produce the P═S group. Poly(phosphine sulfide) **2a** is converted to polyphosphine **11** or to poly(phosphine oxide) **10** via a common phosphorane polymer, **9**. Chelating properties of poly(phosphine sulfide) are also examined.

Introduction

Recently we have reported the cationic ring-opening polymerization of a five-membered deoxophostone (2-phenyl-1,2-oxaphospholane) to give a poly(phosphine oxide)[1] and the reduction of the polymer to a polyphosphine,[2] (eq 1). A kinetic study on the polymerization of the deoxophostone[3] and the preparation of a chelating resin from the same monomer[4] have also been reported.

As an extension of these studies the present paper deals with ring-opening polymerization of five- and six-mem-

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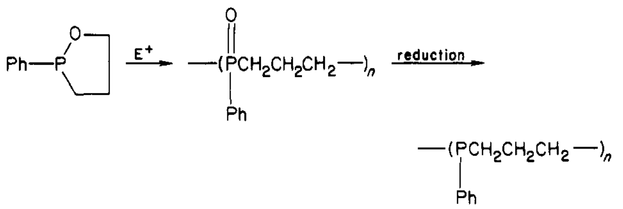
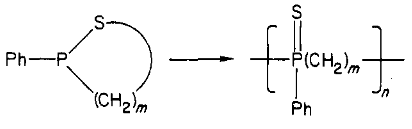


(1)

bered deoxothiolphostones, 2-phenyl-1,2-thiaphospholane (**1a**) and 2-phenyl-1,2-thiaphosphorinane (**1b**), to produce poly(phosphine sulfides) **2a** and **2b**, respectively. Monomer **1a** is a sulfur analogue of the above deoxophostone.


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

The polymerization of **1** to polymer **2** involves the formation of a P=S group via an Arbuzov-type reaction, which is the first instance of polymerization observed with trivalent phosphorus compounds having a P—S bond. In addition, the present paper describes some reactions of product polymer **2a** and chelating properties of **2a**.

Results and Discussion

Synthesis of Monomers 1a and 1b. Monomers **1a** and **1b** are new compounds, which have been prepared by our method of the procedures[5]

$$\mathrm{PhPCl_2 + HS(CH_2)_{\mathit{m}}Cl \xrightarrow{\text{pyridine}} \xrightarrow{\text{Li}} \mathbf{1a}\ (\mathit{m} = 3) + \mathbf{1b}\ (\mathit{m} = 4)}$$

"Deoxothiolphostones" is given as a conventional name for these monomers by a logical extension of the naming of "deoxophostone".[5]

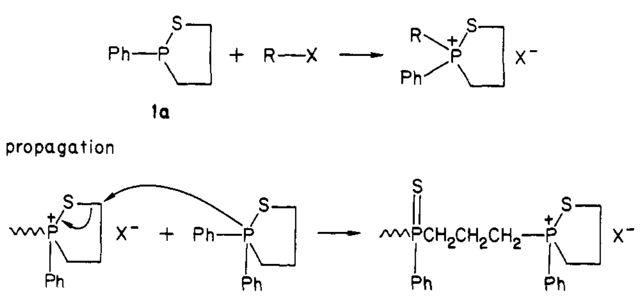
Ring-Opening Polymerization. Table I shows polymerization results of monomers **1a** and **1b**. Cationic initiators such as MeI, $PhCH_2Br$, $MeOSO_2CF_3$ (MeOTf), and $BF_3{\cdot}OEt_2$ are effective for the polymerization of **1a**. At 80 °C, **1a** was not converted to polymer in the absence of initiator. However, at a higher temperature, e.g., 150 °C, the polymerization of **1a** was induced in the absence of initiator. Since the initiators MeI and $PhCH_2Br$ showed better results in catalyst activity for **1a**, they were used for the polymerization of **1b**. These two initiators produced polymer **1b** at 100 °C. Monomer **1b** did not show polymerizability in the absence of initiator even at a higher temperature of 200 °C. An anionic initiator (BuLi) and a radical initiator (AIBN) did not induce the polymerization of either monomer **1a** or **1b**.

