Table VI
Thermodynamic Properties of Hydrolyses

Copolymer		Reaction Solvent (kcal/mol) Water[a]	30% Ethanol[b]
VI-12	ΔH^*	18.3	5.38
	$T\Delta S^{*c}$	−2.46	−16.3
	ΔH	−13.3	9.40
	$T\Delta S^c$	−9.97	13.5
VI-26	ΔH^*	12.6	−5.05
	$T\Delta S^{*c}$	−8.61	−26.8
	ΔH	−6.63	23.2
	$T\Delta S^c$	−2.69	27.2

[a] pH 9.0. [b] pH 9.1. [c] $T = 26.0°$.

in the present study, the cooperative action between imidazole and carboxylic acid moieties was observed. Moreover, the carboxylic acid moiety acts as an attracting moiety for the substrate, ANTI. The attraction was caused by electrostatic interaction. In this action, ΔH was estimated to be $-4 \sim -5$ kcal per mol and ΔG was done to be $-3.3 \sim -3.9$ kcal per mol, respectively.

Acknowledgment. The authors are grateful to Professor Kenichi Fukui for his unfailing encouragement.

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Kinetics and Thermodynamics of the Polymerization of the Cyclic Phosphate Esters. II. Cationic Polymerization of 2-Methoxy-2-oxo-1,3,2-dioxaphosphorinane (1,3-Propylene Methyl Phosphate)[1]

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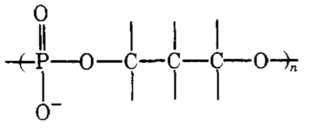
ABSTRACT: Kinetics and thermodynamics of cationic polymerization of 1,3-propylene methyl phosphate, a six-membered cyclic ester of phosphoric acid, have been investigated. The reaction was performed in $(CH_2Cl)_2$ and in bulk, using cationic initiators such as salts of Ph_3C^+ or 1,3-dioxolan-2-ylium with PF_6^-, AsF_6^-, and SbF_6^- counterions. These initiators, in contrast to, *e.g.*, $Ph_3C^+SbCl_6^-$, react quantitatively with the monomer, yielding the propagation cyclic tetraalkoxyphosphonium ion. In the investigated temperature range of 60–155° the polymerization proceeds with marked depropagation. Interaction of the active species with macromolecules leads to chain termination caused by the formation of the nonstrained tetraalkoxyphosphonium ions. The kinetics of the mechanism involving the propagation, depropagation and termination steps was resolved and the respective rate constants determined in the investigated temperature range. Thus, $\Delta H_p^* = 19.5$ kcal/mol, $\Delta S_p^* = -15.6$ eu, $\Delta H_d^* = 20.6$ kcal/mol, $\Delta S_d^* = -10.2$ eu, $\Delta H_t^* = 11.6$ kcal/mol, $\Delta S_t^* = -48.1$ eu, $\Delta H_p = -1.1$ kcal/mol, and $\Delta S_p° = -5.4$ eu. At 25° in bulk $\Delta F_{ls} = -0.78$ kcal/mol.

There are two major methods already explored and used in the preparation of the oligonucleotides. Both are based on the polycondensation principles coupled with chemical activation of the reacting components.[2]

These methods, although limited and demanding the protection of the reactive groups in the nucleotide involved, led to the successful synthesis of various polynucleotides. Reactions of this kind, and further step by step synthesis of the copolynucleotides as well as the polycondensation of blocks of two or more different nucleotides were responsible for the tremendous progress in this field in the last decade.[2b]

In principle, formation of the backbone consisting of a sequence of six atoms

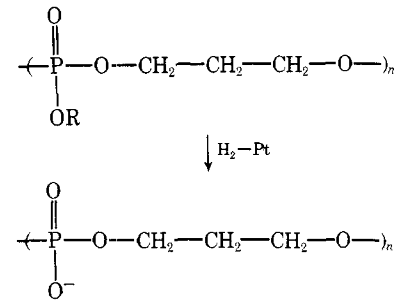


$$-\!\!\left(\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-O\right)\!\!_n$$

should also be possible either by a polymerization of six-membered cyclic phosphate esters or by copolymerization of oxetanes[3] with derivatives of phosphoric acid.

Since the cyclic phosphate bearing an acidic function can not be directly polymerized by any of the ionic mechanisms, this function should be blocked and the blocking group later removed from the polymer. Various temporary blocking groups, that can be removed without altering the degree of polymerization, have already been studied in the classical chemistry of the nucleic acids.

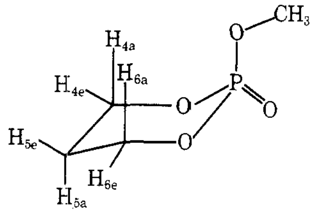
We have, for instance, prepared and polymerized 2-phenoxy- and 2-benzyloxy-2-oxo-1,3,2-dioxaphosphorinanes and converted the resulting polyesters into the polyacid by hydrogenation.[4a]



$$\left(\begin{array}{c}O\\ \|\\ -P-\\ |\\ OR\end{array}-O-CH_2-CH_2-CH_2-O-\right)_n \xrightarrow{H_2-Pt} \left(\begin{array}{c}O\\ \|\\ -P-\\ |\\ O^-\end{array}-O-CH_2-CH_2-CH_2-O-\right)_n$$

The two routes described above (copolymerization of oxetanes and homopolymerization of six-membered cyclic phosphates) are not the only possibilities. The corresponding cyclic phosphite can also be prepared, polymerized, oxidized into a polyphosphate, and then converted into a polyacid.

Alternatively, polyphosphite can be converted into a polyacid and further oxidized. Various routes are being tried in this laboratory to find conditions, that can further be applied to monomers closer in structure to nucleotides or even the cyclic nucleotides. In the present paper the cationic polymerization of a model monomer, containing six-membered 1,3,2-dioxaphosphorinane ring



1

was studied in order to elaborate the kinetics and thermodynamics of polymerization to ascertain the conditions necessary to polymerize monomers of this class.

There are no available kinetic data on the polymerization of cyclic phosphates, the only six-membered cyclic phosphate polymerized earlier being the 2-ethoxy derivative.[4b]

Results and Discussion

Nmr Spectra of a Monomer and Polymer. In order to understand the polymer structure and to determine the polymer content in a monomer-polymer mixture the ^1H nmr spectra were studied to find regions suitable for quantitative determination of both components.

The ^1H nmr spectrum of monomeric 1 was obtained in $CDCl_3$ solution and is given in Figure 1 together with the nmr spectrum of poly-1. Although the whole spectrum of 1 is too complicated to be simply analyzed, the major assignments can be given by analogy with the fully analyzed spectrum of 2-chloro-2-oxo-4-phenyl-1,3,2-dioxaphosphorinane.[5]

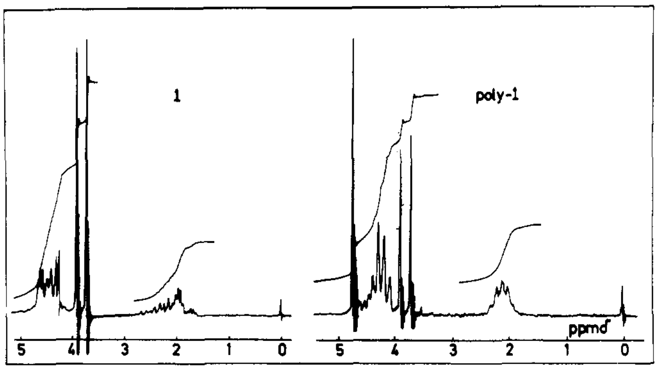


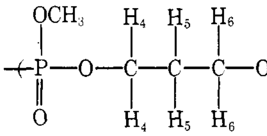
Figure 1. ^1H nmr spectra of 2-methoxy-2-oxo-1,3,2-dioxaphopsphorinane (1) (in $CDCl_3$) and of the corresponding poly-1 (in D_2O).

