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Kinetic Studies on Cationic Ring-Opening Polymerization of 2-Phenyl-1,2-oxaphospholane

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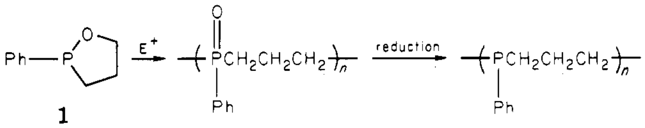
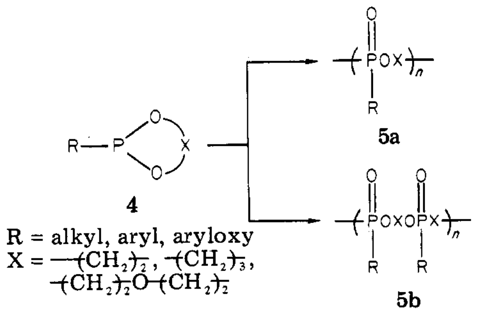
ABSTRACT: A kinetic study on the cationic ring-opening polymerization of a five-membered deoxophostone (2-phenyl-1,2-oxaphospholane (**1**)) was performed with the use of the four initiators $MeOSO_2CF_3$ (MeOTf), MeI, $PhCH_2Br$, and $PhCH_2Cl$. The course of polymerization was monitored by ^{31}P NMR spectroscopy for kinetic analysis. The rate constants and activation parameters of the propagation were obtained. The nature of the propagating species and the rate constant of propagation varied significantly according to the initiators. The polymerization of **1** with MeOTf proceeded via a cyclic phosphonium propagating species. With alkyl halide initiators, on the other hand, the propagating species were of the covalent alkyl halide type. The magnitude of k_p was in the following order: MeI $\gtrsim$ MeOTf > $PhCH_2Br$ > $PhCH_2Cl$. The present study provides the first example that a covalent-type propagating species of an alkyl iodide showed even larger propagation reactivity than an onium type with a OTf^- counteranion.

Recently, we reported the cationic ring-opening polymerization of a five-membered deoxophostone (2-phenyl-1,2-oxaphospholane (**1**)) to give poly(phosphine oxide) **2**[1] and the reduction of the phosphoryl group of **2** to yield polyphosphine **3**.[2] A new polymer having **2** as a graft chain has been shown to exhibit good chelating properties toward heavy-metal ions.[3]



1 **2** **3**

Several cyclic phosphorus(III) compounds (**4**) have been polymerized with a cationic initiator via the Arbuzov-type reaction to give polymers of a phosphinate or phosphonate unit ("normal unit", **5a**).[4-11] During the polymerization, however, a side reaction takes place to form an isomerized unit (**5b**). The amount of the isomerized unit **5b** is dependent on the reaction conditions, and it sometimes exceeds that of a normal unit **5a**.[8,9] Therefore, the kinetics on cationic ring-opening polymerizations of cyclic phosphorus(III) monomers are complicated, and, in fact, the polymerization has not been precisely performed except for the phosphocane polymerization.[11] The cationic ring-opening polymerization of **1** in the present study has been found to be a clean system to yield a polymer consisting exclusively of "normal unit" **2** without isomerization, and hence, is a suitable system for kinetic study.



4 **5a** **5b**

R = alkyl, aryl, aryloxy
X = $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_2O(CH_2)_2-$

Results and Discussion

MeOTf-Initiated System. Figure 1a shows the ^{31}P NMR spectrum of the MeOTf-initiated polymerization system that was recorded immediately after the addition of MeOTf to the monomer solution at 0 °C in PhCN. For the purpose of the kinetic analysis, the monomer/initiator molar ratio was adjusted to 10.0. The two peaks (A and B) were assigned as A (+109 ppm relative to external 85% H_3PO_4 standard) for monomer **1** and B (+101 ppm) for the methylated phosphonium ion (**6**). The initiation reaction was so fast that production of the first propagating species of the cyclic phosphonium (**6**) had already finished. The phosphonium species **6** has been identified also by a model experiment in which an equimolar reaction of **1** with MeOTf in PhCN was carried out. The reaction mixture showed the following characteristic NMR signals for three nuclei: ^{31}P NMR (+101 ppm, single peak), ^{19}F NMR (+0.47 ppm relative to external CF_3CO_2H standard, assignable to $CF_3SO_3^-$), and ^1H NMR (a doublet at δ 2.7 due to CH_3P^+, $^2J_{HP}$ = 14.3 Hz, and double triplets at δ 4.9 due to CH_2OP^+, $^3J_{HP}$ = 10.1 Hz and J_{HH} = 6.0 Hz). These data support cyclic structure **6**, which was stable at a higher temperature, e.g., 60 °C.

