(9) Kops, J.; Hvilsted, S.; Spanggaard, H. *Macromolecules* **1980**, *13*, 1058.
(10) Kops, J.; Spanggaard, H. *Polym. Bull.* **1981**, *4*, 521.
(11) Tanaka, J.; Katagiri, T.; Takabe, K. *Yuki Gosei Kagaku Kyokai Shi* **1970**, *28*, 764; *Chem. Abstr.* **1970**, *73*, 98321.
(12) Richardson, W. H.; Golino, C. M.; Wachs, R. H.; Yelvington, M. B. *J. Org. Chem.* **1971**, *36*, 943.
(13) Bennett, G. M.; Philip, W. G. *J. Chem. Soc.* **1928**, 1937.
(14) Kops, J.; Spanggaard, H. *Makromol. Chem.* **1972**, *151*, 21.
(15) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Oxford, 1966; p 132.
(16) Hvilsted, S.; Kops, J. *Macromolecules* **1979**, *12*, 889.
(17) Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1961**, *83*, 2984.
(18) Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757.
(19) Clouet, F.; Brossas, J. *Makromol. Chem.* **1979**, *181*, 875.
(20) Hoene, R.; Reichert, K.-H. *Makromol. Chem.* **1976**, *177*, 3545.
(21) Cram, D. J.; Hammond, G. S. "Organic Chemistry"; McGraw-Hill: New York, 1959; pp 233–234.
(22) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.
(23) Cram, D. J.; Hammond, G. S. "Organic Chemistry"; McGraw-Hill: New York, 1959; pp 399–403.
(24) Jones, R. A. Y. "Physical and Mechanistic Organic Chemistry"; Cambridge University Press: New York, 1979; p 156.

High Molecular Weight Poly(2-methoxy-1,3,2-dioxaphospholane 2-oxide) by Ring-Opening Catalysis of Tertiary Amines. Initiation and Stepwise Propagation Mechanisms As Studied by the Stoichiometric Reaction with Triethylamine

Hajime Yasuda, Mitsuhiro Sumitani, Keonil Lee, Takeo Araki,† and Akira Nakamura*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received December 3, 1981*

ABSTRACT: Ring-opening polymerization of an unsubstituted cyclic phosphate, 2-methoxy-1,3,2-dioxaphospholane 2-oxide, by catalysis of tertiary amines gave a linear high polymer of $\bar{M}_n = 5 \times 10^4$. The corresponding mono- and dimethyl-substituted cyclic phosphates are also polymerized but with less efficiency. Ionic mechanisms for the initiation and propagation steps were proposed based upon the ^1H, ^{13}C, and ^{31}P NMR data of solution species formed in 1:1, 1:2, and 1:5 reactions between triethylamine and 2-methoxy-1,3,2-dioxaphospholane 2-oxide.

Introduction

Much effort has been devoted to the preparation of high molecular weight polymers containing phosphorus atoms in the main chain.[1] Condensation of a glycol with $P(O)Cl_3$ or $ROP(O)Cl_2$[2] and anionic[3] or cationic[4] ring-opening polymerization of 1,3,2-dioxaphospholane, 1,3,2-dioxaphospholane 2-oxide, and 1,3,2-dioxaphosphorinane in many cases have given low molecular weight polymers. Recently, organometal-catalyzed ring-opening polymerizations of a series of cyclic esters of phosphoric acid to give high molecular weight polymers have been reported by Penczek,[5] and the analysis of microstructure, polymerization mechanisms and interconversion into an acidic polyester have been extensively studied. In a previous paper, we reported a unique method for preparation of acidic polyesters by thermal elimination of isobutylene from poly(2-*tert*-butoxy-1,3,2-dioxaphospholane 2-oxide).[6]

In seeking excellent catalysts for linear polymerization of five- or six-membered cyclic phosphates, we have found that a simple tertiary amine such as triethylamine or pyridine catalyzes the ring-opening polymerization of 2-methoxy-1,3,2-dioxaphospholane 2-oxide to give a high molecular weight linear polymer in good yield. Other characteristics of this type of polymerization are (1) the polymerization procedure and the removal of catalysts are facile and do not require any special techniques and (2) water-insoluble high molecular weight polymers and water-soluble relatively low molecular weight polymers can be prepared at one's option by controlling the ratio between the monomer and catalyst.

High molecular weight polyesters of phosphoric acid thus prepared will be useful as novel functional polymer materials with specific physical properties such as hydrophilicity, nonflammability,[7] thermal stability, high adhesion to glass and metal, etc.[8] If it is possible to convert efficiently $O{=}P(OR)_3$ groups in the main chain into $O{=}P(OH)(OR)_2$ groups, a wide applicability may appear because its polymer backbone is analogous to that of polynucleotides. Preparation of synthetic polynucleotides bearing hydrogen phosphate groups in the main chain has been attempted by condensation of $ROP(O)Cl_2$ with a glycol involving nucleic acid bases.[9] However, the polymer prepared so far has a molecular weight too low for synthetic polynucleotides.

Results and Discussion

1. Polymerization by Tertiary Amine Catalysts. The results of the polymerization of 2-methoxy-1,3,2-dioxaphospholane 2-oxide (1) with tertiary amine catalysis at 90 °C are listed in Table I. The polymer was separated into three fractions according to the solubility or magnitude of the molecular weight by fractional precipitation in methanol and water. The methanol-soluble fraction contains polymers of molecular weight 1×10^3 to 8×10^3 and the water-soluble fraction (but insoluble in methanol) contains polymers of $\bar{M}_n = 8 \times 10^3$ to 5×10^4 as analyzed by VPO (vapor pressure osmometry) and GPC (gel permeation chromatography). The molecular weight of the water-insoluble fraction was estimated to be $>5 \times 10^4$. The degree of cross-linkage for the water-insoluble polymer will be very small because practically no difference was ob-

† Present address: Department of Chemistry, Faculty of Science, Shimane University, Nishikawazu 1060, Matsue 690, Japan.

0024-9297/82/2215-1231$01.25/0

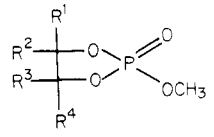
Table I
Yield, Fractional Part, and Molecular Weight of Poly(2-methoxy-1,3,2-dioxaphospholane 2-oxide) Prepared by Tertiary Amine Catalysts

catalyst	total yield of polymer/%[a]	fractional part of polymer: MeOH soluble[b] %	MeOH soluble[b] $\bar{M}_n$	H_2O soluble[c] %	H_2O soluble[c] $\bar{M}_n$	H_2O insoluble, %
$HN(C_2H_5)_2$	81	100	5.2×10^2	0		0
$C_6H_5NH_2$	79	100	6.5×10^2	0		0
$N(C_2H_5)_3$	97	33	8.1×10^3	28	4.8×10^4	39
pyridine	99	35	5.5×10^3	23	5.0×10^4	42
$C_6H_5N(CH_3)_2$[d]	96	37	2.0×10^2	13	4.7×10^4	50

[a] Polymerization was carried out at 100 °C for 15 h. Total yield is expressed as the proportion of ether-insoluble fraction to the charged monomer. [b] Proportion of methanol-soluble part to the total yield of the polymer. [c] Methanol-insoluble part was fractionated with water at 25 °C. [d] 2,6-Dimethylpyridine.

served in the IR spectra between these three fractionated polymers.