Thus, the δ 1.71 and 1.96 bands (all δ values in ppm) can be assigned to the H_{5e} (equatorial) coupled with H_{5a} (axial) (J_{5a5e} = 15 Hz) and split further mainly by the hydrogen atoms in the axial positions (H_{4a} and H_{6a}) as well as by the P atom. This gives the composite J = 3 Hz which is in good agreement with already published data.[5] The seven lines in the region 2.1–2.7 correspond to H_{5a} coupled mainly to H_{5e} and further to the other hydrogen atoms in the ring. The next complicated band is observed at 4.23–4.65. This is due to the hydrogen atoms H_4 and H_6. Here, the influence of the P atoms becomes greater, since the POCH system with a gauche conformation (projected along the C—O axis) is known to give coupling constant of J_g = 1.5–2.3 Hz while J_t (trans) = 22–28 Hz.[5,6]

Hydrogen atoms from the -OCH_3 group absorb at δ 3.8 (δ in ppm) (d) with J_{PH} = 11.0 Hz. This is in agreement with the data reported for $(CH_3O)_3PO$: δ 3.78 and J_{PH} = 11.0 Hz.[7;8] The stability of the chair conformation of phosphorinanes has been shown by a number of authors.[9]

Nmr spectrum of poly-1 is much simpler than that of 1. The source of the H atoms nonequivalence, due to the interactions of H atoms at the axial and equatorial positions, is now eliminated, and a relatively simple spectrum results. This is shown in Figure 1.

In the polymer chain (poly-1)



$$\left(\begin{array}{c}OCH_3\\ |\\ -P-\\ \|\\ O\end{array}-O-\begin{array}{c}H_4\\ |\\ C\\ |\\ H_4\end{array}-\begin{array}{c}H_5\\ |\\ C\\ |\\ H_5\end{array}-\begin{array}{c}H_6\\ |\\ C\\ |\\ H_6\end{array}-O-\right)_n$$

both H_5 are equivalent and absorb at δ 2.09 (quint) with J_{HH} = 6 Hz. H atoms from the -OCH_3 group absorb at δ 3.80 (d), at practically the same position which is observed for these atoms in the monomer molecule.

Both H_4 and H_5 are identical, but instead of a triplet four lines are observed, centered at δ 4.23 and a composite J = 6 Hz. The additional split is due to POCH interaction, since it is known that in RCH_2OP J = 6–7 Hz.[6] Since J_{HH} (*cf.* the δ 2.09 band) is also equal to 6 Hz; this coincidence gives four lines as the superposition of two triplets. This is confirmed by integration, being close to the expected ratio 1:3:3:1.

Thus, integration of the doublet, due to the methoxy groups in the mixture of monomer and polymer, does not depend on composition and can be used as an internal standard. According to the spectra given in Figure 2 a single line arising in the polymer at δ 4.18 can be used as a measure of polymer content. This line is a part of the four lines coming from the superimposed two triplets of the methylene groups: —O—CH_2—CH_2—CH_2—O—.

Unfortunately, the polymerization kinetics could not be directly followed by nmr in bulk, since at high polymer content the spectra loose their sharpness. The method

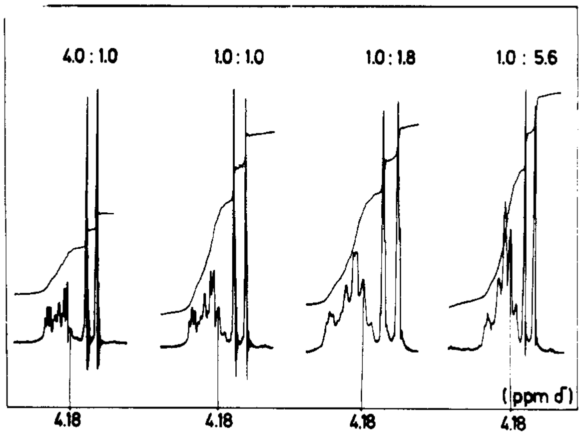


Figure 2. Nmr spectra of the 1-poly-1 mixtures of various compositions.

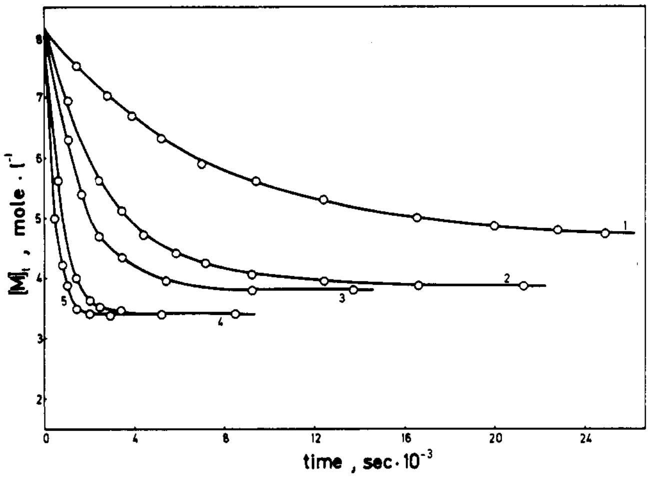


Figure 3. Influence of the [initiator]/[monomer] ratio on the kinetics of polymerization. $[M]_0$ = 8.0 *M*, $[I(Ph_3C^+PF_6^-)]_0$ = (× 10^{-2}): curve 1, 0.36; 2, 0.80; 3, 1.09; 4, 3.03; 5, 7.6 *M*, temperature 125°.

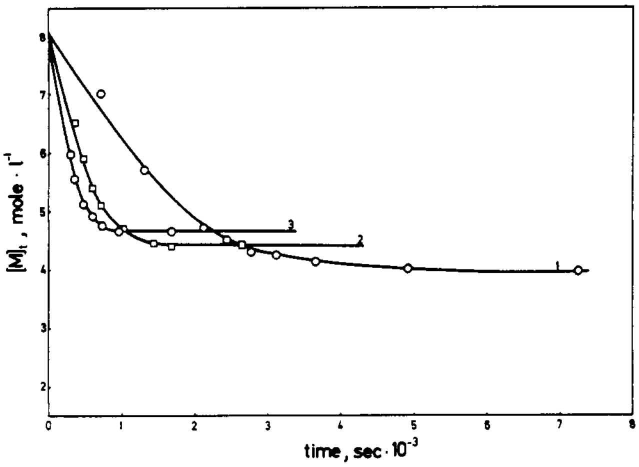


Figure 4. Influence of temperature on the plateau position. $[M]_0$ = 8.0 *M* (at 125°); $[I]_0$ = (× 10^{-2}): curve 1 (125°), 2.2; 2 (135°), 5.1; 3 (155°), 6.97 *M*.

