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Polymerization via Zwitterion. 24. Copolymerization of a Cyclic Acyl Phosphonite with Aromatic Aldehydes

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Summary

Spontaneous copolymerizations of 2-phenyl-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane, a new cyclic acyl phosphonite, (M_N) with p- and o-substituted aromatic aldehydes (M_E) gave 1:2 (M_N : M_E) alternating copolymers. This copolymerization took place without added catalyst affording copolymers 2 via zwitterion 6. The intermediate of spiro acyloxyphosphorane 5 was detected in situ by ^{31}P NMR. The formation of a stabilized intermediate 5 was taken as an important factor to control the 1:2 composition. The scheme of the copolymerization involving a zwitterion 6 was presented. For the comparison with the above system, copolymerizations of ethylene phenyl phosphonite with aromatic aldehydes were also examined.

Introduction

We have explored a series of copolymerizations which take place spontaneously by mixing two monomers of a nucleophilic monomer (M_N) and an electrophilic one (M_E) (SAEGUSA, 1977; SAEGUSA et al, 1975 and 1976; SAEGUSA and KOBAYASHI, 1978a). Phosphorus 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) have recently been found as good M_N monomers. Thus, SPO and SPI were successfully copolymerized with p-benzoquinone derivatives as M_E to produce alternating copolymers (SAEGUSA et al, 1978c) (Eq. 1). In the present paper we report novel copolymerizations of SPO (M_N) with aromatic aldehydes (M_E, 1a ~ 1f) (Eq. 2). The copolymerizations took place without added initiator to produce $M_N : M_E = 1 : 2$ alternating copolymers 2a ~ 2f consisting of both phosphinate and ester groups in the main chain. In the relation to reaction (Eq.2),we have already reported the 1:1 alter-

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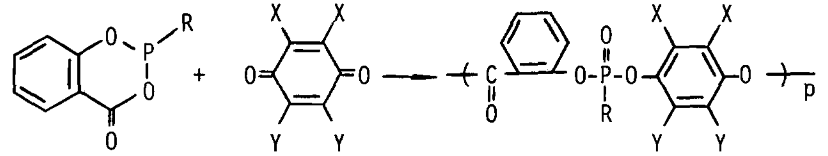

SPO; R=Ph

SPI; R=OPh

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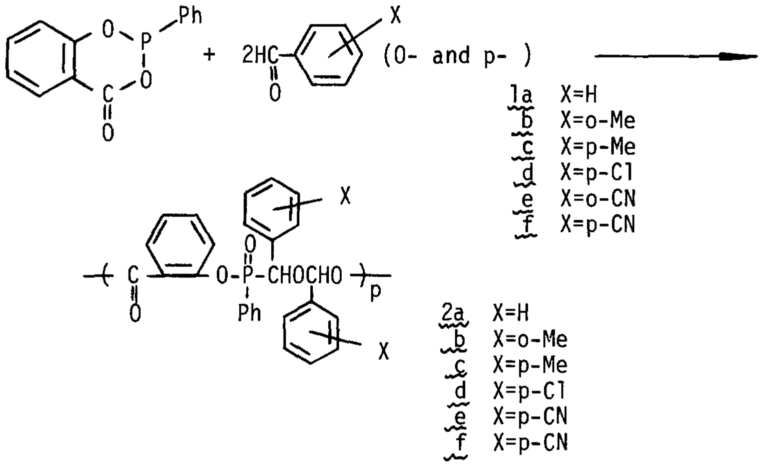


1a X=H
1b X=o-Me
1c X=p-Me
1d X=p-Cl
1e X=o-CN
1f X=p-CN

2a X=H
2b X=o-Me
2c X=p-Me
2d X=p-Cl
2e X=p-CN
2f X=p-CN

(2)

nating copolymerizations of 2-phenyl-1,3,2-dioxaphospholane (ethylene phenyl phosphonite ; EPO) with ortho or para formylbenzoic acids (SAEGUSA et al, 1978b).

Experimental

Matherials SPO was prepared and purified as previously reported (SAEGUSA et al, 1978c). Commercially available aromatic aldehydes were used after purification. All solvents were purified by distillation according to the usual methods.

Copolymerization Procedure. An example of copolymerization procedure was as follow. To 3 ml of solvent containing 3 mmol of SPO, 3 mmol of benzaldehyde 1a was added at room temperature under nitrogen, and the tube was sealed. Then, mixture was kept at 90°C. After the reaction, the mixture was poured into a large amount of diethyl ether to precipitate the copolymer. The resulting copolymer after the reprecipitation was dried in vacuo to give white powder.

