On the other hand, when the sample was prepared by compression molding, the scattering patterns were of two types. One has maximum intensity at particular azimuthal angles $(2n + 1)\pi/4$ (n = 0–3). The other has maximum intensity at $n\pi/2$ (n = 0–3). Using a proper choice of the correlation distance parameter, theoretical calculations were carried out to explain the characteristic azimuthal dependence on the basis of a model associated with orientation disorder of the rodlike lamellae with respect to the spherulitic radius. The calculated pattern became circular with decreasing correlation distance. The calculated results were close to the observed ones with a suitable choice of the parameter R/a. The scattering patterns at various extension ratios were investigated by assuming an affine deformation model of the spherulite. The calculation was restricted to the scattering from a perfect spherulite. The results were rather close to the observed patterns in the case of two kinds of spherulites. That is, the one corresponded to a positive spherulite and the other to a spherulite whose lamellar axes orient in the radial direction and the optical axes orient at 45° to lamellar axis.

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Supplementary Material Available: A list of the coefficients T_i (i = 0–6) in eq 19 (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Presented in part at the 32nd Annual Meeting of Home Economics Science, Japan, Tokyo, Oct 1980.
(2) Cooper, S. L.; Tobolsky, A. T. *J. Appl. Polym. Sci.* **1968**, *10*, 1837.
(3) Kimura, I.; Ishihara, H.; Ono, H.; Yoshihara, N.; Nomura, S.; Kawai, H. *Macromolecules* **1974**, *7*, 355.
(4) Cella, R. J. *J. Polym. Sci., Part C* **1973**, *42*, 727.
(5) Seymour, R. W.; Overton, J. R.; Corley, L. S. *Macromolecules* **1975**, *8*, 331.
(6) Schen, M.; Mehra, U.; Niinomi, M.; Koberstein, J. T.; Cooper, S. L. *J. Appl. Phys.* **1974**, *45*, 4182.
(7) Lilanoitku, A.; West, J. C.; Cooper, S. L. *J. Macromol. Sci., Phys.* **1976**, *B12*, 563.
(8) Matsuo, M.; Sagu, S.; Asai, H. *Polymer* **1969**, *10*, 79.
(9) Inoue, T.; Soen, T.; Kawai, H.; Kukatsu, M.; Kurata, M. *J. Polym. Sci., Part B* **1968**, *6*, 75.
(10) Inoue, T.; Soen, T.; Hashimoto, T.; Kawai, H. *J. Polym. Sci., Part A-2* **1969**, *7*, 1283.
(11) Inoue, T.; Soen, T.; Hashimoto, T.; Kawai, H. *Macromolecules* **1970**, *3*, 87.
(12) Nomura, S.; Kawai, H.; Kimura, I.; Kagiyama, M. *J. Polym. Sci., Part A-2* **1967**, *5*, 479.
(13) Clough, S.; van Aartsen, J. J.; Stein, R. S. *J. Appl. Phys.* **1965**, *36*, 3072.
(14) Stein, R. S.; Chu, W. *J. Polym. Sci., Part A-2* **1970**, *8*, 1137.
(15) Stein, R. S.; Hashimoto, T. *J. Polym. Sci., Part A-2* **1971**, *9*, 517.
(16) Hashimoto, T.; Stein, R. S. *J. Polym. Sci., Part A-2* **1971**, *9*, 1747.
(17) Prud'Homme, R. E.; Yoon, D.; Stein, R. S. *J. Polym. Sci., Part A-2* **1973**, *11*, 1047.
(18) Prud'Homme, R. E.; Stein, R. S. *J. Polym. Sci., Part A-2* **1974**, *12*, 1085.
(19) Stein, R. S.; Stidham, S. N. *J. Appl. Phys.* **1964**, *35*, 42.
(20) Sawatari, C.; Muranaka, T.; Matsuo, M., in preparation.
(21) The coefficients T_i (i = 0–6) in eq 19 are available as supplementary material. See supplementary material paragraph.

Notes

Ring-Opening Polymerization of Spiro(acyloxy)phosphoranes Having a P–H Bond with the Use of a Proton-Trapping Agent

SHIRO KOBAYASHI, TAK YUEN CHOW, and
TAKEO SAEGUSA*

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

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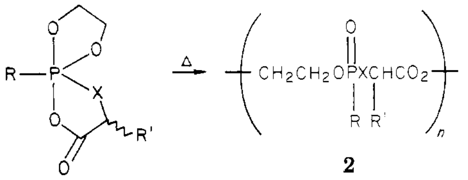
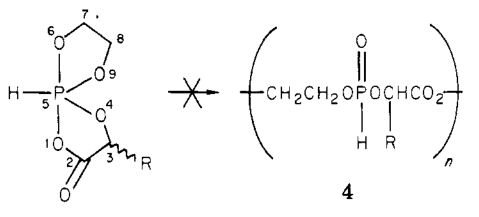
Spiro(acyloxy)phosphoranes (1) are new pentavalent phosphorus species, originally prepared by us. They are reactive monomers and give various types of phosphorus-containing polymers (2).[1,2] Polymerizations of 1 take place by heating, without added initiator.



