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Studies on Phosphorus-Containing Polymers. V. Ring-Opening Polymerization of Tetrahydrofuran Catalyzed by Linear Phosphonitrilic Chloride

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Studies on Phosphorus-Containing Polymers. V. Ring-Opening Polymerization of Tetrahydrofuran Catalyzed by Linear Phosphonitrilic Chloride

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ABSTRACT

It was found that linear phosphonitrilic chloride could be used as a catalyst for ring-opening polymerization of tetrahydrofuran. Bulk polymerizations were carried out in a nitrogen atmosphere. After termination of polymerization, the reaction mixture was poured into water, thereby decomposing the catalyst. The product was dissolved in benzene and then subjected to lyophilization. The polymerization of tetrahydrofuran in the presence of linear phosphonitrilic chloride was found to be an equilibrium and a "living" polymerization. The polymerization product includes little phosphorus, and its infrared absorption spectrum agrees well with that of the polymer obtained with PF_5 catalyst. The results of the polymerization using epichlorohydrin as a promoter show that the number of active sites in the molecule of linear phosphonitrilic chloride is considerably smaller. Consequently

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it is conceivable that the catalytic activity of the linear phosphonitrilic chloride is attributed to its terminal $\sim\sim\text{P}^+\text{Cl}_3\text{PCl}_6^-$ structure. Furthermore we presume that the polymerization of tetrahydrofuran in the presence of this catalyst proceeds through a cationic ring-opening mechanism.

INTRODUCTION

Such phosphorus compounds as phosphorus pentafluoride [1-3] or phosphorus oxychloride [4] are known to be useful as catalysts for ring-opening polymerization of tetrahydrofuran (THF). We found that the cationic ring-opening polymerization of THF monomer and with linear phosphonitrilic chloride (LPNC) as catalyst is a "living" one. We further studied the structure of the polymerization product and the polymerization mechanism.

EXPERIMENTAL

Materials

THF was a commercial preparation of the pure chemical mixed with granulated potassium hydroxide. The mixture is allowed to stand more than one week and then distilled twice.

LPNC was a product synthesized according to the method described in the preceding report [5].

Epichlorohydrin (EPC) was a commercial preparation, twice distilled under reduced pressure before use.

Polymerization

A given weight of LPNC is introduced into a test tube with a ground glass stopper, and THF is poured in. After flushing with nitrogen and stoppering tightly, the test tube is placed in a thermostat for a fixed time for settled-state polymerization.

Separation and Purification of the Polymerization Product

After polymerization, the product is poured into water, the catalyst being completely decomposed. The precipitate is collected by filtration and dissolved in benzene. The solution is washed with water and then subjected to lyophilization.

Analysis of the Products

Molecular weight was determined by vapor pressure osmometry (VPO) or the viscosity method after dissolving the sample in benzene. Phosphorus was determined by the Allen method [6, 7] and chlorine by the Volhard method after decomposition with Na_2O_2 in a micro-autoclave. Hydroxy radical was determined by the following procedure [8, 9]: the unreacted phthalic acid was titrated with sodium hydroxide after completion of reaction with phthalic acid anhydride in pyridine.

RESULTS AND DISCUSSION

Results

In the presence of LPNC, ring-opening polymerization of THF is initiated in a very short time. The polymerization system becomes viscous rapidly. In Fig. 1 are shown the results of bulk polymerizations at various temperatures between 0 and 80°C. A relatively long induction period was observed at 0°C. This is probably due to the fact that the propagating species are produced slowly by the reaction between the catalyst and the monomer at a lower temperature. With

