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Polymerization via Zwitterion
27. No-Catalyst Copolymerization of 2-Phenyl-1,3,2-Dioxaphospholane with β-Hydroxyalkyl Acrylates and Methacrylates

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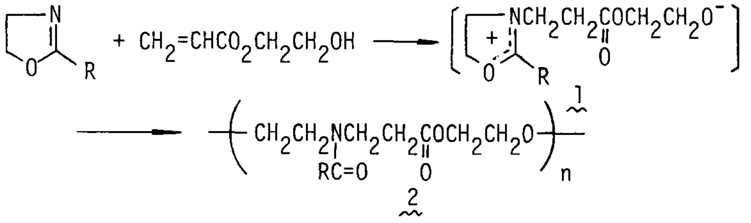
Dedicated to the 60th birthday of Professor C. I. Simionescu

Summary

This paper describes "No-Catalyst Copolymerizations" between ethylene phenylphosphonite (EPO) as M_N and four β-hydroxyalkyl acrylates and methacrylates as M_E. In all combinations polyphosphinate type copolymers were obtained above 130°C without added catalyst. The first step of reaction was a proton-transfer step to yield a transient phosphonium-alkoxide zwitterion 5 and generated a phosphorane intermediate like 6. The subsequent reactions of 6 were rather complicated. It was possible to conceive several zwitterions to lead to polymer units. The liberation of ethylene oxide and/or propylene oxide was observed as a side reaction during polymerization.

Introduction

We have reported that 2-phenyl-1,3,2-dioxaphospholane (ethylene phenylphosphonite; EPO) is a good nucleophilic monomer (M_N) to produce various alternating copolymers in the combinations with electrophilic monomers (M_E) such as acrylic acid, acrylamide, electron-deficient vinyl monomers, carbonyl compounds including α-keto acids, and p-benzoquinones (a recent review, SAEGUSA and KOBAYASHI, 1979). On the other hand, hydroxyalkyl acrylates were found to copolymerize as M_E with M_N monomers of cyclic imino ethers to give amide-ester-ether type polymers such as 2. The reaction involved a zwitterion 1 derived via a proton transfer (SAEGUSA et al, 1977). The present paper



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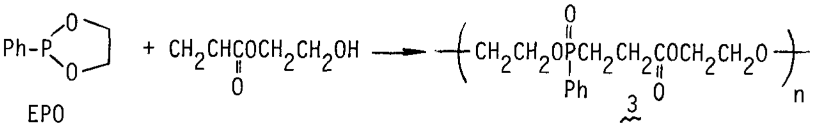
describes the copolymerization of EPO as M_N with hydroxyalkyl acrylates and methacrylates as M_E, which occurred without added catalyst. It was expected that the reaction gives rise to polymer 3 of phosphinate-ester-ether type in an analogous manner as the above reaction. The reaction, however, was rather complicated as



described below.

Experimental

Materials. Solvents of acetonitrile and benzonitrile were purified by distillation under nitrogen. EPO was prepared and purified as previously described (SAEGUSA et al, 1976). β-Hydroxyethyl(HEA) and β-hydroxypropyl acrylates (HPA), and β-hydroxyethyl (HEM) and β-hydroxypropyl methacrylates (HPM) were commercial reagents and purified by distillation under nitrogen.

Copolymerization. A typical run was performed as follows. In a sealed tube EPO and HEA (3 mmol each) were mixed in 0.6 ml of acetonitrile containing a radical inhibitor of p-methoxyphenol (0.1 mol% for HEA) at 0°C under nitrogen. The mixture was then kept at 130°C. After 40 hr the content of the tube was poured into a large amount of diethyl ether to precipitate a polymeric material, which was dried *in vacuo* to give 0.504 g (59.2% yield) of colorless glassy polymer.

Alkaline Hydrolysis of Copolymer. To 50 mg of copolymer in an NMR sample tube was added 0.5 ml of a 10% D_2O solution of NaOH at room temperature, the tube was sealed, and the mixture was heated at 90°C for 20 hr. Then, the reaction mixture was directly subjected to NMR measurement.

Results and Discussion

Reaction of EPO with four electron-deficient vinyl monomers required higher temperatures, e.g. 130°C, in order to obtain copolymers. Table I shows the copolymerization results. The structure of copolymers was examined by ^{31}P, ^{1}H as well as ^{13}C NMR, IR, and alkaline hydrolysis experiments.

