Polymerization via Zwitterion. 26. Thermal Polymerization of a Spiro Thiophosphorane

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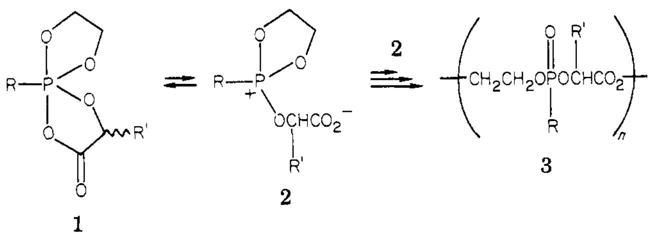
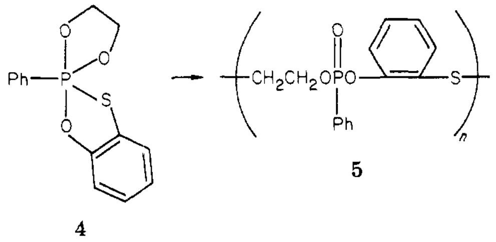
Recently we have disclosed a new thermal polymerization of spiro acyloxyphosphorane 1 to give polyphosphate 3 involving zwitterion 2 as a reaction intermediate.[1,2] The presence of the P-OC(O) group in 1 facilitates the equilibrium between 1 and 2 due to the polarizable P-O bond under polymerization conditions of higher temperatures and hence 1 showed high polymerizability as the monomer. The present paper describes the ring-opening polymerization of a new spiro phosphorane containing sulfur atom 4. The polymerization took place thermally without added initiator to yield polyphosphonate 5.





Results and Discussion

Solid monomer 4 (252 mg) was heated at 170 °C in a sealed tube under nitrogen. The monomer melted and gradually became viscous. After 76 h the reaction product was dissolved in $CHCl_3$ and poured into an excess amount of diethyl ether. A powdery material was obtained in 55.6% yield (140 mg). The molecular weight of the polymer was 3600 by vapor pressure osmometry.

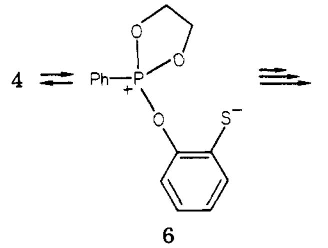
The structure of the polymer was determined by ^1H and ^{31}P NMR and IR spectroscopy as well as elemental analysis. The ^1H NMR spectrum showed broad multiplets at δ 6.8–8.3 due to aromatic protons (9 H), a broad signal at 3.9–4.6 assignable to OCH_2 (2 H), and a signal at 2.7–3.2 due to SCH_2 (2 H). The ^{31}P NMR spectrum of the polymer showed only one signal at δ +15.0,[3] which is reasonably assigned to a phosphonate structure.[4] In the IR spectrum, three characteristic absorptions are seen at 1250 cm^{-1} ($\nu_{P=O}$), at 1210 cm^{-1} (a stretching band of the P-O-aryl group), and at 1030 cm^{-1} (a stretching band of the P-O-alkyl group). Anal. Calcd for $(C_{14}H_{13}O_3PS)_n$: C, 57.53; H, 4.48; P, 10.60. Found: C, 57.52; H, 4.51; P, 10.15. All of the above data are taken to indicate the polymer structure of polyphosphonate 5. Table I summarizes the results of thermal polymerization of 4 under various conditions. The polymerization required higher reaction temperatures of 150 and 170 °C. The polymerization did not take place at 100 °C, a slightly higher temperature than the melting point of monomer 4.

Table I
Thermal Polymerization of Spiro Thiophosphorane 4

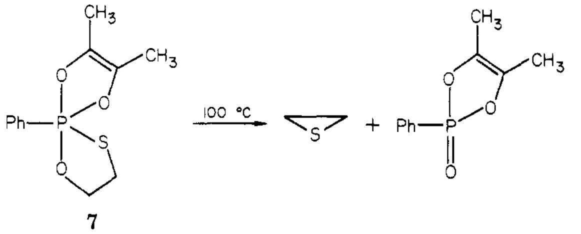
amount of feed monomer 4, mg	reaction temp, °C	reaction time, h	polymer yield mg	polymer yield %	mol wt[c]
252[a]	170	76	140	55.6	3600
715[b]	170	30	152	21.3	2500
491[a]	150	76	387	78.8	2700
357[a]	100	100	0	0	

[a] Bulk polymerization. [b] In 1.0 mL of PhCN. [c] Measured by vapor pressure osmometry in $CHCl_3$ at 35 °C.