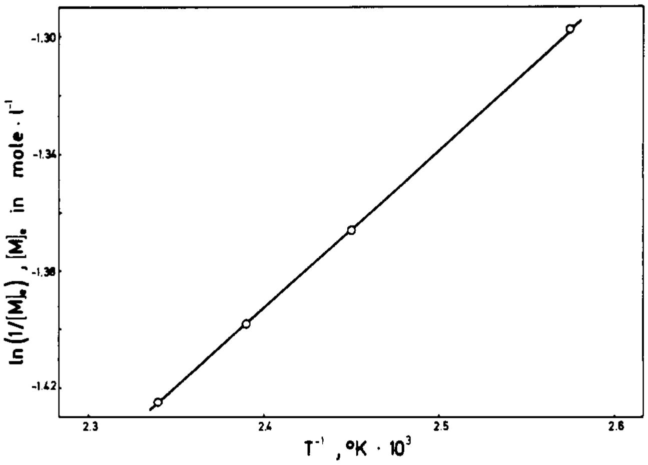


Figure 5. Dependence of ln $(1/[M]_e)$ on reciprocal of the absolute temperature. $[M]_e$ denotes the concentration of monomer at equilibrium. $[M]_0$ = 8.1 *M* (at 115°, corrected for the other temperatures), $[I(PH_3C^+PF_0^-)]_0 = 5.85 \times 10^{-2}$ *M*.

could, however, be used for solutions of monomer–polymer mixtures. Thus, to study the polymerization, dilatometry was used and the conversion factor determined by both gravimetric and nmr methods.

Polymerization Kinetics of 2-Methoxy-2-oxo-1,3,2-dioxaphosphorinane (1). As it can be seen from Figures 3 and 4, 1 polymerizes quite fast in bulk above 100° with the starting initiator concentration in the range 10^{-3}–10^{-2} *M* and the polymerization is finished in just a few hours.

The triphenylmethyl salts 2 are known to be highly active cationic initiators. Their activity, however, at least in the case of the 1,3-dioxolane polymerization, depends on the anion structure.[10] Thus it has been recently shown that in the case of $SbCl_6^-$ as the counterion, the initiator efficiency is more than 10^2 times lower than that observed for SbF_6^- or AsF_6^-.[11] A very similar phenomenon is also observed in the case of 1. Compound 2 with AsF_6^-, PF_6^-, and SbF_6^- counterions give almost identical rates and final conversions while $2(SbCl_6^-)$ is more than 10 times less active, if it is judged from the plateau position.

According to Figures 3 and 4 polymerization of 1 proceeds until a plateau is reached, its height dependent (for $[M]_0$ = const) on the starting initiator concentration $[2]_0$ = $[I]_0$.

There are two possible explanations for these observations: depropagation is important in the range of the temperatures under study and/or an irreversible termination takes place and its activation energy is higher than that of the chain growth.

According to Figure 3 increase of the $[I]_0/[M]_0$ ratio ($[M]_0$ and the temperature being kept constant) has no influence on the polymer yield at the plateau if this ratio passes a certain limit. This clearly indicates a marked reversibility of the chain growth. Analysis of the first-order plots of polymerization shows, however, that the plot of ln $([M]_t - [M]_e)/([M]_0 - [M]_e)$ *vs.* time markedly deviates from linearity. This indicates an irreversible termination.

The dependence of ln $(1/[M]_e)$ = ln K_e on $1/T$ is given on Figure 5. The reversibility of propagation has also been checked by a study of the dependence of the measured overall rate of polymerization, epxressed by d[M]/d*t*, as a function of the starting monomer concentration in ethylene chloride solvent, at 80°. This is shown on Figure 6, results were obtained with $[I]_0 = 1 \times 10^{-2}$ *M*, giving the ratio $[I]_0/[M]_0$ high enough to reach the equilibrium conditions even at the highest $[M]_0$ (*i.e.*, in bulk).

A number of kinetic schemes were tested, including various termination reactions; all kinetic results can be described by a scheme consisting of fast initiation, reversible chain growth and an irreversible bimolecular chain termination, involving reaction of the growing center M′ with a macromolecule (P), whether dead or growing.

Solution of this scheme

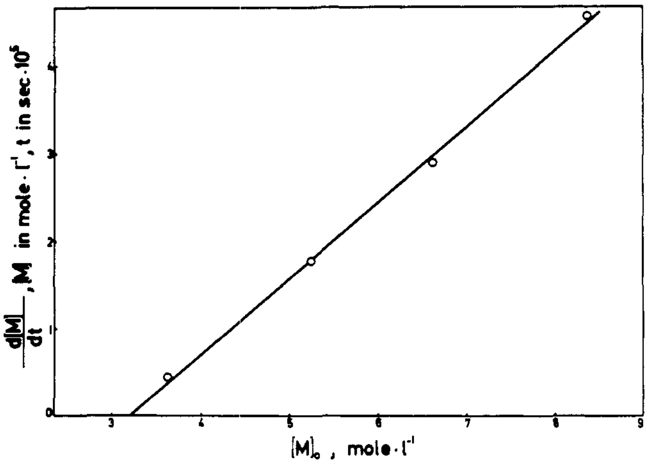


Figure 6. Dependence of the overall polymerization rate d[M]/dt as a function of the initial monomer concentration $[M]_0$ in 1,2-ethylene dichloride solvent, at 80°. $[I(Ph_3C^+PF_6^-)]_0 = 1.0 \times 10^{-2}$ *M*.

$$
\begin{array}{ll}
I + M \xrightarrow{k_i} IM \quad \text{(fast)} & M' + M \underset{k_d}{\overset{k_p}{\rightleftharpoons}} M' \\
IM + M \underset{k_d}{\overset{k_p}{\rightleftharpoons}} IMM \quad (M') & M' + P \xrightarrow{k_t} M'P \\
 & \qquad\qquad \text{(inactive)}
\end{array}
$$

in which I, M, and M′ denote initiator, 1, and active centers, and k_i, k_p, k_d, and k_t rate constants of the initiation, propagation, depropagation, and termination, respectively. Since

$$
\begin{aligned}
d[M']/dt &= k_t[M']([M]_0 - [M]) \\
d[M]/dt &= k_p([M] - [M]_e)[M']
\end{aligned}
$$

we get after dividing d[M′]/dt by d[M]/dt and further rearrangement

$$
\int_{[M']_0}^{[M']} d[M'] = \frac{k_t}{k_p} \int_{[M]_0}^{[M]_t} \frac{([M]_0 - [M]_e)d([M] - [M]_e)}{[M] - [M]_e} \qquad (1)
$$

and eventually

$$
-\frac{d\ln([M]_t - [M]_e)}{dt} = k_p[I]_0 - k_t \times \{([M]_0 - [M]_e) \ln \frac{[M]_0 - [M]_e}{[M]_t - [M]_e} - ([M]_0 - [M]_t)\} \qquad (2)
$$

A very similar equation was derived by one of us recently for a system with no depropagation[12] and successfully used in a description of the polymerization of cyclic ethers.[13] Goethals applied similar treatment to the cationic polymerization of cyclic sulfides.[14] Plesch named figuratively this kind of polymerization a "suicidal polymerization."[15]

Equation 2 has been tested in Figure 7; fairly good straight lines were observed at various temperatures. From the corresponding slopes k_t can be calculated even if $[I]_0$ were unknown. Intercepts are equal to the products $k_p[I]_0$. Thus, to find k_p the true value of $[I]_0$ should be determined.

It was assumed in a derivation of eq 2, that $[I]_0$ is equal to the concentration of the initiator used only if initiation is quantitative; *i.e.*, if one molecule of initiator produces one original active center.

Among 2 tested, the highest and identical polymerization rates were found for AsF_6^-, PF_6^-, and SbF_6^- anions. Besides, 1,3-dioxolan-2-ylium salts (3) with AsF_6^-, PF_6^-, and SbF_6^- anions gave the same rates as 2. Thus, all kinetic and thermodynamic data given below were obtained mainly with 2 (AsF_6^- and PF_6^-) and 3 with the same anions. It was assumed, that for these salts $[I]_0$ is equal to the concentration of the initiator used. This, in turn, allowed the rate constants of propagation k_p to be determined at various temperatures.

