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Polymerization via Zwitterion
25. Alternating Copolymerizations of Cyclic Acyl Phosphonite and Phosphite with Vinyl Monomers Having an Electron Withdrawing Group

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Summary

Spontaneous copolymerizations of cyclic acyl phosphonite (SPO) and phosphite (SPI) with an electron-deficient vinyl monomer such as methyl acrylate (MA), methyl vinyl ketone (MVK), and acrolein (AL), gave the corresponding alternating copolymers. These copolymerizations took place without added initiator and proceeded through zwitterion intermediates. Copolymer structures *1a*, *1b*, *2* and *3* have been established, all of which were derived in a regiospecific manner of ambident anions. The scheme of the copolymerizations is presented.

Introduction

We have hitherto reported a series of new alternating copolymerizations between a nucleophilic monomer (M_N) and an electrophilic one (M_E) which take place spontaneously without any added catalyst and proceed via zwitterion intermediates (SAEGUSA, 1977b; SAEGUSA and KOBAYASHI, 1978a and 1978b). Recently we have found new phosphorous containing monomers of 2-phenyl-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane (salicylyl phenyl phosphonite ; SPO) and 2-phenoxy-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane (salicylyl phenyl phosphite ; SPI), which act as M_N monomers in combination with M_E monomers of p-benzoquinones (SAEGUSA et al, 1979a) and aromatic aldehydes (SAEGUSA et al, 1979b). In the present study SPO and SPI were subjected to copolymerization with another type of M_E monomers of three vinyl compounds having conjugated electron-withdrawing groups. Electron-deficient vinyl monomers examined were methyl acrylate (MA), methyl vinyl ketone (MVK) and acrolein (AL). All copolymerizations produced 1 : 1 alternating copolymers without added initiator.

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In relation to the copolymerizations of the present study, we have already reported the alternating copolymerizations of 2-phenyl-1,3,2-dioxaphospholane (ethylene phenylphosphonite ; EPO) and electron-deficient vinyl monomers such as MA and MVK (SAEGUSA et al, 1977a).

Experimental

Materials. Solvent of chloroform was purified by distillation by a usual manner. SPO and SPI were prepared and purified as previously described (SAEGUSA et al, 1979b). Commercial reagents of MA, MVK, and AL were purified by distillation under nitrogen before use.

Copolymerization. A typical copolymerization was performed as follows. In a sealed tube SPO and MA (3 mmol each) were mixed in 3 ml of chloroform at room temperature under nitrogen. The mixture was then kept at 110°C. After 42 hr the mixture was poured into a large amount of diethyl ether to precipitate a polymeric material, which was separated and dried in vacuo to give 0.53 g (54% yield) of pale yellow powder (hygroscopic). It is soluble in polar solvents such as DMF, acetonitrile, chloroform, and methanol, but insoluble in diethyl ether and n-hexane.

Results and Discussion

Alternating Copolymerizations. Results of four combinations are shown in TABLE I. The structure of the copolymer was determined by spectroscopic methods and elemental analysis.

TABLE I.

Copolymerizations of SPO or SPI (M_N) with Electron Deficient Vinyl Monomers (M_E)*

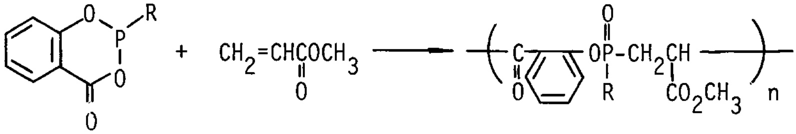
No.	M_N	M_E**	Temp. (°C)	Time (hr)	Copolymer Yield (%)	Copolymer Structure	Mol.Wt.***
1	SPO	MA	110	42	54	*1a*	2380
2	SPO	MA	90	38	43	*1a*	1560
3	SPI	MA	110	51	47	*1b*	1810
4	SPO	MVK	110	46	38	*2*	1160
5	SPO	AL	90	56	58	*3*	2660

* M_N=M_E=3 mmol in 3 ml chloroform.

