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Polymerization via Zwitterions.
22. Alternating Copolymerization of 2-Acryloxypropionic Acid with Cyclic Phosphorus Compounds

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Summary

Alternating copolymerization of 2-acryloxypropionic acid (APA) as a new M_N with two M_N monomers of phosphorus containing ethylene phenyl phosphonite (EPO) and ethylene phenyl phosphite (EPI) have been disclosed. Copolymerizations took place without added catalyst to produce 1:1 alternating copolymers of APA-EPO and of APA-EPI. The structures of the copolymers were determined by IR and NMR spectroscopy, elemental analyses, as well as the identification of the alkaline hydrolysis products. The copolymerizations were explained in terms of a mechanism of zwitterion intermediates involving a hydrogen transfer process.

Introduction

Various combinations of nucleophilic monomers (M_N) and electrophilic ones (M_E) have been explored to produce alternating copolymers via zwitterion intermediates. All of these copolymerizations took place without added catalyst (SAEGUSA, 1977; SAEGUSA et al., 1975 and 1976a; SAEGUSA and KOBAYASHI, 1978). In the present study, 2-acryloxypropionic acid (APA) was used as a new M_E, which is regarded as a dimer of acrylic acid. In connection with the reaction characteristics of acrylic acid in this type of copolymerization (SAEGUSA et al, 1974, 1976b, and 1978), APA was combined with 2-phenyl-1,3,2-dioxaphospholane (ethylene phenyl phosphonite; EPO) and 2-phenoxy-1,3,2-dioxaphospholane (ethylene phenyl phosphite; EPI) which function as M_N. In these copolymerizations alternating copolymers having phosphinate-ester-ester type structures have been obtained.

Experimental

Materials.

2-Acryloxypropionic acid (APA). In a flask equipped with the reflux condenser, acrylic acid monomer, was heated at 150° for 4 hr with copper powder and

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p-methoxyphenol as radical inhibitors. Then, the unreacted acrylic acid monomer was removed under reduced pressure, and APA was isolated by distillation, bp 124-6° (4.5 mmHg) (SHERLIN, 1938).

Methyl 3-(Methoxyphenylphosphono)propionate (3). A mixture of 3 mmol each of dimethoxyphenylphosphine and AA in 0.6 ml of chlorobenzene was kept at 120° for 5 hr. Column chromatography was employed for the isolation of the product (silica gel, ethyl acetate eluent). The isolated material was colorless viscous oil (80% yield). *Anal*. Calcd for $C_{11}H_{15}O_4P$: C, 54.56; H, 6.24; P, 12.80. Found : C, 54.60; H, 6.37; P, 12.80. ^1H NMR ($CDCl_3$) δ 2.38 (m, $PCH_2CH_2CO_2$, 4H), δ 3.65 (s, CO_2CH_3, 3H), δ 3.70 (d, J_{P-H}=11. OHZ, P-OH_3, 3H), δ 7.50 (m, C_6H_5P, 5H); IR (film) 1736, 1220, and 1040 cm^{-1}.

Na Salt of 3-(Phenylphosphono)propionic acid (2). A mixture of the above propionate (87 mg, 0.36 mmol) and a 2N NaOH solution (5 ml) was heated at 70° for 5 hr. After neutralization with 1N HCl (phenolphthalein indicator) water was evapolated. The residue was extracted with 10 ml of ethanol. Evapolation of ethanol gave a white crystal of 2 in a 64% yield: ^1H NMR (D_2O) δ 2.25 (m, $PCH_2CH_2CO_2$, 4H), δ 7.70 (m, C_6H_5P, 5H).

Polymerization Procedure. To 2.0 ml of solvent in a test tube APA, EPO (or EPI) (5.0 mmol each) and 0.02 mmol of p-methoxyphenol (0.4 mol% for APA) as a radical inhibitor were added at room temperature under nitrogen and the tube was sealed. Then, the mixture was kept at a desired temperatuere. After the reaction the reaction mixture was poured into 100 ml of diethyl ether to precipitate the copolymer. The precipitated product was dried *in vacuo* and analyzed by IR, NMR, and elemental analyses as well as by alkaline hydrolysis.