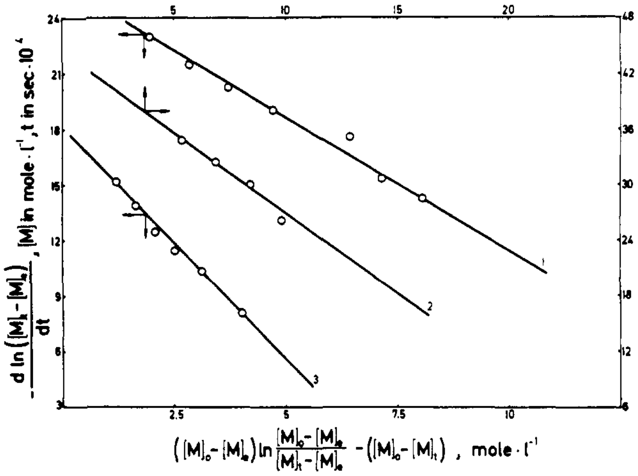


Figure 7. Determination of the rate constants of propagation (k_p) and termination (k_t), according to eq 2. Polymerization in bulk; initiator $Ph_3C^+PF_6^-$: curve 1, $[I]_0 = 2.41 \times 10^{-2}$ *M*, 135°; 2, $[I]_0 = 2.50 \times 10^{-2}$ *M*, 145°; 3, $[I]_0 = 0.97 \times 10^{-2}$ *M*, 155°.

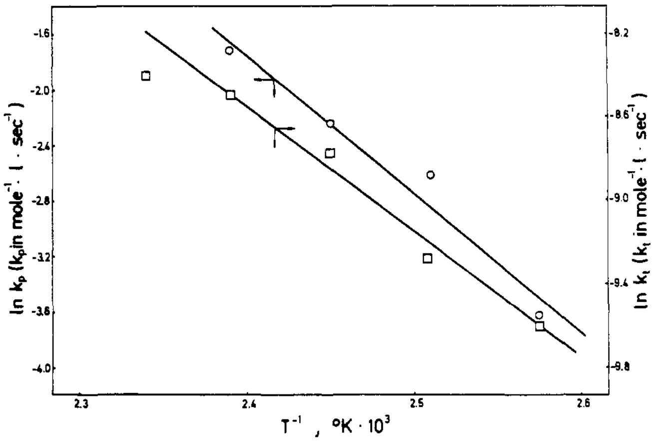


Figure 8. The dependence of ln k_p and ln k_t on the reciprocal of the absolute temperature. Determination of the thermodynamical activation parameters.

Remembering, that $1/[M]_e = K_e$ is valid for sufficiently large polymerization degrees the corresponding equilibrium constants were found for various temperatures. In the determination of constants it was additionally assumed, that only one kind of active centers is formed. Obviously, at high temperatures and in bulk the ion pairs should dominate.

The dependence of ln k_p and ln k_t on reciprocal of the absolute temperature is given in Figure 8, from which the corresponding thermodynamical activation parameters have been determined. Finally, k_d was calculated for various temperatures from $k_d = k_p/K_e$.

The activation parameters as well as the thermodynamic function of the polymerization are given in Table I.

From ΔH_p and $\Delta S_p°$ we obtain $T_c = -65°$ (for a solution in the standard state 1.0 mol l.⁻¹), and T_c (bulk) = 390°. The large difference in these values come from the relatively low enthalpy of polymerization coupled with a low (the absolute value) entropy of polymerization. Thus, the factor $R \ln [M]_e$, being opposite in sign to $\Delta S_p°$, becomes comparable with a standard entropy.

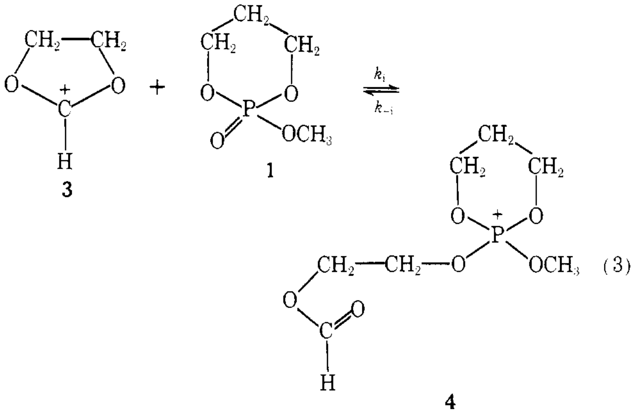
At 25°, $\Delta F_{ls} = \Delta H_{ls}° - T(\Delta S_p° + R \ln [M]') = -0.78$ kcal mol^{-1}, assuming $\Delta H_p = \Delta H_{ls}°$. At this temperature $k_p = 1.1 \times 10^{-5}\ M^{-1}\ sec^{-1}$, $k_d = 3.1 \times 10^{-5}\ sec^{-1}$, and $k_t = 6.0 \times 10^{-7}\ sec^{-1}$. Thus, at this temperature, polymerization is energetically feasible ($\Delta F_{lc} < 0$), yet kinetically inhibited, because of the high activation energy of propagation.

Our preliminary findings in the anionic polymerization of 1 show, that ΔF_{lc} does not depend on the mechanism of polymerization.

Chemistry of the Elementary Steps. In order to realize the significance of the determined values of the activation parameters the chemistry of the elementary steps should be understood first.

Initiation. Two different initiators have been used throughout this work; namely, $Ph_3C^+A^-$ (2) with AsF_6^-, PF_6^-, and SbF_6^- anions and 1,3-dioxolan-2-ylium salts (3) with the same anions.

Initiation with 2 and 3 has been studied in CD_3NO_2 and $C_2H_4Cl_2$ solutions by nmr. The corresponding ^1H nmr spectra of 1 cationated with 3

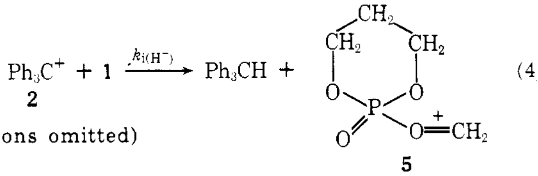


(3)

are given in Figure 9 and Figure 10 (with a heterospin decoupling). The main assignments are given directly in these figures and agree well with the existing knowledge of the structure of the tetraalkoxyphosphonium ions.[16] These ions have the tetrahedral structure and the observed equivalency of the H atoms (in contrast to 1) in 4 strongly suggests that this is a conformationally mobile substance. The replacement of the O═P bond by a R—O—P bond is a main source of the absence of any preferred conformation.

Initiation with 2 proceeds *via* H^- transfer reaction, similarly to the already observed H^- transfer in the polymerization of tetrahydrofuran[17,18] and of 1,3-dioxolane.[19,20] Ph_3CH was observed directly in the nmr spectra and by means of the vpc.

According to the nmr spectra H^- is removed from methoxy group



(4)

The rate of H^- transfer has been studied by monitoring the decrease of the optical density of Ph_3C^+ [λ_{max} 430 nm (ϵ 3.96 × 10^4)],[21] as it was described by one of us previously.

When 2 is dissolved in a solvent containing 1, there are two processes taking place:

(a) fast, reversible formation of a phosphonium ion

Table I[a]

Elementary Reaction	ΔH^* (kcal/mol)	ΔS^* (eu)
Propagation	19.5	−15.6
Depropagation	20.6	−10.2
Termination	11.6	−48.1

[a] From these data $\Delta H_p \cdot (\Delta H_{ls}$ or $\Delta H_{ss}) = 1.1$ kcal/mol, $\Delta S_p° = -5.4$ eu.