All polymers thus obtained are white powdery materials soluble in $CHCl_3$, CH_2Cl_2, DMF, and Me_2SO, partly soluble in acetone and acetonitrile, and insoluble in H_2O, MeOH, toluene, and ethyl acetate. The structures of **2a** and **2b** were determined by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy (Table II). The chemical shift of ^{31}P NMR indicates a structure of phosphine sulfide unit, and the pattern of ^{13}C NMR of **2a** resembles that of poly(phosphine oxide).[1]

Mechanism of Cationic Polymerization. The ring-opening polymerization by cationic initiators such as MeOTf, MeI, and $PhCH_2Br$ is probably expressed as follows by taking monomer **1a** as an example:

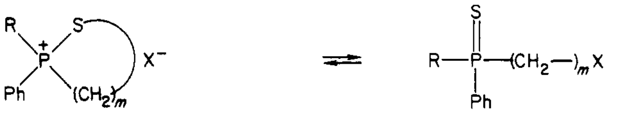
initiation

propagation


1a

The above general scheme can rationalize the formation of the phosphine sulfide unit **2a** from **1a** involving an Arbuzov-type reaction of the P—S bond in the monomer to the P=S group in the polymer. In the polymerization of cyclic phosphorus(III) compounds, this is the first instance of the Arbuzov-type reaction involving the carbon-sulfur bond cleavage instead of a normal Arbuzov reaction involving the carbon-oxygen bond cleavage.

To shed light on the polymerization mechanism, model reactions were undertaken. Monomer **1a** or **1b** was mixed with an equimolar amount of MeOTf, MeI, or $PhCH_2Br$ in $CDCl_3$, and reaction products were examined in situ with ^{31}P NMR spectroscopy. At 35 °C, ^{31}P NMR spectra showed only one peak ascribable to phosphonium species **3** in all cases. When the temperature was raised to 80 °C, **3** was converted to a ring-opened product **4** to reach the equilibrium **3** ⇄ **4** in cases of **4c**–**4e** (Table III) (chemical shift values in parentheses). Structures of **3** were confirmed also by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy (see Experimental Section).

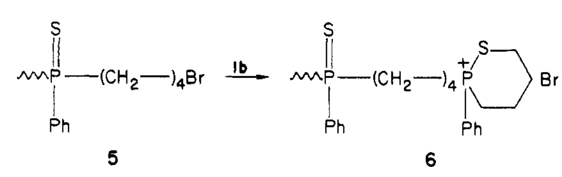

3a, X=TfO; R=Me; m=3 (+74.9)
3b, X=I; R=Me; m=3 (+72.5)
3c, X=Br; R=$PhCH_2$; m=3 (+80.4)
3d, X=I; R=Me; m=4 (+38.3)
3e, X=Br; R=$PhCH_2$; m=4 (+42.9)
4c, X=Br; R=$PhCH_2$; m=3 (+46.1)
4d, X=I; R=Me; m=4 (+39.4)
4e, X=Br; R=$PhCH_2$; m=4 (+45.8)

The stability of **3** depends upon the nature of X and R, the ring size (m value), and reaction solvent as well as reaction temperature. From the data of Table III, the phosphonium species from **1a** is more stable than that from **1b**; i.e., the six-membered phosphonium species, **3d** and **3e**, are more readily susceptible to the nucleophilic attack by the counteranion X^- to open the ring than the five-membered analogues, **3b** and **3c**. It should also be mentioned that phosphonium iodide and bromide derived from a five-membered deoxophostone were not observed even at 35 °C in a more polar solvent of benzonitrile.[3] This clearly indicates that **3b** or **3c** is much more stable than that of the corresponding O-analogue from the deoxophostone.

