Polymer Bulletin

© Springer-Verlag 1981

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

Shiro Kobayashi, Mei Yu Huang* and Takeo Saegusa

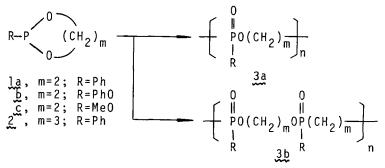
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, 606, Japan

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 PhCH₂Cl 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 PhCH₂Cl 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

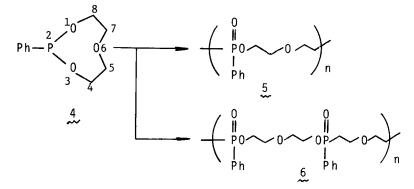
Cationic ring-opening polymerizations of cyclic phosphorus(III) compounds were investigated on 1,3,2dioxaphospholanes (1) (PETROV et al, 1960; MUKAIYAMA et al, 1964; SHIMIDZU et al, 1965 and 1966; HARWOOD and PATEL, 1968; VOGT and AHMAD, 1977) and on 2phenyl-1,3,2-dioxaphosphorinane (2) (HARWOOD and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



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

0170-0839/81/0004/0185/\$01.40

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

<u>Ring-Opening Polymerization of 4</u>. 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 MeOT_f gave polymer and other initiators did²not 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 (CDCI₃, 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)

ТΑ	в	\mathbf{LE}	1
----	---	---------------	---

Polymer Time No Initiator Temp Yield (%) Mol. Wt (°C) (mmol) (hr) 93 2800 PhCH_C1 (0.33)130 195 1 91 2600 2 MeOTf (0.33)60 153 3 BuLi (0.5)90 26 0 (0.5)90 26 0 4 AIBN

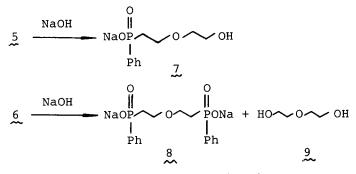
Polymerization of 2-Pheny1-1,3,6,2-trioxaphosphocane (4)^a

а

4=10 mmol in 1.0 ml of PhCN solvent. Determined by vapor pressure osmometry in b CHCl₃ at 35°C.

showed only single peak at +42.5 ppm assignable to a phosphinate unit such as 5. Anal. Calcd for $[C_{10}H_{13}O_{3}P \cdot (H_{2}O)_{0.4}]_n$: C, 54.75; H, 6.34; P, 14.12. Found : C, 54.90; H, 6.35; P, 13.66.

All the above data were taken to indicate the polymer structure of 5. However, more detailed informations as to the polymer structure were obtained by the alkaline hydrolysis of the polymer, which yielded white salt materials quantitatively. The ¹H NMR spectrum of the materials was compatible with the salt 7. The ^{31}P NMR spectrum of the materials in D₂O, however, showed two peaks at +30.3 and +30.1 ppm (the ratio 93:7) which were assigned to salts $\frac{7}{2}$ and $\frac{8}{2}$, respectively.



The above observation was supported by the GLC

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 ³¹P NMR of the hydrolysis products of the polymer.

The structure of the polymer sample No 2 was examined in the same way. The 31p NMR of the polymer showed only one peak at +42.5 ppm in CDC1₃ 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

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

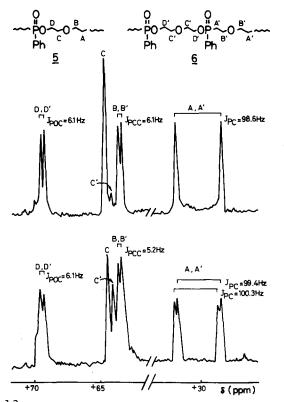
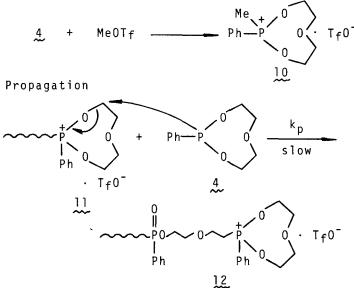


