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Behavior of deoxophostones family as nucleophilic monomers in no-catalyst copolymerization

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Summary

Deoxophostone family(2-phenyl-1,2-oxaphospholane 1a, 2-phenyl-1,2-oxaphosphorinane 1b, and 2-phenyl-1,2-thiaphospholane 1c) copolymerized with acrylic acid without catalyst to produce the corresponding copolymers. The polymerization proceeded via a cyclic acyloxyphosphorane to produce poly(phosphine oxide - ester) 3a(or 3b) from 1a(or 1b) and poly(phosphine oxide - thiolester) 3c from 1c, respectively, with acrylic acid. It is of interest that the copolymer from 1c with acrylic acid was not poly(phosphine sulfide - ester) 4 but 3c. The reactions of 1a or 1b with pyruvic acid or 1,3-propane sultone were also investigated.

Previously, we reported the electrophilic ring-opening polymerization of deoxophostone family (1, 2). In the past decade, on the other hand, the so-called "no-catalyst copolymerizations" have been developed in our laboratory, and many combinations of nucleophilic monomers (M_N) and electrophilic monomers (M_E) have been found out (3). Among them, several cyclic phoshporus(III) compounds(phosphonites and phosphites) are known as typical M_Ns to be copolymerized with several kinds of M_Es such as acrylic derivatives, cyclic disulfide, α-keto acids, and benzoquinone derivatives (3). This paper describes the behaviors of deoxophostone family 1a-1c as nucleophilic monomers in the no-catalyst copolymerization with acrylic acid, pyruvic acid, and 1,3-propane sultone.

Experimental

Materials Deoxophostone family 1a-1c were prepared according to the procedure described in our previous report (4). Acrylic acid, pyruvic acid, and 1,3-propane sultone were purified by distillation. PhCN and

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CH_3CN were distilled over CaH_2. $CDCl_3$ was dried over molecular sieves 3A.

Measurement The following instruments were used; a Hitachi R-20B or R-600 spectrometer for ^{1}H NMR spectrum (60MHz), a Hitachi R-900 spectrometer for ^{31}P{^{1}H}(36.4 MHz) and ^{13}C{^{1}H}(22.6MHz) NMR spectra, a Hitachi 260-50 spectrophotometer for IR spectrum, and a CORONA 117 apparatus for VPO measurement($\overline{Mn}$) in $CHCl_3$ at 40°C.

General procedure for copolymerization Equimolar amounts(0.4-0.5mmol) of 1 and acrylic acid (pyruvic acid or propane sultone) were mixed in 0.2-0.3 ml of PhCN ($CDCl_3$ or CH_3CN) at 0°C under N_2 in a NMR sample tube. After standing overnight at room temperature in a sealed tube, ^{31}P NMR spectroscopy *in situ* indicated generation of an intermediate, whose structure was confirmed by ^{1}H and ^{13}C NMR spectroscopy. Then, the reaction mixture was heated without isolation of the intermediate, and the progress of the reaction was followed by ^{31}P NMR specroscopy. A polymer was isolated by precipitation by pouring into ether, filtered, and dried *in vacuo*.

Spectroscopic data All NMR spectra were measured in $CDCl_3$. The chemical shifts are given in ppm. External standard of ^{31}P NMR spectra is 85% H_3PO_4. In ^{13}C NMR spectra, all signals, which are shown with the coupling constants(J value in Hz) between a carbon atom and a phosphorus atom in the respective parentheses, are doublet, and others without J value are singlet. IR spectra were measured in a $CDCl_3$ or $CHCl_3$ solution. The major peaks are given in cm^{-1}.

2a (5); ^{31}P NMR, -4.4; ^{1}H NMR, 1.33-3.05(m, 8H), 3.10-4.10(m, 2H), and 7.23-8.05(m, 5H).

2b; ^{31}P NMR, -8.0; ^{1}H NMR, 1.2-4.1(m, 12H) and 7.2-8.2(m, 5H); ^{13}C NMR, 22.5(5.1), 25.7(4.0), 27.7(14.3), 30.0(110.9), 30.3(98.7), 65.1(8.1), 128.6(14.2), 131.1(3.1), 132.0(11.2), 132.0(63.0), and 173.6(10.1).