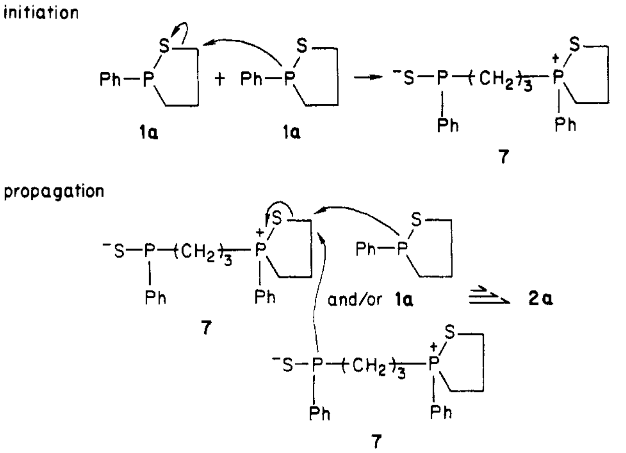
The equilibrium of **3** ⇄ **4** is further supported by the following observations: the temperature of the system involving the ring-opened species **4** was cooled down again to 35 from 80 °C, and **4** converted completely to **3**.

The results of these model reactions are taken to imply the possibility of two types of propagating species, phosphonium and covalent types, in equilibrium. Especially in the case of monomer **1b** with $PhCH_2Br$ initiator, the covalent species **5**, in addition to phosphonium species **6**, may take part in the propagation.

Mechanism of Thermal Polymerization. It is striking that the polymerization of **1a** did occur without initiator at a higher temperature. The mechanism of this

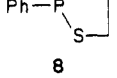


thermal polymerization is not well understood but is best presented as follows involving zwitterions.



Monomer **1a** can act as a nucleophile as well as an electrophile. Thus, two molecules of **1a** produce **7**, a genetic zwitterion. Once **7** is formed, **7** is attacked by another **7** and/or **1a** to produce a phosphine sulfide unit **2a**. It is widely known that a trivalent phosphorus monomer like **1a** behaves as a good nucleophilic monomer.[6] In contrast, the fact that **1a** copolymerized with 2-methyl-2-oxazoline without initiator to give a copolymer can be taken as evidence that **1a** produces electrophilic species such as **7**.[7]

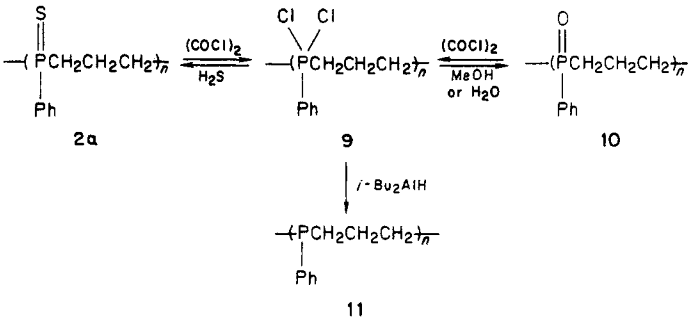
Relevant to the present monomer **1a**, the polymerization of 2-phenyl-1,3,2-dithiaphospholane (**8**) has been examined.



8

This monomer produced a phosphonium species, but did not induced the cationic ring-opening polymerization, although alternating copolymerizations of **8** with acrylic and methacrylic acids have been achieved.[8]

Reduction of Poly(phosphine sulfide). Poly(phosphine sulfide) **2a** was reduced in a similar manner used for the reduction of poly(phosphine oxide) **10**.[2] The reaction of **2a** with oxalyl chloride gave a dichlorophosphorane-type polymer **9**, whose reaction with diisobutylaluminum hydride produced polyphosphine **11**. In turn, **9** could be converted to **10** by the reaction with methanol or water and back to **2a** by the reaction with hydrogen sulfide. Thus, the transformations among **2a** ⇌ **9** ⇌ **10** can readily be performed (Table IV).



Chelating Properties of Poly(phosphine sulfide). It has been reported that tri-*n*-octylphosphine sulfide selectively extracts heavy metal ions.[9] We have described chelating properties of poly(phosphine oxide) chain **10**.[4] Therefore, we have examined here the chelating properties of poly(phosphine sulfide) **2a**. Four heavy metal ions were used for the adsorption with **2a** under various conditions (Table V). Hg^{2+} and Pd^{2+} ions were adsorbed quantitatively in a wide pH range. Cu^{2+} ion was adsorbed more in a weak basic solution rather than in an acidic condition. The adsorption of uranyl ions (UO_2^{2+}) was not remarkable after a contact time of 16 h. The chelating ability of **2a** is compared with that of **10**: **2a** being more effective for Pd^{2+} and Cu^{2+}, comparable for Hg^{2+}, and much less for UO_2^{2+}.[4] Adsorbed UO_2^{2+} was recovered in 50% by treating the polymer with 10% aqueous Na_2CO_3 solution for 16 h.

