

Cationic Ring-Opening Polymerization of 2-Phenyl-1,3,6,2-trioxaphosphocane

Shiro Kobayashi, Mei Yu Huang* and Takeo Saegusa

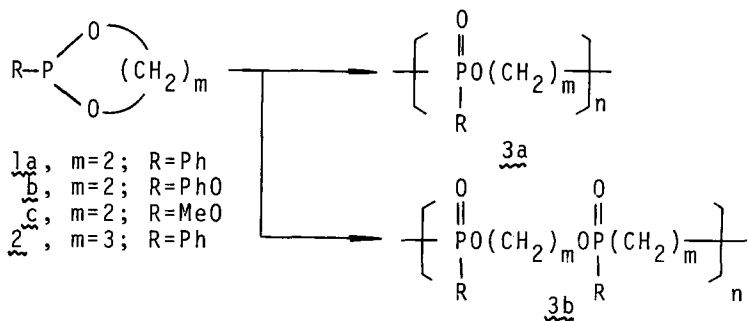
Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Kyoto, 606, Japan

Summary

The ring-opening polymerization of 2-phenyl-1,3,6,2-trioxaphosphocane (4), an eight-membered cyclic phosphonite, has been investigated. Cationic initiators of PhCH_2Cl and MeOTf gave polymers, whereas anionic and radical initiators did not yield polymer. The structure of polymer was examined by IR, ^1H , ^{31}P , and ^{13}C NMR spectroscopy of polymers and elemental analysis as well as the alkaline hydrolysis products. The polymer consisted of two different units, i.e., the major part is the "normal" phosphinate structure 5 and the minor part is the isomerized unit 6 in 7% with PhCH_2Cl initiation and in 34% with MeOTf initiator. The difference in nature of propagating species from these two initiators are discussed in connection with their reactivities.

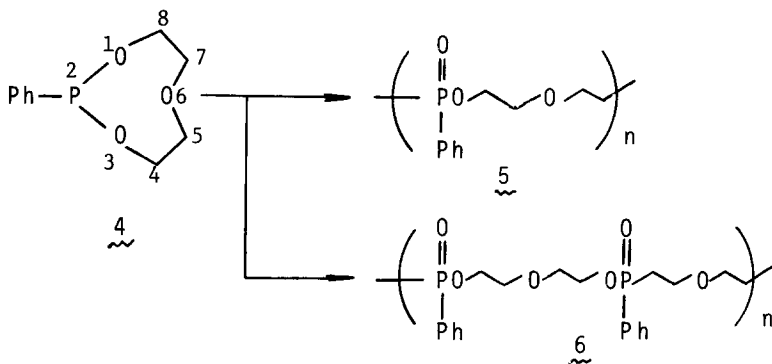
Introduction

Cationic ring-opening polymerizations of cyclic phosphorus(III) compounds were investigated on 1,3,2-dioxaphospholanes (1) (PETROV et al, 1960; MUKAIYAMA et al, 1964; SHIMIDZU et al, 1965 and 1966; HARWOOD and PATEL, 1968; VOGT and AHMAD, 1977) and on 2-phenyl-1,3,2-dioxaphosphorinane (2) (HARWOOD and PATEL, 1968).



* On leave from the Institute of Chemistry, Academia Sinica, Beijing, China

These polymerizations were considered to proceed via the Arbuzov type reactions to give polymers of an expected unit 3a. The structures of the polymers, however, were not simple. It has been pointed out that the polymers contained an expected repeating unit 3a and an isomerized unit 3b, the latter being rather a major part (HARWOOD and PATEL, 1968; VOGT and AHMAD, 1977). The present paper deals with the cationic ring-opening polymerization of 2-phenyl-1,3,6,2-trioxaphosphocane (4), an eight-membered cyclic phosphonite. The product polymer with benzyl chloride catalyst was found to consist of a phosphinate unit 5 and a small amount (7%) of an isomerized unit 6. The extent of isomerization during this polymerization was small. With methyl trifluoromethanesulfonate (MeOTf) catalyst, on the other hand, isomerization took place to an extent of 34%.



Results and Discussion

Ring-Opening Polymerization of 4. Polymerization of 4 was tried with cationic (No 1 and 2), anionic (No 3) and radical (No 4) initiators (TABLE 1). Only cationic initiators of PhCH₂Cl and MeOTf gave polymer and other initiators did not yield any polymeric materials. Polymers are transparent resinous materials (very hygroscopic) soluble in polar organic solvents such as CHCl₃, PhCN and DMF, and insoluble in less polar solvents like diethyl ether and n-hexane and hardly soluble in water.

Structure of Polymer. The ¹H NMR spectrum of polymer sample No 1 (CDCl₃, TMS) showed a multiplet at δ 1.9-2.5 ascribable to methylene protons of PCH₂- (2H), multiplets at δ 3.4-4.2 due to methylene protons of OCH₂ (6H) and a signal at δ 7.3-8.1 assigned to aromatic protons (5H). In the IR spectrum (neat), strong bands at 1210 cm⁻¹ due to P=O and at 1030 cm⁻¹ due to P-O-alkyl group were observed. The ³¹P NMR of the polymer (CDCl₃, with proton-decoupling, δ in ppm with positive sign down-field from external 80% H₃PO₄)

analysis (poly(ethylene glycol) column) of the mother solution of the alkaline hydrolysis mixture, which contained diethylene glycol 9 in 7.6% yield based on the monomeric units in the polymer. The differentiation between 5 and 6 was possible only by ^{31}P NMR of the hydrolysis products of the polymer.

