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Spontaneous Copolymerizations of 2-Phenyl-1,3,6,2-trioxaphosphocane with α,β-Unsaturated Acids and with α-Keto Acids

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Summary

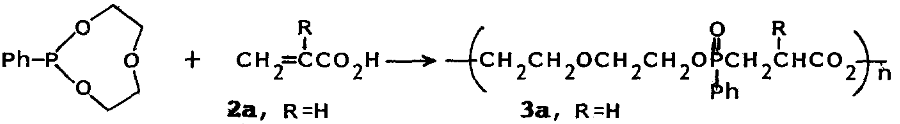
2-Phenyl-1,3,6,2-trioxaphosphocane(**1**), an eight-membered cyclic phosphonite, was copolymerized with α,β-unsaturated acids and with α-keto acids. The copolymerization took place above room temperature without added catalyst. The copolymerizations of **1** with α,β-unsaturated acids of acrylic and methacrylic acids(**2**) afforded polyphosphinates(**3**), alternating copolymers of **1** and **2**. On the other hand, the combinations of **1** with α-keto acids of pyruvic and phenylglyoxylic acids(**5**) gave copolymers(**6**) consisting of alternating unit **6α** and α-ester unit **6β** formed via the deoxygenation of **5** by **1** ("Deoxy-Copolymerization").

Introduction

In the course of studies on the spontaneous copolymerizations proceeding via zwitterion intermediates (reviews:SAEGUSA, 1977; SAEGUSA et al, 1975; SAEGUSA and KOBAYASHI, 1978a, 1978b, and 1979) various phosphorus (III) compounds acted as nucleophilic monomers(M_N) in combination with electrophilic monomers(M_E) such as acrylic acid (SAEGUSA et al, 1976 and 1978c) and α-keto acids (SAEGUSA et al, 1977 and 1978c; KOBAYASHI et al, 1980a and 1980b). The present paper deals with the spontaneous copolymerizations of 2-phenyl-1,3,6,2-trioxaphosphocane(**1**), an eight-membered cyclic phosphonite, as M_N. **1** was combined with four kinds of M_E of acrylic and methacrylic acids(**2**) and of pyruvic and phenylglyoxylic acids (**5**). In connection with this study cationic ring-opening polymerization of **1** has been reported very recently (KOBAYASHI et al, 1981).

Results and Discussion

*Alternating Copolymerization of **1** with Acrylic and Methacrylic Acids (**2**).* The combination of **1** with **2** gave alternating copolymers of polyphosphinate(**3**) (Table 1). Copolymer **3a** (sample No. 2) was a transparent, hygroscopic paste-like material (molecular



1 **2a**, R=H **2b**, R=CH_3 **3a**, R=H **3b**, R=CH_3

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weight=2200) soluble in polar organic solvents such as $CHCl_3$, CH_2Cl_2, and PhCN. The structure of **3a** was determined on the basis of the following data. The ^1H NMR spectrum ($CDCl_3$ with TMS) of the polymer showed multiplet signals at δ 1.9-3.0 due to two methylene protons of $PCH_2CH_2C(O)$ (4H), a signal at δ 3.3-3.8 due to two methylene protons of CH_2OCH_2 (4H), a signal at δ 3.8-4.4 ascribable to $POCH_2$ and CO_2CH_2 (total 4H), and multiplet peaks at δ 7.3-8.1 assignable to aromatic protons (5H). The ^{31}P NMR spectrum of the polymer ($CDCl_3$ with positive values downfield from H_3PO_4 external standard) exhibited a single peak at +44.4 ppm ascribable to a phosphinate structure (**3a**). The IR spectrum of the polymer (neat) showed characteristic strong bands at 1735 (ester, $\nu_{(C=O)}$), 1220 ($\nu_{(P=O)}$) 1120 ($\nu_{(C-O)}$) and 1040 cm^{-1} ($\nu_{(P-O-alkyl)}$). *Anal.* Calcd for $(C_{13}H_{17}O_5P\cdot(H_2O)_{0.4})_n$: C, 53.57; H, 6.16; P, 10.63. Found: C, 53.70; H, 6.02; P, 10.59.

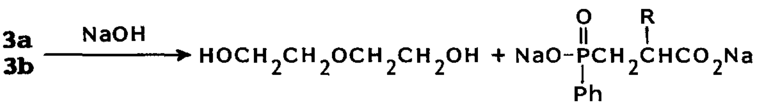
TABLE 1

Alternating Copolymerization of **1** with Acrylic and Methacrylic Acids (**2**)^a

No	M_E	Reaction		Polymer		
		Temp.	Time (hr)	Yield (%)	Structure	Mol.Wt.
1	**2a**	r.t.	232	72	**3a**	1380
2	**2a**	60°C	55	70	**3a**	2200
3	**2a**	90°C	104	88	**3a**	2800
4	**2b**	r.t.	98	41	**3b**	710
5	**2b**	90°C	13	70	**3b**	1440

a) **1**=**2**=3.0 mmol in 1 ml of PhCN

All the above data support the alternating 1:1 structure of **3a**. Further evidence was obtained by an alkaline hydrolysis experiment of the polymer. The GLC analysis of the products revealed that diethylene glycol was formed in 98% yield based on the unit structure (**3a**). In addition, white solid of salt **4a** was obtained in a quantitative yield from the reaction mixture.