Experimental Section

Materials. Monomers **1a** and **1b** were prepared by the reaction of $PhPCl_2$ with 3-chloropropanethiol and 4-chlorobutanethiol, respectively, followed by treatment with Li metal.[5] Initiators were prepared or purified according to the ordinary procedures. A solvent of $CDCl_3$ was dried over 4-Å molecular sieves (Wako Chemical Co.). $CHCl_3$ and CH_2Cl_2 were dried over P_2O_5 and distilled under nitrogen. Oxalyl chloride was purified by distillation, and *i*-Bu_2AlH in hexane (Aldrich Chemical Co.) was used without further purification. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Hitachi R-20B (60 MHz), Hitachi R-900 (23.6 MHz), and Hitachi R-900 (36.43 MHz) spectrometers, respectively.

Polymerization. Monomer **1a** or **1b** was charged in a sealed tube with or without a initiator (2.0–5.9 mol %) under nitrogen. After the reaction mixture was heated for the desired period of time, it became very resinous. The tube was opened, and the mixture was dissolved in $CHCl_3$, which was subject to ^{31}P NMR measurement to determine the conversion of monomer. The $CHCl_3$ solution was then poured into a large amount of diethyl ether to precipitate a polymeric material, which was separated and dried in vacuo. ^{31}P, ^1H, and ^{13}C NMR data of the product polymers **2a** and **2b** are shown in Table II. The IR spectral data $CHCl_3$ solution) are as follows (cm^{-1}): (**2a**) 2960, 1440, 1410, 1280, 1110, 1030, 970, 910, 835, 630, and 590; (**2b**) 2970, 2925, 2870, 1445, 1385, 1350, 1145, 1105, 1070, 1040. Anal. Calcd for CH_3–$(C_9H_{11}PS)_{17.2}$–I (**2a**, sample no. 1 in Table I): C, 57.24; H, 5.95; P, 16.30. Found: C, 57.16; H, 5.95; P, 17.27. Anal. Calcd for CH_3–$(C_{10}H_{13}PS)_{17.1}$–I (**2b**, sample no. 9 in Table I): C, 59.18; H, 6.50; P, 15.18. Found: C, 59.37; H, 6.44; P, 15.40.

Model Reactions. **1a** or **1b** (0.152–0.246 mmol) in $CDCl_3$ (0.2–0.26 mL) was mixed with almost equimolar amounts of MeOTf, CH_3I, or $PhCH_2Br$ in a sealed NMR tube under nitrogen and cooled with ice. By monitoring the reaction with ^{31}P NMR, we found that the reaction finished within 15 min for **1a**–MeOTf, 1.5 h for **1a**–MeI, 17 h for **1a**–$PhCH_2Br$, and 4 h for both **1b**–MeI and **1b**–$PhCH_2Br$ systems at 25 °C to produce phosphonium species **3**.