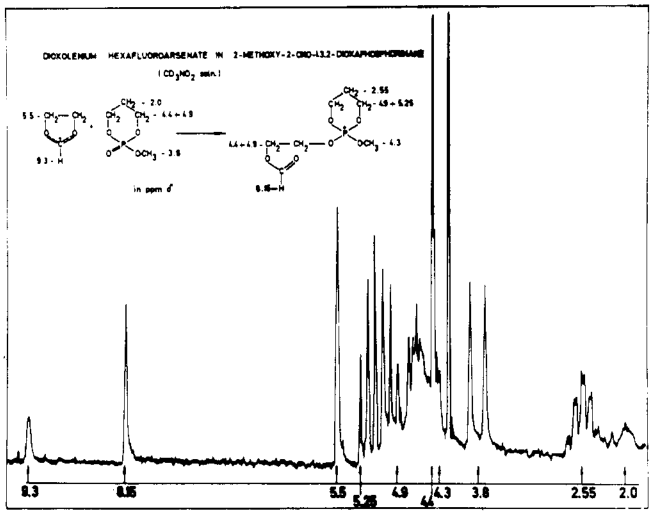
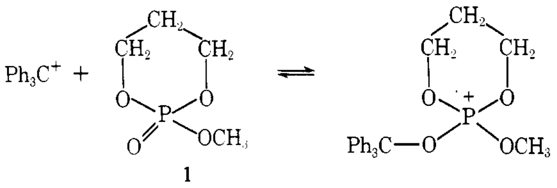


Figure 9. ^1H nmr spectrum of the reaction product of 1,3-dioxolan-2-ylium salt with a monomer: formation of the tetraalkoxyphosphonium cation in the initiation reaction. $[I]_0 = 0.81\ M$, $[M]_0 = 0.98\ M$, CD_3NO_2, 25°.



(5)

(b) slow, and practically irreversible H^- transfer process specified above in eq 4.

Since the extent of cationation is very low, due to the low basicity of 1, this reaction can be neglected in the further treatment.

Thus

$$-\mathrm{d}[5]/\mathrm{d}t = \mathrm{d}[2]/\mathrm{d}t = -k_{i(H^-)}[2][1]$$

and, taking into the account, that

$$[1] = [1]_0 - ([5]_0 - [5]) - [\text{polymer}]$$

and, that at $t \rightarrow 0$, [polymer] $\rightarrow 0$ (t denotes a time) and, finally

$$\mathrm{d}[2]/\mathrm{d}t = -k_{H^-}[2]([1]_0 - [2]_0) - [2]^2$$

solution at this equation leads to the following final expression

$$\ln [1 + ([1]_0 - [2]_0)/[2]] = k_{H^-}([1]_0 - [2]_0)t + \ln [1]_0/[2]_0 \tag{6}$$

This equation allows the $k(H^-)$ values to be determined.

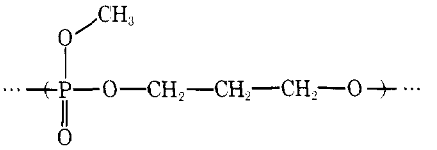
Thus, results of the spectrophotometric study of reaction 4 have been plotted according to eq 6 and from the slope $k(H^-)$ has been determined (Figure 11). Intercepts give the ln $[1]_0/[2]_0$ marked directly in the Figure 11 and in good agreement with the calculated values.

It was also observed that in the lower region of the temperatures studied marked acceleration periods were observed in polymerization when 2 was used as initiator. Treatment of the kinetic data according to the equations describing the nonstationary polymerization with a slow initiation and fast propagation allowed the k_i to be determined. When both $k(H^-)$ and k_i were plotted against $1/T$, all of the points were found on the same straight line with $\Delta H_i{}^* = 18.7$ kcal/mol and $\Delta S_i{}^* = -26.4$ eu. This result confirms the proposed hydride-transfer reaction as a process responsible for initiation (Figure 12).

The temperature coefficient of the H^- transfer is higher than that of propagation, and, therefore, starting from approximately 100° the inequality $k_p > k_i$ holds.

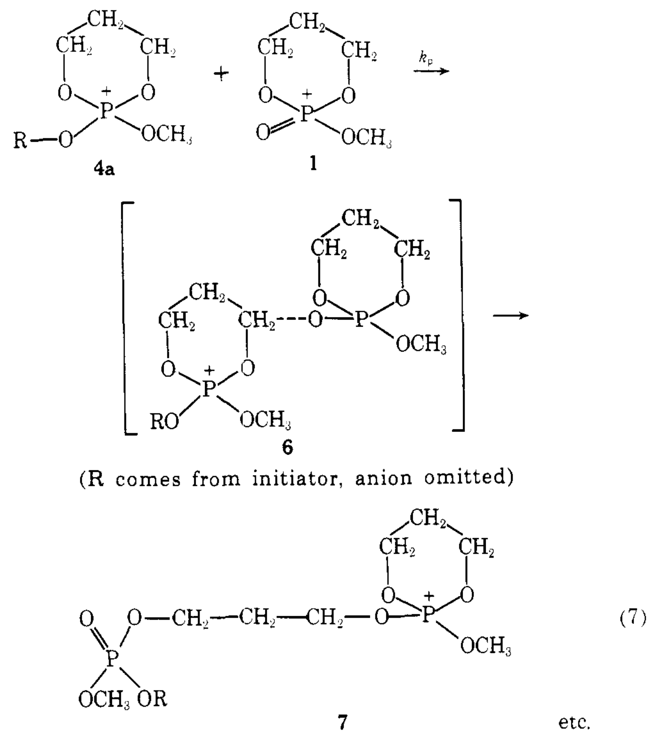
Chain Growth. According to the already discussed ^{1}H nmr spectrum, poly-1 (Figure 1) has a structure of polyester, expected for polymerization proceeding through a simple ring-opening polymerization.

Therefore, besides the end groups, discussed in the next sections, polymer has predominantly the following structure



$$\cdots\!-\!\!\left(\overset{\overset{\displaystyle O-CH_3}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-O-CH_2-CH_2-CH_2-O\right)\!\!-\!\cdots$$

Thus, if we consider initiation through a cationation at the 2-oxo group, then, the first step of the chain growth can be formulated in the following way



4a

1

6

(R comes from initiator, anion omitted)

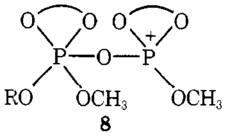
(7)

7

etc.

Structure 6, given in the brackets is only a schematical representation and does not reflect our idea about the transition state.

Although the attack on P^+ and formation of the pyrophosphoric structure



8

might even be kinetically preferred, 8 cannot be a thermodynamic product, since both ^{31}P and ^{1}H nmr spectra do not conform the pyrophosphoric chain.

The presence of the partial positive charge on the C_4 and C_6 carbon atoms, attacked at the chain growth, is also confirmed by the nmr spectrum (Figure 10); $\Delta\delta = \delta_{cat\,1} - \delta_1 = 36$ Hz (downfield) for H atoms attached to these carbon atoms.

Chain Termination. The only indication of the reactions proposed below and leading to the chain termination comes from the study of the reaction kinetics, and from the fact, that the measured constant (k_t) does not depend on the structure of the anion attached to the growing species.