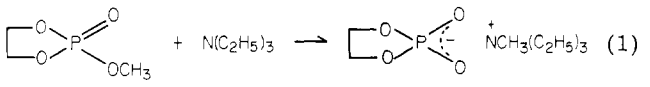
To evaluate the efficiency of the tertiary amine catalyst, we examined polymerization of **1** with typical organometallic catalysts in benzene at 20 °C. Butyllithium gave a methanol-soluble polymer ($\bar{M}_n = 3.5 \times 10^2$) in 82% yield and diethylmagnesium a polymer ($\bar{M}_n = 3.8 \times 10^2$) in 96% yield. The apparent rate of polymerization by butyllithium (32.5 mol/min at a concentration of 1 mol % of catalyst to monomer) and by diethylmagnesium (25.0 mol/min) is larger than that (1.1 mol/min) by tertiary amines. $AlEt_3$–H_2O (1:0.9) and $ZnEt_2$–H_2O (1:0.8) were found to be active catalysts in polymerization of **1**. $AlEt_3$–H_2O (1 mol % of monomer) gave a polymer ($\bar{M}_n = 3.0 \times 10^3$) in 98% yield and $ZnEt_2$–H_2O (1 mol % of monomer) a polymer ($\bar{M}_n = 2.9 \times 10^3$) in 96% yield (polymerization conditions, 100 °C, 15 h, no solvent). The water-modified catalysts were superior to $AlEt_3$ or $ZnEt_2$ alone (pure $AlEt_3$ and $ZnEt_2$ gave only an oily polymer in 5–10% yield when the monomer **1** purified by repeated distillation was used). Catalysis by a tertiary amine is favored over that of organometallic catalysts in the preparation of high molecular weight polymers in good yield. Secondary amines such as diethylamine or aniline gave a low molecular weight oily polymer in 57–85% yield, presumably due to the chain transfer to the monomer. Use of a solvent such as ether, benzene, or dichloroethane lowered the polymer yield and the degree of polymerization. Tertiary amine catalysts required higher polymerization temperatures (>45 °C) than the organometallic catalysts, which induce polymerization at −20 to +20 °C.[5b] Tertiary amine catalysts are also effective for polymerization of 2-methoxy-4-methyl-1,3,2-dioxaphospholane 2-oxide (**2**) and 2-methoxy-4,4-dimethyl-1,3,2-dioxaphospholane 2-oxide (**3**). Reaction



1, $R^1 = R^2 = R^3 = R^4 = H$
2, $R^1 = R^2 = R^4 = H$; $R^3 = CH_3$
3, $R^1 = R^2 = H$; $R^3 = R^4 = CH_3$
4, $R^1 = R^2 = R^3 = R^4 = CH_3$

of **2** or **3** with 2 mol % of triethylamine at 100 °C for 48 h gave polymers with $\bar{M}_n = 3.5 \times 10^2$ (57% yield) and $\bar{M}_n = 3.1 \times 10^2$ (90% yield), respectively. The catalytic activity of triethylamine for these two was less than that of organometallic catalysts. All the tertiary amines examined by us were inactive toward 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-oxide (**4**).

2. Initiation Step of the Polymerization by Tertiary Amine Catalyst. To examine the initiation mechanism of the polymerization, we carried out the 1:1 reaction of **1** with tertiary amines in $CHCl_3$ at 80–100 °C for 20 h in a sealed tube and analyzed the structure of the product by ^1H NMR (100 MH). The spectrum shows the formation of the 1:1 adduct **5** of triethylamine with 2-methoxy-1,3,2-dioxaphospholane 2-oxide in quantitative yield (eq 1). The reaction of excess triethylamine with **1** (3:1 and



1 **5** (1)

5:1) gave a pure sample of identical structure. The ^1H NMR spectrum showed that the doublet (δ 3.59 ppm, J_{PH} = 11.5 Hz) assigned to the methoxy proton signal of **1** changed into a singlet (2.90 ppm) when **1** formed the adduct **5** and the multiplet (4.21 ppm) assigned to OCH_2C-H_2O of **1** changed into a doublet (3.84 ppm, J_{PH} = 11.1 Hz), indicating the persistence of the ring. Similar ionic structures have been known for the product obtained from cyclic or acyclic phosphate triesters and tertiary amines.[10]

In the reaction of 2-phenoxy-1,3,2-dioxaphospholane 2-oxide with dimethylamine, the ring-opened zwitterion structure has been proposed for the 1:1 product, while 2-phenoxy-4-methyl-1,3,2-dioxaphospholane 2-oxide is known to produce the cyclic (ring-retained) ionic structure.[11] The ring-opened zwitterion structure was excluded for the present 1:1 adduct because its $^{31}P\{^1H\}$ NMR spectrum (in $CDCl_3$) showed a peak at −17.5 ppm (assuming the signal of H_3PO_4 as 0.0 ppm), a characteristic position for the five-membered cyclic phosphates.[12] The ^{31}P chemical shift value of the starting monomer **1** was −18.4 ppm. The ^{13}C NMR spectrum ($CDCl_3$ solution) of the 1:1 adduct showed a singlet assigned to the $POCH_2$ group at 64.12 ppm (i.e., two carbon atoms on the OCH_2CH_2O group are magnetically equivalent) and sharp singlets at 46.26, 55.80, and 8.09 ppm, the signals of NCH_3, NCH_2, and CH_3CH_2 of $^+NCH_3(C_2H_5)_3$. Thus the ^{13}C NMR studies also support the cyclic ionic structure. The ^{13}C NMR signals for the $POCH_2$ and $POCH_3$ groups of monomer **1** appeared at 66.2 (singlet) and 54.8 ppm (doublet, J_{PC} = 6.4 Hz).

The rate of formation of **5** depends on the pK_a value of amines, and the kinetic plots suggest that the reaction is second order (Table II; the rate of reaction is defined by k_2[cyclic phosphate][tertiary amine]). The P=O stretching vibration of **5** in the IR spectrum was shifted to higher wavelength by 20–60 cm^{-1} with increasing amine pK_a value. The increased ionic character of the adduct will account for the higher wavelength shift.