On heating at 70 °C two new signals appeared (Figure 1b). Signal C (+38 ppm) was ascribed to phosphine oxide unit **2** and signal D (+34 ppm) was assigned as a terminal

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Table I
Propagation Rate Constants and Activation Parameters in the Polymerization of 1[a]

	initiator			
	MeOTf	MeI	$PhCH_2Br$	$PhCH_2Cl$
$k_p \times 10^4$, L/(mol·s)	3.52 (50 °C)	4.53 (50 °C)	2.13 (70 °C)	1.88 (130 °C)
	9.27 (60 °C)	11.5 (60 °C)	4.34 (80 °C)	3.89 (140 °C)
	24.3 (70 °C)	25.0 (70 °C)	7.99 (90 °C)	5.45 (150 °C)
	40.3 (80 °C)	43.8 (80 °C)	15.0 (100 °C)	10.5 (160 °C)
k_p at 50 °C	3.52×10^{-4}	4.53×10^{-4}	(4.75×10^{-5})[b]	(5.38×10^{-7})[b]
$\Delta H^{\ddagger}$ at 50 °C, kJ/mol	73.3	66.7	63.5	74.3
$\Delta S^{\ddagger}$ at 50 °C, J/(K·mol)	−84.8	−103	−132	−136

[a] $[M]_0$ = 1.25 mol/L and $[I]_0$ = 0.125 mol/L in PhCN solvent. [b] Calculated values.

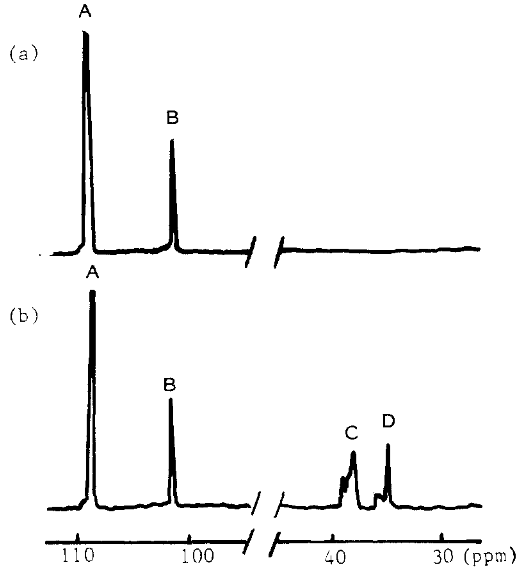
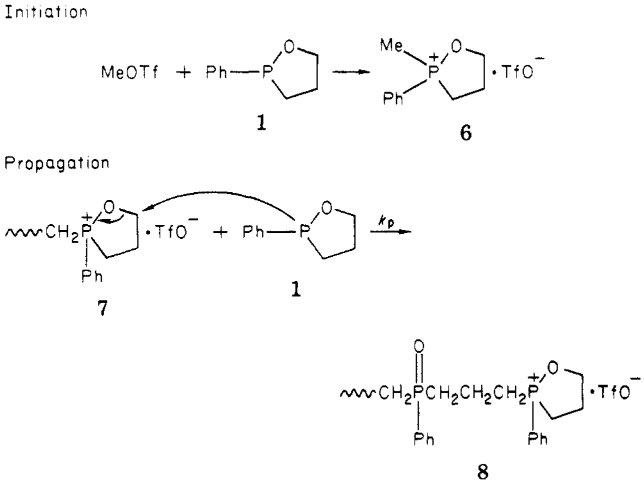


Figure 1. $^{31}P\{^1H\}$ NMR spectra of the cationic ring-opening polymerization of 1 initiated with MeOTf in PhCN ($[M]_0$ = 1.25 mol/L and $[I]_0$ = 0.125 mol/L): (a) before heating; (b) after 30 min at 70 °C.

Scheme I



phosphine oxide group ($MePhP(=O)CH_2\sim$) derived from 6. Cyclic phosphonium species such as 7 and 8 showed the same chemical shift as 6. Therefore, the polymerization of 1 with MeOTf can be given generally as shown in Scheme I.