Results and Discussion

Copolymerization of SPO with Aromatic Aldehydes. Some typical results of the copolymerization are shown in TABLE I. The structure of copolymers was established by spectroscopic analyses and by elemental analyses. IR and ^{31}P NMR data of **2a** are as follows : IR (KBr) 1740 cm^{-1} (νC=O), 1235 cm^{-1} (ν P=O), and 1200 cm^{-1} (νP-O-Ar); ^{31}P NMR ($CHCl_3$) δ= +34.0 ppm (down field from 80% H_3PO_4). These spectral data strongly support the structure of copolymer **2a**. In the ^1H NMR spectra of the copolymers, signals due to phenyl and methyne protons overlaped and therefore ^1H NMR was not helpful to the structure analysis. The results of the elemental analyses (TABLE II) were in good agreement with the calculated value of **2a** unit. Data of ^{31}P NMR and of elemental analyses are listed in TABLE II. It should be noted that the copolymer composition was 1:2 (M_N:M_E) in all cases. Copolymers 1-4 were white powder, and 5 and 6 were light brown powdery materials. All copolymers were soluble in polar solvents such as chloroform, partially soluble in benzene, and insoluble in diethyl ether or n-hexane.

TABLE I

Copolymerizations of SPO(M_N) with Aromatic Aldehydes (M_E)*

No.	M_E	Time (hr)	Yield (%)	Copolymer Structure	Molecular** Weight
1	**1a**	32	52	**2a**	2350
2	**1b**	36	43	**2b**	1160
3	**1c**	36	46	**2c**	1690
4	**1d**	31	41	**2d**	2180
5	**1e**	28	38	**2e**	2010
6	**1f**	26	56	**2f**	2260

* M_N=M_E=3 mmol in 3 ml chloroform at 90°C.

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

TABLE II

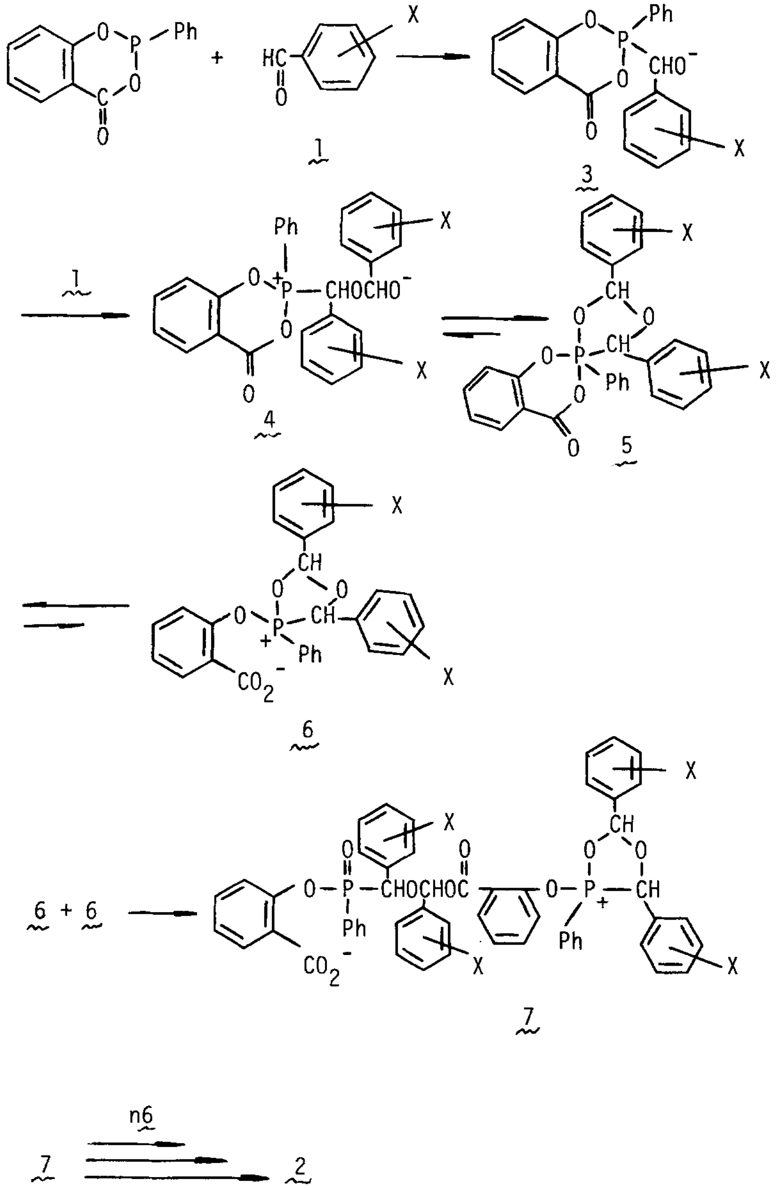
Results of ^{31}P NMR and Elemental Analyses of 1:2 Alternating Copolymers