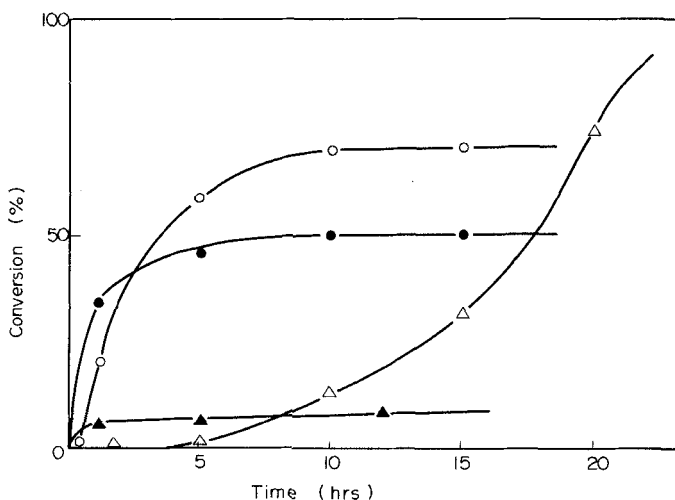


FIG. 1. Relationship between % conversion and polymerization time at various temperatures: (Δ) 0°C; (\circ) 30°C; (\bullet) 50°C; (\blacktriangle) 80°C. THF, 12.2 mole/liter; LPNC, 2.04×10^{-2} mole/liter.

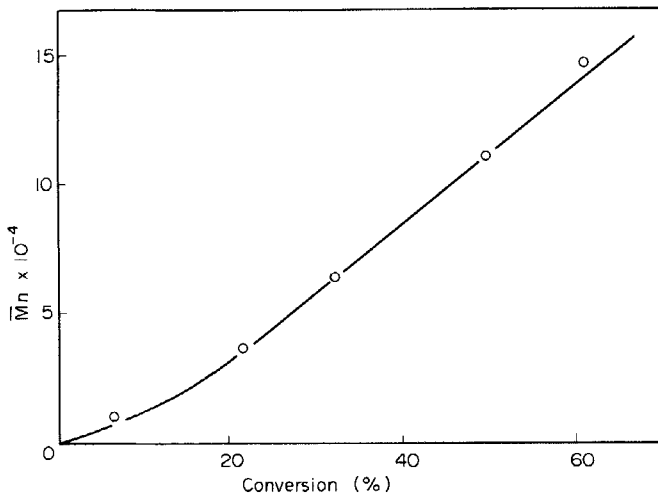


FIG. 2. Relationship between % conversion and molecular weight \bar{M}_n in polymerization at 30°C. THF, 12.2 mole/liter; LPNC, 2.04×10^{-2} mole/liter.

the rise of the temperature of polymerization, the polymerization rate of THF becomes higher and the equilibrium conversion becomes less, because, as is conceivable, the polymerization of THF is reversible [10] and consequently the equilibrium between the produced polymer and the monomer shifts to the monomer side with rising temperature.

In Fig. 2, the relationship between conversion and molecular weight is shown by a straight line except for the initial stage of polymerization. Provided the concentration of propagating species remains constant during polymerization and accordingly the so-called living polymerization occurs without termination, the concentration of propagating species at the portion of straight line in Fig. 2 is calculated at 4.40×10^{-3} mole/liter and the initiation efficiency of LPNC catalyst is 0.213 at 30°C.

Structure of the Polymerization Product

The product of polymerization of THF with LPNC catalyst agrees well in the infrared absorption spectrum with that obtained with conventional catalyst [11], and the absorptions attributable to phosphorus bonds [12], such as P-O-C (in the vicinity of 1000 cm^{-1}) or P=O (1200 cm^{-1}), are very weak.

Phosphorus, chlorine, and hydroxy radicals were determined for the polymerization product having a molecular weight of 3490. The

polymer contains little phosphorus, 0.943 mole of hydroxy radical, and 0.963 mole of chlorine, respectively, in 1 mole polymer. The results obtained on the phosphorus content and the infrared absorption spectrum are in agreement. Accordingly the disappearance of the absorption attributed to the P-N bond (in the vicinity of 1300 cm^{-1}) is due to the decomposition of the catalyst by water. Also, the results indicate that a molecule of the polymer contains one hydroxy group and one chlorine atom. In view of the living polymerization system and the use of water for termination of the polymerization, it is conceivable that the hydroxy radical combines at the end of termination while chlorine combines at the end of initiation. Hence the polymerization product is assumed to have the structure, $\text{Cl}-\text{C}_4\text{H}_8-\left(\text{OC}_4\text{H}_8\right)_n-\text{OH}$.