Propagating ends were cyclic phosphonium ions such as 7 and 8, which were opened by nucleophilic attack of monomer 1 to produce a unit of *P*-phenyltrimethylenephosphine oxide 8 via the Arbuzov-type reaction. On the basis of the results of the kinetic analysis shown below, the propagation has been found to be an S_N2 reaction between 1 and 7, and its rate constant (k_p) is obtained by the equation

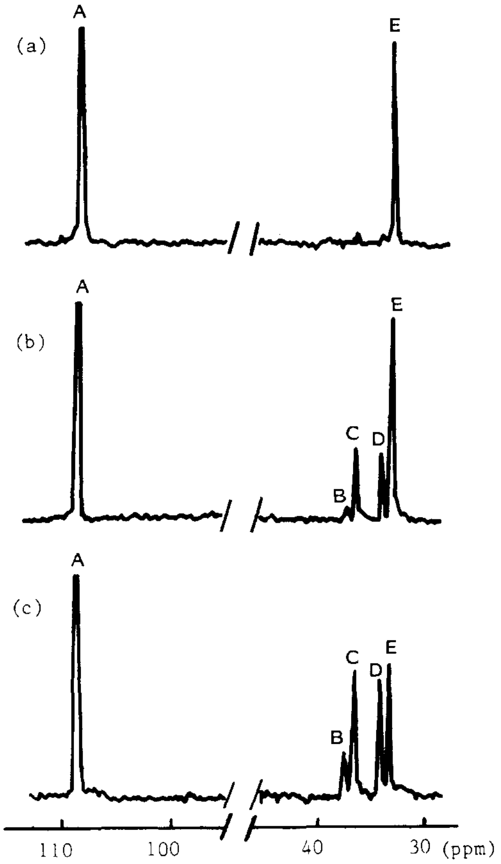


Figure 2. $^{31}P\{^1H\}$ NMR spectra of the cationic ring-opening polymerization of 1 initiated with MeI ($[M]_0$ = 1.25 mol/L and $[I]_0$ = 0.125 mol/L): (a) after 1 min at 70 °C, (b) after 10 min at 70 °C; (c) after 20 min at 70 °C.

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

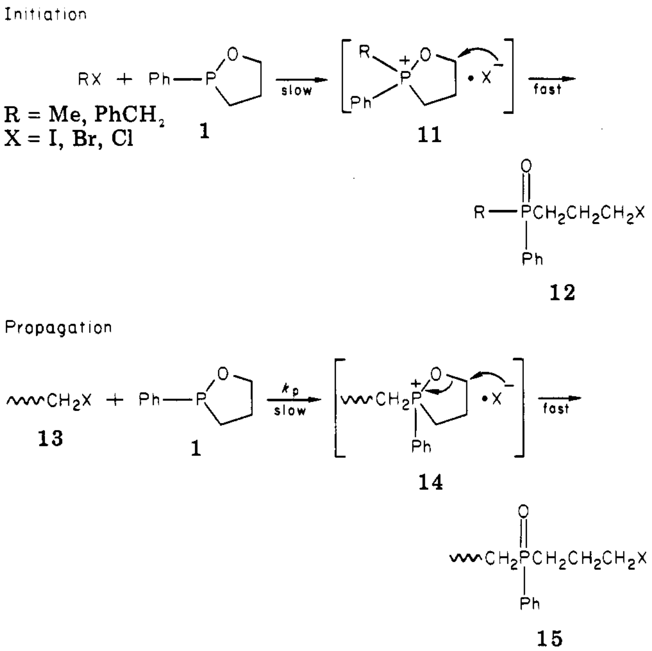
where $[P^*]$ and $[M]$ are the concentrations of propagating species and monomer. Kinetic analysis was carried out by monitoring the polymerization system with ^{31}P NMR spectroscopy. It was found that the concentration of propagating phosphonium species was equal to that of initiator charged, which remained constant throughout the polymerization. Therefore, the integrated form of the above equation is given by

$$\ln \{[M]_1/[M]_2\} = k_p[P^*](t_2 - t_1) \quad (1)$$

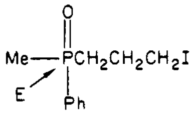
Plots of $\ln \{[M]_1/[M]_2\}$ vs. $t_2 - t_1$ showed a linear relationship, from which k_p values were obtained. Arrhenius plots of k_p values at four temperatures gave a straight line, whose slope led to the activation parameters (Table I).

Alkyl Halide Initiated Systems. Figure 2 shows the ^{31}P NMR spectra of the MeI-initiated polymerization

Scheme II

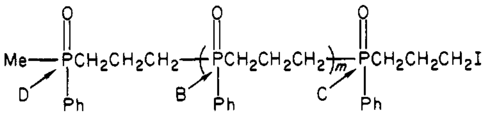


system at 70 °C at the reaction times of 1 min (a), 10 min (b), and 20 min (c). Besides a large peak A (+109 ppm) due to 1, four peaks (B–E) ascribable to the following phosphine oxide groups are observed. At an early stage of polymerization, peak E (+33 ppm) appeared, which was ascribed to the first propagating species (9).