It has been observed in the polymerization of all of the heterocyclics, that the inevitable chain termination proceeds through the reaction of the growing species with a polymer segment. This is a reaction similar to that of the chain growth, but leading to the nonstrained onium ions, unable to reinitiate the chain growth (polymerization of cyclic acetals is an exception).

By an analogy with the chain growth, chain termination can be visualized in reaction 8.

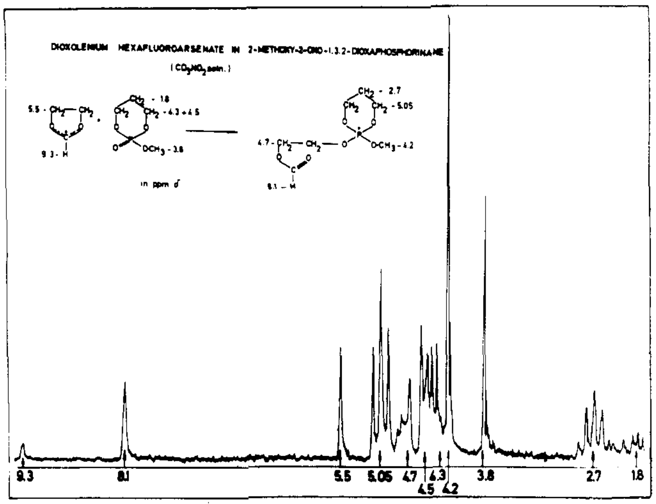


Figure 10. The same as in Figure 9, but ^{1}H spectra decoupled from ^{31}P.

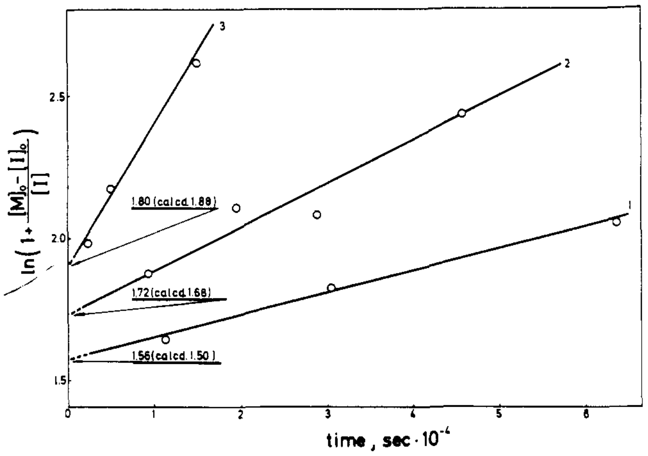
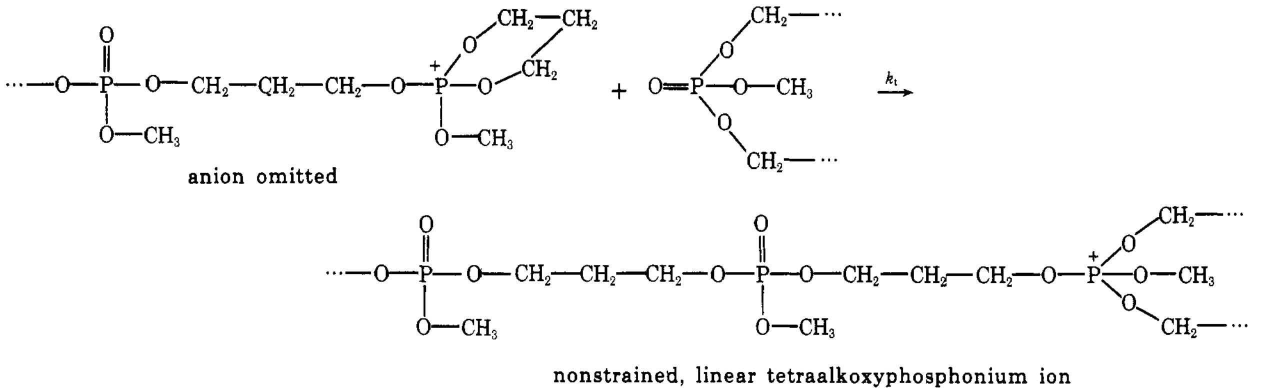


Figure 11. Kinetic plots of the H^- transfer from monomer to $Ph_3C^+A^-$ plots: curve 1, $[1]_0 = 1.32\ M$; $[2]_0 = 0.30\ M$; 60°, $k(H^-) = 7.8 \times 10^{-6}\ M^{-1}\ sec^{-1}$; 2, $[1]_0 = 1.72\ M$; $[2]_0 = 0.32\ M$; 70°, $k(H^-) = 1.1 \times 10^{-5}\ M^{-1}\ sec^{-1}$; $[1]_0 = 1.92\ M$; $[2]_0 = 0.32\ M$; 80°, $k(H^-) = 3.3 \times 10^{-5}\ M^{-1}\ sec^{-1}$.



(8)

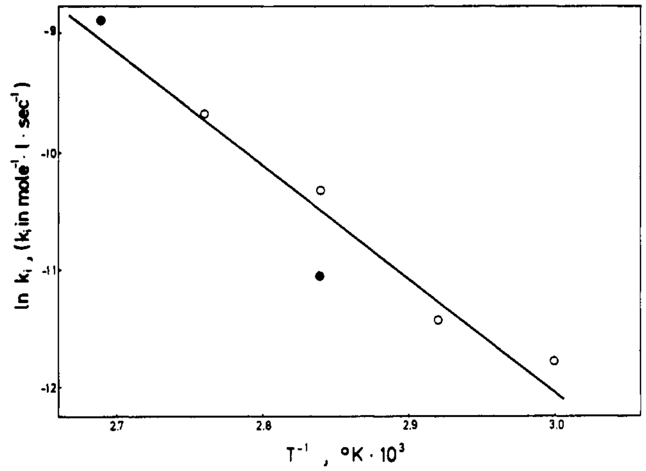


Figure 12. Dependence of $k(H^-)$ and k_i (from kinetic curves) on the reciprocal of the absolute temperature $1/T$ (°K). Determination of ΔH_i^* and ΔS_i^*: (●) $k(H^-)$, from H^- transfer measurement; (○) k_i, from the study of the polymerization kinetics.

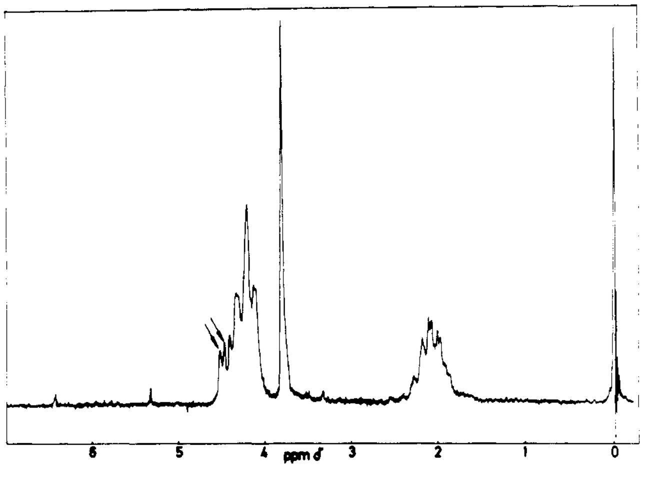
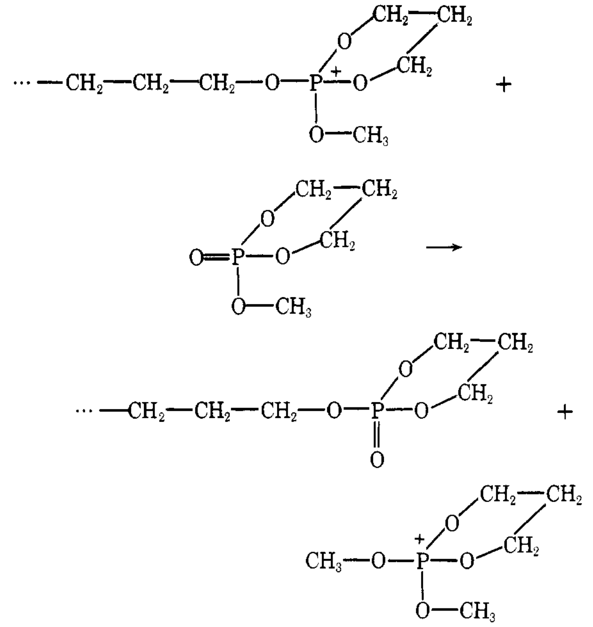


Figure 13. ^{1}H nmr spectra decoupled from ^{31}P of poly-1, showing the presence of some cyclic structures in the macromolecules (the arrow shows the region of the contribution of cyclic structures in the linear macromolecule).