1, X = O, CH_2

2

Spiro(acyloxy)phosphoranes having a P–H bond (2-oxo-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonanes 3) are known.[3] We examined the polymerizability of 3 in order to obtain polyphosphonates having a P–H bond (4). It turned out, however, that 4 was not formed by simple heating of 3. The present paper reports a novel polymerization of 3 with the aid of the carbonyl compounds benzaldehyde, *p*-benzoquinone, and methyl acrylate. The function of these carbonyl compounds is to accept an acidic hydrogen ("proton-trapping agent").



3

4

Results and Discussion

First, monomers **3a,b** were prepared by a new ester-exchange reaction; i.e., the reaction of 2-phenoxy-1,3,2-dioxaphospholane (5) with α-hydroxy acid **6** quantitatively gave **7** with liberation of phenol. Compound **7** is in equilibrium with **3** as shown by ^{31}P NMR analysis; **3** is a

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Table I
Polymerization of 3 Using Proton-Trapping Agent[a]

no.	3	proton-trapping agent	solvent	temp, °C	time, h	polymer yield, %	polymer structure	polymer mol wt[b]	polymer appearance
1	**3a**	PhCHO	PhCN	130	45	54	**8a**	5000	white powder
2	**3a**	PhCHO	$CHCl_3$	90	60	52	**8a**	3500	white powder
3	**3b**	PhCHO	$CHCl_3$	90	60	68	**8b**	3100	white powder
4	**3a**		PhCN	130	40	67	**9**	4500	brown powder
5	**3a**	MA[c]	PhCN	130	35	43	**10**	2900	paste

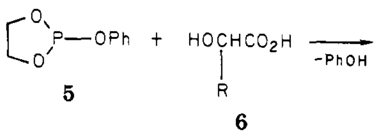
[a] **3** was prepared from **5** and **6** in situ. **3** and the proton-trapping agent (each 3.0 mmol) were dissolved in 1.5 mL of solvent under nitrogen. The mixture was subjected to polymerization. [b] Determined by vapor pressure osmometry in $CHCl_3$ at 35 °C. [c] Methyl acrylate.

Table II
Spectroscopic Data of Polymers

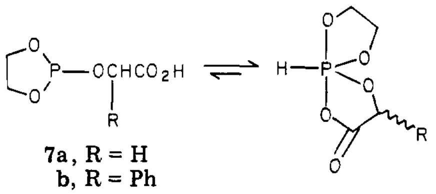
sample no.	IR (neat), cm^{-1}	^1H NMR ($CDCl_3$)[a]	^{31}P NMR[b] ($CDCl_3$)
1	3300 (OH), 1760 (C=O), 1260 (P=O)	3.8-5.2 (m, OCH_2CH_2O, $CH_2C(O)$, CH, 7 H), 7.1-7.7 (m, C_6H_5, 5 H)	+18.9
3	3350 (OH), 1755 (C=O), 1255 (P=O)	3.8-5.2 (m, OCH_2CH_2O, CH, 5 H), 5.7-6.0 (m, OCH, 1 H), 6.8-7.7 (m, C_6H_5, 10 H)	+15.8
4	3250 (OH), 1770 (C=O), 1265 (P=O)	3.8-5.0 (m, OCH_2CH_2O, $CH_2C(O)$, 6 H), 6.8-8.1 (m, C_6H_4, 4 H)	−5.8
5	1755 (C=O), 1260 (P=O)	2.8-3.0 (m, $PCH_2CH_2C(O)$, 4 H), 3.7 (s, CH_3, 3 H), 4.0-5.0 (m, 4 H, OCH_2CH_2O)	+17.8

[a] Chemical shifts relative to Me_4Si. [b] Chemical shifts are negative upfield from external 80% H_3PO_4 standard.

more stable form than **7**. The failure of polymer **4** to form from **3** is probably due to the equilibrium **3** $\rightleftharpoons$ **7**.