Sample No.	^{31}P NMR* (ppm)	Formula	Anal.									
			Calcd.**					Found				
			C	H	P	N	Cl	C	H	P	N	Cl
1	+34.0	$(C_{27}H_{21}O_5P)_n$	60.71	6.29	9.21			60.72	6.31	9.18		
2	+34.6	$(C_{29}H_{25}O_5P)_n$	71.89	5.20	6.39			71.57	4.97	6.48		
3	+34.4	$(C_{29}H_{25}O_5P)_n$	71.89	5.20	6.39			71.91	5.18	6.27		
4	+33.8	$(C_{27}H_{19}O_5PCl_2)_n$	61.73	3.65	5.90		13.50	61.58	3.59	5.68		13.41
5	+33.5	$(C_{29}H_{19}O_5PN_2)_n$	68.77	3.78	6.12	5.53		68.73	3.86	6.19	5.38	
6	+33.8	$(C_{29}H_{19}O_5PN_2)_n$	68.77	3.78	6.12	5.53		68.65	3.81	6.11	5.58	

* Chemical shift is positive to the down-field from the external standard of 80% H_3PO_4.

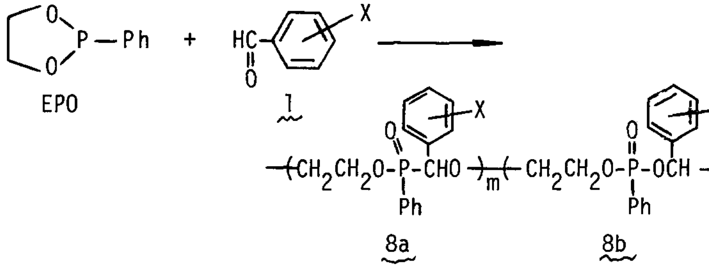
** For the $M_N:M_E=1:2$ composition of copolymers.

Scheme of Copolymerizations. The present copolymerization is understood by the scheme which is based on the general pattarn of the spontaneous alternating copolymerization and the additional experimental findings in the present study.



The reaction between SPO and 1 induces a bond formation between the phosphorus atom and the carbonyl carbon of 1 to lead 3, followed by an additional attack of 1 onto 3 to produce a transient species 4 having 1:2 composition. 4 is converted to the more stabilized species 5 which is in equilibrium with another zwitterion 6, an important key intermediate for both the initiation and propagation. At 35°C, spiro acyloxyphosphorane 5 is spectroscopically detected in situ. The ^{31}P NMR spectrum showed a signal at -13.5 ppm assignable to 5 in the SPO-1a system together with the signal due to the copolymer. Reactions of P(3) compounds and aromatic aldehydes generally gave phosphoranes (RAMIREZ, 1966 and 1974). The corresponding phosphorane 5 in this study, however, is not stable enough to be isolated. The reaction between two molecules of 6 produces the initial propagating zwitterion 7, in which the phosphonium ring of the one molecule is opened by nucleophilic attack of the carboxylate anion of the other molecule. 7 grows to 2 by the successive reaction with 6 to give the M_N:M_E=1:2 alternating copolymer 2. The formation of a stabilized intermediate 5 controls the 1:2 composition.

In comparison with the copolymerizations of the above study the combination of EPO and aromatic aldehydes produced copolymers of the 1:1 composition without added catalyst. The copolymers, however, consisted of two kinds of unit in which the phosphorous atom of EPO is bound to C atom and to O atom of the carbonyl group. The ratio of C attack and O attack was dependent on the substituted group (Eq. 3). The ratio of m:n in 8 was determined by ^{31}P NMR ; a signal at



(3)

X=H m:n = 2.5:1
X=o-CN m:n = 2.0:1

+34.8 assignable to phosphinate unit 8a and other one at +18.5 due to phosphonate unit 8b. Copolymers were light brown powder soluble in highly polar solvents such as DMF.

References

RAMIREZ, F. : Bull. Soc. Chim. Fr. 1966, 2443
RAMIREZ, F. : Synthesis 1974, 90
SAEGUSA, T., S. KOBAYASHI, Y. KIMURA and H. IKEDA : J. Macromol. Sci., Chem. A-9, 641 (1975)
SAEGUSA, T., S. KOBAYASHI and Y. KIMURA : Pure Appl. Chem. 48, 307 (1976)
SAEGUSA, T. : Angew. Chem. Int. Ed. Engl. 16, 826 (1977)
SAEGUSA, T. and KOBAYASHI, S. : Pure Appl. Chem. 50, 281 (1978a)
SAEGUSA, T., T. YOKOYAMA, Y. KIMURA and S. KOBAYASHI : Polymer Bull., in press (1978b)
SAEGUSA, T., T. KOBAYASHI, T. Y. CHOW and S. KOBAYASHI : Macromolecules, submitted (1978c)

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