A polymerization mechanism is postulated, involving a zwitterion intermediate 6 derived from 4. The generation of 6 is the most important factor for the occurrence of the polymerization. The phosphorus–sulfur bond of phosphorane 4 is more reactive than the phosphorus–oxygen bond[5] and enables the scission of the P–S bond to generate 6. No reaction was observed with the O analogue of 4 even above 170 °C. The P–S bond scission, however, requires more activation energy than the phosphorus–acyloxy bond of 1, and hence higher temperatures are necessary for the polymerization of 4 than for that of 1.[1] After the generation of the key intermediate 6, which is in equilibrium with 4, the polymerization proceeds through the intermolecular reactions between the zwitterions.[2]



The following reaction is to be referred to as a study relevant to the present polymerization. Spiro thiophosphorane 7 did not undergo the ring-opening polymerization on heating but readily gave ethylene sulfide and cyclic phosphonate.[6] Monomer 4 consisting of the *o*-hydroxybenzenethiol moiety does not allow the formation of a three-membered sulfide and cyclic phosphonate and hence gave linear polymer 5.



Experimental Section

Materials. Benzonitrile was purified as previously reported.[1] 2-Phenyl-1,3,2-dioxaphospholane was prepared by the reaction of phenyldichlorophosphine with ethylene glycol in the presence of triethylamine in benzene;[7] bp 58–59 °C (0.2 mm) (lit.[7] bp 79–80 °C (0.8 mm)). *o*-Hydroxybenzenethiol was prepared according to the reported procedure,[8] i.e., *o*-aminophenol was diazotized and the resulting *o*-hydroxybenzenediazonium was reacted with potassium xanthogenate followed by alkaline hydrolysis to give *o*-hydroxybenzenethiol: bp 91–92 °C (13 mm); ^1H NMR ($CDCl_3$) δ 2.98 (s, SH, 1 H), 6.30 (s, OH, 1 H), 6.48–7.40 (m, aromatic protons, 4 H). Diisopropylchloroamine was obtained according to the procedure reported.[9] Diisopropylamine should be handled carefully, since *N*-chloroamine is generally unstable toward light and heat.

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Preparation of 2,3-Benzo-5-phenyl-1,6,9-trioxa-4-thia-5-phospha(V)spiro[4.4]nona-2-ene (4).[10] Into an equimolar amount of *o*-hydroxybenzenethiol and 2-phenyl-1,3,2-dioxaphospholane (30 mmol each) in 100 mL of dry diethyl ether was dropwise added 30 mmol of diisopropylchloroamine in 50 mL of diethyl ether at −78 °C with stirring. On the addition, white precipitate was formed. After the addition the reaction system was allowed to warm to room temperature and stirred for 3 h. The solid salt was separated by filtration and washed with 30 mL of dry benzene. The filtrate was combined with benzene washing and solvents were evaporated in vacuo to give an oily residue. *n*-Hexane (50 mL) was added to the residue, and the mixture was stirred to form a white solid, which was separated. After recrystallization from a chloroform/diethyl ether mixed solvent, 4 was obtained in 70% yield: mp 96–97 °C (lit.[9] 96–97 °C); ^{1}H NMR ($CDCl_3$) δ 3.5–4.5 (m, OCH_2, 4 H), 6.6–8.2 (m, aromatic protons, 9 H); ^{31}P NMR (CH_3CN) δ +3.8.[3] Anal. Calcd for $C_{14}H_{13}O_3PS$: C, 57.53; H, 4.48; P, 10.60. Found: C, 57.61; H, 4.64; P, 10.09.

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References and Notes

(1) T. Saegusa, T. Yokoyama, Y. Kimura, and S. Kobayashi, *Macromolecules*, **9**, 724 (1976).
(2) (a) T. Saegusa and S. Kobayashi, *J. Macromol. Sci., Chem.*, **13**, 295 (1979); (b) T. Saegusa, *Angew. Chem., Int. Ed. Engl.*, **16**, 826 (1977).
(3) The positive sign means the lower magnetic field relative to external standard of 80% H_3PO_4.
(4) T. Saegusa, T. Kobayashi, T.-Y. Chow, and S. Kobayashi, *Macromolecules*, **12**, 533 (1979).
(5) T. Mukaiyama, R. Matsueda, and M. Suzuki, *Tetrahedron Lett.*, 1901 (1970).
(6) A. P. Stewart and S. Trippett, *J. Chem. Soc., Chem. Commun.*, 1297 (1970).
(7) T. Mukaiyama, T. Fujisawa, Y. Tamura, and Y. Yokota, *J. Org. Chem.*, **29**, 2572 (1964).
(8) (a) H. F. Wilson and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 5200 (1950); (b) D. Greenwood and H. A. Stevenson, *J. Chem. Soc.*, 1514 (1953).
(9) H. Bock and K. L. Kompa, *Chem. Ber.*, **99**, 1347 (1966).
(10) J. I. G. Cadogan, N. J. Stewart, and N. J. Tweddle, *J. Chem. Soc., Chem. Commun.*, 191 (1979).

