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Polymerization via Zwitterion.
23. Terpolymerization Among 2-Phenyl-1,3,2-dioxaphospholane, Methyl Acrylate, and Carbon Disulfide

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Summary

The present paper describes the terpolymerization involving 2-phenyl-1,3,2-dioxaphospholane, methyl acrylate, and carbon disulfide, which took place without any added initiator in benzonitrile or dimethylformamide. The structure and composition of terpolymer were determined by NMR and IR spectra, as well as by elemental analysis. A reaction scheme proceeding via zwitterion 5 was proposed (Eq. 2-5).

Introduction

Various combinations of spontaneous copolymerizations betwen nucleophilic (M_N) and electrophilic monomers (M_E) have been found by us (SAEGUSA, 1975 and 1977; SAEGUSA et al., 1975, 1976, 1977, and 1978). A zwitterion $^+M_N-M_E^-$ which is formed by the reaction between M_N and M_E functions as the key intermediate of copolymerization. The present paper describes a terpolymerization involving 2-phenyl-1,3,2-dioxaphospholane (ethylene phenylphosphonite, EPO), methyl acrylate (MA), and carbon disulfide (CS_2). Previously a 1:1:1 alternating terpolymerization of EPO, MA, and carbon dioxide was reported by us (SAEGUSA et al., 1977b).

Results and Discussion

Terpolymerization of EPO-MA-CS_2. In the terpolymerization of the present study, EPO behaves as M_N and both MA and CS_2 function as M_E. It has been found that EPO and CS_2 are copolymerized with each other (SAEGUSA et al., unpublished). In order to avoid the binary copolymerization between EPO and CS_2, EPO and MA were first reacted with each other to form a phosphorane 2 in situ which was a 1:1 adduct and present in equilibrium with a zwitterion 1. Then, 2 was subjected to copolymerization with CS_2 (Eq. 1).

Thus, 3 mmol each of EPO and MA were mixed in 1.0 ml of benzonitrile, and the mixture was maintained at 50° under nitrogen. After 10 hr 3 mmol of CS_2 was added to this solution system and the glass tube was sealed, which was then maintained at 50° for 10 hr.

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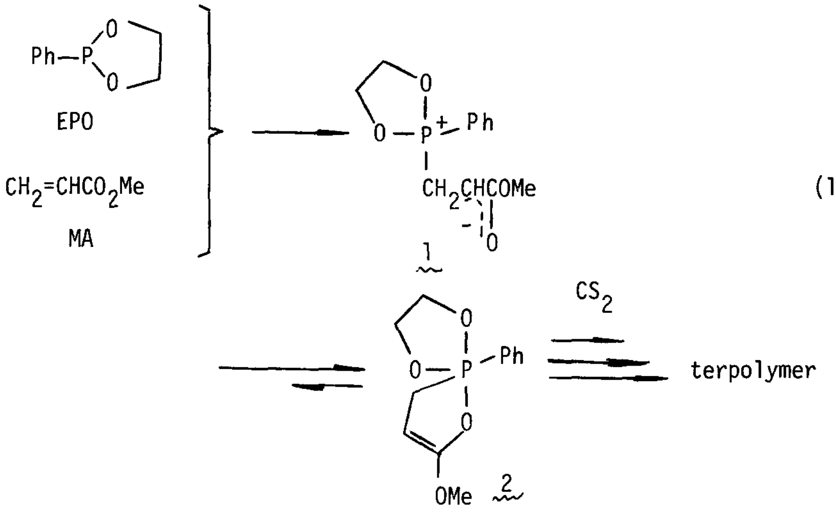
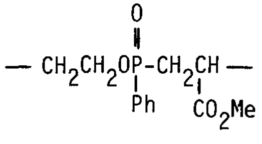


(1)

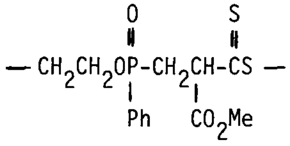
Finally, the temperature was raised and kept at 130° for 70 hr. The mixture was then poured into a large amount of diethyl ether to precipitate a polymeric material, which was purified by another reprecipitation with a chloroform (solvent)-diethyl ether (non-solvent) system. The isolated polymer was dried in vacuo and weighed. The results are shown in TABLE 1 (No. 1 and 2). The polymer is a dark-red powder melting at 50-70°. The color might due to dithiocarboxylic acid ester group (or so-called xantate). The terpolymer thus obtained was soluble in polar solvents such as chloroform, dimethylformamide, and methanol but insoluble in diethyl ether, benzene, and water.