$Me-P(=O)(Ph)CH_2CH_2CH_2I$

9



$Me-P(=O)(Ph)CH_2CH_2CH_2-(P(=O)(Ph)CH_2CH_2CH_2)_m-P(=O)(Ph)CH_2CH_2CH_2I$

10

With the progress of polymerization, peak D (+34 ppm) increased in compensation for the decrease of peak E. Therefore, peak D was ascribed to the terminal phosphine oxide group of 10. Peaks B (+38 ppm) and C (+37 ppm) was ascribed respectively to the internal phosphine oxide units of 10 and to the propagating terminal unit having the 3-iodopropyl group shown as 10. In contrast to the MeOTf-initiated system, no peak due to phosphonium species was detected under polymerization conditions of higher temperatures such as 70 °C. Therefore, it is reasonable to conclude that the propagating ends are alkyl iodide species such as 12, 13, or 15 as shown in Scheme II.

The rate-determining steps of both initiation and propagation are the reactions between an alkyl iodide and monomer 1 generating transient phosphonium species such as 11 and 14, which are converted quickly into covalent alkyl iodide species, e.g., 12 and 15, by nucleophilic attack of the iodide counteranion. The plot of the second-order kinetics of eq 1 for the propagation was also linear, in which [P*] was equal to the concentration of the charged MeI after the initiation was over, e.g., 1 min at 70 °C.

In order to obtain more information about the stability of the phosphonium iodide species (11), a model reaction was carried out. An equimolar amount of MeI and 1 was mixed in PhCN at 0 °C in an NMR sample tube under nitrogen. Within 1 min after mixing, the ^{31}P NMR spectrum of the reaction mixture showed three peaks: +109 ppm (remaining monomer 1), +101 ppm, ascribable to a cyclic phosphonium (11), and +33 ppm (phosphine oxide of 9). Then the mixture was kept at room temperature. After 30 min, peaks due to 1 and 11 disappeared and only a peak due to 9 was observed, indicating that 11 is not stable at room tempature. The quantitative production of 9 was further confirmed by ^1H NMR of the reaction mixture with the following observations: a doublet at δ 1.8 ($CH_3P(=O)$), $^2J_{HP} = 12.0$ Hz) and a triplet at δ 3.3 ($\sim CH_2I$, $J_{HH} = 6.0$ Hz).

Similarly, benzyl bromide and benzyl chloride initiated systems were also shown to proceed via alkyl halide propagating ends as stable species. Transient phosphonium species such as 11 or 14 with bromide or chloride counteranion should be less stable than that with iodide counteranion because of the increased nucleophilic reactivity of Br^- or Cl^- compared with that of I^- in aprotic polar solvents such as PhCN. These kinetic results are given in Table I.

The k_p values are very much dependent upon the counteranion that is derived from initiator. The relative reactivities at 50 °C are in the following order: MeOTf:MeI:$PhCH_2Br$:$PhCH_2Cl$ = 654:842:88.3:1.0. As seen above, the propagating species of the MeOTf-initiated system were of the cyclic phosphonium ion type whereas those of the alkyl halide initiated systems were of the covalently bonded alkyl halide type. The difference in mechanism is due to that of the nucleophilicity of the anions TfO^- and X^- (X = I, Br, Cl), affecting the stability difference of the cyclic phosphonium species. This difference is relfected by $\Delta S^{\ddagger}$ values; i.e., the reduced reactivity with systems such as $PhCH_2Cl$ and $PhCH_2Br$ is due to the less favorable entropy term in comparison with the MeOTf system. This may be explained in terms of solvation–desolvation phenomena. With the MeOTf system the rate-determining step is an ion (7)–dipole (1) reaction to form a phosphonium ion (8). In the course from the initial state to the transition state, therefore, the extent of solvation is decreased. With $PhCH_2Cl$ and $PhCH_2Br$ systems, on the other hand, the reaction between a dipole of the alkyl halide species (13) and a dipole (1) is rate determining to form an unstable phosphonium ion (14). In this case the solvation at the transition state is much increased compared with that of the initial state. Thus the entropy change from the desolvated initial state to the solvated transition state with the alkyl halide systems is less favorable than that with the MeOTf system.