The rate of formation of the 1:1 adducts is greatly affected by alkyl substituent on the ring of **1**. It decreased remarkably with increasing number of methyl groups

Table II
Rate of Reaction between Tertiary Amines and 2-Methoxy-1,3,2-dioxaphospholane 2-Oxide and the IR Frequency of P=O for the Adducts

amine	pK_a	k_2/(dm^3 mol^{-1} h^{-1})	ν(P=O)/cm^{-1}	Δ(P=O)/cm^{-1} [a]
$HN(C_2H_5)_2$	10.94	(2.22) [b]	1228	60
$N(C_2H_5)_3$	10.64	0.74	1238	50
pyridine	5.19	0.07 (5)	1257	30
$C_6H_5N(CH_3)_2$	5.12	0.03 (2)	1271	17

[a] Shift from the P=O frequency (1288 cm^{-1}) of 2-methoxy-1,3,2-dioxaphospholane 2-oxide (solvent, $CHCl_3$). [b] Though the kinetic plots deviated from a straight line, an approximate value is given for comparison.

Table III
^{1}H NMR (100 MHz) Chemical Shifts and Coupling Constants (Hz) for the Triethylamine-2-Methoxy-1,3,2-dioxaphospholane 2-Oxide 1:n Adducts and the Polymer in $CDCl_3$ [a]

n for the adducts	polymer end			polymer chain	
	OCH_2CH_2O		CH_3O	OCH_2CH_2O	CH_3O
	H_a	H_b	H_c	H_d	H_e
2	3.89 (d, 10.0)	3.74 (m)	3.54 (d, 11.1)		
3	3.89 (d, 9.9)	3.80 (m)	3.60 (d, 11.0)	4.00 (m)	3.54 (d, 11.2)
5	3.98 (d, 10.0)	3.90 (m)	3.64 (d, 11.0)	4.13 (m)	3.59 (d, 11.1)
polymer [b]				4.25 (t, 8.5)	3.74 (d, 11.1)

[a] ppm downfield from external Me_4Si. Subscript letters of H_a-H_e follow the numbering system given in eq 4. d, t, and m indicate doublet, triplet, and multiplet. [b] Methanol-soluble fraction was used.

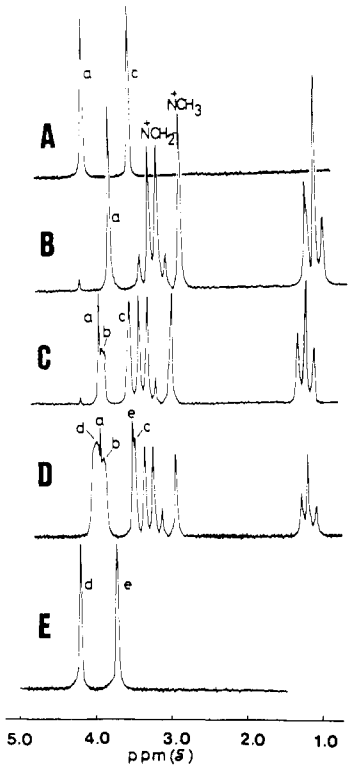
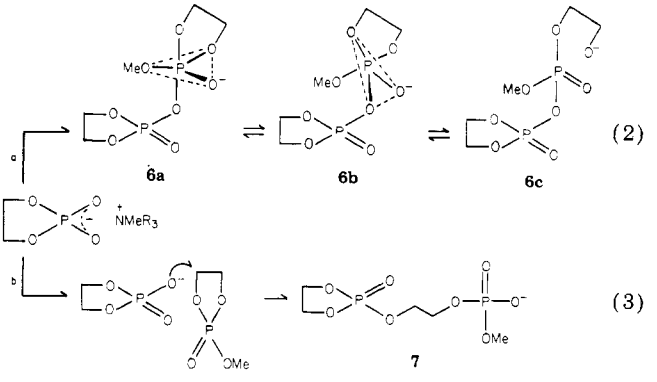


Figure 1. 100-MHz ^{1}H{^{31}P} NMR spectra of 2-methoxy-1,3,2-dioxaphospholane 2-oxide (A), the triethylamine–2-methoxy-1,3,2-dioxaphospholane 2-oxide 1:1 (B), 1:2 (C), and 1:5 (D) adducts, and the polymer (E) in $CDCl_3$ at 30 °C. Symbols used to specify the signals follow the numbering system given in eq 4.

substituted on the ring; i.e., the rate constant for **1** (0.74 dm^3 mol^{-1} h^{-1}) > **2** (0.26 dm^3 mol^{-1} h^{-1}) > **3** (0.16 dm^3 mol^{-1} h^{-1}) > **4** (0.074 dm^3 mol^{-1} h^{-1}). The decrease in the rate constant is due to the increase of electron density on the P atom, which contributes to weakening of the interaction between phosphates and tertiary amines. The formation of the 1:1 adduct seems necessary for initiation of the polymerization but is not sufficient to allow the propagation of the polymerization. Thus cyclic phosphate **4** forms the adduct in good yield in 5 days at 60 °C but no polymerization occurred when a mixture of 20 equiv of **4** and the adduct was heated to 120 °C for 1 day (**4** was recovered).

3. Nuclear Magnetic Resonance Studies on the Propagation Step. 2-Methoxy-1,3,2-dioxaphospholane 2-oxide **1** was chosen for the NMR study on the propagation step of the polymerization, since the molecular weight of the oligomer prepared by stoichiometric reaction of **1** with triethylamine was found to increase in proportion to the ratio of **1** to triethylamine. GPC (eluent, methanol) analysis of the product obtained by 1:2 reaction of triethylamine with **1** at 60 °C for 20 h showed that it comprises the 1:2 adduct (92%), the 1:3 adduct (4%), and unreacted **1** (4%), in line with the ^{1}H NMR assignments (Table III). Correct ^{1}H NMR assignment was made with the aid of the ^{1}H{^{31}P} NMR spectrum, in which ^{1}H–^{31}P coupling disappears (Figure 1). ^{1}H NMR data permit two structures for the 1:2 adduct. One is **6** formed by nucleophilic attack of the phosphoryl oxygen (PO^-) on the phosphorus atom of **1**, leading to **6** with P–O–P bonding (eq 2). Attack of the anion from the apical position is most plausible based on the accepted theory of base-catalyzed hydrolysis of cyclic phosphates.[13] The other candidate is **7**, which is formed by nucleophilic attack of the phosphoryl oxygen atom on the CH_2 group (eq 3). ^{31}P{^{1}H} NMR



(2)

(3)

spectra will serve as a useful tool to distinguish these two

Table IV
^{13}C NMR Chemical Shifts (ppm) and Coupling Constants (Hz) for the Triethylamine-2-Methoxy-1,3,2-dioxaphospholane 2-Oxide 1:*n* Adducts and the Polymer in $CDCl_3$ [a]

n for the adducts	polymer end			polymer chain	
	OCH_2CH_2O		CH_3O	OCH_2CH_2O	CH_3O
	C_a	C_b	C_c	C_d	C_e
2	61.5 (6.7)	61.4 (m)	50.1 (5.8)		
3	61.6 (6.8)	61.4 (m)	49.9 (5.6)	65.4 (m) 65.8 (m)	52.3 (5.6)
5	61.9 (6.7)	61.6 (m)	50.1 (5.8)	65.9 (m) 66.3 (m)	53.8 (5.6) 54.1 (5.6)
polymer				66.8 (6.1)	55.0 (5.5)

[a] ppm downfield from external Me_4Si. Subscript letters of C_a-C_e follow the numbering system given in eq 4.

