Much work remains to be carried out in the field of NCA polymerization. The physical factors such as the conformation of the growing chain,[24] effects of heterogeneity and monomer absorption on the active ends of growing chains,[25] effects of counterions, and the modes of molecular weight distributions of polymers all require further elucidation.[26]

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(26) **Note Added in Proof:** After submission and acceptance of our manuscript, a paper appeared by H. R. Kricheldorf, *Makromol. Chem.*, **178**, 1959–1970 (1977), in which he clearly demonstrated that the "active monomer" mechanism is valid for NCA polymerizations. In earlier papers, he showed the formation of NCA anions by the essentially quantitative *N*-silylation and *N*-sulfenylation of NCA's [H. R. Kricheldorf, *Angew. Chem.*, **85**, 86 (1973) and H. R. Kricheldorf, and M. Fehrle, *Chem. Ber.*, **107**, 3533–3547 (1974)].

Cationic Polymerization of 2-Alkoxy-2-oxo-1,3,2-dioxaphosphorinanes (1,3-Propylene Alkyl Phosphates)

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ABSTRACT: Kinetics, thermodynamics, and mechanism of polymerization of 1,3-propylene alkyl phosphates, the six-membered cyclic esters of phosphoric acid, have been investigated. The reaction was performed in bulk, using cationic initiators such as salts of Ph_3C^+ with stable anions (PF_6^-, AsF_6^-). The kinetics of polymerization was resolved and the elementary steps were described. Propagation is reversible, as in case of the previously studied 1,3-propylene methyl phosphate where the enthalpies and entropies of the propagation–depropagation equilibria gave a linear isoequilibrium plot. ΔH_p and ΔS_p both increase with the size of the exocyclic groups. Only the polymerization of 1,3-propylene methyl phosphate is exothermic; polymerizations of monomers with larger exocyclic groups are endothermic and possible because of the positive entropy change. Apparently, the mobility of the large exocyclic groups, having restricted rotation in monomers, increases in polymers and the gain in the rotational entropy, also not too large (a few entropy units), is sufficient to shift the propagation–depropagation equilibrium to the polymer side. ^1H and ^{31}P NMR spectra indicate that polymers are linear with cyclic end groups, formed because of the extensive chain transfer to monomer of the positively charged exocyclic groups from the growing centers.

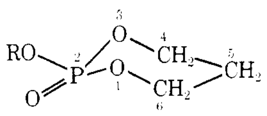
In our previous paper, describing the kinetics and thermodynamics of the cationic polymerization of 2-methoxy-2-oxo-1,3,2-dioxaphosphorinane (1,3-propylene methyl phosphate) (1), we stressed the importance of the chain transfer to monomer (eq 1) responsible for the formation of polyesters of limited polymerization degrees.[1] The competition between chain propagation and chain transfer is shown in the Scheme I below.

Thus, for both propagation and transfer, involving nucleophilic attack of the phosphoryl oxygen atom, there is a common transition state proposed, and the mechanism of transfer, illustrated above, leads to the formation of macromolecules with cyclic end groups. The presence of these end groups was confirmed by ^1H, ^{31}P, and ^{13}C NMR.[1,2]

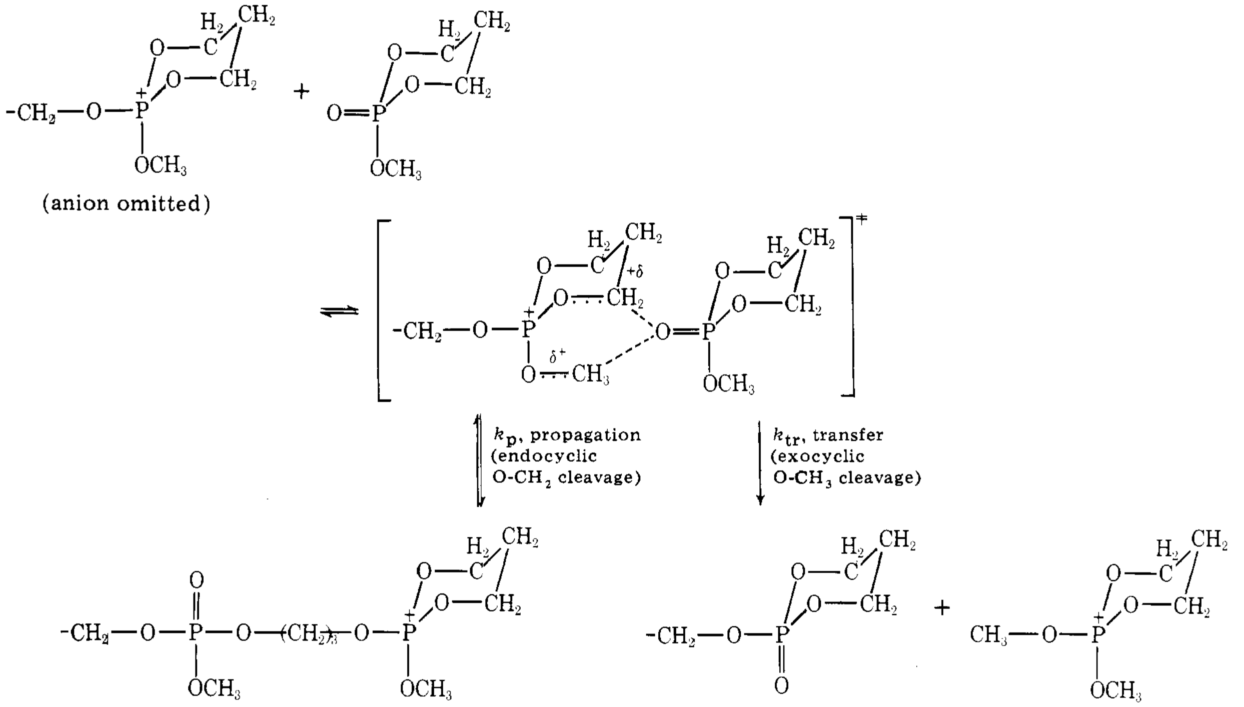
For the methoxy exocyclic group the polymerization degrees of polymers prepared at 100 °C were close to 10, indicating that the ratio k_p/k_{tr} (eq 1) is of the same magnitude.

