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Alternating Copolymerizations of Dioxaphospholanes with Acrylic Acid Derivatives and with α-Keto Acids. New Synthesis of Polyphosphonates

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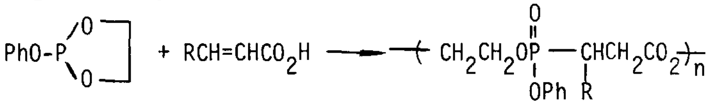
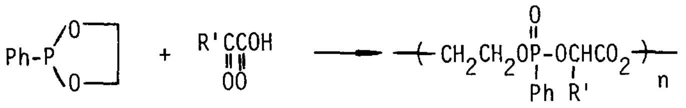
Introduction

This paper reports new copolymerizations of 2-phenoxy-1,3,2-dioxaphospholane (**1**) with acrylic acid (**2**) and of 2-phenyl-1,3,2-dioxaphospholane (**4**) with α-keto acid (**5**) to give polyphosphonates (**3**) and (**6**), respectively.



(1)

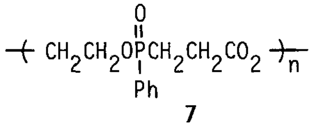
1 **2a**, R=H **2b**, R=CH_3 **2c**, R=Ph **3a**, R=H **3b**, R=CH_3 **3c**, R=Ph



(2)

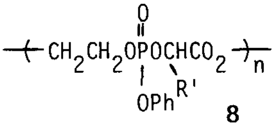
4 **5a**, R'=CH_3 **5b**, R'=Ph **6a**, R'=CH_3 **6b**, R'=Ph

We have developed a series of new copolymerizations which occur without added catalyst and proceed through zwitterion intermediates (SAEGUSA et al, 1975a, b; 1976a; 1977a). In these copolymerization, a monomer of nucleophilic reactivity (M_N) reacts with another monomer having electrophilic reactivity (M_E) to generate a key intermediate of zwitterion $^{+}M_N-M_E^{-}$. On the basis of this concept we found new polymer synthesis reactions to form polyphosphinate **7** from **4** and **2a** (SAEGUSA et al, 1976b) and polyphosphate **8** from **1** and **5** (SAEGUSA et al, 1977b). In both cases, **1** and **4** acted as nucleophilic monomer (M_N) and **2** and **5**



$$-\!\!\left(CH_2CH_2O\overset{O}{\underset{Ph}{P}}CH_2CH_2CO_2\right)_{\!n}-$$

7



$$-\!\!\left(CH_2CH_2O\overset{O}{\underset{OPh}{P}}O\underset{R'}{C}HCO_2\right)_{\!n}-$$

8

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behaved as an electrophilic one (M_E). In the present study, alternative two combinations of M_N and M_E, i.e., **1**-**2** and **4**-**5** were examined. In both cases polyphosphonates were produced. Before this study preparation of polyphosphonates was performed by ring-opening polymerization of cyclic phosphonites (MUKAIYAMA et al, 1964; HARWOOD and PATEL, 1968).

Results and Discussion

Alternating Copolymerization of 2-Phenoxy-1,3,2-dioxaphospholane (**1**) with Acrylic Acid Derivatives (**2**). An equimolar mixture of **1** and **2** was allowed to kept at 100°C in acetonitrile or DMF solvent under nitrogen. Copolymerization took place and gave resinous or powdery materials after usual work-up procedures (TABLE).

TABLE

Alternating Copolymerization between M_N (**1** and **4**) and M_E Monomers (**2** and **5**)[a]

M_N	M_E	Solvent	Reaction Temp (°C)	Reaction Time (hr)	Yield (%)	Mol.Wt.[c]	Structure
1	**2a**	CH_3CN	100	31	74	1710	**3a**
1	**2b**[b]	CH_3CN	100	37	63	2110	**3b**
1	**2c**[b]	DMF	100	20	48	1570	**3c**
2	**5a**	PhCN	120	22	49	1410	**6a**
2	**5a**	CH_3CN	100	37	52	1280	**6a**
2	**5b**	CH_3CN	120	30	37	1870	**6b**

[a] M_N=M_E=3.0 mmol in 1.5 ml solvent under N_2 in a sealed tube.

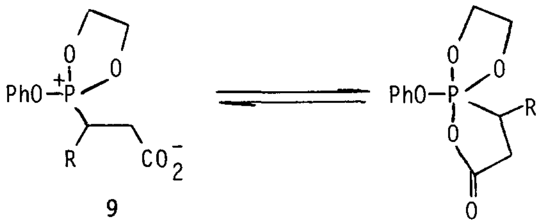
[b] Trans-isomer.

[c] Determined by vapor pressure osmometry in $CHCl_3$ at 35°C.