The terpolymers were not 1:1:1 alternating ones, but were found to be consisted of the following two kinds of segments 3 and 4. FIGURE 1 shows a typical



$$-CH_2CH_2O\overset{O}{\overset{\|}{P}}(Ph)-CH_2CH(CO_2Me)-$$

3



$$-CH_2CH_2O\overset{O}{\overset{\|}{P}}(Ph)-CH_2CH(CO_2Me)-\overset{S}{\overset{\|}{C}}S-$$

4

NMR spectrum of the terpolymer (sample No. 2). Broad peak B (δ 2.35) is ascribed to methylene protons adjacent to phosphorus group (P-CH_2). Peak C (δ 2.76) is reasonably assigned to methylene protons of CS_2-CH_2. Peak D (δ 3.40), E (δ 3.52), and F (δ 4.08) are due to a methyne proton of $-CH{<}^{CS_2}_{CO_2Me}$, methyl protons of CO_2-CH_3 and methylene ones of P-O-CH_2, respectively.

Peak G (δ 7.40) is ascribed to the phenyl group. Besides, a small peak A around δ 1.75 is clearly detected as a shoulder on peak B, which is to be assigned to the protons of the methylene group in $P\text{-}OCH_2\text{-}\underline{CH_2}\text{-}CH\!\lessdot_{CO_2Me}$ of 3 as was investigated in EPO-MA copolymerization (SAEGUSA et al., 1977a). The signals of other protons of 3 are overlapped with those of 4, i.e., with B, D, E, F, and G. The itensity of them, therefore, was found as A+C:B:D:E:F:G=2.0:2.0:1.0:3.0:2.0:5.0. From the relative intensities of A and G the composition of 4/3 was calculated at 2.0/1.0. The ratio was also calculated by its elemental analysis, which was found as 62/38. Both values from NMR and elemental analysis are in good agreement with each other. In FIGURE 2 the IR spectrum of the terpolymer (sample No. 2) is shown in which characteristic absorptions of ester carbonyl (ν C=O) at 1735 cm^{-1}, ν P=O at 1220 cm^{-1}, ν C=S at 1080 cm^{-1}, and $\nu_{P\text{-}O\text{-}C}$ at 1030 cm^{-1} are noticed.

The elemental components of the structure of the EPO-MA-CS_2 terpolymer are similar to those of the EPO-MA-CO_2 terpolymer. However the terpolymer involving CS_2 is not a 1:1:1 alternating one. Binary alternating diad 3 of EPO and MA is incorporated. It is due to the polymerization of 2 through 1 without reaction with CS_2.

Copolymerization of Isolated 2 with CS_2. The isolation of 2 was previously reported (SAEGUSA et al., 1977a). Since 2 is very hygroscopic special care is required. When a mixture with 3 mmol each of EPO and MA in 3 ml n-hexane was kept at 50° for 15 hr under nitrogen, a colorless liquid product was separated from the solution, which was washed throughly with n-hexane and dried in vacuo. Then a mixture of 1.0 ml of dimethylformamide and 3.0 mmol of CS_2 was added to 2. The tube was sealed and heated to 130° after maintained at 50° for 10 hr. After 50 hr the terpolymer was isolated as before (see No. 4 in TABLE 1). Similarly, a mixture of 0.5 ml of benzonitrile and 1.5 mmol of CS_2 was added to 1.38 mmol (0.46 g) of 2 and the terpolymerization was undertaken as described above. The result is shown in TABLE 1 (No. 3). The use of the isolated 2 could not realize the 1:1:1 alternating terpolymerization.

Scheme of the Terpolymerization. On the basis of the above findings and various results of this type of copolymerizations including EPO-MA-CO_2 terpolymerization, the following sheme is proposed to explain the present terpolymerization. The first step is the formation of 1 from EPO and MA, which falls into the penta-covalent phosphorane 2 being in equilibrium with each other. The formation of 1 or 2 is very rapid compared with the formation of the binary copolymer 3.