Table V
^{31}P NMR Chemical Shifts (ppm) and P-P Coupling Constants (Hz) for the Triethylamine-2-Methoxy-1,3,2-dioxaphospholane 2-Oxide 1:*n* Adducts and the Polymer in $CDCl_3$ [a]

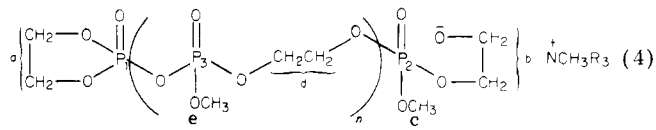
n for the adducts	polymer end		polymer chain
	P_1	P_2	P_3
2	−17.2 (15.1)	0.15 (15.2)	
3	−17.2 (14.9)	0.16 (s)	−0.34 (15.0)
5	−17.2 (15.0)	0.16 (s)	−0.31 (s), −0.34 (15.1)
polymer			−0.31 (s)

[a] Spectra were measured at 40.32 MHz at 30 °C with aqueous H_3PO_4 as an external standard. P_1-P_3 in eq 4 specify the P nuclei.

structures because ^{31}P–^{31}P coupling will be observed for **6a** or **6c** but not for **7**. Actually, the spectrum showed a ^{31}P–^{31}P coupling of 15.1 Hz), a value consistent with the P–O–P coupling value of 16 ± 3 Hz reported for pyrophosphoric acids.[14] Therefore, the structure of the 1:2 adduct was concluded to be **6a** or **6c**. Though the species **6c** may be in equilibrium with **6b** and **6a**, the observation of two signals of P nuclei at −17.2 and 0.15 ppm indicates that **6c** is preferred over **6a** (the positional change of the growing end at the apical position of **6a** to the equatorial position by pseudorotation will lead to **6b** and cause one end of the five-membered ring of **6b** to be freed from the apical position, giving **6c**). If the adduct involves two cyclic phosphates expressed as **6a** or **6b**, chemical shifts of both P nuclei should appear at −15 ± 2 ppm. Chemical shift values of P nuclei for acyclic phosphate triesters are generally 0.5 ± 2 ppm.[15] A similar ring-opened ionic structure is known for the base-hydrolyzed product of 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-oxide.[16]

The product obtained by the 1:3 reaction of triethylamine with 1 at 55–90 °C for 45 h consists of the 1:3 adduct (78%), the 1:2 adduct (102%), and others (10%) as evidenced by GPC and $^1H\{^{31}P\}$ NMR spectra. The $^1H\{^{31}P\}$ NMR signals of the 1:3 adducts are readily assigned to the structure given in eq 4, the structure expected from eq 2.

$$(n+2)1 + NR_3 \rightarrow$$



(4)

The separation of the 1:4 adduct from the 1:5 or 1:6 adduct by GPC or discernment by $^1H\{^{31}P\}$ NMR has failed due to insufficient resolution. Therefore, the peak assignment for the 1:5 adduct was made by referring to the relative signal intensity ratio of the end group (cyclic phosphate) to the main chain.

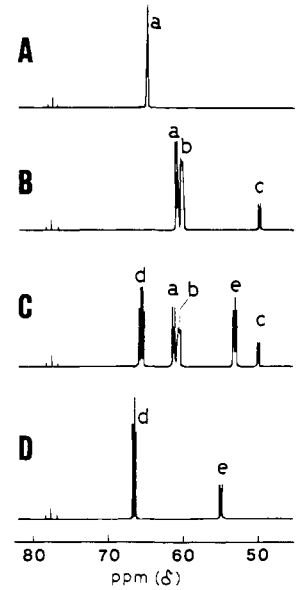
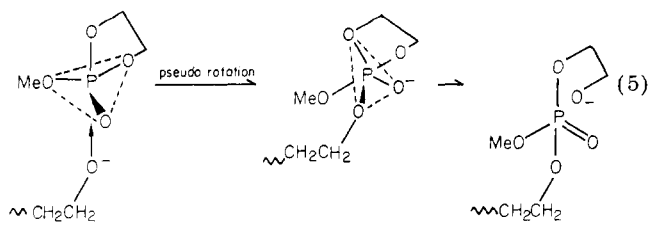


Figure 2. ^{13}C NMR spectra of the triethylamine–2-methoxy-1,3,2-dioxaphospholane 2-oxide 1:1 (A), 1:2 (B), and 1:5 (C) adducts and the polymer (D) in $CDCl_3$. Symbols used for signal assignment are given in eq 4. Signals of the countercation, $^+NCH_3(C_2H_5)_3$, are omitted for clarity. A triplet at 77.5 ppm shows the signal of $CDCl_3$.

The ^{13}C NMR spectral data for the 1:*n* adducts and the polymer are shown in Table III and Figure 2 (symbols used to specify the signals are given in eq 4). The assignment of the ^1H NMR spectrum was done with reference to the corresponding ^{13}C NMR spectrum, which supports the structure given in eq 4. The ratio of the number of cyclic phosphates at the polymer end to those in the main chain was determined by the $^{31}P\{^1H\}$ NMR spectrum (Table IV), in which the P signal of cyclic phosphates appeared at a significantly lower field compared to that of acyclic phosphates. On the basis of these data, we can resonably propose a mechanism (eq 5) of chain propagation for the



(5)

tertiary amine catalyzed polymerization, which is essentially the same as the mechanism proposed by Penczek for anionic polymerization of 2-alkoxy-1,3,2-dioxaphosphorinane 2-oxide.[4e] The attack of the growing end (alcoholate anion) is directed along the apical position to form an

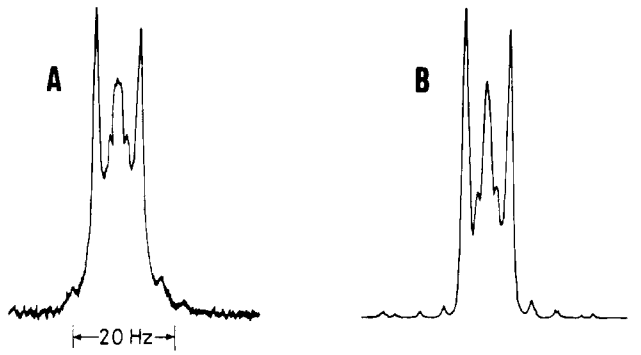
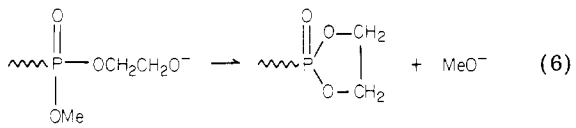


Figure 3. 100-MHz ^1H NMR spectrum of the $POCH_2CH_2O$ part of poly(2-methoxy-1,3,2-dioxaphospholane 2-oxide): (A) observed; (B) simulated.

intermediate with a trigonal-bipyramidal structure. Change of the methoxy group from an equatorial to an apical position by pseudorotation results in the liberation of the growing end from the apical position to reinitiate the chain growing. The degree of polymerization calculated from the $^{31}P\{^1H\}$ NMR spectrum (assuming one cyclic end group in every macromolecule) was larger than the value determined by the VPO method. This will be due to the gradual ring opening of the end group by protolysis with D_2O (used as a solvent) during the NMR measurement. An acyclic phosphate–amine adduct catalyst prepared from $OP(OMe)_3$ and triethylamine also gave a high molecular weight polymer under the same polymerization conditions as described above (yield, 92%; water-soluble fraction 58% and insoluble fraction 42%). This result clearly shows that this type of polymerization does not necessarily require the strained five-membered ring phosphate as the polymer end.