Chain-Transfer Processes, Polymerization Degree, and the Polymer End Groups. According to the proposed mechanism of the elementary reactions, polymers of high polymerization degree should be formed. Thus, at $[I]_0 = 10^{-3}$ *M* and $[M]_0 = 8.05$ *M* (bulk, 125°) $\overline{DP}_n$ should be of the order of 10^3 ($[M]_{final} \simeq 4.0$ *M*). Instead, $\overline{DP}_n$ did not surpass 8 and polymers of M_n (vapor pressure osmometry) not higher than 1200 were obtained. At the same time in the ^{1}H and ^{31}P nmr spectra of polymers bands typical for cyclic structures have been observed. The expanded part of the spectra with these bands is shown in Figure 13.

Because of the overlap of the nmr spectra of the cyclic part of the macromolecule with that of the linear segments the calculation of the $\overline{DP}_n$ assuming one cyclic endgroup per macromolecule on the basis of the nmr spectra is difficult. Approximate calculations give however results close to $\overline{DP}_n$ determined by the vpo methods.

The chemical process, responsible for the discussed above chain-transfer reaction is assumed to be as follows

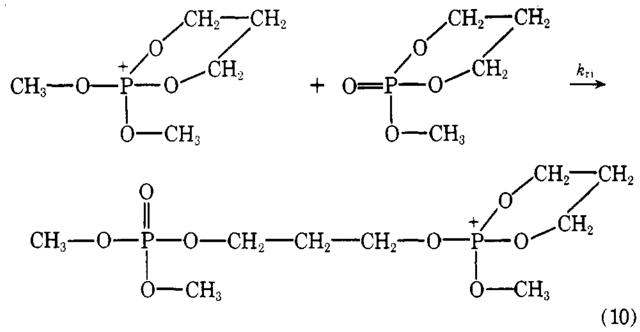


(9)

9

Reinitiation should proceed with a rate similar to that of propagation, since the structure of **9** is identical with that of the growing species **7**. Therefore, no retardation is observed.

Reinitiation with **9** proceeds similarly to the initiation with **4a**



(10)

where $k_{ri} \simeq k_p$

Thus, the majority of macromolecules, independently of the initiator used, contain cyclic structure from one end, formed through the chain-transfer reaction.

In the polymers prepared with **3** as initiators a strong absorption in the ir region at 6.39 μ was observed. Polymers obtained with **2** did not absorb in this region at all. According to the proposed mechanism of initiation with **3** (cationation of **1** and formation of the formate group) this absorption could be due to the carbonyl group. However, carbonyl groups in the low molecular weight formates absorb usually at 5.8 μ, a region 6.2–6.4 μ being characteristic for carboxylic acids.[22] This discrepancy is not understood at present.

Discussion of the Thermodynamic and Kinetic Parameters. No kinetic or thermodynamic data were available until now for a polymerization of cyclic phosphates.

Our values $\Delta H_p = -1.1$ kcal mol^{-1} and $\Delta S_p° = -5.4$ cal deg^{-1} mol^{-1} are close to those one could expect on the basis of the thermodynamic parameters known for a polymerization of various cyclic monomers.[23] Although $\Delta F_{lc}°$ calculated for six-membered cycloalkanes are (at 25°) strongly positive, a number of six-membered ring compounds are known to polymerize quite easily.[23] Negative values of $\Delta F_{lc}°$ (at 25°) were reported for puckered six-membered cyclic esters (*e.g.*, δ-valerolactone, ethylene oxalate, etc.).[24]

The bond angles in a monomeric **1** and these in the open-chain ester are almost identical (**1** has a chair conformation in a solid state[9]). Therefore, the observed negative ΔH_p is probably caused by a conformational and transannular strain (nonbonded intramolecular interactions between the H atoms).

Our value of $\Delta S_{lc}° = -5.4$ eu can easily be explained on the basis of the usually considered individual contributions of the component entropy changes.[24] This value is to be compared with $\Delta S_{lc}°$, calculated for a hypothetical polymerization of cyclohexane (−2.5 eu), methylcyclohexane (−7.6 eu), or a six-membered lactam (−6.6 eu).[24]

The only work, in which activation parameters were determined for both propagation and degradative chain transfer to polymer (termination) is a paper recently published by Goethals and concerning the cationic polymerization of cyclic sulfides. It is remarkable that in his work, as well as in our present study, the activation enthalpy of polymerization is much higher than that of termination, and the entropy of activation of the termination reaction is much more negative than that of propagation.

The observed difference in enthalpy of activation between the propagation and termination reactions can be attributed to the difference in basicities between monomer (pK_a = 3.1) and a linear polymer segment (pK_a = 3.8) (both measured by us on the basis of the optical density shift in CH_3OD). The large difference in entropies of activation may be due. to the freezing of a much larger number of atoms when a polymer segment is immobilized in the activated complex.

Experimental Section

Materials. Monomer. Preparation, purification, and determination of its purity. 2-Methoxy-2-oxo-1,3,2-dioxaphosphorinane (**1**) was prepared according to known methods by first condensing $P(O)Cl_3$ with CH_3OH.[25] The resulting $CH_3OP(O)Cl_2$ was purified by distillation and condensed with 1,3-propylene glycol in the presence of 2,6-dimethylpyridine.[25] Monomeric **1** was further purified by distillation [101° (5 × 10^{-2} mm)] in the presence of Na, $LiAlH_4$, or $HAl(i\text{-}Bu)_2$. In the presence of sodium distillation was accompanied by partial polymerization.

The purity of **1** was checked by glc, although at high temperature (250°) some decomposition was noted. Therefore, cryoscopic method was adopted, taking advantage of the fact that the melting point of **1** is close to the room temperature. The same method had earlier been elaborated by one of us for 3,3-bis(chloromethyl)oxetane[26] and based on the dynamic cryometry of Rossini.[27]

By adding known amounts of the known impurity the cryoscopic constant (A) of **1** has been determined and further used in the determination of the purity of **1**, according to

$$X = (T_{f_0} - T_f) \times A \times 100 \text{ (in mol \%)}$$

where X = total content of impurities, A = 0.425 mol % deg^{-1}. Compound **1** is highly hygroscopic and should be stored in the closed container. Its purity after a number of distillations was better than 99.90 ± 0.05 mol %, according to the described above cryometric measurements.

Triphenylmethyl salts (2) (Ozark-Mahoning Co., Tulsa, Okla.), were purified by dissolution in CH_2Cl_2, filtration, and precipitation with CCl_4. All of these operations were made in the closed system, attached to the high-vacuum line.