Spectral data of ^1H NMR ($CDCl_3$, J values in Hz) and $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ relative with Me_4S: and J values in Hz) for **3a**–**3e** are as follows: (**3a**) ^1H NMR δ 1.8–4.1 (m, 6 H, d centered at 2.6, $^2J_{HP} = 14.0$, 3 H), 7.2–8.4 (m, 5 H); ^{13}C NMR δ 13.0 (d, $^1J_{CP} = 49.7$), 29.3 (s), 32.1 (d, $^1J_{CP} = 42.7$), 39.5 (d, $^2J_{CP} = 4.3$), 121.5 (d, $^1J_{CP} = 79.3$), 130.1 (d, $^2J_{CP} = 14.0$), 132.0 (d, $^3J_{CP} = 12.2$), 135.1 (d, $^4J_{CP} = 3.5$); ^{19}F NMR ($CDCl_3$) showed a singlet at +0.5 ppm (with external CF_3CO_2H standard) assignable to $CF_3SO_3^-$. (**3b**) ^1H NMR δ 1.9–4.1 (m, 6 H, d centered at 3.0, $^2J_{HP} = 14.0$, 3 H), 7.2–8.5 (m, 5 H); ^{13}C NMR δ 15.3 (d, $^1J_{CP} = 48.8$), 29.7 (s), 32.8 (d, $^1J_{CP} = 42.7$), 40.5 (d, $^2J_{CP} = 4.4$), 121.5 (d, $^1J_{CP} = 79.3$), 130.0 (d, $^2J_{CP} = 13.9$), 132.5 (d, $^3J_{CP} = 11.3$), 135.0 (d, $^4J_{CP} = 2.6$). (**3c**) ^1H NMR δ 1.7–4.1 (m, 6 H), 4.4–5.5 (m, 2 H), 6.7–8.6 (m, 10 H); ^{13}C NMR δ 29.5 (s), 30.8 (d, $^1J_{CP} = 40.0$), 34.3 (d, $^1J_{CP} = 38.7$), 39.4 (d, $^2J_{CP} = 4.8$), 121.0 (d, $^1J_{CP} = 72.8$), 128.0 (d, $^2J_{CP} = 10.2$), 128.5 (d, $^5J_{CP} = 4.7$), 129.0 (d, $^4J_{CP} = 4.0$), 129.7 (d, $^2J_{CP} = 13.6$), 131.0 (d, $^3J_{CP} = 6.1$), 133.0 (d, $^3J_{CP} = 10.8$), 134.6 (d, $^4J_{CP} = 3.4$). (**3d**) ^1H NMR δ 1.7–4.0 (m, 8 H, d centered at 2.8, $^2J_{HP} = 13.8$, 3 H), 7.5–8.6 (m, 5 H); ^{13}C NMR δ 14.5 (d, $^1J_{CP} = 49.7$), 20.9 (d, $^2J_{CP} = 6.1$), 23.7 (d, $^1J_{CP} = 44.5$), 25.3 (d, $^3J_{CP} = 6.1$), 29.6 (d, $^2J_{CP}$

Table I
Ring-Opening Polymerization of Five- and Six-Membered Deoxothiolphostones 1a and 1b[a]

no.	monomers	initiators, mol %	temp, °C	time, h	polymer convn, %[b]	polymer yields, %[c]	polymer mol wt[d]
1	**1a**	MeI (2.0)	80	40	78	62	3000
2	**1a**	MeI (5.0)	80	80	97	81	4100
3	**1a**	$PhCh_2Br$ (2.8)	80	40	76	53	2300
4	**1a**	MeOTf (2.8)	80	125	66	41	1400
5	**1a**	BF_3OEt_2 (2.6)	80	100	32	18	1600
6	**1a**	none	80	40	0		
7	**1a**	none	150	60	100	81	4700
8	**1a**	none	150	24		63	4500
9	**1b**	MeI (5.9)	100	60	97	90	3500
10	**1b**	$PhCH_2Br$ (2.8)	100	60	69	56	4200
11	**1b**	none	100	60	0		
12	**1b**	none	150	110	0		
13	**1b**	none	200	60	*e*		

[a] Bulk polymerization under nitrogen. [b] Conversions determined by ^{31}P NMR spectroscopy before the workup. [c] The amount obtained after the workup procedures. [d] Measured by vapor pressure osmometry in $CHCl_3$ at 40 °C. [e] Complicated reactions such as isomerization and decomposition took place, and only a small portion of oligomeric materials showing several unidentified ^{31}P NMR signals were obtained after precipitation procedures.