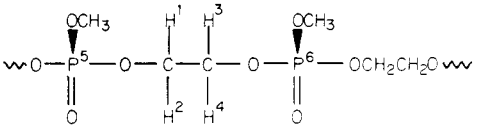
Extensive chain transfer occurred when a secondary amine was used as a catalyst in the present work. A possible mechanism for the chain transfer is the elimination of MeO^- anion at the growing end of the polymer (eq 6), resulting in the formation of a cyclic end group. The



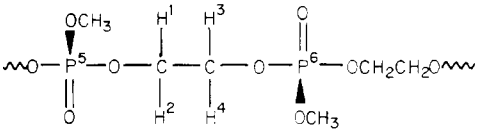
(6)

liberated MeO^- anion may attack the monomer to reinitiate the polymerization or combine with countercation, $^+NHMeEt_2$, to produce a catalytically active tertiary amine ($NMeEt_2$ together with MeOH). The enhanced chain transfer may be attributed to hydrogen transfer from $^+NHMeEt_2$ to the growing end because the pK_a value of $HNEt_2$ is similar to that of NEt_3 and no difference was observed between the structures of the 1:1 adduct of $HNEt_2$ and of $HNEt_3$.

4. Polymer Structure Determined by NMR. Poly(2-methoxy-1,3,2-dioxaphospholane 2-oxide) thus obtained was stable in water in the pH range 2.0–12.0 at least for 20 h at ambient temperature, though it decomposed rapidly in 6 N HCl or 6 N NaOH. The ^1H, $^1H\{^{31}P\}$, $^{31}P\{^1H\}$ and ^{13}C NMR spectra of the polymer prepared by the present method coincided in chemical shifts and coupling constants with the NMR data reported by Penczek.[5b] The $^1H\{^{31}P\}$ NMR spectrum possesed singlets at 3.74 (CH_3OP) and 4.25 (CH_2OP) ppm downfield from Me_4Si. The $^{31}P\{^1H\}$ NMR spectrum showed simply a singlet at −0.3 ppm (H_3PO_4 was used as an internal standard (0.0 ppm)). The ^{13}C NMR spectrum consists of a doublet (J_{PH} = 6.1 Hz) at 55.0 ppm and a triplet (J_{PH} = 5.5 Hz) at 66.8 ppm. The ^1H NMR signal assignment of the polymer has not been established due to its complexity. An iterative computer simulation (six spin system) of the spectrum in $CDCl_3$ provided the following parameters for the $POCH_2CH_2O$ group: J_{12} (J_{34}), −8.0; J_{13} (J_{24}), 6.5; J_{14} (J_{23}), 13.0; J_{15} (J_{25}, J_{46}), 8.6; J_{16} (J_{26}, J_{35}, J_{45}), −0.1; J_{56}, 0.08 Hz. The $^3J_{PH}$ value for $POCH_3$ group is 11.1 Hz. The observed and simulated spectra with respect to the $POCH_2CH_2O$ group of the polymer are given in Figure 3. The magnitude of J_{15} and J_{16} are similar to those of $^3J_{PH}$ (8.0–8.5 Hz) and $^4J_{PH}$ (<0.5 Hz), respectively, reported for acyclic phosphates such as $C_2H_5OPCl_2$ and $(C_2H_5O)_3PO$.[17] Free rotation around the C–O and P–O bonds of the polymer chain is probable because $J_{15} = J_{25}$ and $J_{36} = J_{46}$. Magnetic equivalence of protons and P atoms in the polymer chain does not give any meaningful information on the isotactic placements



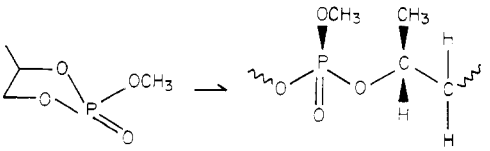
isotactic



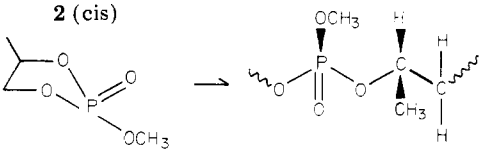
syndiotactic

for poly(2-methoxy-1,3,2-dioxaphospholane 2-oxide), although these placements in terms of dyads are possible for poly(2-alkoxy-1,3,2-dioxaphospholane) and poly(2-alkoxy-1,3,2-dioxaphospholane 2-oxide). The J values of J_{15} (11.35–14.26 Hz) and J_{25} (8.05–9.25 Hz) for monomer **1**[18] and related cyclic phosphates[19] are known to be different from each other, reflecting the trans and cis configuration with respect to H and $POCH_3$ groups.

Though no peak splitting attributable to the syndio- or isotactic conformation was observed for the polymer obtained from **1**, the ^{13}C NMR spectrum of the polymer obtained from **2** by reaction with triethylamine (concentration, 1 mol %; polymerization at 80 °C for 20 h) showed peak splittings ascribable to the conformations. The spectrum gave two sets of parameters, i.e., 75.25 ($POCH_2$, 5.7 Hz), 70.98 (POCH, 5.7 Hz), 54.25 ($POCH_3$, 6.3 Hz), and 19.20 (CH_3, 6.5 Hz) and 74.92 ($POCH_2$, 5.7 Hz), 69.5 (POCH, 5.7 Hz), 54.49 ($POCH_3$, 6.3 Hz), 17.85 (CH_3, 6.5 Hz) ppm. The intensity ratio of each of the signals from the former to the latter is 35:65. If the polymerization occurred with retention of configuration of the monomer (39:69 cis–trans mixture), the parameter of the former may readily be ascribed to the disyndiotactic or erythro–diisotactic placement and the latter to the threo–diisotactic placement. The preparation of single diastereomers of **2** is required to make an accurate microstructural analysis of the polymer.