According to the proposed structure of the transition state (eq 1), it would be necessary to destabilize the carbenium ion of the exocyclic group, partially developed in the transition state, in order to increase the k_p/k_{tr} ratio and in this way to increase the polymerization degree.

We report in this paper on the polymerization of 2-alkoxy-2-oxo-1,3,2-dioxaphosphorinanes of the general formula:



Scheme I



(1)

Table I
Properties of 2-Alkoxy-2-oxo-1,3,2-dioxaphosphorinanes (Monomers), ^1H and ^{31}P NMR Chemical Shifts of Monomers and of Corresponding Polymers

	RO	bp, °C (mm of Hg)	mp, °C	Density	$^1H\{^{31}P\}$ NMR (exocyclic group)[a]			$^{31}P\{^1H\}$ NMR (ppm from 85% H_3PO_4)		
						δ, ppm from TMS	J, Hz	Monomer	Polymer c	Polymer d
2	C_2H_5O	111 (0.7)	8	$d^{25}_4 = 1.2556$	$-OCH_2-$	4.26 (q)	7.5	+7.5	+1.0	+7.25
		(110 (0.2[5]))			$-CH_3$	1.40 (t)	7.5			
3	n-C_3H_7O[b]	137 (5×10^{-2})		$d^{25}_4 = 1.2012$	$-OCH_2-$	4.04 (t)	6.5	+7.25	+1.1	+7.4
					$-CH_2-$	1.5–2.6 (m)				
					$-CH_3$	0.98 (t)	7.0			
4	i-C_3H_7O[b]	103 (10^{-2})		$d^{25}_4 = 1.1953$						
					$-CH<$	4.68 (sep)	6.0	+8.7		
					$-CH_3$	1.37 (d)	6.0			
5	n-C_4H_9O[b]	111 (2×10^{-2})		$d^{21}_4 = 1.1641$	$-OCH_2-$	4.13 (t)	7.5	+7.5		
					$(-CH_2)_2-$	1.2–1.5 (m)				
					$-CH_3$	0.98 (t)	6.0			
6	$C_6H_{11}O$[b]		59		$-C_6H_{11}$	1.25–2.13 (m)		+8.6		
7	$C_6H_5CH_2O$[b]		73		$-C_6H_5$	7.35 (s)		+7.5		
					$-CH_2-$	5.05 (s)				
8	$(CH_3)_3SiO$[b]	112–3 (1.1)		$d^{21}_4 = 1.14$	$-CH_3$	0.32 (s)		+15.8		
9	CCl_3CH_2O	(148 (0.05[6]))	74		$-CH_2-$	4.65 (s)		+9.0		
10	CF_3CH_2O	120 (0.3)		$d^{25}_4 = 1.4742$	$-CH_2-$	4.52 (q)	8.7	+8.4		
		(104 (0.05[6]))								
11	$CNCH_2CH_2O$[b]		45–6		$-OCH_2-$	4.33 (t)	6.0	+7.75		
					$-CH_2-$	2.60 (t)	6.0			

[a] ^1H NMR of the ring protons is described in detail in ref 1, 7, 8. [b] Prepared for the first time. [c] P atoms in linear segment. [d] P atoms in the cyclic end group.

We expected, first of all, to confirm by using these monomers the generality of the mechanism of chain transfer, described by eq 1, and, further on, we expected that a proper choice of R could lead to polymers of higher polymerization degrees.

Experimental Section

Materials. 2-Alkoxy-2-oxo-1,3,2-dioxaphosphorinanes. Monomers 2–7 and 9–11 were prepared according to Arbuzov's methods[3] with some modifications. Thus a mixture of a suitable alcohol with pyridine as an acceptor of HCl was gradually introduced to the solution of 2-chloro-2-oxo-1,3,2-dioxaphosphorinane in benzene at 20–25 °C. Then, the mixture was stirred for 5 h and filtered off from pyridine hydrochloride, and the resulting filtrate was distilled under vacuum (monomers **2**, **3**, **4**, **5**, **10**). Monomers **6**, **7**, **9**, **11** were precipitated from this solution with cyclohexane.