Copolymer structure was determined by ^1H NMR and IR spectroscopy. ^1H NMR spectrum of copolymer from **1** and **2a** in $CDCl_3$ showed a multiplet peak at δ 2.0-3.0 due to $O=PCH_2CH_2C=O$ (4H), a broad peak at δ 4.0-4.6 due to two methylenes of OCH_2 (4H), and a phenyl peak at δ 7.0-7.6 (5H). In the IR spectrum of the same copolymer very strong absorption bands at 1735 cm^{-1} ($\nu_{C=O}$), 1240 cm^{-1} ($\nu_{P=O}$) and 1195 cm^{-1} (ν_{P-OPh}) were observed. These data along with those of our previous copolymers **7** and **8** were taken to support the alternating copolymer structure of polyphosphonate **3a**. ^1H NMR and IR data of copolymers of **3b** and **3c** are as follows. ^1H NMR signals of **3b** in $CDCl_3$; δ 1.0-1.6 (CH_3, 3H), δ 2.2-3.1 ($O=P-CHCH_2-C=O$, 3H), δ 4.0-4.6 (two OCH_2, 4H), and δ 7.0-7.5 (Ph, 5H) and IR absorption data of **3b**; 1735 cm^{-1} ($\nu_{C=O}$) and 1240 cm^{-1} ($\nu_{P=O}$). ^1H NMR signals of **3c** in $CDCl_3$; δ 2.7-3.4 ($O=P-CHCH_2C=O$, 3H), δ 3.4-4.5 (two OCH_2, 4H), and δ 6.9-7.7 (two Ph, 10H) and IR absorption data of **3c**; 1710 cm^{-1} ($\nu_{C=O}$), 1240 cm^{-1} ($\nu_{P=O}$) and 1200 cm^{-1} (ν_{P-OPh}).

Alternating Copolymerization of 2-Phenyl-1,3,2-dioxaphospholane (**4**) with α-Keto Acids (**5**). Similarly, combination of **4** and **5** gave alternating copolymer of polyphosphonate **6** when an equimolar mixture of both monomers was heated above 100°C (TABLE). ^1H NMR spectrum of the copolymer from **4** and **5a** in $CDCl_3$ showed a peak at δ 1.3-1.9 due to CH_3 (3H), a peak at δ 4.0-4.6 assignable to two OCH_2 (4H), a broad signal at δ 5.1-5.4 due to POCH (1H) and phenyl signal at δ 7.1-8.0 (5H). IR spectrum of the copolymer indicated characteristic two bands at 1750 cm^{-1} ($\nu_{C=O}$) and at 1245 cm^{-1} ($\nu_{P=O}$). These data support the alternating copolymer structure **6a**. ^1H NMR ($CDCl_3$) and IR spectral data of **6b** were as follows: δ 3.7-4.5 (two OCH_2, 4H), δ 5.6-6.2 (POCH, 1H), and δ 6.8-8.0 (two Ph, 10H); 1750 cm^{-1} ($\nu_{C=O}$) and 1255 cm^{-1} ($\nu_{P=O}$).

Copolymerization Mechanism. It is reasonable to assume intermediates of zwitterion and/or phosphorane in the above reactions. In reaction (1) a zwitterion **9** is formed from **1** and **2** involving a hydrogen transfer, which is the key intermediate in the copolymerization between **1** and **2**.



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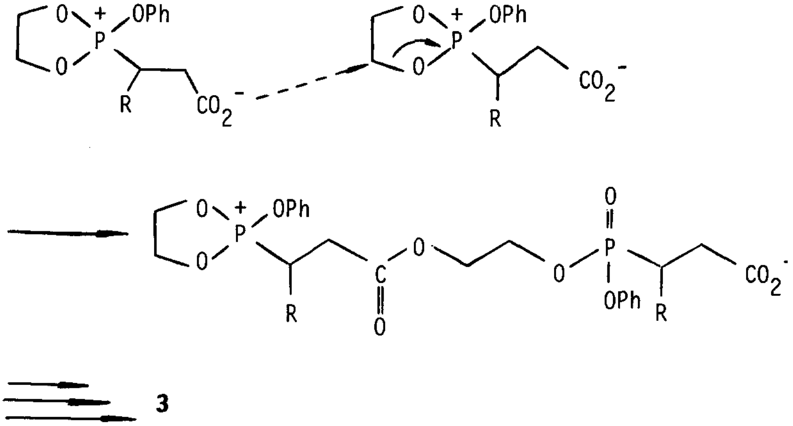
A zwitterion **9** is assumed to be in equilibrium with a spiro phosphorane **10**, although **10** has not been isolated yet as a stable species. The propagation proceeds via the opening of cyclic phosphonium group by the attack of carboxylate anion of another zwitterion.



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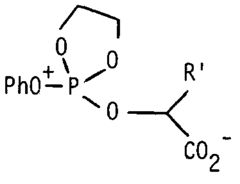
In the combination of **4** and **5**, however, a spiro phosphorane **12** has actually been isolated at a lower temperature, e.g., at room temperature. The copolymerization between **4** and **5** proceeds also through the opening of phosphonium ring by the attack of carboxylate group of another zwitterion.



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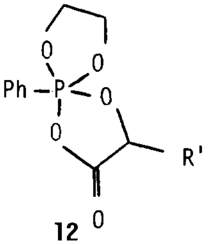

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Summary

The present paper describes alternating copolymerizations of 2-phenoxy-1,3,2-dioxaphospholane **1** with acrylic acid derivatives **2** and of 2-phenyl-1,3,2-dioxaphospholane **4** with α-keto acids **5**. At temperatures above 100°C, these copolymerizations took place without added initiator to give low molecular-weight polyphosphonates, **3** and **6**, respectively. In both cases **1** and **4** acted as nucleophilic monomers and **2** and **5** served as electrophilic ones. Key-intermediates for the

respective copolymerizations were postulated and presented.

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