2 (cis)



2 (trans)

5. Conversion of Polyesters into Poly(hydroxy-

ethylene Phosphate). Conversion of poly(2-methoxy-1,3,2-dioxaphospholane 2-oxide) into poly(2-hydroxy-1,3,2-dioxaphospholane 2-oxide) was examined according to the procedure reported by Penczek.[5a] The $\bar{M}_n = 2.2 \times 10^4$ polymer of 1 was reacted with aqueous trimethylamine (30%) at 50 °C for 10 h in a sealed tube, and the solution was passed through a cation exchange resin (Dowex 50W in a 3 × 30 cm column) to exchange the $^+N(CH_3)_4$ ion by protons. The ^1H NMR spectrum of the resulting polymer in D_2O is essentially the same as those reported earlier.[5a,6] The interconversion of $O{=}P(OR)_3$ groups in the polymer into $O{=}P(OH)(OR)_2$ groups exceeds 90% as revealed by NMR. The yield is ca. 85% (15% of the polymer was adsorbed on the resin and remained in the column). Thus the polymer having a backbone analogous to that of polynucleotides was prepared in good yield. The introduction of nucleic acid bases into the side chain of the polymer is now being attempted.

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were taken on a Varian Model XL-100 instrument and $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ NMR spectra on a JEOL Model FX100. IR spectra were recorded on a Hitachi EPI-2 spectrometer. Elemental analysis was carried out with a Yanagimoto Model MT-2 CHN analyzer. Molecular weight of the polymer was measured by vapor pressure osmometry with a Mechrolab Model 302 instrument and by gel permeation chromatography on a Shimadzu-Du Pont Model 830 GPC fitted with SE-100 and SE-500 columns (Shimadzu Co.) using methanol–water as eluent. Triethylamine, pyridine, diethylamine, and chloroform were dried over calcium hydride and distilled before use.

Preparation of 2-Methoxy-1,3,2-dioxaphospholane 2-Oxide. To a mixture of ethylene glycol (55 mL, 1.0 mol), pyridine (162 mL, 2.0 mol), and dry ether (300 mL) was added dropwise an ether solution (120 mL) of phosphorus trichloride (87 mL, 1.0 mol) over a 5-h period with vigorous mechanical stirring. The reaction temperature was controlled to −15 ± 5 °C with ice–salt during the reaction. After separation of pyridine hydrochloride salt by filtration with a sintered glass filter, ether was removed by evaporation, and the residue was distilled in vacuo to give 2-chloro-1,3,2-dioxaphospholane [48 °C (17 mmHg)] in 42% yield (70 g, 0.55 mol). In a 1-dm^3 three-necked flask fitted with a mechanical stirrer, a Dimroth condenser, and a separatory funnel, 2-chloro-1,3,2-dioxaphospholane (63 g, 0.5 mol) was dissolved in pentane (400 mL) and cooled to −20 °C. Then a mixture of dry methanol (20 mL, 0.5 mol) and triethylamine (70 mL) was added dropwise through the funnel over a 5-h period with mechanical stirring. After removal of triethylamine hydrochloride salt by filtration, the pentane solution was distilled to give 2-methoxy-1,3,2-dioxaphospholane. Typical yield was 55% (29 g, 0.24 mol) based on 2-chloro-1,3,2-dioxaphospholane. The sample was distilled twice in vacuo [54 °C (25 mmHg)] to obtain 2-methoxy-1,3,2-dioxaphospholane of 99% purity (20 g). The oxidation of 2-methoxy-1,3,2-dioxaphospholane was carried out by bubbling dinitrogen tetraoxide through a mixture of 2-methoxy-1,3,2-dioxaphospholane (20 g) and pentane (100 mL) cooled to −20 °C with ice–salt. Dinitrogen tetraoxide was generated by Besson's method.[20] As oxidation proceeded, the solution separated into two layers. End of the reaction was indicated by the appearance of a brown color in the upper pentane layer due to NO_2 or formation of a pale green color in the lower layer. After removal of pentane and excess dinitrogen tetraoxide by evaporation, the residue was distilled in vacuo to give a colorless liquid [95 °C (2 mmHg)] of 2-methoxy-1,3,2-dioxaphospholane 2-oxide (19 g, 0.18 mol) in 82% yield. The purity was ca. 98% estimated by gas chromatographic analysis and the ^1H NMR spectrum: ^1H NMR ($CDCl_3$) 3.82 (3 H, d, J_{HP} = 11.8 Hz, OCH_3), 4.45 (4 H, m, J_{HP} = 10.1 Hz, CH_2) ppm; IR (neat), 2960, 2920, 2860, 1415, 1373, 1293 (s), 1213, 1188, 925 (s), 869, 846, 768 cm^{-1}. Anal. Calcd for $C_3H_7O_4P$: C, 26.10; H, 5.11. Found: C, 26.04; H, 5.30. $d^{25} = 1.44$.

Preparation of 2-Methoxy-4-methyl-1,3,2-dioxaphospholane 2-Oxide. 2-Methoxy-4-methyl-1,3,2-dioxaphospholane was prepared by reaction of 1,2-propanediol (74 mL, 1 mol) with phosphorus trichloride (87 mL, 1 mol) followed by alkoxylation with methanol in essentially the same manner as described for 2-methyoxy-1,3,2-dioxaphospholane: bp 91 °C (2 mmHg); yield, 56% based on 1,2-propanediol. Oxidation with dinitrogen tetraoxide was carried out at −40 °C. Immediately after completion of the reaction, dinitrogen tetraoxide was evaporated at this temperature because the rise in temperature to room temperature in the presence of N_2O_4 resulted in a decrease in the yield due to the spontaneous polymerization of 2-methoxy-4-methyl-1,3,2-dioxaphospholane 2-oxide. Distillation of the pentane solution gave 2-methoxy-4-methyl-1,3,2-dioxaphospholane 2-oxide [bp 93 °C (1 mmHg)] in 89% yield based on 2-methoxy-4-methyl-1,3,2-dioxaphospholane. The compound consists of trans and cis isomers in a 69/31 ratio as determined by ^1H NMR, referring to the reported data:[21] ^1H NMR ($CDCl_3$) 1.44 (3 H, d, J_{PH} = 6.41 Hz, CH_3O of cis isomer), 1.48 (3 H, d, J_{PH} = 6.4 Hz, CH_3O of trans isomer), 3.87 (3 H, d, J = 11.9 Hz, CH_3), 4.00–5.20 (3 H, m, $CHCH_3$ and CH_2) ppm; ^{13}C NMR ($CDCl_3$) 75.42 ($POCH_2$), 72.05 (POCH), 54.75 ($POCH_3$, trans, 6.2 Hz), 54.69 ($POCH_3$, cis, 6.2 Hz), 19.00 (CH_3, trans, 6.5 Hz), 18.80 (CH_3, cis, 6.5 Hz) ppm; IR (neat) 1290, 1061, 1012, 854 cm^{-1}. Anal. Calcd for $C_4H_9O_4P$: C, 31.59; H, 5.96. Found: C, 31.56; H, 6.05.