Random-Coil Configurations of the Polyformals [$CH_2O(CH_2)_yO$]. 5. Dipole Moments, Unperturbed Dimensions, Optical Anisotropies, and Molar Kerr Constants for 1,3-Dioxolane Polymers Containing Structural Irregularities

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Experimental values of the dipole moments of poly(1,3-dioxolane) were recently reported[2] and successfully interpreted[2] in terms of the rotational isomeric state theory.[3] The theoretical values of the dipole moments had been calculated assuming all of the repeat units in the chain to be identical. This polymer, however, is generally prepared by ring-opening polymerization of the monomer $\overline{CH_2\text{–}O\text{–}(CH_2)_2O}$.[2,4] Bond scissions occurring exclusively at bonds of the first type shown or exclusively at bonds of the second type would yield the same, perfectly-regular polymer [$CH_2O(CH_2)_2O$]. Scissions occurring at both types of bonds, however, would introduce the irregular sequences CH_2OCH_2O and $(CH_2)_2O(CH_2)_2O$, arising from the presence of the two different repeat units $CH_2O(CH_2)_2O$ and $(CH_2)_2OCH_2O$. The fact that the experimental and theoretical values of the dipole moments were in good agreement[2] thus supported the regular structure for this polymer, but the sensitivity of the dipole moment to the structural irregularities was not known. Also, polymerization may be more complex in the case of other formals,[4-7] particularly those of more complicated structure. Additional calculations could therefore provide valuable guidance in the choice of configuration-dependent properties for characterizing this class of chain molecules.

Previous studies have shown that the dipole moment generally has a sensitivity to structure which is much larger than that shown by the unperturbed dimensions.[8,9] Specific examples are its sensitivity to chemical composition and sequence distribution in chemical copolymers and to stereochemical structure in vinyl polymers. This enhanced sensitivity is due to the fact that skeletal bonds or polymer repeat units can generally vary much more in polarity than they can in length. One would therefore expect the dipole moment (and also the optical anisotropy and the molar Kerr constant) to be particularly sensitive to structure in the case of asymmetric units in which the side chains contribute significantly to the property being measured.[10] This has been found to be the case.[8-16]

It is thus obviously of considerable interest to investigate a wide variety of configuration-dependent properties for polyformals having symmetrically substituted units which can be irregular with regard to the sequence of skeletal atoms and others having unsymmetrically substituted units which can be irregular with regard to stereochemical structure. Of particular interest will be the identification of those properties which should be most sensitive to a particular variation in structure and therefore most promising for experimental investigations. The present study is part of this general program. It focuses on poly(1,3-dioxolane) and how the irregular sequences CH_2OCH_2O and $(CH_2)_2O(CH_2)_2O$ affect the chain's dipole moments, unperturbed dimensions, optical anisotropies, and molar Kerr constants.

Theory

General Features of the Rotational Isomeric State Model. As in the previous study[2] of poly(1,3-dioxolane), skeletal bond angles were assumed to be tetrahedral, and rotational states were located at dihedral angles of 0, 120, and −120°. The two alternative repeat units $CH_2O(CH_2)_2O$ and $(CH_2)_2OCH_2O$ were designated types 1 and 2, respectively. The chains investigated had $n = 200$ skeletal bonds and, in the case of those having structural irregularities, Monte-Carlo methods were used to generate 15 representative chains having Bernoullian placements of the structures 1 and 2.[3] The conformational energies employed were those presented and discussed elsewhere.[2] Standard matrix methods[3,17] were used to generate the values of the statistical properties of interest, at 25 °C.

Dipole Moments. The calculated values of the mean-square dipole moment $\langle \mu^2 \rangle$ were expressed as the dipole moment ratio $\langle \mu^2 \rangle / n\mu_0^2$, where μ_0^2 is the average square of the bond moments. The required bond moments, μ_{CO} and μ_{CC}, were assigned the values 1.07 and 0.00 D, respectively.[2]

Unperturbed Dimensions. The values calculated for the mean-square end-to-end distance pertain only to the chains in the absence of excluded volume interactions and are thus designated as the unperturbed values $\langle r^2 \rangle_0$. These results are expressed as the characteristic ratio $\langle r^2 \rangle_0 / nl^2$,

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