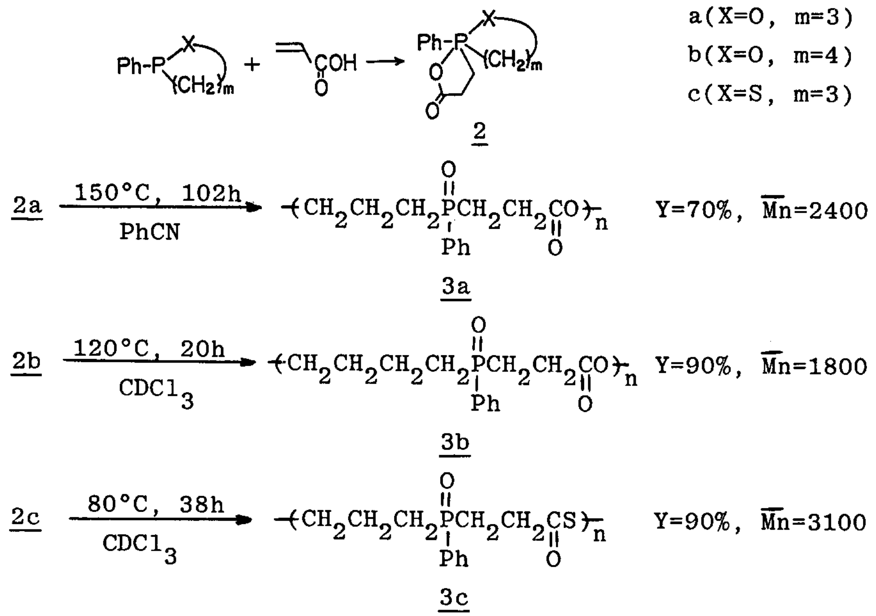
2c; ^{31}P NMR, -7.8; ^{1}H NMR, 1.0-3.7(m, 10H) and 7.1-8.1(m, 5H); ^{13}C NMR, 25.4, 28.7(3.1), 31.2(92.6), 31.7(9.2), 34.1(90.6), 128.5(14.3), 128.8(11.1), 130.3(3.1), 135.9(126.4), and 172.9(10.1).

3a; ^{31}P NMR, +37.8; ^{1}H NMR, 1.2-2.8(b, 8H), 3.8-4.2(b, 2H), and 7.1-8.0 (b, 5H); ^{13}C NMR (ppm), 20.1(1.8), 24.2(68.7), 25.3(1.8), 25.7(60.6), 64.4(14.8), 128.7(11.3), 129.7(8.7), 130.2(95.0), 131.3, and 171.8 (15.9); IR, 1740(νC=O), 1420(δP-Ph), and 1190(νP=O).

3b; ^{31}P NMR, +39.7; ^{1}H NMR, 1.4-3.2(b, 10H), 3.7-4.3(b, 2H), and 7.0-8.5 (b, 5H); ^{13}C NMR, 18.1(2.1), 24.9(68.2), 26.2(2.0), 29.4(69.2), 29.5 (15.3), 64.1, 129.0(11.2), 130.5(9.2), 131.5(66.1), 132.2, and 172.3 (15.2); IR, 1730(νC=O), 1435(δP-Ph), and 1160(νP=O).

3c; ^{31}P NMR, +38.7; ^{1}H NMR, 1.7-3.1(b, 10H) and 7.3-8.0(b, 5H); ^{13}C NMR, 21.8, 25.2(69.2), 29.0(68.1), 29.5(15.2), 35.6(2.0), 129.2(10.2), 130.6(9.1), 130.9(82.4), 132.3, and 197.3(15.2); IR, 1685(νC=O), 1435(δP-Ph), and 1170(νP=O).