The ^{31}P NMR spectrum of glassy polymer obtained from EPO and HEA showed only one peak at δ +44.7 (from 85% H_3PO_4 external standard) in $CDCl_3$, indicating that the polymer has phosphinate type structure of $\sim\sim OP(O)(Ph)CH_2\sim\sim$. The ^{1}H NMR spectrum of the polymer (Figure 1, a) showed three kinds of peaks; peak A at δ 7.1-8.0 due to aromatic protons, signal B at δ 3.5-4.4 ascribed to methylene protons of

$\sim\sim OCH_2CH_2O\sim\sim$, and signal C at δ 1.8-2.6 assignable to methylene protons of $>P(O)CH_2CH_2C(O)$ in a integral ratio of 5.0 : 7.0 : 4.0. If the copolymer had the 1:1 alternating structure **3** as expected, the integral ratio should be 5.0 : 8.0 : 4.0. The smaller integration of signal B was due to the elimination of ethylene oxide during the polymerization as described below. The ^{13}C NMR spectrum of the copolymer was very complicated, but two characteristic peaks ascribable to the spiro carbon of ortho ester structure at δ 122.5 and 121.7 (from TMS) were observed. In the IR spectrum of the copolymer, three characteristic stretching bands were observed at 1740 cm^{-1} due to ester carbonyl at 1230 cm^{-1} due to P=O, and at 1040 cm^{-1} of P-O-alkyl.

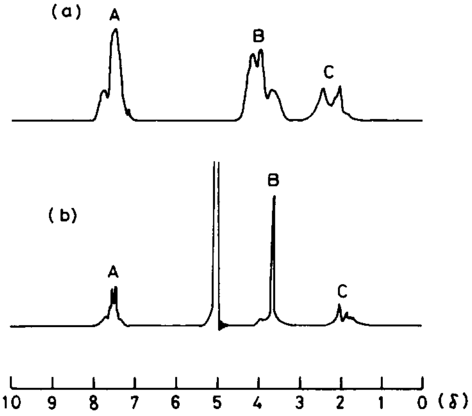


Fig. 1 ^1H NMR spectra of the copolymer obtained from EPO and HEA in $CDCl_3$ (a) and of the alkaline hydrolysis mixture of the copolymer in D_2O (b)

The copolymer was subjected to alkaline hydrolysis in D_2O in an NMR tuble and its ^1H NMR spectrum was recorded (Figure 1, b). Three kinds of peaks due to aromatic protons(A), methylene protons of ethylene glycol unit(B), and two methylenes of $P(O)CH_2CH_2C(O)$ (C) were observed. The peak area of peak C decreased since the H-D exchange took place under the reaction conditions. The peak ratio of A:B:C was, therefore, 5.0:6.9:2.9. The spectrum b was very close to that of a 1:1 mixture of authentic samples of $HOP(O)(Ph)-CH_2CH_2CO_2H$ and $HOCH_2CH_2OH$ (SAEGUSA et al, 1978).

Furthermore, the hydrolysis mixture was neutralized and the organic substances were extracted several times with a large amount of diethyl ether. The organic layer was subjected to GC analyses. It was found that a main product was ethylene glycol and only a trace amount of diethylene glycol was detected;

again the structure 3 is improbable.

It was found that ethylene oxide was produced during the reaction. The reaction of EPO with HEA at 130°C was monitored. The amount of ethylene oxide formed and the production of copolymer were given on the basis of the amount of EPO as follows; 3% and 20% after 10 hr, 8% and 50% after 30 hr, and, 13% and 70% after 60 hr. The amount of ethylene oxide was much less than that of the total copolymer units. Ethylene oxide was also detected in the reaction system of EPO with HEM. With the combination of EPO and HPA as well as HPM having β-hydroxypropyl group, on the other hand, not only ethylene oxide but also propylene oxide were produced.

TABLE 1

Copolymerization of EPO(M_N) with β-Hydroxyalkyl Acrylates and Methacrylates (M_E)[a]

No	M_E	Temp. (°C)	Time (hr)	Copolymer		
				Yield(%)	MW[c]	^{31}P NMR(δ)
1	HEA	130	40	59	1270	+ 44.7
2[b]	〃	160	30	76	1970	+ 44.5
3	HEM	130	30	59	1440	——
4	HPA	130	30	51	3540	+ 45.6
5	HPM	130	30	13	1440	+ 43.7
6	HEA	90	20	60	330	- 20.5
7	HEM	90	40	52	400	- 20.9

[a] EPO = M_E = 3.0 mmol each in 0.6 ml of CH_3CN under nitrogen in the presence of p-methoxyphenol (0.1 mol% for EPO) as a radical inhibitor.

[b] Benzonitrile was used instead of CH_3CN.

[c] Determined by vapor pressure osmometry in DMF at 55°C.

From the above results it was considered that the copolymer structure is not simple and composed of a mixture of units 13——16 as given in Scheme. Table 2 shows results of the elemental analysis of copolymers. All copolymers are very hygroscopic and, therefore, the carbon values were generally less than the calculated ones whereas the hydrogen values were more than the calculated ones. The carbon to phosphorus atomic ratio was less than the calculated one due to the liberation of ethylene and/or propylene oxides.