Monomers were purified by distillation under vacuum or by crystalization from benzene–cyclohexane mixture (cf. Table I).

2-Trimethylsilyloxy-2-oxo-1,3,2-dioxaphosphorinane (**8**) was obtained from **1**. In the first step a sodium salt of cyclic 1,3-propylene hydrogen phosphate (**12**) was prepared in reaction of **1** with NaI according to the known procedure.[4] The resulting **12** was dissolved in distilled water and passed through a column with Dowex 50 W (H^+ form) and after concentration and drying on the vacuum line the cyclic 1,3-propylene hydrogen phosphate (**13**) resulted. **13** was reacted with BSA (N,O-bis(trimethylsilyl)acetamide) in Et_2O to give as a final product 8. Crude 8 was redistilled under vacuum.

Triphenylmethyl salts (Ozark-Mahoning Co., Tulsa, Okla.) were purified as described previously.[1]

Ethyl trifluoromethanesulfonate (Cationics, Inc., Cleveland, Ohio) was distilled under vacuum into thin glass bulbs (vials) which were sealed off and stored at −10 °C.

Kinetic Measurements. Polymerization was carried out by using dilatometers filled in high vacuum from a rotating trap, as described in our previous paper[1] as well as in glass ampules sealed off or closed by Teflon stopcocks (for identification of the gaseous by-products). It has been shown that the overall rate of polymerization does not depend on the anion (PF_6^-, AsF_6^-, or $CF_3SO_3^-$) structure. Isolation of polymers and determination of their microstructures and polymerization degrees was also described previously.[1]

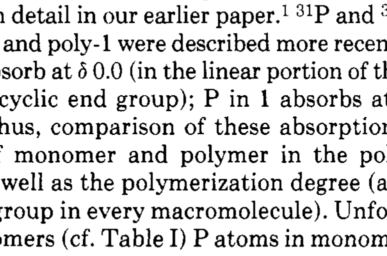
NMR spectra (both ^1H and ^{31}P) were measured with a 60-MHz Jeol Model JNM-DBT-8T in D_2O or $CDCl_3/CHCl_3$ solutions. Polymerization degrees were determined with a Hewlett Packard Vapor Pressure Osmometer Model 302 B. GLC–mass spectroscopy analysis was performed with an GCMS LKB-2091 apparatus provided with a PDP-11/05 e computer.

Results and Discussion

NMR Spectra of Monomers and Polymers. Some properties, including ^1H and ^{31}P NMR spectra of monomers, used throughout this work are given in Table I. In the same table chemical shifts for ^{31}P NMR of the corresponding polymers are included for comparison.

The ^1H and $^1H\{^{31}P\}$ NMR spectra of 1 and of poly-1 were described in detail in our earlier paper.[1] ^{31}P and $^{31}P\{^1H\}$ NMR spectra of 1 and poly-1 were described more recently.[2] P atoms in poly-1 absorb at δ 0.0 (in the linear portion of the chain) and at δ +7.0 (cyclic end group); P in 1 absorbs at δ 6.0 (from H_3PO_4). Thus, comparison of these absorptions gives proportions of monomer and polymer in the polymerization mixture as well as the polymerization degree (assuming one cyclic end group in every macromolecule). Unfortunately, in other monomers (cf. Table I) P atoms in monomer and in cyclic end group have almost identical chemical shifts. Apparently, when the size of the exocyclic group increases the difference vanishes between the magnetic environment of P atoms in the monomer molecule and in the corresponding polymer end group. However, as it will be shown, comparison of the expanded spectra of the polymerization mixture and isolated polymers allowed the determination of the polymer yields on the basis of $^{31}P\{^1H\}$ NMR spectra.

The $^1H\{^{31}P\}$ NMR spectrum of poly(1,3-propylene ethyl phosphate) (poly-2) is shown in Figure 1; a spectrum of a mixture of 2 and poly-2 is given in Figure 2. In the $^1H\{^{31}P\}$ NMR spectrum of poly-2 the following chemical shifts are observed (cf. also Table I, where *J* are listed): CH_3CH_2 δ 1.40 (t), CH_2CH_2O δ 2.12 (quint), CH_2CH_2O δ 4.33 (t), and CH_3CH_2O δ 4.26 (quart: 4.45, 4.33, 4.20, 4.07). At lower field



$$(\text{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O-CH_2-CH_3}{|}}{P}}-O-CH_2-CH_2-CH_2-O\text{-})$$

poly-2

additional lines are observed, partially superimposed with a δ 4.33 triplet. There are four lines coming from a cyclic part of the macromolecule (CH_2CH_2O) distinctly seen: δ 4.67, 4.62, 4.54, and 4.49. The appearance of four lines of the same intensity can be accounted for by a slight deformation of the six-membered ring. Then, if H_4 and H_6 atoms are magnetically equivalent and both are split by two nonequivalent H_5 atoms (axial and equatorial) with coupling constants J = 7.8 Hz (H_{5a}) and J = 3.0Hz (H_{5e}), the four lines should result. Similar observations were reported earlier for 2-phenoxy-2-oxo-1,3,2-dioxaphosphorinane (14), where $(J_{4a,5a} + J_{4e,5a})/2$ = 8.3 Hz (comparable to our 7.8 Hz) and $J_{4a,5e} = J_{4e,5e}$ = 2.7 Hz (comparable to our 3.0 Hz).[7]