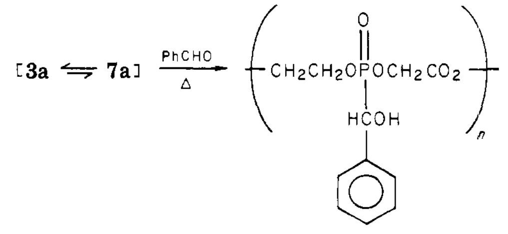
5 **6**



7a, R = H
b, R = Ph

3a, R = H
b, R = Ph

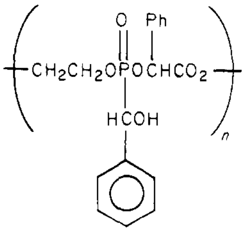
It is well-known that P(III) compounds are very reactive toward various electrophiles. Therefore, the electrophile benzaldehyde was employed to achieve the polymerization of **3a** by modification of the P(III) species **7a** (see Reaction Mechanism). Then, it became possible to produce polymer **8a** (Table I). Polymer **8a** is a white powdery material soluble in polar organic solvents such as $CHCl_3$, CH_3CN, DMF, and PhCN but insoluble in water and in the less polar organic solvents diethyl ether and hexane.



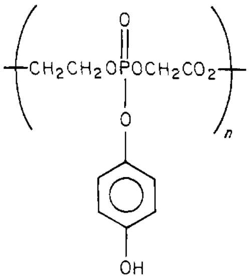
8a

The structure of polymer sample no. 1 was determined to be **8a** on the basis of spectroscopic data (Table II) as well as elemental analysis (Table III).

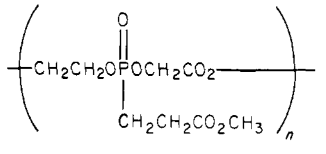
Similarly, **3b** and benzaldehyde gave polymer **8b**. *p*-Benzoquinone and methyl acrylate function as electrophiles, too, and were found to give polymers **9** and **10**, respectively. The **3**:electrophile composition of these polymers is 1:1.



8b



9



$$\left[-CH_2CH_2OP(=O)(CH_2CH_2CO_2CH_3)OCH_2CO_2-\right]_n$$

10

Reaction Mechanism. The reaction of **3a** with benzaldehyde was followed by ^{31}P NMR (Figure 1). First, **3a** was prepared in situ by the reaction of **5** with glycolic acid (**6**, R = H). Figure 1A shows the quantitative production of **3a** having a P-H bond (J_{PH} = 892 Hz centered at −27.0 ppm). Then, benzaldehyde was added to the system, which was kept at 90 °C for 1 h. In the ^{31}P NMR spectrum of the system (Figure 1B) two new peaks appeared in addition to those of **3a**. The peak at +18.9 ppm is due to polymer **8a** and the other peak at −23.8 ppm was assigned

Table III
Analytical Data of Polymers

no.	formula	calcd % C	calcd % H	calcd % P	found % C	found % H	found % P
1	$(C_{11}H_{13}O_6P)_n$	48.54	4.81	11.38	48.58	4.90	11.04
3	$(C_{17}H_{17}O_6P)_n$	58.62	4.92	8.89	58.47	5.02	8.62
4	$(C_{10}H_{11}O_7P)_n$	43.80	4.04	11.30	43.97	3.91	10.94
5	$(C_8H_{13}O_7P)_n$	38.10	5.20	12.28	38.48	5.39	11.97