Table II
^{31}P, ^1H, and ^{13}C NMR Spectroscopic Data ($CDCl_3$) of Poly(phosphine sulfides) 2a and 2b

	2a	**2b**
$^{31}P\{^1H\}$ NMR,[a] ppm	+45.3 (single peak)	+46.1 (single peak)
^1H NMR, δ	0.7–3.0 (6 H, broad)	0.8–3.1 (8 H, broad)
	6.7–8.1 (5 H, broad)	6.9–8.2 (5 H, broad)
$^{13}C\{^1H\}$ NMR,[b] ppm	15.9 (s)	23.1 (d, $^3J_{CP}$ = 17.5 Hz)
	33.1 (dd, $^1J_{CP}$ = 53.2 Hz, $^3J_{CP}$ = 12.2 Hz)	32.6 (d, $^1J_{CP}$ = 54.9 Hz)
	128.8 (d, $^2J_{CP}$ = 10.5 Hz)	128.7 (d, $^2J_{CP}$ = 11.3 Hz)
	131.0 (d, $^3J_{CP}$ = 9.6 Hz)	130.9 (d, $^3J_{CP}$ = 9.6 Hz)
	131.9 (s)	131.7 (s)

[a] Chemical shifts are from 85% H_3PO_4 external standard. [b] Signals due to the aromatic carbon bound to the phosphorus atom directly were not observed as separate peak(s).

Table III
Equilibrium between 3 and 4 in $CDCl_3$

monomers	X	3:4, %[a] at 35 °C	3:4, %[a] at 80 °C
1a	TfO	100:0	100:0
1a	I	100:0	100:0
1a	Br	100:0	87:13
1b	I	100:0	92:8
1b	Br	100:0	72:28

[a] The 0 values mean "not detected". The accuracy of the detection is ±2%.

Table IV
Results of Polymer Reactions

starting polymer (mol wt)	product polymer structure	yield, %	mol wt	purity, %[a]
2a (4700)	**11**	71	5100	89
2a (4700)	**10**	76	4000	95
10 (4000)	**2a**	91	5000	98
10 (3500)	**11**	75	4100	100[b]

[a] Determined by ^{31}P NMR. [b] From ref 2.

Table V
Adsorption of Heavy-Metal Ions with 2a

conditions[a]	amount of metal ions adsorbed, % Hg^{2+}	Pd^{2+}	Cu^{2+}	UO_2^{2+}
pH 1	100	100	54	2
pH 4	100	100	88	27
pH 6	100	100	88	25
pH 8	100	100	100	24

[a] See Experimental Section.

= 2.7), 119.5 (d, $^1J_{CP}$ = 80.2), 130.5 (d, $^2J_{CP}$ = 13.1), 132.2 (d, $^3J_{CP}$ = 11.3), 135.3 (d, $^4J_{CP}$ = 3.5). (**3e**) ^1H NMR δ 1.5–4.0 (m, 8 H), 4.7 (d, $^2J_{HP}$ = 14.1, 2 H), 7.1–8.5 (m, 10 H); ^{13}C NMR δ 20.6 (d, $^2J_{CP}$ = 6.9), 21.4 (d, $^1J_{CP}$ = 41.8), 25.4 (d, $^3J_{CP}$ = 6.1), 29.0 (d, $^2J_{CP}$ = 3.5), 34.6 (d, $^1J_{CP}$ = 41.8), 117.7 (d, $^1J_{CP}$ = 75.0), 127.0 (d, $^2J_{CP}$ = 10.5), 128.6 (d, $^5J_{CP}$ = 4.3), 129.0 (d, $^4J_{CP}$ = 3.5), 130.2 (d, $^2J_{CP}$ = 12.2), 130.6 (d, $^3J_{CP}$ = 5.3), 132.9 (d, $^3J_{CP}$ = 10.5), 135.0 (d, $^4J_{CP}$ = 2.6).

Synthesis of 2a from 10. To 40.8 mg (0.246 mmol) of **10** dissolved in CH_2Cl_2 (3 mL) was added 26 μL (0.295 mmol) of $(COCl)_2$ under nitrogen with stirring at room temperature to produce a solid product of **9**. After 0.5 h, dry H_2S gas, which was produced by the reaction of saturated aqueous NaSH solution with saturated aqueous $MgCl_2$ solution, was passed through the reaction mixture, and a clear solution was obtained. Pouring the solution into diethyl ether produced **2a**, which was separated and dried in vacuo to give 40.6 mg of white powdery materials (91% yield).