Figure 1. ¹³C FT-NMR (22.6 MHz) spectra of polymer samples No 1 (upper) and No 2 (lower) in CDCl₂ (with TMS)

regions. Possible signal assignments were made and are given in the figure. Signals of the upper spectrum are sharper than those of the lower one due to the less content of unit 6. The most striking difference is the relative ratio of two peaks at +64.5 and 64.0, which are assignable respectively to the methylene carbon C of 5 and C' of 6. Thus, the relative ratio of peaks C and C' reflects the content of units 5 and 6 in the polymer, i.e., peak C' in the lower spectrum is much greater than in the upper one. In the case of sample No 2 containing 34% of 6 (lower spectrum), signals due to A and A' are splitted into two doublets.

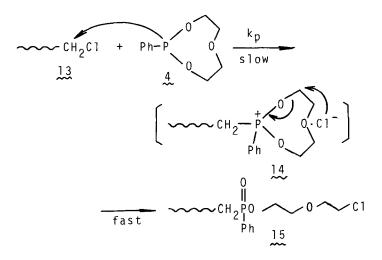
Polymerization Mechanism. With MeOTf catalyst the polymerization course is given as follows.

Initiation



The initiation step of producing 10 was very rapid. The propagating species is a cyclic phosphonium 11, whose opening.by the nucleophilic attack of 4 produces the normal phosphinate unit. Elucidation of the mechanism for the production of the isomerized unit 6 is not clear at the present time.

With PhCH₂Cl initiator, on the other hand, the propagating end is an alkyl chloride species 13 (or 15) which produced via the Arbuzov type ring-opening reaction of the cyclic phosphonium 14 by the nucleophilic attack of Cl⁻. The difference from the case of MeOTf catalyst is due to the difference in nucleophilic reactivity of Cl⁻ from OT_f^- .



Based on the assumption that the propagations are S_N^2 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 kp values of 0.72×10^{-4} 1/mol·sec for MeOTf at 60°C in PhCN and 2.8 × 10⁻⁴ 1/mol·sec for PhCH₂Cl at 150°C in PhCN, respectively.

Experimental

<u>Materials</u>. Monomer (4) was prepared by the reaction of phenyldichlorophosphine with diethylene glycol in the presence of triethylamine in benzene, bp 120°C/0.4 mm (30% yield). 31P NMR +168.3 ppm (PhCN) in comparison with +168 (C_6D_6) (DUTASTA et al, 1979). Anal. Calcd for $C_{10}H_{13}O_3P$: 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. MeOT_f was prepared from $T_{f}OH$ 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 PhCH₂Cl 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 CHCl₃ as solvent and diethyl ether as precipitant solvent and dried <u>in</u> 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.

References

DUTASTA, J.-P. ROBERT, J.-B., and VINCENS, M.: Tetrahedron Lett., 933 (1979). HARWOOD, H. J., and PATEL, N. K.: Macromolecules <u>1</u>, 233 (1968). MUKAIYAMA, T., FUJISAWA, T., TAMURA, Y., and YOKOTA, Y.: J. Org. Chem. <u>29</u>, 2572 (1964). PETROV, K. A., NIFENTEV, E. E., and SOPIKOVA, I. I.: Vysokomol. Soedin. <u>2</u>, 685 (1960). SHIMIDZU, T., HAKOZAKI, T., KAGIYA, T., and FUKUI, K.: J. Polymer Sci. Part B, <u>3</u>, 871 (1965); Bull. Chem. Soc. Jpn. <u>39</u>, 562 (1966). VOGT, W., and AHMAD, N. U.: Makromol. Chem. <u>178</u>, 1711 (1977).

Received and accepted January 21, 1981