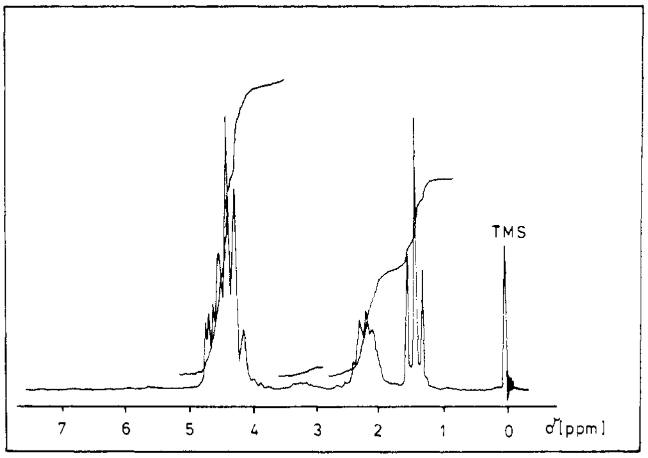


Figure 1. $^1H\{^{31}P\}$ NMR spectrum of poly(2-ethoxy-2-oxo-1,3,2-dioxaphosphorinane) (poly-2) in $CDCl_3$.

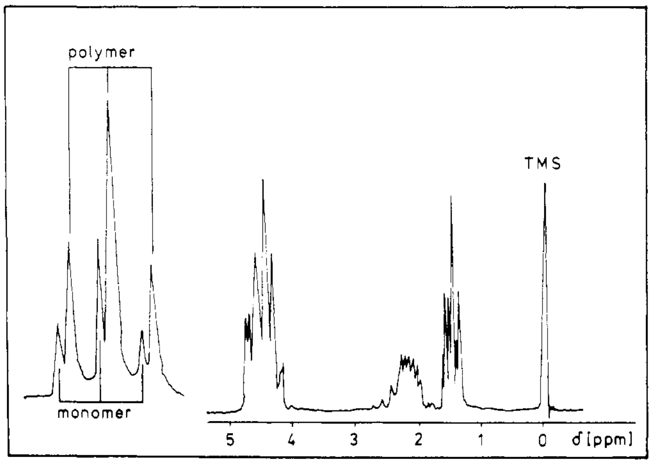


Figure 2. $^1H\{^{31}P\}$ NMR spectrum of a mixture of 2 and poly-2 in $CDCl_3$. The expanded triplet (five times) from CH_3CH_2O groups in 2 and poly-2.

The expanded $^1H\{^{31}P\}$ NMR spectrum of a polymer–monomer mixture gives a better separation of the CH_3CH_2 triplets from monomer and polymer (cf. Figure 2). This separation is sufficiently good (δ 1.40 and 1.38) to permit an independent integration and determination in this way of the proportion of both components.

The ^{31}P NMR spectrum of 2 shows a septet at δ 7.5 (from 85% H_3PO_4), reduced in $^{31}P\{^1H\}$ NMR to a single line. The $^{31}P\{^1H\}$ NMR spectrum of poly-2 contains two lines: a larger one at δ 1.0 and a smaller one at δ 7.25 (cyclic end group). A mixture of polymer and monomer gives three lines (Figure 3) and expansion of the region from δ 7.0 to 7.5 gives a possibility to determine the polymer yield on the basis of integration of a singlet due to monomer and a singlet due to polymer end group. This determination requires that every macromolecule of poly-2 contains one cyclic end group.

Analysis of $^{31}P\{^1H\}$ and $^1H\{^{31}P\}$ NMR spectra of reaction mixtures of 2 and poly-2 permitted, in accordance with methods described above, the determination of polymer yield and gave consistent results. On the other hand, the polymer yields determined by gravimetrical method (monomer distilled off after addition of the terminating agent) were substantially lower. Apparently, some lower oligomers (e.g., dimers) were also distilled off at our conditions (100 °C (0.1 mm of Hg)).

Analyses of $^1H\{^{31}P\}$ NMR spectra of mixtures of 1,3-propylene *n*-propyl phosphate (3) and poly-3 did not allow the

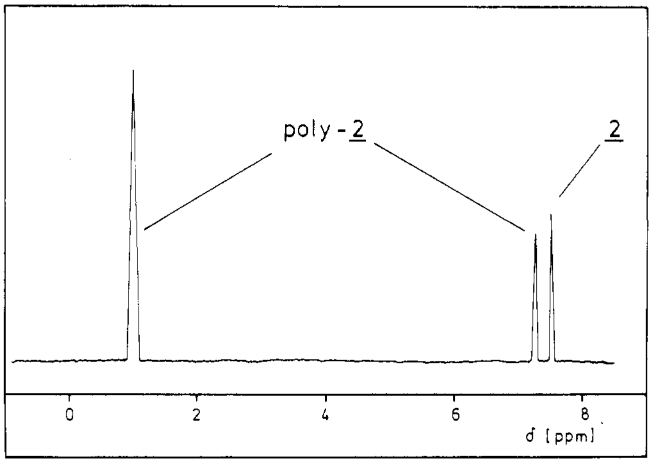


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of a mixture of 2-ethoxy-2-oxo-1,3,2-dioxaphosphorinane (2) and poly-2 in $CHCl_3$ (in δ ppm from 85% H_3PO_4).