Kinetics of the Polymerization

The living polymerization system [13] which is reversible consists of two following elementary reactions: initiation and propagation [Eqs. (1) and (2)]:



where P^* is the propagating species, I is initiator, M is monomer, and k_i , k_p , and k_{-p} are the rate constants of initiation, propagation, and depropagation, respectively.

In the polymerization system with LPNC catalyst, the rate of initiation is substantially greater than that of the propagation reaction, so that the concentration of the propagating species [P^*] may be regarded as constant except for the very early stage of polymerization. This is supported by the results given in Fig. 2. From the propagation reaction equation (2), we can obtain Eq. (3) for the polymerization:

$$-d[\text{M}]/dt = k_p[\text{P}^*][\text{M}] - k_{-p}[\text{P}^*] \quad (3)$$

In the equilibrium state, the rates of polymerization and depolymerization are equal to each other; hence

$$k_p[\text{P}^*][\text{M}]_e = k_{-p}[\text{P}^*]_e/k_p = [\text{M}]_e \quad (4)$$

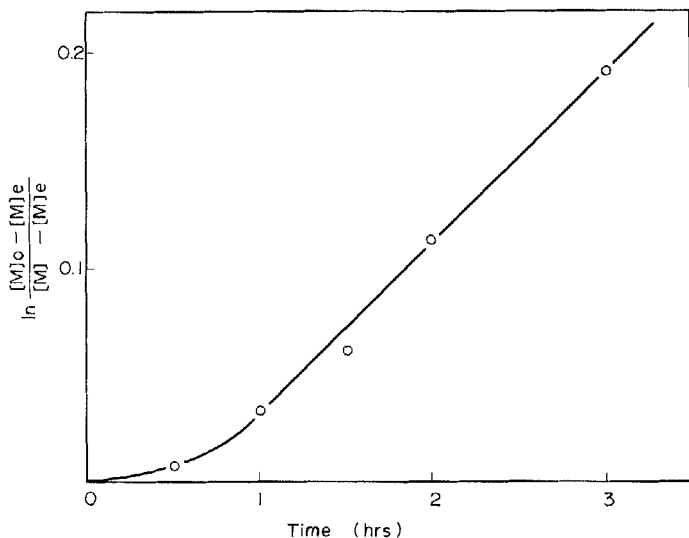


FIG. 3. Relationship between time of polymerization and monomer concentration. $[P^*]$, 4.40×10^{-3} mole/liter; temperature of polymerization, 30°C .

Applying Eq. (4) to Eq. (3), we obtain Eq. (5)

$$-d[M]/dt = k_p [P^*] ([M] - [M]_e) \quad (5)$$

By integrating Eq. (5), Eq. (6) is obtained:

$$\ln \left(\frac{[M]_0 - [M]_e}{[M] - [M]_e} \right) = k_p [P^*] t \quad (6)$$

where $[M]_0$ and $[M]_e$ are the initial and equilibrium monomer concentrations, respectively.

Between the left-hand side of Eq. (6) and the time t , as shown in Fig. 3, there exists a good linear relationship except for the early stage of polymerization. This substantiates the claim that the polymerization system is shown by Eq. (6) and that the above-mentioned assumption is correct.

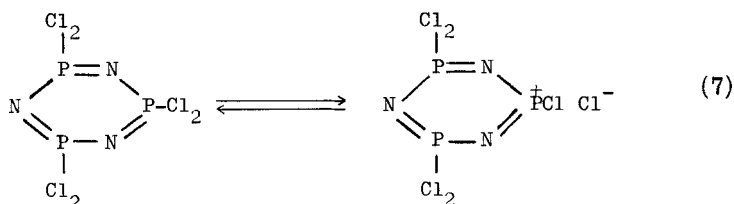
$[P^*]$ was 4.40×10^{-3} mole/liter at 30°C , as described above. From Eq. (6), k_p was calculated as $k_p = 4.21 \times 10^{-2}$ liter/mole-sec.