Scheme 1



$$\left(\mathrm{CH_2CH_2CH_2}\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle Ph}{\underset{|}{P}}}}\mathrm{CH_2CH_2}\underset{\displaystyle O}{\underset{\|}{C}}\mathrm{O}\right)_n \quad \left(\mathrm{CH_2CH_2CH_2CH_2}\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle Ph}{\underset{|}{P}}}}\mathrm{CH_2CH_2}\underset{\displaystyle O}{\underset{\|}{C}}\mathrm{O}\right)_n \quad \left(\mathrm{CH_2CH_2CH_2}\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle Ph}{\underset{|}{P}}}}\mathrm{CH_2CH_2}\underset{\displaystyle O}{\underset{\|}{C}}\mathrm{S}\right)_n$$

7a (5); ^{31}P NMR, +2.6 and +2.0; ^{1}H NMR, 1.03-2.80(m, 7H, including two doublet peaks (J=7Hz) at 1.35 and 1.58), 3.40-4.25(m, 2H), 4.25-4.90 (m, 1H), and 7.10-8.15(m, 5H).

8a; ^{31}P NMR, +46.7; ^{1}H NMR, 1.0-1.7, 1.7-2.3, 3.8-4.3, 4.7-5.3, and 7.4-7.9

10c; ^{31}P NMR, +80.6; ^{1}H NMR, 1.3-4.3(m, 12H) and 7.0-8.7(m, 5H); ^{13}C NMR, 19.5, 24.8(47.8), 29.5, 30.5(41.7), 39.4, 51.2(17.3), 121.0(75.3), 130.0(12.2), 132.3(11.2), and 134.7.

11; ^{31}P NMR, +40.0; ^{1}H NMR, 1.4-2.8, 2.8-3.8, 3.9-4.4, and 7.2-8.1; ^{13}C NMR, 14.4, 16.5, 21.7, 25.1(52.3), 25.9(70.6), 30.3(61), 46.3, 50.0(10.5), 67.4, 69.9(13.0), 129.0(7.9), 130.4 (6.9), 132.3 (α-position of Ph ring was buried in noises); IR, 1360(ν_{as}S=O), 1180 (νP=O and ν_sS=O).

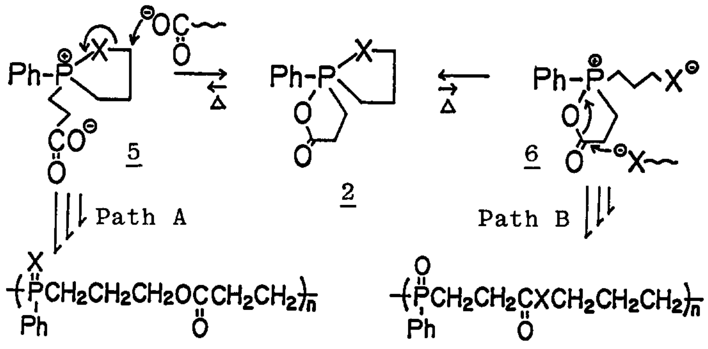
Results and Discussion

Alternating Copolymerization of 1a-1c with acrylic acid

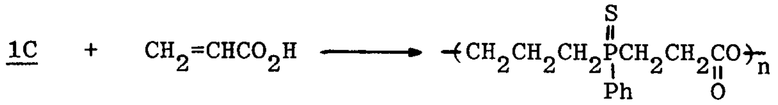
Deoxophostone family 1a-1c reacted with acrylic acid at 0°C to give penta-coordinated acyloxyphosphoranes 2 quantitatively. This was confirmed by in situ ^{31}P NMR spectropcopy. Without isolation, 2a-2c were heated to give the polymers 3a-3c, respectively (Scheme 1) (5).