Preparation of 4,4-Dimethyl- and 4,4,5,5-Tetramethyl-2-methoxy-1,3,2-dioxaphospholane 2-Oxide. 2-Methoxy-4,4-dimethyl-1,3,2-dioxaphospholane 2-oxide and 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-oxide were prepared starting from 1,2-isobutylene glycol and pinacol, respectively, under the same reaction conditions as described for 2-methoxy-1,3,2-dioxaphospholane 2-oxide. The isolated yields were 13 and 15%, respectively, based on the glycols. The 4,4,5,5-tetramethyl derivative was purified by sublimation at 100 °C (0.1 mmHg).

2-Methoxy-4,4-dimethyl-1,3,2-dioxaphospholane 2-oxide: bp 85 °C (1 mmHg); ^1H NMR ($CDCl_3$) 1.48 (3 H, s, CH_3), 1.52 (3 H, s, CH_3), 3.82 (3 H, d, J_{PH} = 12.2 Hz, OCH_3), 4.11 (1 H, d, J_{PH} = 10.8 Hz), 4.32 (1 H, d, J_{PH} = 9.3 Hz) ppm; IR (neat) 2980, 2960, 2910, 2835, 1417, 1393, 1380, 1365, 1295 (s), 1242, 1176, 1155, 1062, 1021 (s), 983 (s), 921 (s), 862, 851, 797, 752 cm^{-1}. Anal. Calcd for $C_5H_{11}O_4P$: C, 36.15; H, 6.68. Found: C, 36.06; H, 6.84. d^{25} = 1.25.

2-Methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-oxide: mp 100.5 °C; ^1H NMR ($CDCl_3$) 1.42 (6 H, s, CH_3), 1.47 (6 H, s, CH_3), 3.82 (3 H, d, J_{PH} = 11.2 Hz, OCH_3) ppm; IR (KBr) 2985, 1400, 1379, 1285 (s), 1269 (s), 1209, 1170, 1149, 1150 (s), 1112, 966 (s), 941 (s), 895 (s), 834, 802, 778 cm^{-1}. Anal. Calcd for $C_7H_{17}O_4P$: C, 43.30; H, 7.79. Found: C, 43.25; H, 7.65.

Preparation of $AlEt_3$–H_2O (1:0.9) and $ZnEt_2$–H_2O (1:0.8) Catalysts. The catalyst $AlEt_2$–H_2O was prepared as previously reported.[22] $ZnEt_2$–H_2O catalyst was prepared in the following manner. A toluene solution (30 mL) of diethylzinc (1.2 g, 10 mmol) was added dropwise to a stirred suspension of water (0.14 g) in toluene (30 mL) at 0 °C. After gas evolution ceased, the resulting yellow solution was heated to 80 °C for 2 h and evaporated to dryness. After the addition of benzene (30 mL) to the residue and separation of the precipitate by filtration, the benzene-soluble part was used as catalyst.

Polymerization of 2-Methoxy-1,3,2-dioxaphospholane 2-Oxide. Polymerization was carried out by means of a high-vacuum technique under an argon atmosphere with or without the use of solvent. Monomer (1.0 g), solvent, and triethylamine (1 mol % of monomer) were charged into a Schlenk tube at 0 °C and the tube was sealed. The mixture was held at 100 °C for 10 h to induce polymerization and the contents were poured into ether (80 mL) containing methanol (5 mL). The ether-insoluble part was taken as the total yield. The polymer dried in vacuo for 20 h was powdered and dissolved in methanol (100 mL) at 25 °C. The methanol-insoluble part was then poured into water (100 mL) for fractionation. Water-insoluble polymer: Anal. Calcd for $(C_3H_7O_4P)_n$: C, 26.10; H, 5.11. Found: C, 26.12; H, 5.32. IR (KBr) 2955, 1460, 1275 (s), 1186, 1125, 1030 (s), 982 (s), 836 (s) 815 (s), 748 cm^{-1}. The methanol-soluble polymer showed the same IR spectrum irrespective of the tertiary amine used as catalyst.

Preparation of the Tertiary Amine–Cyclic Phosphate 1:1 Adducts. To a chloroform (10 mL) solution of 2-methoxy-1,3,2-dioxaphospholane 2-oxide (0.7 g, 5 mmol) was added triethylamine (1.4 mL, 10 mmol) in a Schlenk tube (1.5 × 10 cm) under an argon atmosphere. After the tube was sealed, the

mixture was heated to 80 °C for 10 h and then evaporated to dryness. The resulting compound comprises the 1:1 adduct of 98% purity as confirmed by the ^{1}H NMR spectrum: ^{1}H NMR ($CDCl_3$) 3.84 (d, J = 10.0 Hz, $POCH_2$), 3.43 (q, J = 7.5 Hz, NCH_2), 2.90 (s, NCH_3), 1.31 (t, CH_3) ppm. Anal. Calcd for $C_9H_{22}O_4NP$: C, 45.19; H, 9.21; N, 6.73. Found: C, 45.05; H, 9.03; N, 6.45. The 1:1 triethylamine adduct of 2-methoxy-4-methyl-1,3,2-dioxaphospholane 2-oxide was prepared by reaction of triethylamine (1.4 mL, 10 mol) with 2-methoxy-4-methyl-1,3,2-dioxaphosholane 2-oxide (0.76 g, 2 mmol) in $CHCl_3$ (10 mL) at 60 °C for 20 h: ^{1}H NMR ($CDCl_3$) 3.87–3.56 (m, $POCH_2$ and POCH), 3.32 (q, J = 7.6 Hz, NCH_2), 2.90 (s, NCH_3), 1.74 (t, CH_3), 1.18 (d, CH_3). The adduct of 2-methoxy-4,4-dimethyl-1,3,2-dioxaphospholane 2-oxide was prepared by reaction at 80 °C for 20 h: ^{1}H NMR ($CDCl_3$) 3.49 (d, J = 10.8 Hz, $POCH_2$), 3.24 (q, J = 7.5 Hz, NCH_2), 2.82 (s, NCH_3), 1.06 (t, NCH_2). The reaction of triethylamine (1.4 mL, 10 mmol) with 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-oxide (0.97 g, 5 mmol) was carried out at 80 °C for 20 h in chloroform (10 mL). Evaporation of the reaction mixture gave the 1:1 adduct of 87% purity in 80% yield: ^{1}H NMR ($CDCl_3$) 3.41 (q, J = 7.6 Hz, NCH_2), 3.03 (s, NCH_3), 1.15 (br s, CH_3).