This value agrees approximately with that obtained with a different catalyst system [4].

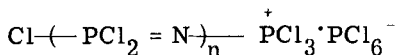
Consideration of the Polymerization Mechanism

Linear phosphonitrilic chlorides (LPNC) have catalytic ability for polymerization while cyclic phosphonitrilic chlorides (CPNC) do not.

CPNC is said [14] to dissociate in the solution as shown in Eq. (7).



On the other hand the LPNC has the structure [5]:



For example, concerning response to nucleophilic reagents, CPNC is considerably inferior to LPNC. Particularly chlorine combined with the ionic terminal phosphorus atom of LPNC is very reactive. Accordingly, in the polymerization of THF with LPNC, the THF first actively attacks the phosphorus atoms to produce oxonium ions which are the propagating species of the polymerization. With CPNC, however, this stage seems to occur only with difficulty.

Differences of LPNC from CPNC consist not only in reactivity but also in that LPNC gives PCl_6^- while Cl^- dissociates from CPNC. Owing to the living polymerization system, the counteranions must be less nucleophilic and consequently stable. Thus Cl^- , because of its enormous nucleophilic property, is not suitable as a counteranion for the living polymerization system. This is probably why no polymerization occurs with CPNC.

Accordingly we carried out the following experiment [15]: LPNC was heated at 250–260°C to convert the PCl_6^- moiety into the Cl^- moiety. With this converted PNC, polymerization of THF was attempted. After allowing the mixture to stand 24 hr at room temperature, the unreacted THF was evaporated. The residue was a brown liquid which was probably the LPNC catalyst. The infrared absorption spectrum showed that no polymer was produced. Therefore, it will be possible to say that the PNC in the absence of PCl_6^- anion cannot function as a catalyst for the polymerization. In this