$$\mathbf{3a},\ \mathbf{3b} \xrightarrow{NaOH} HOCH_2CH_2OCH_2CH_2OH + NaO\text{-}\underset{Ph}{\overset{O}{\overset{\|}{P}}}CH_2\overset{R}{C}HCO_2Na$$

4a, R=H
4b, R=CH_3

Analogously **1** was subjected to copolymerize with methacrylic acid (**2b**) to give polyphosphinate (**3b**), a 1:1 alternating copolymer of **1** and **2b**. The following data supported the structure **3b**: ^1H NMR ($CDCl_3$ with TMS) δ 1.0-1.4 (3H, m), 1.6-3.1 (3H, br m), 3.4-3.9 (4H, broad singlet-like), 3.9-4.4(4H, broad singlet-like), and 7.3-8.1(5H, br m); ^{31}P NMR ($CDCl_3$ with external H_3PO_4) +43.1 and 43.6 ppm with equal intensity due to the presence of a chiral carbon atom; IR(neat) 1730($\nu_{(C=O)}$), 1200($\nu_{(P=O)}$), 1120($\nu_{(C-O)}$), 1030 cm^{-1}($\nu_{(P-O-alkyl)}$). The alkaline hydrolysis of the copolymer gave diethylene glycol (92% yield determined by GLC analysis) and salt **4b**.

Copolymerization of ***1*** *with α-Keto Acids(****5****) Involving the Deoxygenation of the Acids.* The reaction of **1** with pyruvic acid **5a** at room temperature for 168 hr gave polymer **6a** in 26% yield after reprecipitation with diethyl ether. **6a** is a transparent, hygroscopic, waxy material(molecular weight=1500) which is consisted of phosphonic acid ester unit **6α** and α-hydroxy-carboxylic acid ester unit **6β**. Unit **6α** is an alternating unit of monomers **1** and **5a** whereas unit **6β** is produced by deoxygenation of the keto-oxygen atom of **5a** with **1**. Polymer **6** can be taken as a copolymer of units **6α** and **6β**("Deoxy-Copolymerization") (KOBAYASHI et al, 1980a). In the deoxygenating step **1** was oxidized to cyclic phosphonate **7**.

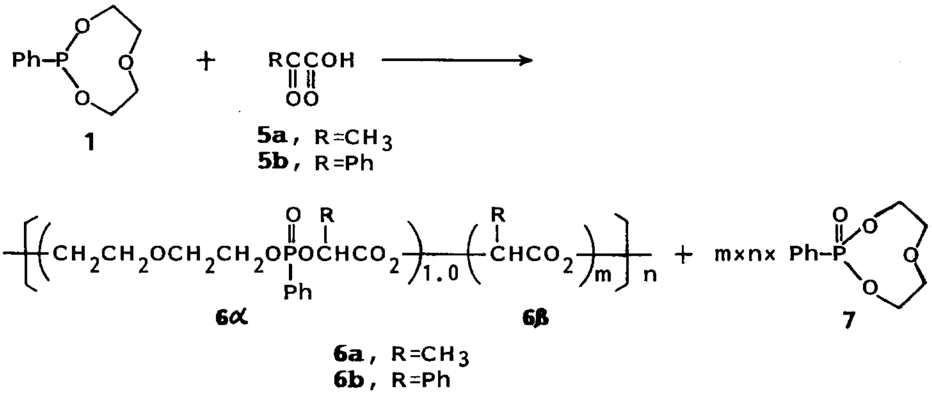


TABLE 2

Deoxy-Copolymerization of **1** with Pyruvic and Phenylglyoxylic Acids(**5**)[a]

No	M_E	Reaction Temp.	Reaction Time(hr)	Polymer Yield(%)	Polymer Structure	Polymer m-value	Polymer Mol.Wt.
6	**5a**	r.t.	168	26	**6a**	0.5	1500
7	**5a**	60°C	51	24	**6a**	0.4	1330
8	**5b**	r.t.	48	37	**6b**	2.1	1470
9	**5b**	90°C	11	31	**6b**	2.3	2670

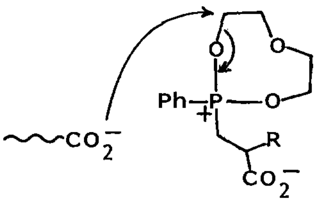
a) **1**=**5**=3.0 mmol in 1 ml of PhCN

The structure of **6a** was determined on the basis of following data. The ^1H NMR of **6a** in $CDCl_3$ showed five signals at δ 1.2-1.7(4.5H, CH_3), 3.5-3.9(4H, CH_2OCH_2), 4.0-4.5(4H, $POCH_2$ and CO_2CH_2), 4.8-5.4(1.5H, CH), and 7.3-8.1(5H, C_6H_5). From these results of the integration the m-value in **6a** is equal to 0.5. The ^{31}P NMR of **6a** in $CDCl_3$ showed a singlet peak at +19.7 ppm assignable to phosphonate unit **6α.** The IR spectrum of the polymer showed strong bands at 1740($\nu_{(C=O)}$), 1220($\nu_{(P=O)}$), 1130($\nu_{(C-O)}$), and 1040 cm^{-1}($\nu_{(P-O-alkyl)}$).

