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Cationic Ring-Opening Polymerization of Spirophosphorane, 5-Phenyl-1,4,6,9-tetraoxa-5-phosphaspiro[4,4]nonane

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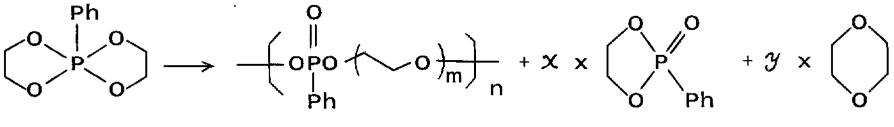
Summary

This paper reports new cationic ring-opening polymerization of a spirophosphorane, 5-phenyl-1,4,6,9-tetraoxa-5-phosphaspiro(4,4)nonane, 1. The polymerization of 1 was induced by cationic initiators such as methyl trifluoromethanesulfonate (MeOTf), $BF_3 \cdot OEt_2$, and $Et_3O^+ \cdot BF_4^-$ to give polymer 2 consisting of two different units, 2a and 2b. During the reaction cyclic phosphonate 3 and 1,4-dioxane were simultaneously produced. The formation of unit 2b is considered to be due mainly to the cationic ring-opening polymerization of 3.

Introduction

Cationic ring-opening polymerizations of cyclic phosphorus (III) compounds have been extensively studied (PETROV et al, 1960 and 1962 ; MUKAIYAMA et al, 1964 ; SHIMIDZU et al, 1965 and 1966 ; HARWOOD and PATEL, 1968 ; VOGT and AHMAD, 1977 ; SINGH, 1979 ; KOBAYASHI et al 1981a and 1981b). On the contrary, the ring-opening polymerization of cyclic phosphoranes (pentacovalent phosphorus species) has not been reported so far. The present paper describes the first instance of the cationic ring-opening polymerization of a new monomer of spirophosphorane, 5-phenyl-1,4,6,9-tetraoxa-5-phosphaspiro(4,4)nonane (1). The product polymer (2) is consisted of two different phosphonate units, 2a and 2b. By-products of a cyclic phosphonate (3)and 1,4-dioxane were formed during the polymerization.



1

2a ; m=1

2b ; m=2

3

Results and Discussion

The cationic polymerization of 1 was carried out by three initiators at 60°C or 90°C in $CHCl_3$ under nitrogen. Polymeric materials were obtained after usual work-up procedures (TABLE 1). Radical (AIBN at 60°C) and anionic initiators ($NaOCH_3$ at 60°C) did not give polymer.

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TABLE 1
Cationic Ring-Opening Polymerization of 1 [a]

No	Initiator	Temp (°C)	Time (hr)	Polymer Yield(%)	Mol.Wt.[b]
1	MeOTf	60	36	44	1050
2	MeOTf	90	11	40	1200
3	$BF_3 \cdot OEt_2$	60	80	21	4100
4	$BF_3 \cdot OEt_2$	90	11	27	2600
5	$Et_3O^+ \cdot BF_4^-$	60	102	36	1500

a) (1)=3.0 mmol and (initiator)=2 mol% for 1 in 2.0 ml of $CHCl_3$ under nitrogen, CH_2Cl_2 being used as solvent for No 5.
b) Determined by vapor pressure osmometry in $CHCl_3$ at 35°C.

The polymer structure was determined by ^1H and ^{31}P NMR as well as IR spectroscopy and by analysis of the hydrolysis products of the polymer. The ^1H NMR of polymer in $CDCl_3$ (sample No 1 in TABLE 1) showed three kinds of signals; a signal at δ7.0-8.1 due to phenyl protons (5H), a broad singlet at δ3.7-4.4 assignable to methylene protons of $P(O)OCH_2$(4H), and a broad singlet at δ3.1-3.7 ascribed to methylene protons of CH_2OCH_2(1.1H). From these peak areas, the ratio of the units 2a to 2b was calculated as 27:73. The ^{31}P NMR of the polymer (in $CDCl_3$) showed only a single peak at +19.2 ppm (lower field from external H_3PO_4 standard), which was reasonably assigned to a phosphonate structure 2. The IR spectrum of the polymer showed a characteristic band of $\nu_{P=O}$ at 1240 cm^{-1}.