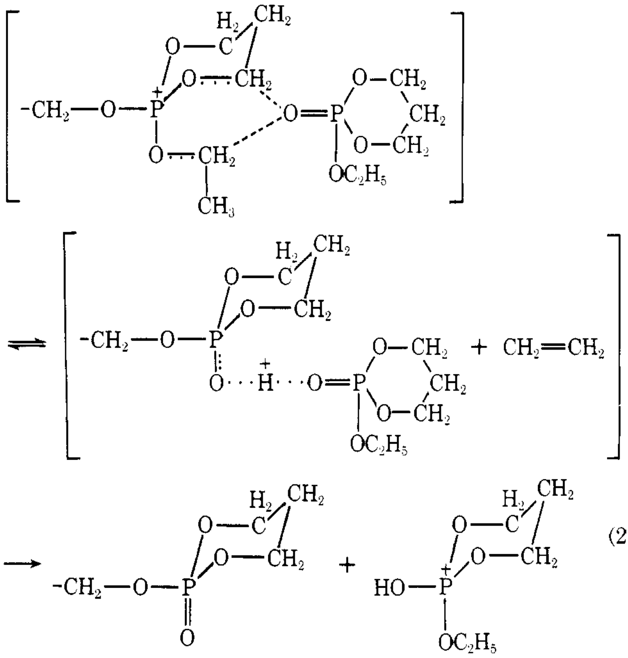
determination of polymer yields based on integration of either region δ 3.90/4.20 or region δ 0.80/1.20. Integration of the expanded region from δ 7.2 to 7.5 of the $^{31}P\{^1H\}$ NMR spectra (assuming that every macromolecule contains one cyclic end group) gives separately the monomer and polymer concentrations. The reliability of this method was proved by the gravimetric method.

The NMR spectra discussed above confirm our assumption that, as in the case of poly-1, polymers are of rather low molecular weight and that the polymerization degree is mostly governed by an extensive chain transfer, leaving cyclic end groups in macromolecules.

GLC-Mass Spectroscopy Analysis of the Volatile Products and Mechanism of the Chain Transfer. During a polymerization of several monomers listed in Table I we observed that evolution of gaseous products and/or formation of solid or liquid by-products accompanied the actual polymerization process. In order to study the gaseous products, polymerization of a given monomer was studied in an apparatus equipped with a port closed with a self-sealing rubber stopper and located over the surface of the liquid polymerization mixture. Samples of the gaseous products were taken and injected into the GLC-mass spectroscopy apparatus. The following major components were identified according to the mass spectra:

R in monomer	parent peak
C_2H_5	M = 28.0; $C_2H_4^+$
i-C_3H_7	M = 42.0; $C_3H_6^+$
n-C_4H_9	M = 56.0; $C_4H_8^+$

Scheme II



(2)

In the polymerization of a monomer with exocyclic group R = cyclohexyl, cyclohexane was isolated and identified by its ^1H NMR spectrum. Polymerization of a benzyl monomer led to the formation of a small amount (apart from a corresponding benzylic polyphosphate) of a solid product, identified as polybenzyl; its elemental analyses gives a formula $C_{21}H_{20}$ (C_7H_6 calculated for a mer of polybenzyl) and the ^1H NMR spectrum consists of two absorptions, δ 3.90 (s) ($-C_6H_4-CH_2-C_6H_4-$) and 7.05/7.20 (m) ($-CH_2-C_6H_4-CH_2-$), with an integration ratio 1:2 and in agreement with a known spectrum of an authentic polybenzyl.[9]

These facts indicate that a scheme of chain transfer, according to eq 1, has to be completed with an additional process, in which carbenium ion, partially developed in the transition state (e.g., methylium cation in eq 1), expels a proton, eventually transferred to the incoming monomer molecules; thus, for 1,3-propylene ethyl phosphate see Scheme II.

Scheme II requires that at least a part of the macromolecules have one acidic (HO-P(O)<) and one cyclic end group.

The proportion of these acidic macromolecules can be found by comparing an apparent $\overline{DP}_n$, determined from base titration of the polymeric acids, with a $\overline{DP}_n$ determined either from the cyclic end groups or by direct measurements. This proportion should also be in agreement with the amount of the

Table II
Polymer Yields and Polymerization Degrees Calculated from $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ NMR Spectra of Poly-2 and Poly-3, and Compared with Direct Measurement (VPO)