Preparation of the 1:2 Triethylamine–2-Methoxy-1,3,2-dioxaphospholane 2-Oxide Adduct. Into a chloroform solution (20 mL) of the 1:1 triethylamine–2-methoxy-1,3,2-dioxaphospholane 2-oxide adduct (1.2 g, 5 mmol) in a Schlenk tube was syringed 2-methoxy-1,3,2-dioxaphospholane 2-oxide (0.7 g, 5 mmol). After the tube was sealed, the mixture was stirred for 30 h at 55 °C, then stirred for 10 h at 70 °C, and finally heated to 90 °C for 5 h. The resulting compound contained the 1:2 adduct of >90% purity as revealed by the ^{1}H NMR spectrum. A rapid rise in temperature must be avoided because it causes the formation of higher oligomers. The 1:2 adduct was also obtained by direct reaction of triethylamine (1.0 mL, 10 mmol) with 2-methoxy-1,3,2-dioxaphospholane 2-oxide (1.4 g, 10 mmol) in chloroform (20 ml). The mixture was stirred at 55 °C for 30 h, then stirred at 70 °C for 10 h, and heated to 100 °C for 4 h. The reaction was monitored by the ^{1}H NMR spectrum until completion. The 1:2 adduct was obtained as an oily material in 95–95% yield by evaporation of the solution to dryness. Anal. Calcd for $C_{12}H_{29}NO_8P_2$: C, 38.20; H, 7.75; N, 3.71. Found: C, 38.09; H, 7.89; N, 3.48.

Preparation of the 1:5 Adduct. A chloroform solution (10 mL) of 2-methoxy-1,3,2-dioxaphospholane 2-oxide (2.8 g, 20 mmol) was added to a chloroform solution (30 mL) of the 1:1 adduct (1.2 g, 5 mmol) in a Schlenk tube at ambient temperature. The tube was sealed and the solution was stirred at 55 °C for 15 h, heated to 80 °C for 20 h, and heated to 100 °C for 10 h. Evaporation of the resulting solution gave the 1:5 triethylamine–2-methoxy-1,3,2-dioxaphospholane 2-oxide adduct as an oily product in 98% yield (3.9 g). Anal. Calcd for $C_{21}H_{50}NO_{20}P_5$: C, 31.87; H, 6.37; N, 1.77. Found: C, 31.75; H, 6.40; N, 1.53.

References and Notes

(1) (a) Sander, M.; Steinger, E. *J. Macromol. Sci., Rev. Macromol. Sci.* **1967**, *1*, 91. (b) Vandenberg, E. J. *J. Polym. Sci., Part A-1* **1971**, *9*, 2451. (c) Corfield, G. C.; Monks, H. H. *J. Macromol. Sci., Chem. A9*, 1113.

(2) (a) Vives, J.-P.; Navech, J.; Petit, J. *C. R Hebd. Seances Acad. Sci.* **1959**, *249*, 922. (b) Maiboroda, V. D.; Datskevich, L. A. *Polym. Sci. USSR (Engl Transl.)* **1965**, *6*, 2113.

(3) (a) Majoral, J. P.; Mathis, F. M.; Munoz, A.; Vives, J.-P.; Navech, J. *Bull. Soc. Chim. Fr.* **1968**, 4455. (b) Vogt, W.; Pfluger, R. *Makromol. Chem., Suppl.* **1975**, *1*, 97.

(4) (a) Lapienis, G., Penczek, S. *Macromolecules* **1977**, *10*, 1301. (b) *Ibid.* **1974**, *7*, 166. (c) Yamashita, Y. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 56*, 477. (d) Fujisawa, T.; Yokota, Y.; Mukaijama, T. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 147. (e) Lapienis, G.; Penczek, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 371.

(5) (a) Kalużynski, K.; Libiszowski, J.; Penczek, S. *Macromolecules* **1976**, *9*, 365. (b) Libiszowski, J.; Kalużynski, Penczek, S. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1275. (c) Kalużynski, K.; Libiszowski, J.; Penczek, S. *Makromol. Chem.* **1977**, *178*, 2943.

(6) Yasuda, H.; Sumitani, M.; Nakamura, A. *Macromolecules* **1981**, *14*, 458.

(7) Sanders, H. J. *Chem. Eng (N.Y.)* **1978**, 21.

(8) (a) Coover, H. W., Jr.; McConnel, R. L.; McCall, M. A. *Ind. Eng. Chem.* **1960**, *52*, 409. (b) Wright, H. R.; Zenftman, H. *Chem. Ind. (London)* **1952**, 244.

(9) (a) Seita, T.; Yamauchi, K.; Kinoshita, M.; Imoto, M. *J. Makromol. Sci.* **1971**, *148*, 321. (b) Kawabata, T.; Ueda, N.; Takemoto, K. *Chem. Lett.* **1973**, 55. (c) Amarnath, V.; Broom, A. D. *Chem. Rev.* **1977**, *77*, 183.

(10) (a) Revel, M.; Navech, J.; Mathis, F. *Bull. Soc. Chim. Fr.* **1971**, 105. (b) Revel, M.; Navech, J. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1971**, 706. (c) Thuong, M. T.; Clergue, M. C.; Larraut, E.; Chabrier, P. *Bull. Soc. Chim. Fr.* **1964**, 1407.

(11) (a) Brault, J.-F.; Chabrier, P. *Bull. Soc. Chim. Fr.* **1974**, 677. (b) Revel, M.; Navech, J. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1969**, 121.

(12) (a) Blackburn, G. M.; Cohen, J. S.; Todd, L. *Tetrahedron Lett.* **1964**, 2873. (b) Blackburn, G. M.; Cohen, J. S.; Weatherall, I. *Tetrahedron* **1971**, *27*, 2903.

(13) (a) Mislow, K. *Acc. Chem. Res.* **1970**, *3*, 321. (b) Kluger, R.; Kerst, F.; Lee, D. G.; Dennis, E. A.; Westheimer, F. H. *J. Am. Chem. Soc.* **1969**, *91*, 6066.

(14) (a) Jesson, J. P.; Meekin, P.; Kneissel, G. *J. Am. Chem. Soc.* **1973**, *95*, 618. (b) Glonek, T.; Costello, A. J. R.; Meyer, T. C.; Van Wazer, J. R. *J. Phys. Chem.* **1975**, *79*, 1214.

(15) (a) Jones, R. A. Y.; Katritzky, A. R. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 32. (b) Jones, R. A. Y.; Katritzky, A. R. *J. Chem. Soc.* **1960**, 849.

(16) Cox, J. R., Newton, M. G. *J. Org. Chem.* **1969**, *34*, 2600.

(17) (a) Takahashi, K.; Yamashita, T.; Miyazima, G. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2787. (b) Duval, E.; Bene, G. J. *Helv. Phys. Acta* **1967**, *40*, 501.

(18) Revel, M.; Navech, J. *Bull. Soc. Chim. Fr.* **1973**, 1195.

(19) Cox, R. H.; Campbell, B. S.; Newton, M. G. *J. Org. Chem.* **1972**, *37*, 1557.

(20) Moeller, V. T., Ed. "Inorganic Synthesis"; McGraw-Hill: New York, 1977; Vol. 1, p 87.

(21) Mikolajczk, M.; Witczak, M.; Wieczorek, M.; Bokijao, N. G.; Struchkov, Y. *J. Chem. Soc., Perkin Trans.* **1976**, 371.

(22) Storr, A.; Jones, K.; Laubengayer, W. *J. Am. Chem. Soc.* **1968**, *90*, 311. See also: Ueyama, N.; Araki, T.; Tani, H. *Inorg. Chem.* **1973**, *12*, 2218.