In the ring-opening polymerization, cyclic onium propagating species are usually more reactive than covalently bonded ones, e.g., superacid macroester-type species in the cyclic ether polymerization[12,13] and alkyl halide type species in the cyclic imino ether polymerization.[14] However, it should be emphasized that the MeI-initiated polymerization of 1 proceeded even faster than the MeOTf-initiated system, although the difference in rate is small. To the best of our knowledge, this is the first example of covalent propagating species showing a higher reactivity than ionic propagating ones.

Experimental Section

Materials. PhCN solvent was dried over P_2O_5 and distilled under nitrogen. Initiators were prepared or purified according to ordinary procedures. Monomer 1, bp 69–71 °C (0.4 mmHg) was prepared according to the reported method[15] and also according to our new method involving reaction of dichlorophenylphosphine with 3-chloro-1-propanol.[16]

Kinetics. A general procedure is given as follows. Monomer 1 (0.25 mmol) and an initiator (0.025 mmol) were placed in 0.17

mL of PhCN under nitrogen and kept at a constant temperature in a sealed NMR sample tube. The reaction was monitored by ^{31}P FT NMR with a Hitachi R-900 (36.43 MHz) spectrometer with proton decoupling, and the kinetic analysis was performed by determining the instantaneous concentrations of the monomer, propagating ends, and polymer units. The ^{31}P NMR spectrum was recorded after 8 scans with a pulse interval of 2 s. The time (16 s) to record the spectrum was so short that it was not necessary to take it into account for the kinetic analysis. The concentrations of the respective species were obtained directly from the integral intensity of the spectrum. The reaction system was homogeneous throughout the kinetic run.

Spectral Measurements. ^{1}H and ^{19}F NMR spectra were recorded on a Hitachi R-20B NMR spectrometer (60 and 56.46 MHz, respectively).

Registry No. 1, 16324-17-7; MeOTf, 333-27-7; MeI, 74-88-4; benzyl bromide, 100-39-0; benzyl chloride, 100-44-7.

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Dynamic Light Scattering Study of Copolymers Prepared in the Pregel State by the Radical Copolymerization of Styrene–*m*-Divinylbenzene

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ABSTRACT: Dynamic light scattering experiments have been performed on benzene solutions of macromolecular clusters prepared by radical copolymerization of styrene with *m*-divinylbenzene. The hydrodynamic radius of the clusters was found to diverge at the gel point. The law of variation of the cluster size with the monomer consumption indicates a critical behavior of the system.

Introduction

Gelation mechanisms have been apprehended over the past 30 years through the fundamental theory introduced by Flory[1-3] and Stockmayer[4,5] or, more recently, through the cascade model developed by Gordon and co-workers.[6-10] These theories allow one to predict for an irreversible gelation both the gel point and the evolution of some structural characteristics of the branched aggregates when the gel point is approached (from both the pregel and postgel sides). As a matter of fact, experience on *f*-functional random polycondensations has given strong support to the Flory–Stockmayer model. More specifically, both the gel point and the increase in the weight-average molecular weight with the extent of the reaction were found to be in satisfactory agreement with the theoretical predictions.[1,11] However, the Flory–Stockmayer model neglects excluded volume effects, steric hindrance, and cyclic bonds. The latter effect, which is known from the very early works to delay the gel point,[1,11] has given rise to a large number of studies.[12,23] Recently, percolation models have been applied to polymer gelling systems. As in the classical mean field models, the properties are defined by only one parameter, the conversion factor p, defined as the ratio of the actual number of bonds between monomers at a given time to the maximally possible number of such bonds. In the bond percolation model, which is the most widely used, the monomers occupy all the sites of a lattice, and between two nearest neighbors of lattice sites a bond is formed randomly with probability p. A cluster is defined as a group of lattice sites connected directly or indirectly by bonds. The infinite cluster that appears for p larger than the percolation threshold p_c is identified with the gel. Such a model takes into account excluded volume, cyclization, and possibly solvent effects.[24-28] It does not predict the gel point, as the p_c value depends on the choice of the lattice, but, on the other hand, it allows for a variation of p_c with the polymer volume fraction for gelations performed in the presence of a solvent.[24-28] However, the most important feature of the percolation models is that they predict critical exponents that differ drastically from those of the classical theories. As for the critical phenomena, the percolation model should apply only in the vicinity of the gel point, so that one expects to observe a crossover from classical to percolation behavior as p approaches to p_c. Up to now, there has been no clear experimental evidence for such a crossover but one must underline the paucity of experimental data (and there are far more theoretical papers

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