Then in this system is added CS_2, and it attacks the carbanion of 1 to give the second zwitterion 5 which is the key intermediate of the terpolymerization. Two molecules of 5 afford a dimeric zwitterion 6. The propagation proceeds via successive attack of 5 onto 6 to form a macrozwitterion 7. However, competitive propagations involving binary zwitterion 1 participate in this system to lead a biased incorporation of the segment 3 in the terpolymer (Eq. 5).

SCHEME

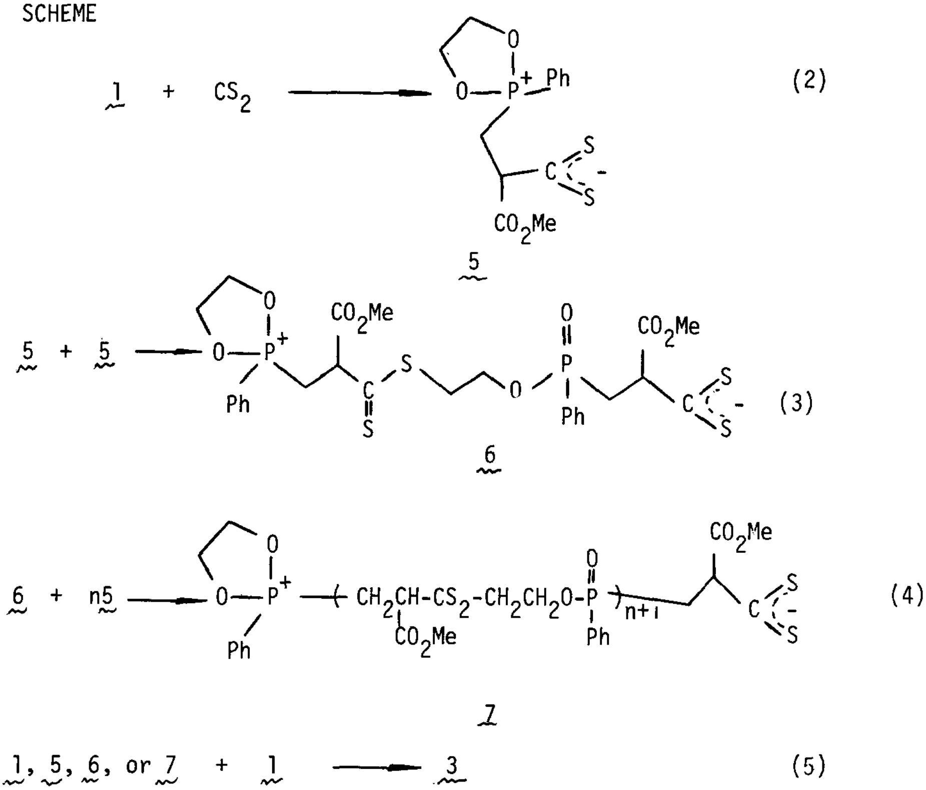


TABLE 1

Terpolymerization Involving EPO, MA, and CS_2.

No.	Monomers[a]			Solvents (ml)		Temp.[c] °C	Time[d] hr	Terpolymer Yield %	Molecular Weight[e]
1	EPO	MA	CS_2[b]	benzonitrile	(1.0)	130	70	74	1780
2	"	"	"	"	(")	120	150	52	2610
3	**2** (46%)[f]		CS_2 (1.5)[g]	"	(0.5)	130	70	10	1310
4	**2** (94%)[f]		CS_2 (3.0)[g]	dimethyl-formamide	(1.0)	130	50	60	1030

a) 3 mmol of each, otherwise specifically noted.

b) Added after maintained for 10 hr at 50°.

c) The terpolymerization mixture was kept at these temperatures after CS_2 monomer was heated with the EPO-MA reaction product at 50° for 10 hr.

d) Time for c) operation.

e) Determined by vapor pressure osmometry in dimethylformamide at 55°.

f) Obtained yield of **2** from the reaction between EPO and MA.

g) The amount added to **2**.