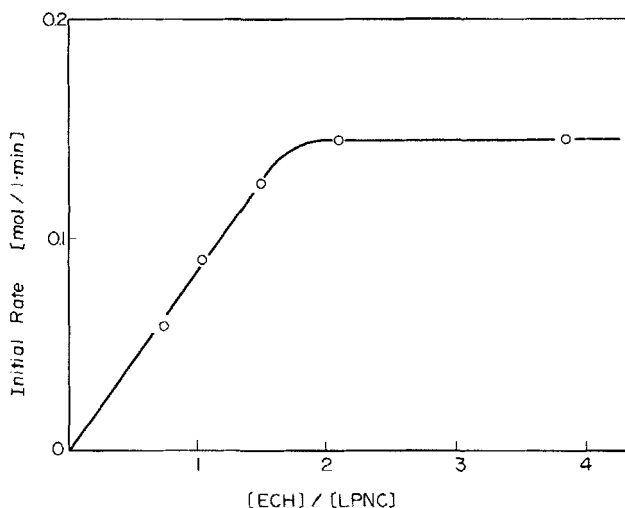


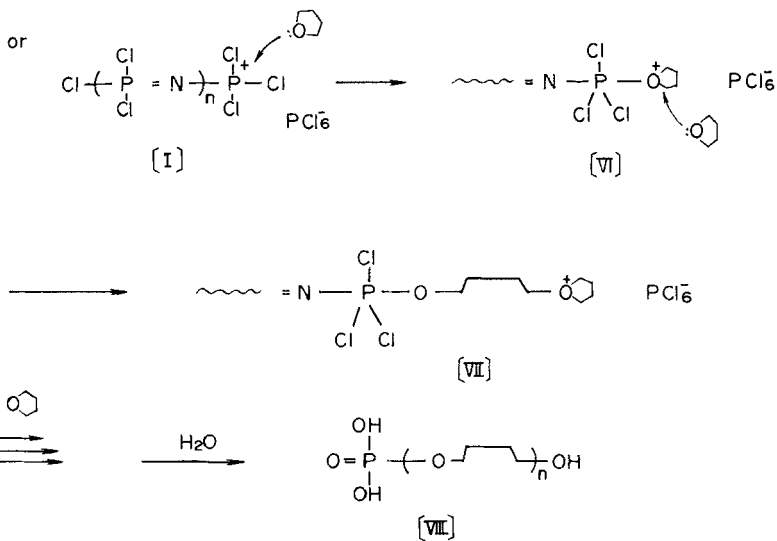
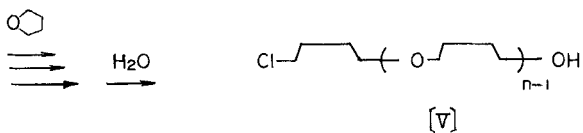
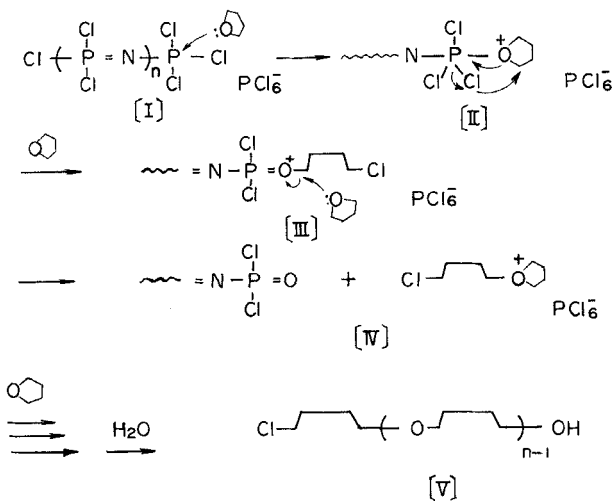
FIG. 4. Influence of epichlorohydrin (ECH) as a promoter for polymerization at 30°C, THF, 12.2 mole/liter; LPNC, 5.10×10^{-3} mole/liter.

way we presumed that the active point of LPNC was the ionic terminal phosphorus atom.

In an attempt to ascertain this, we investigated the effect of epichlorohydrin as promoter. Figure 4 shows the results obtained as the relationship of the polymerization to $[ECH]/PNC$ unit. The initial rate of polymerization increases approximately proportional to the concentration of ECH in the range of small added quantities of ECH and reaches an upper limit value at the addition rate of about two molecules per molecule of LPNC. It remains at the upper limit value, however, even though further addition is made. From this, we can see that LPNC has a very small number of active points in one molecule. These findings support the presumption that the terminal portion has catalytic activity for the polymerization and PCl^- acts as a stable counteranion.

Furthermore we speculated on the polymerization mechanism with LPNC catalyst. First, the lone electron pair of oxygen in the THF attacks the terminal phosphorus atom which is most deficient in electrons (I), thereby producing an oxonium ion (II). Then the highly reactive chlorine combined with the terminal phosphorus atom attacked by oxygen attacks nucleophilically the carbon alpha to the positive oxygen (II). The splitting of the P-Cl bond probably contributes to the fact that the oxonium ion, type III, is more stable than type II, owing to the conjugation of the double bond in III. Consequently the

Mechanism:



oxonium ion is attacked by the THF monomer to become IV. The catalyst separates in this stage, and after that the oxonium salt plays the role of the propagating species. In this way the propagation proceeds as in the regular case (V).

This presumption that the polymerization proceeds through a mechanism of I- II - III - IV → V corresponds well with the above-mentioned

analytical results of the polymerization product. Detection of a very small amount of phosphorus, however, suggests that the polymerization is carried out partially through the mechanism I - VI - VII - VIII.

In any case the function of LPNC as an initiator for cationic polymerization is attributed to the specific property of its terminal structure.

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