						$\overline{DP}_n$	
Monomer	$[Ph_3C^+, PF_6^-]_0 \times 10^2$, mol L^{-1}	$[M]_0$, mol L^{-1}	Temp, °C	Time, h	Polymer yields, % wt	Calcd from NMR spectra	Determined by VPO method
2	1.47	7.13	105	13	51	4.0	4.8
2	3.22	7.17	95	11	55	4.2	4.0
2	2.30	7.09	115	7	71	5.0	4.4
2	1.67	6.93	145	3.5	79	4.2	3.9
2	1.45	7.03	125	2	68	3.6	4.1
3	1.70	6.16	140	4.5	77		4.4
3	1.34	6.14	145	3.5	68	2.9	3.2
3	2.92	6.37	95	7	67		3.0

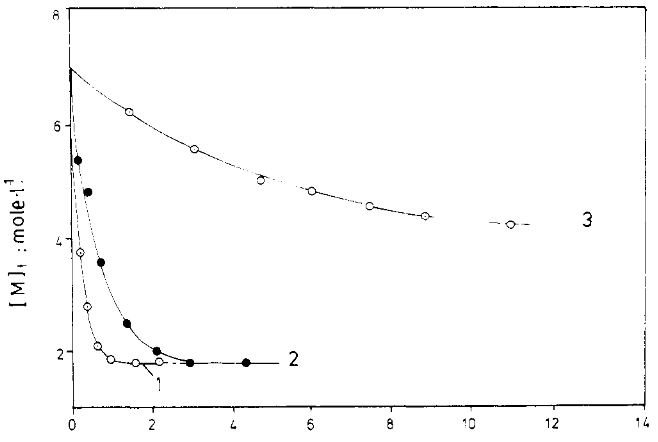


Figure 4. Kinetics of polymerization of 2-ethoxy-2-oxo-1,3,2-dioxaphosphorinane (2) with Ph_3C^+, PF_6^- in bulk at 125 °C: $[2]_0 = 7.03$ M; $[Ph_3C^+, PF_6^-]_0$, curve 1 1.09×10^{-2} M, curve 2 2.46×10^{-3} M, and curve 3 1.00×10^{-3} M.

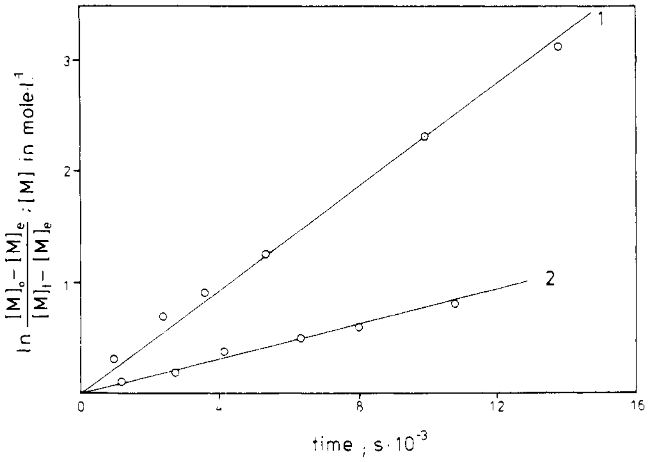
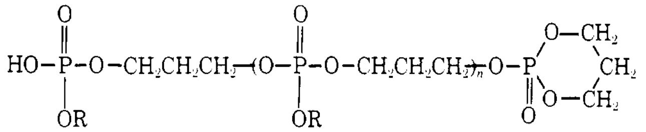


Figure 5. Kinetics of polymerization of 2-trimethylsilyloxy-2-oxo-1,3,2-dioxaphosphorinane (8) with $CF_3SO_3C_2H_5$ as initiator: (1) 130 °C, $[M]_0 = 5.05$ M, $[I]_0 = 1.08 \times 10^{-2}$ M; (2) 105 °C, $[M]_0 = 5.15$ M, $[I]_0 = 1.78 \times 10^{-2}$ M.

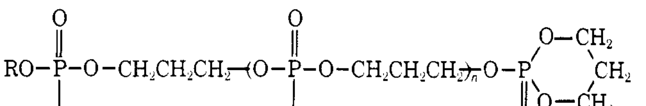
given olefin evolved. Thus, for example: polymerization of 3 at 125 °C ($[Ph_3C^+, PF_6^-] = 3.58 \times 10^{-2}$ mol L^{-1}) gives 56% of poly-3 and 27.4 mL (at 25 °C) of propylene. $\overline{DP}_n \approx 17.3$ (from base titration) agrees with $\overline{DP}_n \approx 13.4$ obtained from the measured volume of propylene. This latter value exceeds, according to expectations, the actual value of $\overline{DP}_n$ for poly-3 (Table II) approximately three times.

Thus, on the basis of the data given in Table II and measurements of the olefin evolved, the structure of polymers of higher 1,3-propylene alkyl phosphates can be presented as the mixture of macromolecules with two different kinds of end groups:



$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR}{|}}{P}}-O-CH_2CH_2CH_2\!\!+\!\!\left(O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR}{|}}{P}}-O-CH_2CH_2CH_2\right)_{\!n}\!\!-O-\underset{\underset{\displaystyle O}{\|}}{P}\genfrac{}{}{0pt}{}{/O-CH_2\backslash}{\backslash O-CH_2/}CH_2$$

and



$$RO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR}{|}}{P}}-O-CH_2CH_2CH_2\!\!+\!\!\left(O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR}{|}}{P}}-O-CH_2CH_2CH_2\right)_{\!n}\!\!-O-\underset{\underset{\displaystyle O}{\|}}{P}\genfrac{}{}{0pt}{}{/O-CH_2\backslash}{\backslash O-CH_2/}CH_2$$

The proportion of the acidic form does not exceed 20–30% at the polymerization conditions used in our work.