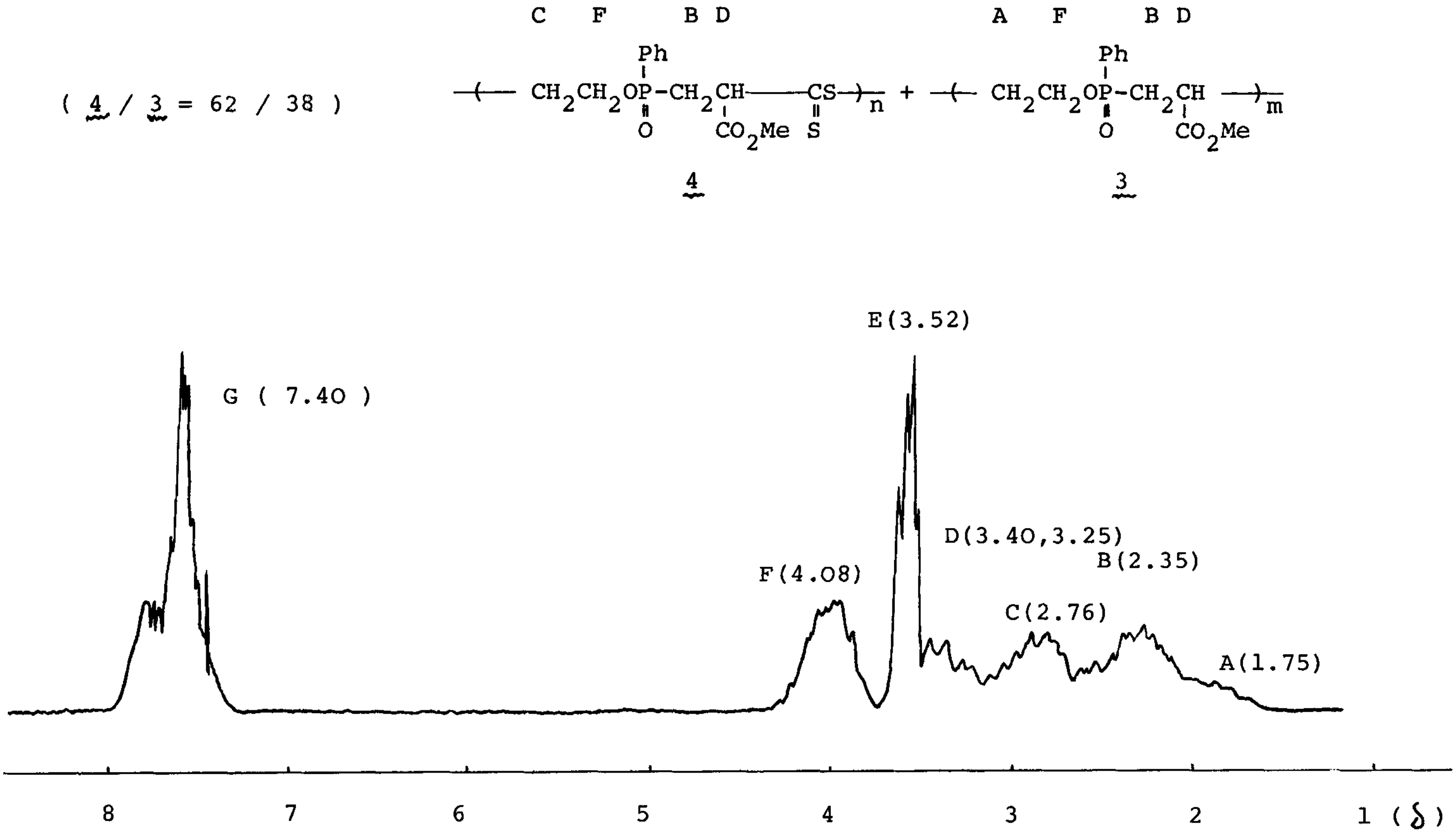
TABLE 1 (continued)

No.	Terpolymer Appearance	(mp)	Terpolymer Unit Structure[h] **4**/**3**	Analyses[i] C	H	P	S
1	dark red powder		49/51	49.43	5.75	10.61	9.57
2	〃	(63-66°)	62/38	49.84	5.13	10.18	13.20
3	〃	(50-54°)	71/29[j]				
4	dark red gum		69/31[j]				

h) Estimated from elemental analyses based on the assumption that EPO/MA unit is 1/1.