Synthesis of 10 from 2a. Polyphosphorane **9** was obtained in situ by the reaction of 20.7 mg (0.114 mmol) of **2a** with 15 μL (0.17 mmol) of $(COCl)_2$ in CH_2Cl_2 (2 mL). MeOH (0.1 mL) was added to this reaction mixture, and stirring was continued for 1 h. With the addition of powdered $NaHCO_3$ to the mixture to remove HCl liberated, stirring was continued for additional 0.5 h. The mixture was filtrated and poured into diethyl ether to precipitate the product **10**, which was separated and dried in vacuo to give 14.3 mg of solid polymer (76% yield).

Synthesis of 11 from 2a. The procedure was similar to that reported previously for the synthesis of **11** from **10**.[2] From 23 mg (0.126 mmol) of **2a**, 13.4 mg of polyphosphine **11** was obtained (71% yield).

Adsorption of Heavy-Metal Ions with 2a. A general procedure was as follows. Powdered materials of **2a** (20 mg, 0.1 mmol of phosphine sulfide) was suspended in 1 mL of a buffer solution of a heavy-metal salt (1 × 10^{-4} mol/L) which was respectively from $HgCl_2$, $PdCl_2$, $CuSO_4$, or $UO_2(OAc)_2$. The following buffer systems were used: pH 1, KCl-HCl buffer; pH 4 and 6, AcOH-AcONa buffer for Hg^{2+} and Pd^{2+} and potassium hydrogen phthalate-NaOH buffer for Cu^{2+} and UO_2^{2+}; pH 8, NH_4Cl-NH_4OH buffer for Hg^{2+}, Pd^{2+}, and Cu^{2+}, and H_3BO_3, KCl-NaOH, Na_2CO_3 buffer ($[Na_2CO_3]$ = 2 × 10^{-3} mol/L) for UO_2^{2+}. After 16 h of stirring, the polymer **2a** was filtered off, and the amount of the metal ion remaining in the filtrate was determined by spectrophotometric analysis according to the reported procedures for Hg^{2+},[10] Pd^{2+},[11] Cu^{2+},[12] and UO_2^{2+},[13] respectively.

Acknowledgment. S. K. is indebted to the Ministry of Education, Science, and Culture for partial support of 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.

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

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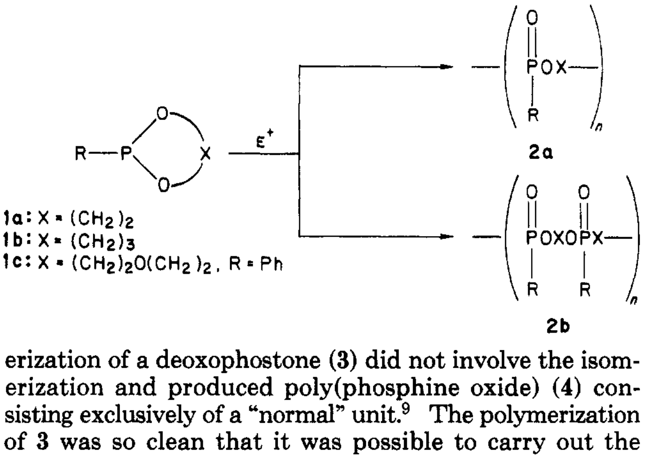
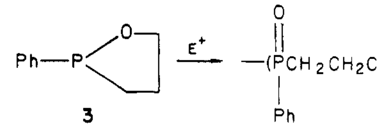
ABSTRACT: Cationic ring-opening polymerization of 2-phenyl-1,3,2-dioxaphosphepane (a seven-membered cyclic phosphonite, **5**) has been investigated. The polymerization of **5** with MeI initiator produced polyphosphinate consisting exclusively of "normal" unit **6**. A Lewis acid and an oxonium initiator 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

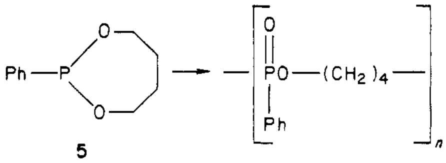
The following cyclic trivalent phosphorus monomers are known to have undergone cationic ring-opening polymerization: phospholanes[1-8] and deoxophostones[9,10] (five membered), phosphorinanes (six membered),[3,5,11] and a phosphocane (eight membered).[12] Cyclic phosphonite monomers (**1**) produced 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



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

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