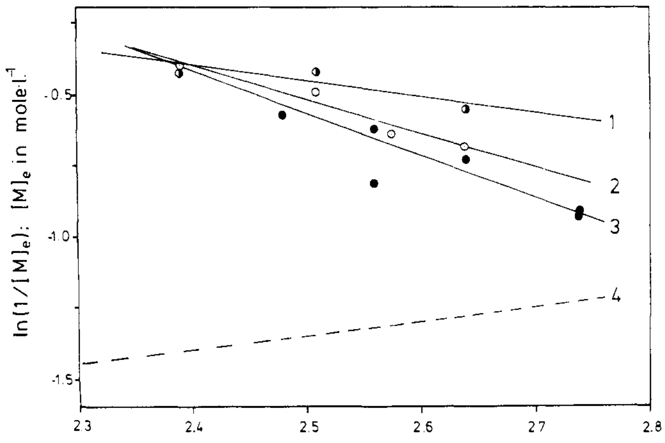


Figure 6. Dependence of ln $(1/[M]_e)$ on the reciprocal of the absolute temperature in cationic polymerization of 2-alkoxy-2-oxo-1,3-dioxaphosphorinanes: (1) (◑) ethoxy (2); (2) (○) n-propoxy (3); (3) (●) trimethylsilyloxy (8); (4) methoxy (1).[1]

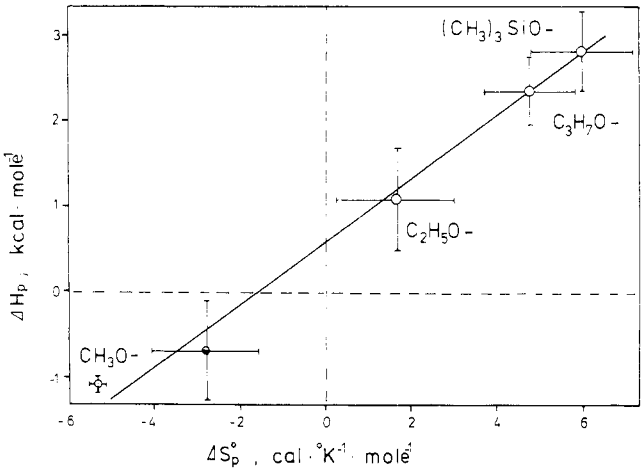


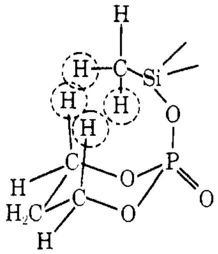
Figure 7. Isoequilibrium dependence in the cationic polymerization of 2-alkoxy-2-oxo-1,3,2-dioxaphosphorinanes (standard deviations of thermodynamic parameters are shown directly on the plot): (⊖) anionic polymerization of 1.[2]

Thermodynamics and Kinetics of Polymerization. Polymerization of 1 was described by a kinetic scheme, consisting of initiation, propagation, chain transfer, and chain termination, due to the reaction of the polymer segment with growing species and producing a linear tetraalkoxy phosphonium ion. Kinetic curves, at low concentration of an initiator, showed limited conversions resulting from a kinetic termination. At sufficiently high starting concentration of initiator the polymer–monomer equilibrium comes first and the final concentration of monomer becomes equal to the equilibrium monomer concentration.[1] The same phenomenon was observed in the polymerizations of 2 and in 1,3-propylene n-propyl phosphate (3) initiated with $Ph_3C^+PF_6^-$. This is shown in Figure 4, where three kinetic runs for 2 are given. Apparently, curves 1 and 2 go to the same thermodynamic plateau whereas polymerization described by curve 3 stops for kinetic reasons.

Polymerization of 2-trimethylsilyloxy-2-oxo-1,3,2-dioxaphosphorinane (8) shows simpler kinetics behavior (Figure 5). Kinetics can be described by reversible propagation up to high conversions (taking into account the equilibrium monomer concentration). This indicates that termination becomes very much hampered in monomers with exocyclic groups of larger volume, like the trimethylsilyloxy group.

From the kinetic curves of both kinds, namely with termination for **2** and **3** and without termination for **8**, we were able to determine the equilibrium monomer concentrations at various temperatures for three monomers. This dependence is given in Figure 6 together with a similar dependence (broken line) determined previously for **1**. It is remarkable that the "normal" behavior ($\Delta H_p < 0$, $\Delta S_p < 0$), observed for **1**, is replaced, in the case of monomers with larger exocyclic groups, by endothermic polymerizations, which are made possible because of the positive change of entropy. Although our data (cf. isoequilibrium dependence, Figure 7) are not accurate enough to draw any conclusion based on the actual values, an increase of the entropy of polymerization with an increase in size of the exocyclic group seems to be a genuine feature of these polymerizations.