The structure of the product polymer was examined also by the analysis of its hydrolysis, which was carried out in aqueous NaOH at 40°C for 1 hr. Then, the reaction mixture was neutralized with aqueous HCl solution. The GLC analysis of the mixture revealed that ethylene glycol and diethylene glycol were formed in a molar ratio of 71:29. No other products of alcohol have not been detected. This result indicates the ratio of the units of 2a:2b = 29:71, which is very close to that obtained by ^1H NMR method. TABLE 2 summarizes the results of polymer samples No 1, 3 and 5.

TABLE 2
Unit Contents of Polymers (2)

Sample No	From ^1H NMR		From Hydrolysis	
	2a(%)	2b(%)	2a(%)	2b(%)
1	27	73	29	71
3	38	62	38	62
5	28	72	—	—

In order to elucidate the reaction course, by-products in the diethyl ether layer (non-solvent for the reprecipitation) were examined. Two by-products, cyclic phosphonate 3 (19% yield based on 1 analyzed by ^{31}P NMR) and of 1,4-dioxane (25% molar yield for 1 analyzed by GLC), were found. The formation of one molecule of 1,4-dioxane is expected to be accompanied by the production of two melecules of 3, and therefore the deficit part of 3 (25 x 2 - 19 = 31%) is assumed to have been consumed by cationic ring-opening polymerization.

Althouth the polymerization of various cyclic phosphonates was once reported (KORSHAK et al, 1957), the cationic ring-opening polymerization of 3 was examined in the present study (TABLE 3).

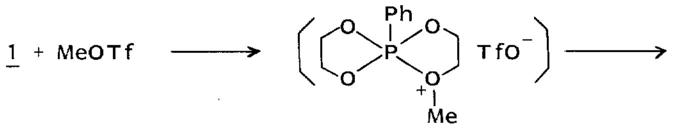
TABLE 3
Cationic Ring-Opening Polymerization of 3 [a]

No	Initiator	Polymer Yield(%)	Mol.Wt.[b]
6	MeOTf	45	1020
7	$BF_3 \cdot OEt_2$	22	1260

a) 3.0 mmol of 3 in 2.0 ml of $CHCl_3$ in the presence of 2 mol % initiator for 3 at 60°C for 40 hr.
b) Determined by vapor pressure osmometry in $CHCl_3$ at 35°C.

The polymer structure was determined as the unit 2b by ^1H and ^{31}P NMR and IR spectra. The ^1H NMR of the polymer (sample No 7, in $CDCl_3$) showed only two signals at δ 7.0-8.1 assigned to phenyl protons (5H) and at δ 3.7-4.4 due to methylene protons of $P(O)OCH_2$(4H). The ^{31}P NMR of the polymer ($CDCl_3$) showed a singlet at +19.2 ppm. The IR spectrum was very similar to that of the polymer sample No 1.

Polymerization Mechanism. Based on the above observations the following reaction courses are considered with MeOTf initiator. 1 and MeOTf first form an intermediate oxonium 4 which rearranges to phosphonium 5. Under the reaction conditions at temperature above 60°C 5 is not stable and the Arbuzov type reaction take place in two paths; path A to produce a phosphonate-triflate 6 which is a reaction mode to lead to unit 2a and path B to produce 3 and ß-methoxyethyl triflate 7.