** MA : methyl acrylate, MVK : methyl vinyl ketone, AL : acrolein.

*** Determined by vapor pressure osmometry in chloroform at 35°C.

The SPO-MA system gave polymer *1a*, whose structural determination was based on the following data. The ^1H NMR spectrum in $CDCl_3$ showed a broad multiplet at δ 1.3-2.3 (with TMS) due to P-CH_2 (2H), a singlet at 3.6 assignable to OCH_3, a broad signal at 4.8-5.2 due to CCHC(O) (1H), and a multiplet signal at 6.8-8.4 of aromatic protons (9H). No olefinic protons were detected. The ^{31}P NMR showed only one peak at δ +37.8 (with external 80% H_3PO_4 standard) which was reasonably assigned to a phosphinate structure. The IR spectrum of the copolymer indicated the existance of two carbonyl groups at 1735 cm^{-1} of an ester and at 1700 cm^{-1} of a ketone besides P=O group at 1230 cm^{-1} (TABLE II, No. 1). Furthermore, the elemental analysis of the copolymer was in good agreement with the 1:1 composition of SPO-MA by taking the adsorbed water into account. All these findings supported the copolymer structure of the phosphinate-ester *1a*.



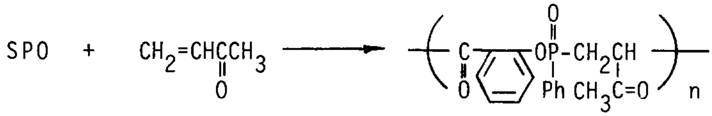
SPO; R=Ph
SPI; R=PhO

MA

1a; R=Ph
b; R=PhO

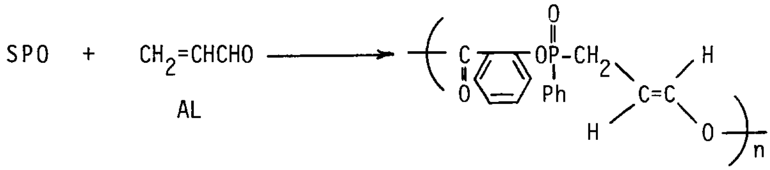
Similarly, the SPI-MA system gave rise to the 1:1 alternating copolymer of structure *1b*.

Two combinations of SPO with MVK and with AL produced the corresponding 1 : 1 alternating copolymers, *2* and *3* , respectively.



MVK

2



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The structures of *1b*, *2*, and *3* were determined on the basis of spectroscopic (TABLE II) and analytical data (TABLE III).

TABLE II

NMR and IR Spectroscopic Data of Alternating Copolymers

Sample No.	Structure	NMR and IR Spectroscopic Data
1	*1a*	^{1}H NMR*; δ 1.3—2.3 (broad m, P-CH$_2$-, 2H), 3.6 (s, CO$_2$CH$_3$, 3H), 4.8—5.2 (broad m, -C-CH-C-, 1H), 6.8—8.4 (m, aromatic protons, 9H). ^{31}P NMR**; δ +37.8. IR***; 1735 ($\nu_{C=O}$, ester), 1700 ($\nu_{C=O}$, ketone, shoulder), 1230 ($\nu_{P=O}$), 1200 cm^{-1} (ν_{P-OAr}).
3	*1b*	^{1}H NMR*; δ 1.5—2.1 (broad m, P-CH$_2$, 2H), 3.6 (s, CO$_2$CH$_3$, 3H), 4.7—5.1 (broad m, -CCHC-, 1H), 6.8—8.1 (m, aromatic protons, 9H). ^{31}P NMR**; δ +24.3. IR***; 1735 ($\nu_{C=O}$, ester) 1700 ($\nu_{C=O}$, ketone, shoulder), 1250 ($\nu_{P=O}$) 1195 cm^{-1} (ν_{P-OAr}).
4	*2*	^{1}H NMR*; δ 1.2—2.2 (broad m, P-CH$_2$, 2H), 2.2 (s, CH$_3$-C-(=O), 3H), 6.3—6.7 (broad m, -CCHC-, 1H), 6.9—8.6 (m, aromatic protons, 9H). ^{31}P NMR**; δ +38.2. IR***; 1720 ($\nu_{C=O}$, ketone), 1235 ($\nu_{P=O}$), 1190 cm^{-1} (ν_{P-OAr}).
5	*3*	^{1}H NMR*; δ 1.5—2.3 (broad m, P-CH$_2$, 2H), 6.6—8.5 (m, CH=CH, 2H and aromatic protons, 9H). ^{31}P NMR**; δ +35.6. IR*** 1750 ($\nu_{C=O}$, ester), 1240 ($\nu_{P=O}$), 1200 (ν_{P-OAr}), 975 cm^{-1} (δ=C-H, trans).

* In CDCl$_3$ with TMS standard

** In CHCl$_3$ with external 80% H$_3$PO$_4$ standard. The chemical shift is positive to the downfield from the standard.