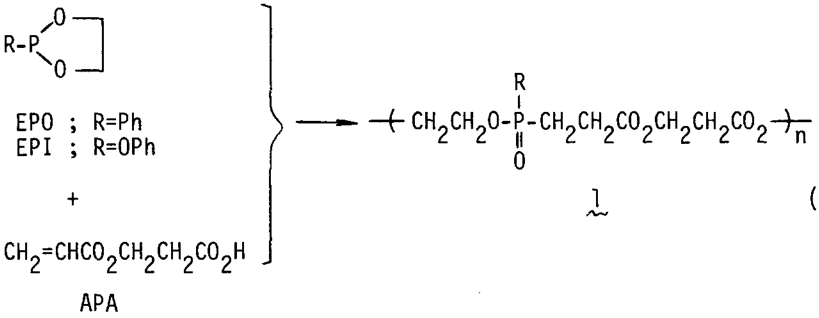
Alkaline Hydrolysis of the Copolymer. To 0.05 g of the copolymer was added 0.5 ml of 10% D_2O solution of NaOH at room temperature and the mixture was heated at 90° for 10 hr. Then the reaction mixture was subjected to NMR measurement.

Molecular Weight Determination. The molecular weight of the copolymer was measured by vapor pressure osmometry (Hitachi Perkin-Elmer Model 115) in dimethylformamide at 55°.

Results and Discussion

Copolymerizations of APA with EPO or EPI. A typical example (No. 2 of Table I) is as follows. An equimolar mixture of APA and EPO (5 mmol each) in 2 ml of acetonitrile was kept at 60°. With the progress of the reaction the mixture became highly viscous. After 21 hr the mixture was poured into a large amount of diethyl ether to precipitate the copolymer. The copolymer was dried *in vacuo* to give 1.29 g (82.7% yield) of a colorless, hygroscopic material. The structure of the copolymer was determined by IR, NMR spectroscopy, elemental analysis and the identification of the alkaline hydrolysis product. The IR spectrum of the copolymer shows strong absorption bands at 1220 cm^{-1} due to P=O and at 1735 cm^{-1} due to C=O group. The NMR spectrum of the copolymer shows the broad signals at δ 8.1-7.3 (5H); δ 4.6-3.7 (6H); and δ 2.8-1.9 (6H). These paks are assigned respectively to protons of C_6H_5; $-OCH_2CH_2O-$ + $-CO_2CH_2$; $P-CH_2CH_2$ + $-CH_2CO_2$.

These spectral data strongly indicate that the copolymer is composed of the phosphinate-ester structure 1, an alternating arrangement of EPO and APA arising by hydrogen transfer from APA.



(1)

TABLE 1

Alternating Copolymerizations of EPO or EPI with APA under Various Conditions[a]

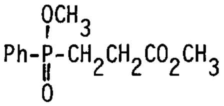
No	M_N	Solvent	Reaction temp. °C	Reaction time hr	Yield (%)	P (%)	Mol Wt[b]
1	EPO	benzonitrile	100	2.5	77	9.82	2270
2	〃	acetonitrile	60	21	83	9.78	3190
3	〃	chlorobenzene	100	5	81	9.81	2350
4	EPI	〃	100	73	51	9.38	1010
5	〃	benzonitrile	120	69	59	9.40	1410

a) The charged monomer was 5 mmol of each in 2.0 ml of solvent containing p-methoxyphenol (0.4 mol% for APA) as a radical inhibitor. M_N/M_E ratios of the copolymers were in all cases 1.0/1.0 determined by the P content and by NMR spectroscopy.

b) The molecular weights were determined by vapor pressure osmometry in DMF at 55°.

The elemental analysis of the copolymer further supported the 1:1 composition of EPO and APA. Anal. Calcd for $C_{14}H_{17}O_6P$: C 53.85, H 5.49, P 9.92 : C 53.42, H 5.59, P 9.78

The alkaline hydrolysis of the copolymer was carried out to confirm the copolymer structure. To 50 mg of the copolymer was added 0.5 ml of 10% NaOH in D_2O. The reaction of the hydrolysis mixture at 90° for 10 hr gave an equimolar mixture of disodium salt of 3-(phenylphosphono)propionic acid 2, sodium 2-hydroxypropionate and ethylene glycol. The sodium salt of 2 was generated in an aqueous NaOH solution from methyl 3-(methoxyphenylphosphono)propionate, 3.



$$\mathrm{Ph{-}\overset{\overset{\textstyle OCH_3}{|}}{\underset{\underset{\textstyle O}{\|}}{P}}{-}CH_2CH_2CO_2CH_3}$$