TABLE 2

Elemental Analyses of Copolymers

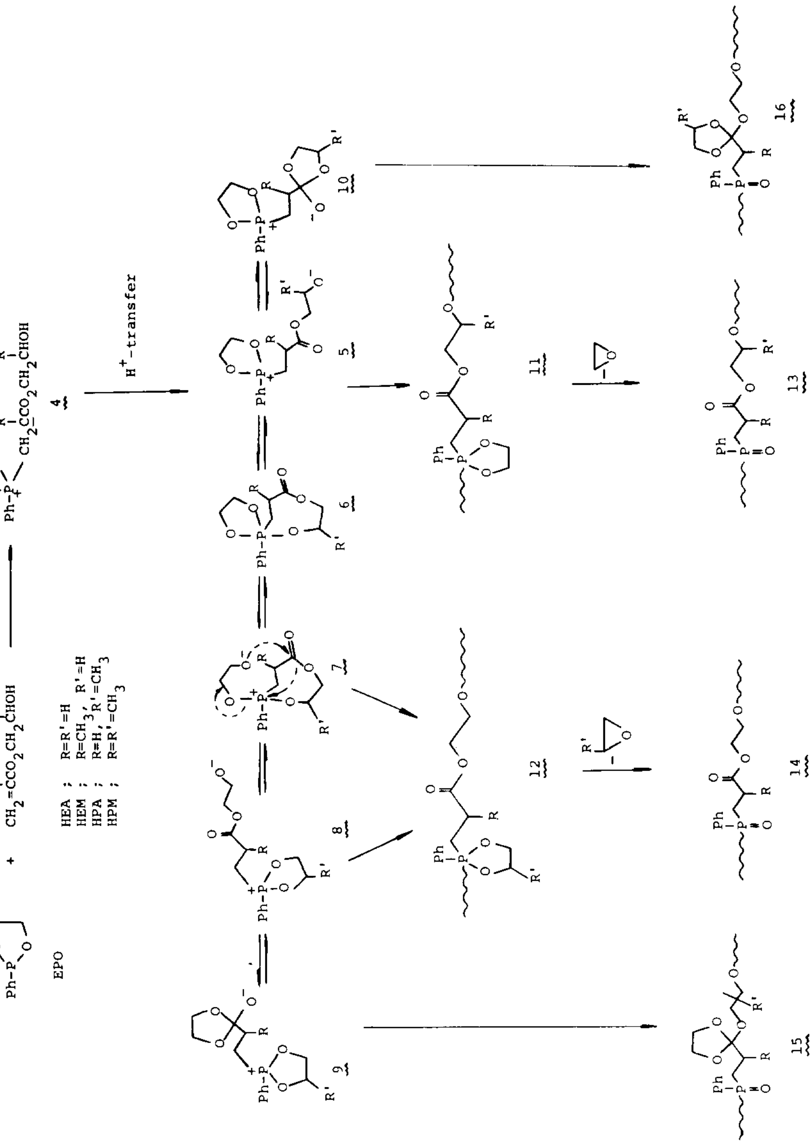
Sample No.		C(%)	H(%)	P(%)	C/P atomic ratio
1	Calcd	54.93	6.03	10.90	13.00 (12.84)[a]
	Found	51.40	7.17	10.48	12.66
3	Calcd	56.39	6.42	10.38	14.00
	Found	55.10	6.99	10.06	13.42
4	Calcd	56.39	6.42	10.38	14.00
	Found	54.24	6.88	10.39	13.46
5	Calcd	57.69	6.78	9.92	15.00
	Found	55.75	7.80	10.01	14.36

[a] The ratio calculated on the assumption that 8 molar percent of ethylene oxide (toward the total polymer units) was liberated.

The reaction was very sensitive to the temperature. At 90°C the reaction of EPO with HEA did not give any polymeric units but yielded products indicating ^{31}P NMR signal at δ -20.5 assignable to phosphorane species. The species was isolated and heated to 130°C, and then produced polymer exhibiting ^{31}P NMR peak at δ +44.7. Therefore, the species was presumed as a reaction intermediate. The isolated species had ester carbonyl group but no ortho ester group. From these observations the structure of the species was assumed to be a phosphorane type of 6.

Reaction Scheme

All above findings are compatible with the general Scheme in the following page. The first step of the reaction of EPO with four electron-deficient olefins is the formation of phosphonium-enolate anion intermediate 4 which is followed by a proton-transfer to generate zwitterion 5. If 5 were a genetic key-


EPO
HEA ; R=R'=H
HEM ; R=CH$_3$, R'=H
HPA ; R=H, R'=CH$_3$
HPM ; R=R'=CH$_3$
4
H$^+$-transfer
5
6
7
8
9
10
11
12
13
14
15
16

Scheme

zwitterion and were responsible for both initiation and propagation, polymer having structure **3** would have been obtained. In the present systems, however, **5** further changed to phosphorane **6** before the propagation stage. **6** is considered to be stable at 90°C. At higher temperatures, e.g., above 130°C, **6** arranges to several conceivable zwitterions **7**-**9**, **5**, and **10**. Zwitterions **9** and **10** lead to polymer units **15** and **16**, respectively, which are main units in the polymer. Zwitterion **5** gives a phosphorane type unit **11** which liberates ethylene oxide under reaction conditions to form phosphinate unit **13**. The generation of ethylene oxide from a cyclic phosphorane having ethylene glycol unit such as **11** has been known (DENNY and JONES, 1969). Zwitterions **7** and **8**, on the other hand, produce another phosphorane unit **12**, which in turn gives propylene oxide (R'=CH_3) with formation of phosphinate unit **14**.

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