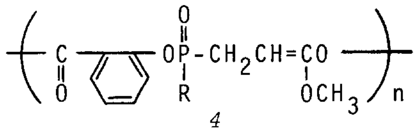
*** Neat.

TABLE III

Analytical Data of Alternating Copolymers

Sample No.	Formula	Calcd for the 1:1 Composition			Found		
		C	H	P	C	H	P
1	$(C_{17}H_{15}O_5P)(H_2O)_{0.20}$	67.41	5.12	10.23	67.38	5.24	10.38
3	$(C_{17}H_{15}O_6P)(H_2O)_{0.15}$	58.51	4.42	8.88	58.32	4.07	8.53
4	$(C_{17}H_{15}O_4P)(H_2O)_{0.36}$	63.66	4.94	9.66	63.24	4.93	9.83
5	$(C_{16}H_{13}O_4P)$	64.00	4.36	10.32	63.71	4.18	10.05

As to the structure of *1* for the product of SPI-MA system , another possible one *4* derived from the enolate form of MA was ruled out. In the SPO-MVK



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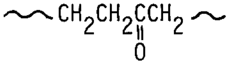
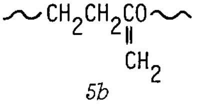
system conceivable unit structures of MVK such as *5a*-*5c* are also absent in the polymer *2*.



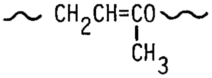
$\sim\sim CH_2CH_2\underset{\underset{O}{\|}}{C}CH_2\sim$

5a



$\sim CH_2CH_2\underset{\underset{CH_2}{\|}}{C}O\sim\sim$

5b

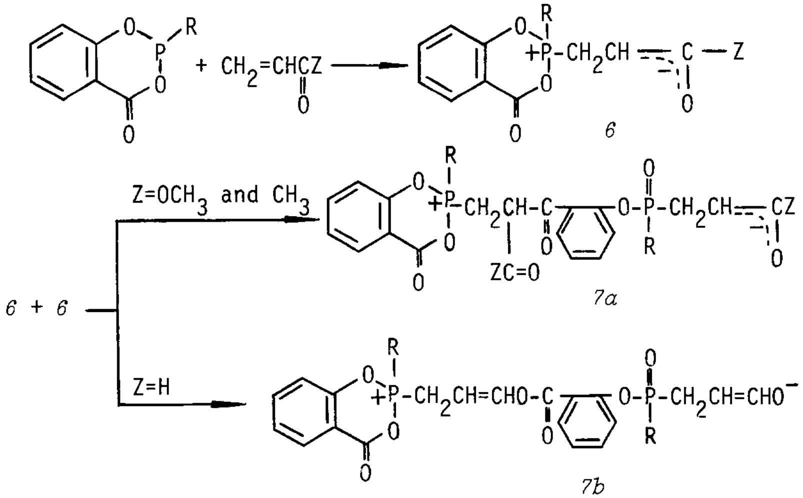


$\sim CH_2CH{=}\underset{\underset{CH_3}{|}}{C}O\sim\sim$

5c

Copolymers *1* and *2* produced from MA and MVK contain their units of the typical vinyl type structures. On the other hand, the copolymer from the SPO-AL combination has no formyl group and its structure of trans-propenyl benzoate type *3* is due to the reaction at the oxygen atom of the enolate anion derived from AL.

Mechanism of Alternating Copolymerizations. The scheme of the present alternating copolymerizations is explained within a framework of the general pattern of polymerizations via zwitterion intermediates developed in our laboratory. At the first step, a Michael-type addition between M_N and M_E takes place to produce a genetic zwitterion *6*, which is responsible for both initiation and propagation. The anionic part of *6* is of an ambident nature. In the cases of MA and MVK the carbon atom of the ambident anion is a reaction site



7b

which attacks the carbonyl carbon atom of the phosphonium ring of another zwitterion and, thus, two molecules of *6* produce a dimeric zwitterion *7a*. In the case of AL, on the contrary, the oxygen atom of the anionic part in *6* reacted and two molecules of *6* gave *7b*. Successive attacks of *6* onto *7a* or *7b* in the similar mode of reaction produced the 1:1 alternating copolymers. It should be noted that in the above four combinations the reactions proceeded in a regiospecific manner. In a previous paper we reported that the copolymerization of EPO with MVK gave a copolymer having the vinyl type unit as well as unit *5a* from MVK (SAEGUSA et al, 1977a). Euclidation of the above regiospecificity of the copolymerizations in the present study requires further study.

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