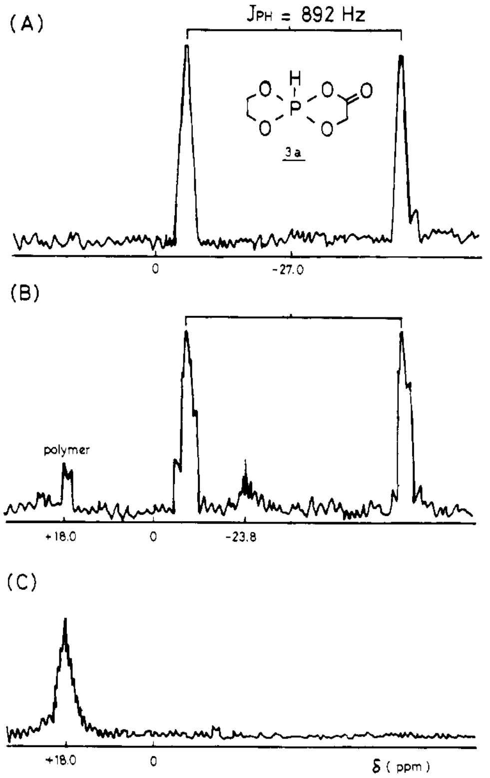
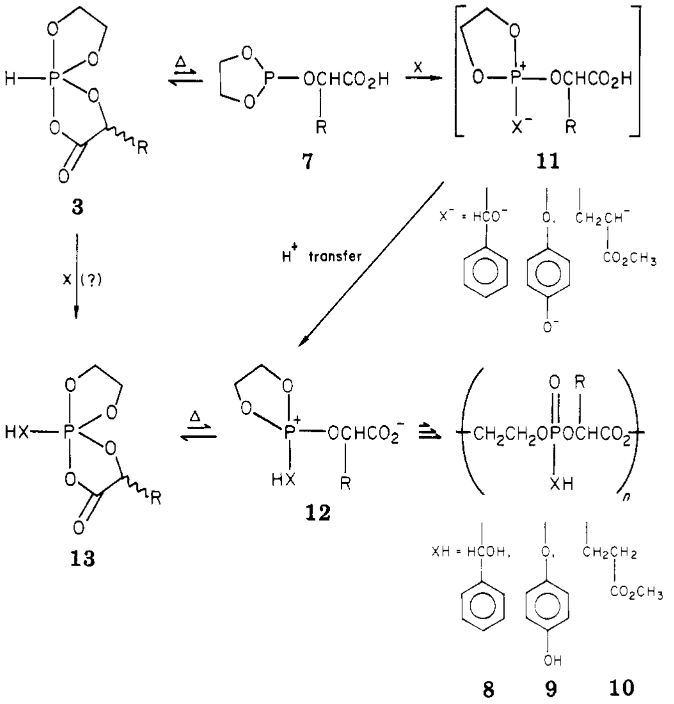


Figure 1. ^{31}P NMR spectra: (A) **5** + glycolic acid; (B) benzaldehyde added to system (A); (C) after polymerization was complete.

Scheme I



to a new spiro(acyloxy)phosphorane, **13**. After further reaction at 90 °C for 18 h only one peak, due to polymer **8a**, was observed (Figure 1C).

From these results a possible reaction course is given in Scheme I. An electrophile X reacts with **7** to give a transient zwitterion **11**. Since **11** has an acidic hydrogen on the carboxyl group, proton transfer takes place to give a more stable phosphonium–carboxylate zwitterion **12**. This species is in equilibrium with spiro(acyloxy)phosphorane **13**, which was actually observed directly by ^{31}P NMR during the reaction as a stable intermediate (Figure 1B). It is also conceivable that the direct reaction between **3** and X gives rise to **13**. Intermediate **12** is the key intermediate of the polymerization responsible for the production of polymers **8–10**.

In order to express the above functions of the electrophile X, we wish to call X a "proton-trapping agent". The reactivity of **3** is modified by X and **3** becomes polymerizable.

Experimental Section

Materials. Glycolic acid and mandelic acid were commercial reagents, which were purified by recrystallization. 2-Phenoxy-1,3,2-dioxaphospholane (**5**) was prepared according to the reported method; bp 65 °C (0.2 mmHg).[4] Solvents were dried over P_2O_5 and fractionally distilled before use under nitrogen.

Polymerization Procedure. A typical run was as follows. At room temperature glycolic acid and **5** (3.0 mmol each) were placed in benzonitrile (1.5 mL) in an ampule under nitrogen and allowed to stand for 0.5 h to give **3** quantitatively. Into this mixture 3.0 mmol of benzaldehyde was added and the ampule was sealed and kept at 130 °C for 45 h. Then, the ampule was opened and the benzonitrile was distilled out in vacuo from the mixture. Chloroform was added to dissolve the polymer and the solution was poured into a large amount of diethyl ether to precipitate the polymer. This reprecipitation procedure was repeated 3 times to separate the polymer, which was then dried in vacuo to give 0.44 g (54% yield) of a white powdery polymeric material (**8a**).

References and Notes

(1) Saegusa, T.; Kobayashi, S. *J. Macromol. Sci., Chem.* **1979**, *A13*, 295.
(2) Kobayshi, S.; Saegusa, T. *Pure Appl. Chem.* **1981**, *53*, 1663.
(3) Munoz, A.; Sunchez, M.; Koenig, M.; Wolf, R. *Bull. Soc. Chim. Fr.* **1974**, 2193.
(4) Ayres, D. C.; Rydon, H. N. *J. Chem. Soc.* **1957**, 1109.

On the Applicability of Raman Scattering to the Study of Reorientational Motions in Polymers

G. D. PATTERSON

Bell Laboratories, Murray Hill, New Jersey 07974.
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A paper appeared in *Macromolecules*[1] which claimed to obtain reorientation times for phenyl groups in polystyrene

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