1,3-Dioxolan-2-ylium salts (3) were prepared and purified as it was earlier described by one of us.[28] Both **2** and **3** were finally distributed into the thin glass bulbs (vials), sealed off and stored at −10 to −20° in dark until used.

Solvent. $ClCH_2$–CH_2Cl was purified as described,[10] and finally stored on the high-vacuum line with CaH_2.

Kinetic Measurements. Polymerization was carried out in bulk or in 1,2-dichloroethane solvent by using dilatometers filled in high vacuum. Dilatometers were first opened from the bottom and a sealed vial with a known amount of initiator and a solid glass hammer were put in. In the next step dilatometers were sealed at the bottom and attached to the rotating trap connected with the high-vacuum line. Monomer was transferred into the dilatometers from the rotating trap and distilled into this trap from a graduated reservoir.

The contraction factor was determined using gravimetrical and nmr methods. Agreement between these methods within 5% was obtained when polymer yield was determined for the same kinetic run for a number of points.

Polymer Isolation, Determination of Structure, and Polymerization Degree. Poly-**1** was isolated by precipitating in diethyl ether, in which **1** is soluble, from homogeneous solution in methanol. Poly-**1** was usually obtained as a viscous, or tacky semisolid, colorless or slightly yellow material, hygroscopic, and easily soluble in water.

Nmr spectra (both ^1H and ^{31}P) were determined with a Jeol Model JNM-DBT-8P apparatus in D_2O or $CDCl_3$ solutions.

Polymerization degree was determined with a vapor pressure osmometer (molecular weight apparatus Hitachi Perkin-Elmer Model 115).

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Optically Active Polymers of 1-Alkynes

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ABSTRACT: The already-known polymers of (*S*)-3-methylpentyne (I) and (*S*)-4-methyl-1-hexyne (II) as well as the new ones from (*S*)-5-methyl-1-heptyne (III), (*S*)-6-methyl-1-octyne (IV), and (*S*)-3,4-dimethylpentyne (V) have been prepared by iron tris(acetylacetonate)–aluminum triisobutyl catalyst. The primary structure with alternate double bonds along the main chain has been confirmed for all above polymers. Spectroscopic data (ir, nmr, and uv) show that conjugation is only partial according to a nonplanar conformation of the chains due to mutual steric repulsion of side chains in "1,3" relative positions. The CD spectra from 400 down to 200 nm show, according to absorption spectra, a system of optically active bands attributed to the presence of an inherently chiral polyene chromophore in the macromolecules main chains.

The polymerization of 1-alkynes gives, in the presence of the catalytic system obtained by reacting iron(III) chelates with aluminum trialkyls or dialkyl hydrides, head-to-tail linear macromolecules with alternate double bonds along the main chain.[2-6]

The first optically active 1-alkyne, (*S*)-4-methyl-1-hexyne, was polymerized in 1967 and it was demonstrated that no racemization occurs during the polymerization.[3] Analogous polymers of (*S*)-3-methylpentyne (I) and (*S*)-4-methyl-1-hexyne (II) were more recently investigated.[7,8]

In the present paper the synthesis of polymers of additional optically active 1-alkynes, such as (*S*)-5-methyl-1-heptyne (III), (*S*)-6-methyl-1-octyne (IV), and (*S*)-3,4-dimethylpentyne (V), is described. The chiroptical properties down to 200 nm of these last polymers as well as those of the polymers from I and II are investigated and related to the conformational equilibrium in solution.

Experimental Section

Materials. The solvents used were purified according to standard procedures; they were deoxygenated by distillation under nitrogen and by bubbling dry nitrogen through them.

$Al(i\text{-}C_4H_9)_3$ was obtained by distillation from a 25% commercial solution in *n*-heptane.

Iron tris(acetylacetonate) was prepared as reported in the literature[9] and purified by two crystallizations from methanol-water mixture.

The monomers I–IV and 3,3-dimethylbutyne (VI) were prepared by adding bromine to the corresponding olefins and causing the obtained dibromides to react with $NaNH_2$ in mineral oil at 160°.[10] Their purity was checked by gas chromatography. A sample of V was kindly supplied by Dr. A. M. Caporusso.

Polymerization Experiments. All experiments were carried out under nitrogen atmosphere in a two-necked 100-ml flask fitted with magnetic stirrer. Catalyst was prepared by introducing in the flask $Fe(AcAc)_3$; this last was dried under vacuum (0.5 mm) at 60–65° for several hours. A few milliliters of *n*-heptane were then introduced and $Al(i\text{-}C_4H_9)_3$ was added under stirring. The flask was heated for 15 min at 60° and the monomer was successively added at room temperature. The polymerization was interrupted by dissolving the polymer in diethyl ether and by decomposing the catalyst with deoxygenated HCl (1:1). The organic layer was then washed with deoxygenated water, treated with saturated $NaHCO_3$ solution, and finally washed with water.

Polymer was precipitated by methanol from the ethereal solution, isolated by filtration, and dried under vacuum. Details concerning each polymerization run are reported in Table I.

Measurements. Fractionation of the polymers and viscosity measurements were carried out as previously reported.[3]

Nuclear magnetic resonance spectra were obtained with a Jeol JNM-100 spectrometer on polymer solution in CCl_4; all chemical shifts are reported in δ (ppm) with Me_4Si as internal standard.

Infrared spectra were obtained with a Perkin-Elmer double-beam spectrophotometer Model 225. The spectra were recorded at 25° on polymer films, prepared by evaporation of the solvent from solution of the polymer in CS_2, placed on NaCl plates.

Ultraviolet spectra were recorded at room temperature by a Cary 14 spectrophotometer. Polymers solutions in Spectrograde *n*-heptane with concentrations between 0.3 and 0.5 g per l. were used.

Optical rotatory power at 589 nm was measured with a Schmidt–Haensch polarimeter. Polymer solutions in Spectrograde *n*-heptane with concentrations between 3 and 5 g per l. were used.

Circular dichroism spectra were carried out on a Roussel Jouan Model II dichrograph. The solutions were the same used for uv spectra. For the low-temperature spectra, ellipticities were calculated assuming as density of the solution the density of the solvent at each temperature. No correction has been made for refractive index of the solvent.

Results and Discussion

Polymerization. No detailed kinetic studies have been performed, but the collected data (Table I) already show that the polymerization rate is strongly affected by monomer structure and particularly by the steric obstruction of the alkyl group bound to the triple bond. In fact the homologous series from I to IV, where the methyl branching goes from the α position in I to the δ position in IV, the polymerization rate seems to increase in the order, even if high conversion can be reached for all monomers I–IV in a few hours. A remarkable decrease in polymerization rate is observed going from I to V and even more to VI. This decrease of capability to polymerize must be attributed to steric reasons. In fact V in addition to the methyl in the α position, as in I, has a second methyl group in the β position. In VI the carbon atom bound to the triple bond is fully substituted and in each monomer conformation the approach of the catalyst to the unsaturation is strongly hindered. Accordingly the corresponding α-olefin, *tert*-butylethylene[11] does not polymerize at all.

The marked steric effect resembles that observed[12] in the α-olefins polymerization by Ziegler–Natta catalysts. This supports the formation of main chain double bonds having a predominantly "cis" or "trans" configuration as observed in the polymerization of nonchiral 1-alkynes.[4,13]

Polymer Structure. The polymerization of terminal acetylenes[3-6] and of acetylene[14] by ferric acetylacetonate or dimethylglyoximate and organoaluminum leads to linear