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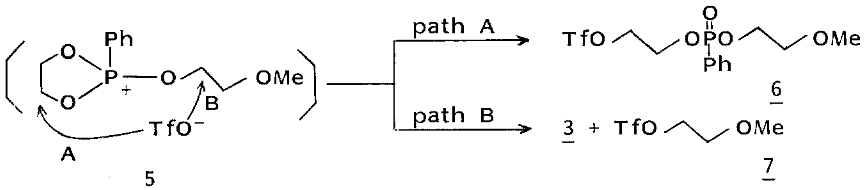

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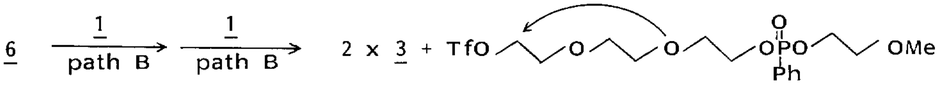

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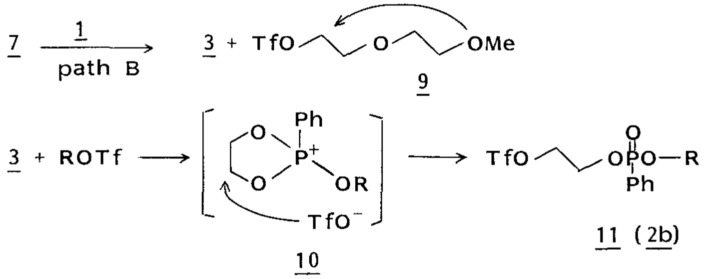

Triflate species, 6 and 7 for example, propagate by reacting with 1 via path A to form unit 2a or via path B. During these propagations in which triflates like $TfO(CH_2CH_2O)_nR$ ($n \geq 2$) having an oxygen atom capable of back-biting as exemplified by 8 and 9 are formed, back-biting reaction takes place predominantly to produce 1,4-dioxane (KOBAYASHI et al, 1975 and 1979). This explains why the alkaline hydrolysis produced only ethylene and diethylene glycols and not the higher ethylene glycols. The cationic ring-opening polymerization of 3 can be explained by the reaction with a propagating triflates, ROTf, to form an intermediate phosphonium 10 and to give 11 of unit 2b.

Experimental

Materials. Monomer 1 was obtained by the reaction of 2-phenyl-1,3,2-dioxaphospholane with ethylene glycol (MALAVAUD et al, 1975; BONE and TRIPPETT, 1976); mp 132–134°C in a capillary under N_2; ^{31}P NMR ($CHCl_3$) −19.2 ppm. Cyclic phosphonate 3 was prepared by the oxidation of 2-phenyl-1,3,2-dioxaphospholane in benzene with bubbling oxygen gas; bp 150°C (0.3mmHg); ^{31}P NMR ($CHCl_3$) + 36.7 ppm. MeOTf was prepared by the reaction of trifluoromethanesulfonic acid with dimethyl sulfate, bp 96–99°C. The oxonium salt, $Et_3O^+ \cdot BF_4^-$ was obtained by the Meerwein's method. All solvents and $BF_3 \cdot OEt_2$ were purified by distillation under nitrogen.

Polymerization. A typical run (No 1) was as follows. Into a tube under nitrogen 3.0 mmol of 1 and 0.06 mmol of MeOTf were placed in 2.0 ml of $CHCl_3$. The tube was sealed and kept at 60°C for 36 hr. The tube was opened and 2.0 ml of $CHCl_3$ was added to the reaction mixture. Then, the mixture was poured into 50 ml of diethyl ether to precipitate the polymeric materials. The precipitation procedure was repeated twice to give 0.30 g (44%) of paste like materials after drying in vacuo.

Alkaline Hydrolysis of Polymer. In a 0.5 ml of 0.2N-NaOH solution 10 mg of polymer sample was placed and the system was kept at 40°C for 1 hr. Then, the reaction mixture was neutralized with 0.5N-HCl. The GLC analysis was performed after 1.0 ml of MeOH containing methyl n-nonanoate as an internal standard was added to the mixture.

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