i) Calcd. for the 1:1:1-terpolymer; $C_{13}H_{15}O_4PS_2$: C, 47.27; H, 4.58; P, 9.38; S, 19.41.
Calcd. for the 1:1-copolymer of EPO-MA; $C_{12}H_{15}O_4P$: C, 56.70; H, 5.95; P, 12.18.

j) Estimated by NMR.



$$\left(\mathrm{CH_2CH_2O\overset{Ph}{\underset{O}{P}}\text{-}CH_2\underset{CO_2Me}{CH}\text{—}\underset{S}{CS}}\right)_n + \left(\mathrm{CH_2CH_2O\overset{Ph}{\underset{O}{P}}\text{-}CH_2\underset{CO_2Me}{CH}}\right)_m$$

FIGURE 1. NMR spectrum of the EPO-MA-CS_2 terpolymer in d_1-chloroform (Sample No.2).

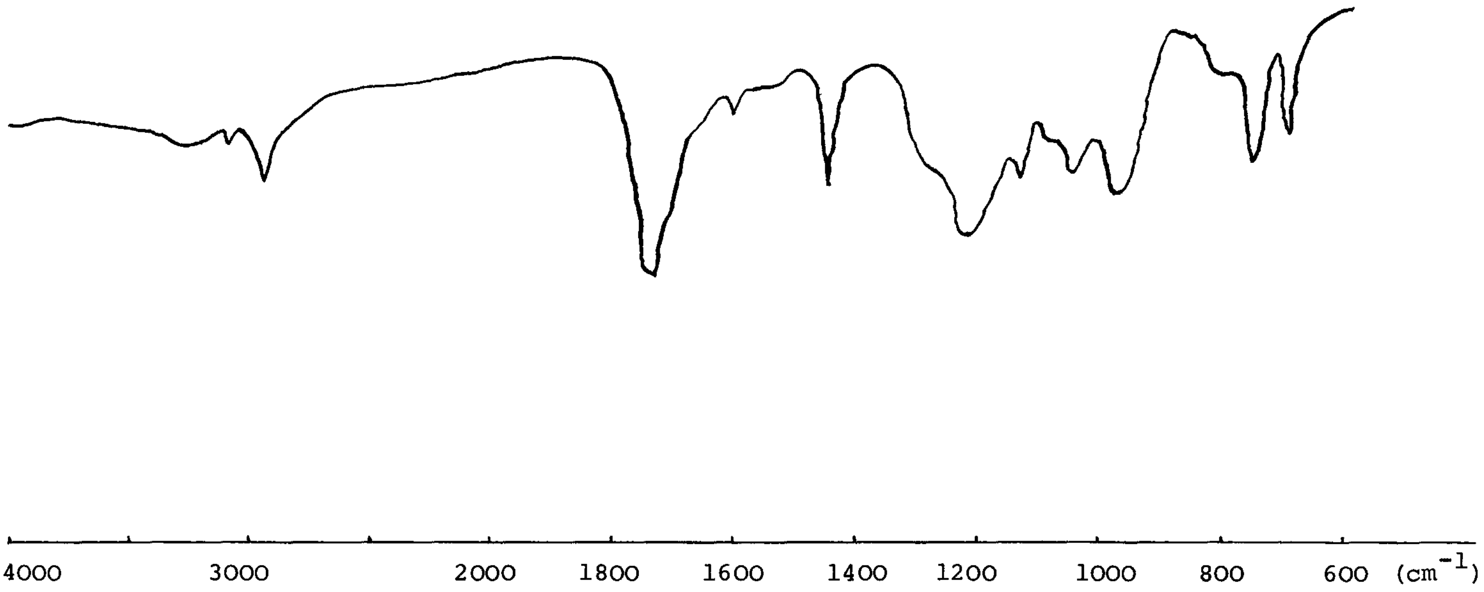


FIGURE 2. Infrared spectrum of the EPO-MA-CS$_2$ terpolymer (KBr) (Sample No.2).

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