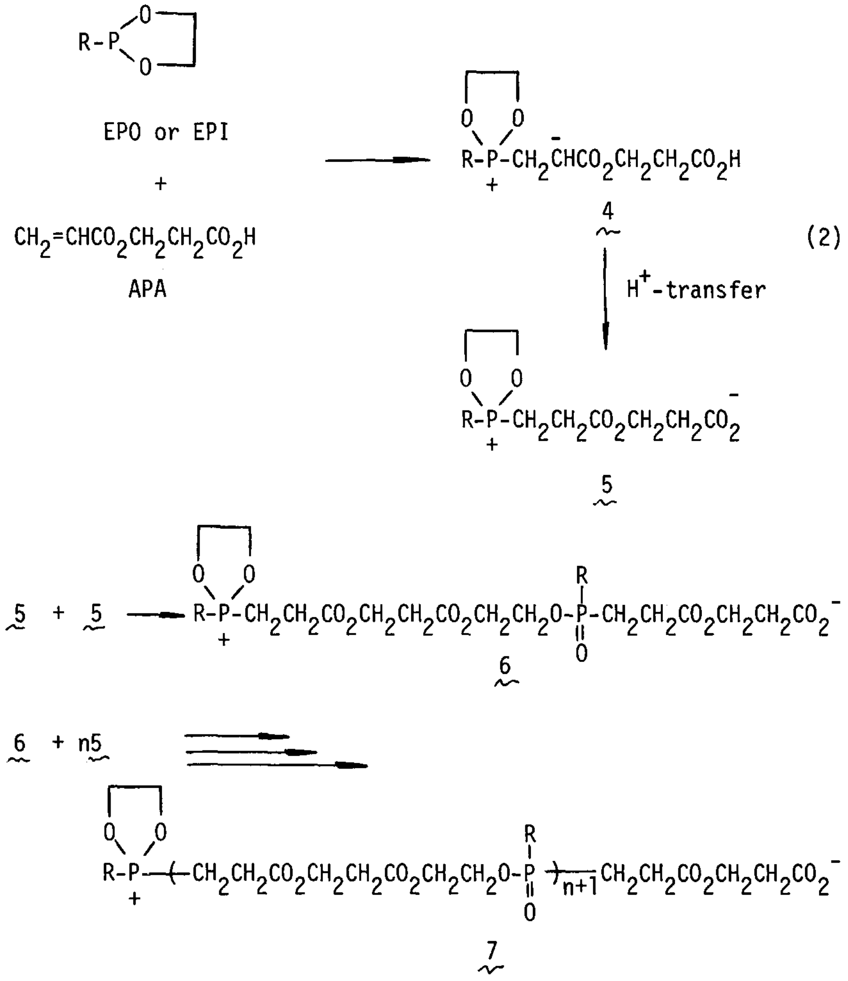
3

The NMR spectrum of the mixture of alkaline hydrolysis of copolymer was almost identical with that of a 1:1:1 mixture of the authentic samples, 3, 2-hydroxypropionic acid and ethylene glycol in D_2O solution of NaOH. All the above findings strongly support the phosphinate-ester -ester structure 1.

Similarly, the copolymerization of EPO or EPI with APA was examined under various reaction conditions (Table 1). The copolymer from EPI with APA gave the phosphonate-ester-ester structure. The copolymer composition was determined by elemental analysis (P% in the copolymer) and by NMR spectroscopy. Both methods gave very close values. In all cases, the copolymerizations took place to produce 1:1 alternating copolymers of EPO-APA, and EPI-APA, respectively.

Copolymers derived from EPO-APA and EPI-APA are soluble in chloroform, methanol acetonitrile and DMF, whereas insoluble in water, benzene, ether and other common organic solvents.

The structures of copolymers are well explained by the following scheme, which has been constructed on the bases of the reactivity characteristics of APA, EPO and EPI as well as the results of this type of copolymerizations in previous publications of us. The first step is the reaction of EPO or EPI with APA to produce a carbanion intermediate 4 followed by a proton-transfer giving the genetic zwitterion 5, which is an important key intermediate in both the initiation and propagation. The reaction of 2 mol of 5 gives dimeric zwitterion 6. The subsequent steps of the propagation involve the attack of 5 to 6 to yield a macrozwitterion 7.



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