Inspection of molecular models of trimethylsilyloxy monomer revealed that, at least in one of the conformers (exo substituent in the axial position), there is a restricted rotation of this group in the monomer, because of the interaction of the hydrogen atoms from the methyl groups and axial protons from the CH_2O group:



This restriction does not appear in the macromolecule any more and the gain of the rotational entropy, which usually does not exceed a few entropy units, becomes a driving force of polymerization.

Increase of the free energy of the ground state in polymers with larger exocyclic groups (increased number of the degrees of freedom) leads eventually to the positive change of enthalpy in polymerization.

Thus, in these polymerizations a floor temperature appears instead of a ceiling temperature, calculated for **1**. We are not giving the values of the floor temperatures because of the already mentioned low accuracy of our measurements of ΔH_p and ΔS_p.

Our values for ΔH_p and ΔS_p differ slightly from values given tentatively in our recent review paper.[10]

Kinetic Parameters. Polymerization curves of **2** and **3** can be converted into their linear anamorphoses by using a kinetic scheme already discussed in detail for the polymerization of **1**. The final kinetic equation for a scheme

$$\begin{gathered}
\mathrm{I} + \mathrm{M} \xrightarrow{k_i} \mathrm{IM}^* \text{ (fast)} \\
\mathrm{IM}^* + \mathrm{M} \underset{k_d}{\overset{k_p}{\rightleftharpoons}} \mathrm{IMM}^* \text{ (M}') \\
\mathrm{M}' + \mathrm{M} \underset{k_d}{\overset{k_p}{\rightleftharpoons}} \mathrm{M}' \qquad (3) \\
\mathrm{M}' + \mathrm{P} \xrightarrow{k_t} \mathrm{M}'\mathrm{P} \text{ (inactive)}
\end{gathered}$$

in which I, M, and M′ denote initiator, monomer, and active centers and k_i, k_p, k_d, and k_t denote rate constants of initiation, propagation, depropagation, and termination, respectively, is given below.

$$-\frac{\mathrm{d} \ln [\mathrm{M}]}{\mathrm{d}t} = k_p[\mathrm{I}]_0 - k_t \left\{([\mathrm{M}]_0 - [\mathrm{M}]_e) \ln \frac{[\mathrm{M}]_0 - [\mathrm{M}]_e}{[\mathrm{M}] - [\mathrm{M}]_e} - ([\mathrm{M}]_0 - [\mathrm{M}])\right\} \qquad (4)$$

Table III
Rate Constants and Activation Parameters in the Cationic Polymerization of 2-Alkoxy-2-oxo-1,3,2-dioxaphosphorinanes[a]

		Monomer		
		CH_3O[1]	C_2H_5O	$(CH_3)_3SiO$
$10^2 \times k_p$		1.0	0.82	0.54
$10^2 \times k_d$	at 100 °C	3.6	0.45	1.35
$10^5 \times k_t$		3.5	0.26	
$\Delta H^{\ddagger}_p$		20	21	19
$\Delta S^{\ddagger}_p$		−16	−12	−20
$\Delta H^{\ddagger}_t$		12	9	
$\Delta S^{\ddagger}_t$		−48	−59	

[a] k_p, k_t in L mol^{-1} s^{-1}; k_d in s^{-1}; $\Delta H^{\ddagger}$ in kcal mol^{-1}; $\Delta S^{\ddagger}$ in cal mol^{-1} deg^{-1}.

Some amount of monomer is also consumed in transfer processes; thus, the scheme above should be supplemented by the transfer reaction. The proportion of monomer used in transfer and determined from the polymerization degree is close to 20% of the total monomer used (for $\overline{\mathrm{DP}}_n = 5$). This value allowed the consumption of monomer in transfer to be neglected, because accuracy of determination of the rate constants does not exceed 15–20% of the measured value.

Determination of the rate constants k_p and k_t for the polymerization of **2** was based (for details see ref 1) on the linear plots, in which the left-hand side of eq 4 was plotted against the second term (variable) of its right-hand part.

The values of k_p and k_t and the corresponding activation parameters are given in Table III together with these values previously determined for **1**.

Analysis of the data from Table III leads to the following conclusions: Increase of the size of the exocyclic group decreases the rate constants k_p and k_t. This decrease seems to be due to the increase of the negativeness of the entropy of activation. Indeed, the larger exo substituents have a larger number of degrees of freedom frozen in the transition state; this observation is in agreement with our interpretation of the ΔS_p data of the monomer–polymer equilibrium.

In order to increase the polymerization degrees, by increasing the ratio of k_p/k_{tr}, we attempted to polymerize a series of monomers with stronger electron-withdrawing exocyclic groups. These, namely 1,1,1-trifluoroethoxy-, 1,1,1-trichloroethoxy-, and 1-cyanoethoxy- (cf., **9**, **10**, and **11** in Table I), did not, however, polymerize in our polymerization conditions.

We expected that the destabilization of the carbenium ion that should precede the transfer of the exocyclic group should also decrease k_{tr}. Unfortunately, the electron-withdrawing effect of these groups appears to be too strong, because polymerization of **9**, **10**, and **11** could not be induced at all. Apparently, the electron density on the P atom in these monomers is too low.

References and Notes

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