The order of the polymerizability was 2c>2b>2a. The structures of the obtained copolymers were elucidated by spectroscopic analysis such as IR and ^{1}H, ^{13}C, and ^{31}P NMR (see Experimental). It is noticeable that the

Scheme 2



structure of the copolymer produced from 1c with acrylic acid was not poly(phosphine sufide - ester) 4 but poly(phosphine oxide - thiolester) 3c (6). That is interesting contrast to the homopolymerization of 1c giving poly(phosphine sulfide) (2).



$$\underline{1C} + CH_2{=}CHCO_2H \longrightarrow -\!\!\left(CH_2CH_2CH_2\overset{\overset{S}{\|}}{\underset{\underset{Ph}{|}}{P}}CH_2CH_2\underset{\underset{O}{\|}}{C}O\right)_{\!n}$$

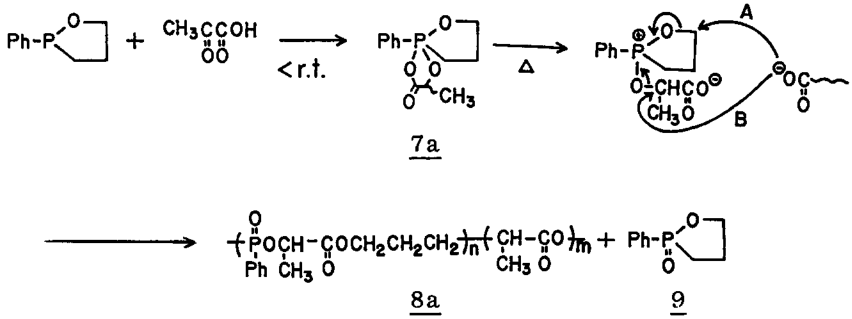
4

The polymerization mechanism of 1a(and 1c) with acrylic acid is shown in Scheme 2(the same mechanism is proposed concerning 1b). There are two possible paths(A and B) for the polymerization of spirophosphorane 2, which is produced below room temperature. Two zwitterionic intermediates 5(path A) and 6(path B) are generated by the thermal dissociation of 2. When X=O(2a), both paths give the same polymer. However, path A is assumed to be predominant because phosphonium carboxylate 5a is much more stable than phosphonium alcoholate 6a. On the other hand, when X=S(2c), path A and path B give the different product, i.e., 4 via path A and 3c via path B. The structure of 3c is taken to indicate exclusiveness of path B. There are two possibilities for the reaction path B. The dissociation of 2c into 6c take place exclusively or the rate of polymerization of a zwitterion 6c is much higher than that of 5c which is present in the reaction system. At the present moment, the mechanism has not been elucidated.

Reaction of 1a and 1c with pyruvic acid

The five-membered deoxophostone 1a reacted with pyruvic acid to give phosphorane 7a quantitatively, whose ^{31}P NMR spectrum *in situ* showed two signals(+4.8 and +5.0 ppm in CH_3CN) having the almost same intensity due to the two stereoisomer (5). Then, 7a was heated at 80°C and the progress of the reaction was followed by ^{31}P NMR spectroscopy, which indicated that 7a produced not only the alternating coplymer(+46.7 ppm) but also phostone 9 (2-phenyl-2-oxo-1,2-phospholane, +57.5 ppm). After 90 hr at 80°C, the

Sheme 3



7a

8a

9

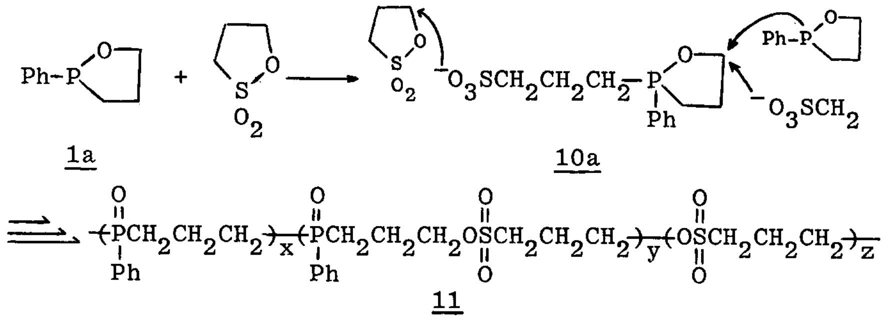
^{31}P NMR spectrum of the reaction mixture showed that the consumption of 7a was about 90%, 83% of which formed 9 and 17% of which formed the alternating units of the copolymer. Pouring the reaction mixture into diethyl ether gave an oligomeric material 8a in 56% yield (based on the polymer structure). The ^{1}H NMR spectrum indicated the lower content of the unit from 1a, which was calculated to be 18% from the integral ratio of the signal due to the phenyl group to that due to the methyne group. The mechanism of this reaction is shown in Scheme 3. The alternating copolymer unit is produced by the attack via A course, and phostone 9 is produced by the attack via B course together with the generation of poly(α-ester) unit. So, deoxophostone 1a partially polymerized with pyruvic acid but mainly deoxygenated the keto-carbonyl of pyruvic acid to produce polyester and phostone 9. Thus, two types of polymerizations, "Redox Copolymerization" (3) and "Deoxy Polymerization" (3) occurred concurrently.