The structure of the polymer sample No 2 was examined in the same way. The ^{31}P NMR of the polymer showed only one peak at +42.5 ppm in CDCl_3 in this case, too. Then, the alkaline hydrolysis products exhibited two peaks at +30.3 and +30.1 ppm in a ratio of 66% : 34%. The GLC analysis of the hydrolysis mixture revealed that diethylene glycol 9 was formed in 33.0% yield. These results show that the polymer sample No 2 consists of units 5 (66%) and 6 (34%).

The above results are supported by ^{13}C FT-NMR spectra of the polymer samples No 1 and 2. Figure 1 shows the expanded ^{13}C NMR spectra of the samples No 1 (upper) and No 2 (lower) of the aliphatic carbon

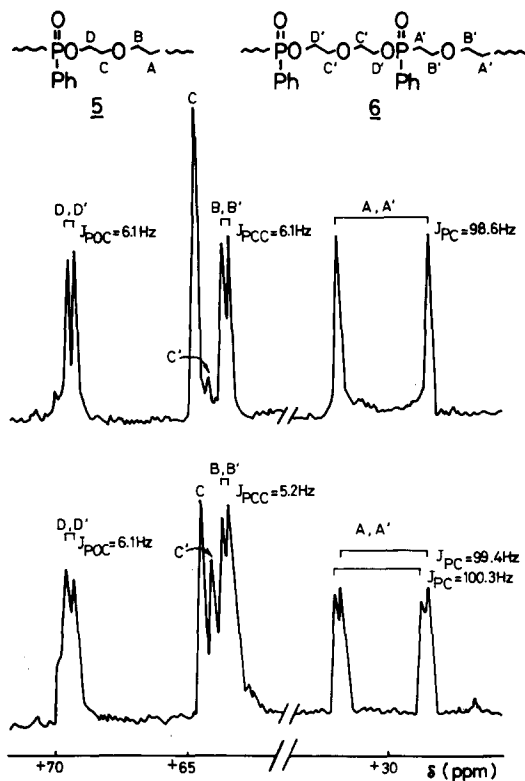
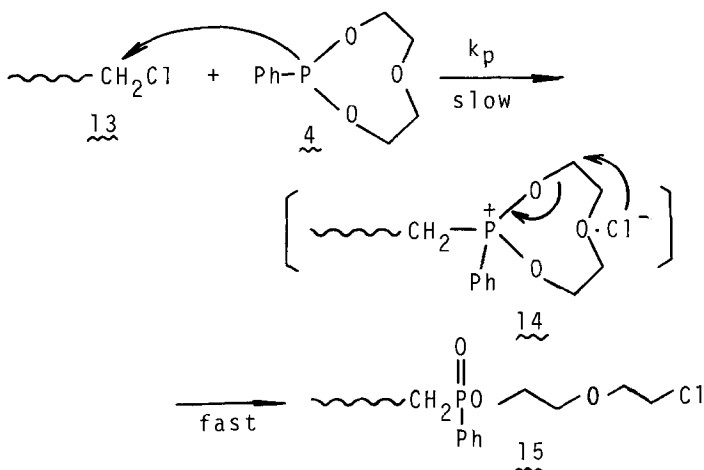


Figure 1. ^{13}C FT-NMR (22.6 MHz) spectra of polymer samples No 1 (upper) and No 2 (lower) in CDCl_3 (with TMS)



Based on the assumption that the propagations are S_N2 reactions of monomer 4 onto cyclic phosphonium propagating species 11 or onto 13 (or 15), the apparent propagating rate constant (k_p) was determined for each case. A preliminary result gave k_p values of 0.72×10^{-4} l/mol·sec for MeOTf at 60°C in PhCN and 2.8×10^{-4} l/mol·sec for PhCH_2Cl at 150°C in PhCN, respectively.

Experimental

Materials. Monomer (4) was prepared by the reaction of phenyldichlorophosphine with diethylene glycol in the presence of triethylamine in benzene, bp $120^\circ\text{C}/0.4$ mm (30% yield). ^{31}P NMR +168.3 ppm (PhCN) in comparison with +168 (C_6D_6) (DUTASTA et al, 1979). Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{O}_3\text{P}$: C, 56.60; H, 6.18; P, 14.60. Found: C, 56.37; H, 6.29; P, 14.33.

Benzonitrile and chloroform solvents and benzyl chloride were purified by distillation under nitrogen. MeOTf was prepared from TfOH and dimethyl sulfate, bp 96 – 98°C . Azobisisobutyronitrile (AIBN) and BuLi in hexane were used without further purification.

Polymerization. A typical run was as follows. In a sealed tube 10 mmol of monomer 4 and 0.33 mmol of PhCH_2Cl were placed in 1.0 ml of PhCN under nitrogen and kept at 130°C for 195 hr. Then, the mixture was poured into a large amount of diethyl ether. The polymer was separated, which was purified by reprecipitation procedure (three times) using CHCl_3 as solvent and diethyl ether as precipitant solvent and dried in vacuo.

Alkaline Hydrolysis of Polymer. Polymer sample No 1 (1.00 g = 4.7 unit mmol) was placed in 1.2 ml of water containing 6.5 mmol of NaOH and kept at 50°C for

30 min. During the reaction the system became homogeneous. Then, the aqueous solution was poured into 30 ml of 1,4-dioxane to precipitate salt materials which were dried in vacuo to give 1.18 g of solid (mp 83-86°C, 4.7 mmol based on the assumption that the salts are consisted of 100% of slat 7). Similarly, polymer sample No 2 was hydrolyzed and salts were obtained quantitatively.

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Received and accepted January 21, 1981