From the etheral solution an oxidation product **7** was actually isolated (39% yield based on **1**): mp 95-96°C (from $CHCl_3$); ^1H NMR ($CDCl_3$ with TMS) δ 3.2-4.8(m, 8H), 7.0-7.9(m, 5H) ^{31}P NMR ($CDCl_3$ with H_3PO_4) +17.5 ppm. *Anal.* Calcd for $C_{10}H_{13}O_4P$: C, 52.64; H, 5.74. Found: C, 53.28; H, 5.70.

In the combination of **1** with **5b**, white powdery polymer **6b** was obtained, in which α-ester unit **6β** was incorporated more than in copolymer **6a**; m-value being >2. The ^1H NMR spectrum of sample No 8 ($CDCl_3$) showed peaks at δ 3.0-3.5(4H, CH_2OCH_2), 3.6-4.2(4H, CH_2OP and CO_2CH_2), 5.7-6.1(2,9, CH) and 6.9-7.5 (20.5H, C_6H_5). From the integration ratio of methylene and aromatic protons m-value of 2.1 was obtained. The ^{31}P NMR of the polymer ($CDCl_3$) showed a peak at +19.7 ppm assignable to phosphonate unit **6α.** In addition to this main peak a small signal at +41.7 ppm was observed, whose assignment has not been made yet. In the IR spectrum of **6b** the following strong bands were observed: 1750($\nu_{C=O}$)), 1240($\nu_{(P=O)}$), and 1030 cm^{-1} ($\nu_{(P-O-alkyl)}$).

Reaction Mechanism. Copolymerization of **1** with **2** probably involves an intermediate zwitterion **8**, which is responsible



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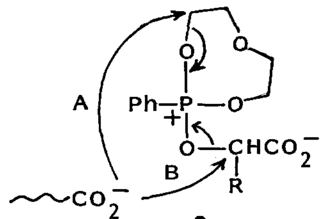

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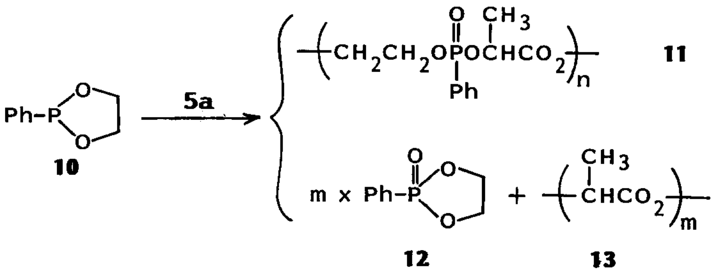
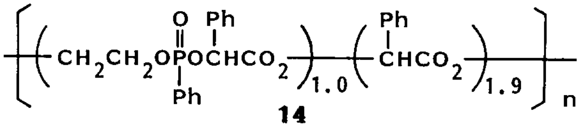
for both the initiation and propagation via the Arbuzov type reaction to yield alternating copolymer **3**. In the copolymerization of **1** with **5**, on the other hand, an intermediate zwitterion **9** is attacked by a carboxylate anion at the ring-methylene carbon (course A) to give an alternating unit(**6α**) and at the exo-carbon of $^+P-O-C$ (course B) to yield an α-ester unit(**6β**) and **7** (Deoxygenation process). Course B was rather a main process (>70%). The α-ester unit constitutes ether-insoluble and ether-soluble parts of polymer **6**. Therefore, the isolated yield of polymer **6** (ether-insoluble) was not high.

In relevance to the deoxy-copolymerization of **1** with **5**, we examined again the previously reported copolymerization system of 2-phenyl-1,3,2-dioxaphospholane(**10**) and **5** (SAEGUSA et al, 1978c). The reaction of **10** with **5a** in $CHCl_3$ at 130°C for 51 hr gave polymer in 53% yield after reprecipitation from diethyl ether (molecular weight = 1800). The isolated polymer had the phosphonate structure **11**, an alternating structure derived from **10** and **5a** as reported previously. This combination, however, involved the deoxygenation step to give 2-phenyl-2-oxo-1,3,2-dioxaphospholane(**12**) and products having α-ester unit **13**. Products **12** and **13** were soluble in diethyl ether and not found in the isolated polymer. The reaction of **10** with **5b** in $CHCl_3$ at 90°C for 20 hr yielded polyphosphonate in 20% yield, the formation of **12** being a major course. The polymer structure is given by **14** (^{31}P NMR signal=+19.8 ppm), indicating that the deoxy-copolymerization took place.





$$\left[\left(CH_2CH_2O\overset{O}{\underset{Ph}{P}}O\overset{Ph}{C}HCO_2\right)_{1.0}\left(\overset{Ph}{C}HCO_2\right)_{1.9}\right]_n$$

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