On the other hand, the reaction of 1c with pyruvic acid gave not the expected phosphorane but many unidentified products even at -78°C.

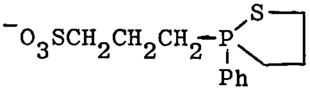
Reaction of 1a and 1c with 1,3-propane sultone

The reaction of 1a with 1,3-propane sultone was also followed by the change of the ^{31}P NMR spectrum. After 24 hr at room temperature in PhCN, the following signals were observed; +108.9 ppm(1a, 77.7%), +100.7 ppm(10a, 11.7%), +55.3 ppm(9, 1%), and 35.3 ppm(a phosphine oxide group, 9.7%). The generation of phosphonium ion 10a, which is the adduct of 1a with 1,3-propane sultone, was observed. The appearance of the last signal(at +35.3 ppm) is taken to indicate that the polymerization had already started even at room temperature. After 44 hr at 40°C, the reaction mixture became heterogenous, to which $CHCl_3$ was added to disolve the insoluble part. Then, the ^{31}P NMR spectra of the reaction mixture showed that the integral proportions of the above four signals changed as follows; 1 (0.7%), 10a (1.4%), 9(2.1%), and a phosphine oxide group (95.7%). The growth of the last signal is indicative of the progress of the polymerzation. The precipitation of the reaction mixture in diethyl ether gave a white powdery materials 11, whose $\overline{Mn}$ was 2350 (VPO), in 42% yield(based on 100% conversion of both monomers). The ^{1}H NMR spectrum indicated that 11 was not a clear alternating copolymer but it contained the units more from 1a

Scheme 4



than from propane sultone. The ratio of the former to the latter was 65:35, calculated from the integral proportions of peaks by the ^{1}H NMR spectrum. In addition, the ^{13}C NMR spectrum indicated that 11 consisted of the alternating unit of 1a and propane sultone, of the homo-diad of 1a, and of the homo-diad of propane sultone. The latter content, however, was low (Scheme 4).



10c

In a separate experiment, the reaction of 1c with propane sultone was carried out at 110°C for 33 hr to give 10c (+80.6 ppm on the ^{31}P NMR spectrum, conversion 89%), whose struture was confirmed by the ^{13}C NMR spectrum *in situ*. However, 10c was too stable to be polymerized. The heating at 150°C for a prolonged time caused a complex reaction.

The present authors dedicate this paper to the late Mr. Ken Mizuno.

References and Notes

1) S. Kobayashi, M. Suzuki, and T. Saegusa, Polym. Bull. 4, 315(1981).
2) S. Kobayashi, M. Suzuki, and T. Saegusa, Macromolecules 19, 462(1986).
3) S. Kobayashi, and T. Saegusa, "Alternating Copolymers" edited by J. M. G. Cowie; Plenum Press: New York, 1985; pp189-238, and references cited therein.
4) S. Kobayashi, M. Suzuki, and T. Saegusa, Bull. Chem. Soc. Jpn. 58, 2153(1985).
5) 2a and 7a are isolable and structurally confirmed; see Y. Narukawa, "Sntheses, Reactions and Polymerizations of Cyclic Acyloxyphosphoranes", PhD thesis(Kyoto University), 1983.
6) The similar reaction has been observed in the polymerization of 2-phenyl-1,3,2-dithiaphospholane with acrylic acid; see ref. 3, p227.

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