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(22) Polymerized at 75 °C for 24 h; details will be reported in a future paper.

(23) The further data and peak assignments of the IR spectrum of 5 were as follows: 1500, 1215, 1140, 980 (α-NpSi); 1310, 1105, 725, 705 (SiPh); 1260 (SiMe). For the peak assignments, see reference cited in note 21b.

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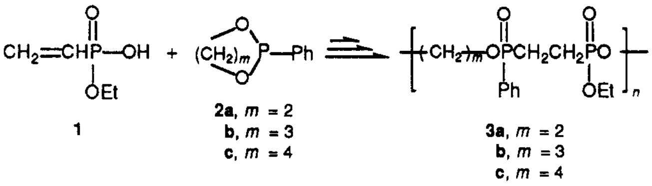
Received May 16, 1989;
Revised Manuscript Received August 29, 1989

Hydrogen-Transfer Alternating Copolymerization of Vinylphosphonic Acid Monoethyl Ester with Cyclic Phosphonites. A New Oxidation–Reduction Copolymerization

In a series of studies on the alternating copolymerization via zwitterion intermediates,[1] several monomers are known to undergo a hydrogen-transfer copolymerization; the monomers have an acidic hydrogen such as acrylic acid,[2] α-keto acids,[3] and ethylenesulfonamide.[4] These reactions occur spontaneously without any added catalyst to give the corresponding 1:1 alternating copolymers.[1] The present paper reports a new copolymerization of vinylphosphonic acid monoethyl ester (1)[5] with cyclic phosphonites 2 to give alternating copolymers 3 having two kinds of phosphorus atoms in the main chain. During the copolymerization, monomer 1 was reduced involving a hydrogen-transfer process and monomer 2 was oxidized; the oxidation state of the phosphorus atom of monomer 2 is changed from trivalent to pentavalent ("oxidation–reduction copolymerization"). It is to be noted that monomer 1 has not previously been employed in the field of polymer chemistry.



When an equimolar mixture of monomer 1 and a five-, six-, or seven-membered cyclic phosphonite (**2a, 2b,** or **2c**) was heated in a solvent or bulk at 80 or 150 °C, the copolymerization occurred without catalyst to afford the corresponding copolymer 3 in good yields (Table I). The molecular weight of the resulting copolymer depends mainly upon the reaction temperature; copolymers of higher molecular weight were obtained when the reaction was carried out at 150 °C, whereas copolymers of lower molecular weight were produced at 80 °C. The copolymers of higher molecular weight are soluble in highly polar solvents such as *N,N*-dimethylformamide, methanol, and water. The copolymers of lower molecular weight are soluble not only in these solvents but also in chloroform.

The following is a typical procedure for the copolymerization betweeen 1 and **2b**: An equimolar mixture of vinylphosphonic acid monoethyl ester (1; 136 mg, 1.0 mmol) and 2-phenyl-1,3,2-dioxaphosphorinane (**2b**; 182 mg, 1.0 mmol) in benzonitrile (0.3 mL) was heated under argon at 150 °C for 90 h. After precipitation from diethyl ether, the product was dried in vacuo to give 210 mg of copolymer **3b** (66% yield).

Figure 1 shows the ^1H NMR spectrum of the copolymer obtained from 1 and **2b** at 150 °C in benzonitrile (entry

0024-9297/89/2222-4390$01.50/0

Table I
Copolymerization of Vinylphosphonic Acid Monoethyl Ester (1) with Cyclic Phosphonites 2

entry	cyclic phosphonite 2	solv	temp, °C	time, h	yield,[a] %	mol wt[b]
1	**2a**	PhCN	150	90	78	37 000
2	**2a**		150	20	71	28 000
3	**2a**		80	100	52	590
4	**2b**	PhCN	150	90	66	36 000
5	**2b**	PhCN	150	24	36	8 300
6	**2b**	DMF	150	20	95	30 000
7	**2b**		150	20	63	23 000
8	**2b**		80	100	49	640
9	**2c**	PhCN	150	24	61	29 000
10	**2c**		150	25	90	24 000
11	**2c**		80	96	72	1 200

[a] Isolated yield. [b] Determined by gel permeation chromatography (GPC): eluent, water; flow rate 1.0 L/min; column, GL-W520 and GL-W530 (Hitachi Co.) at 60 °C.

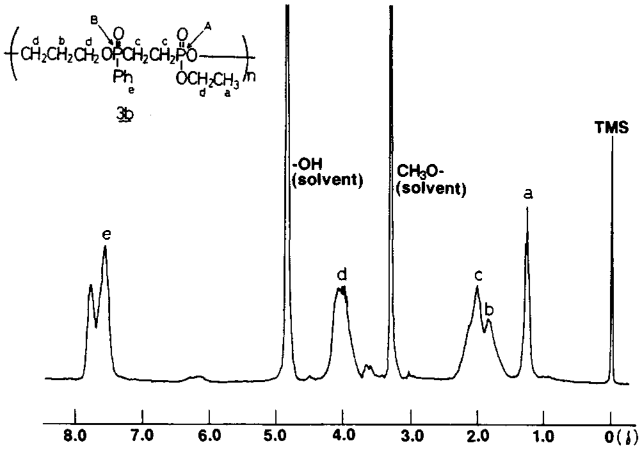
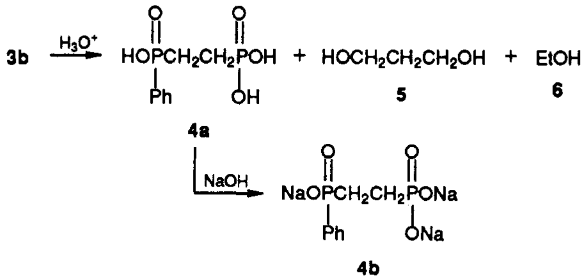


Figure 1. ^{1}H NMR spectrum of copolymer (entry 5) in CD_3OD (250 MHz).

5). The signal at δ 1.24 is assigned to the methyl protons of ethyl group. The broad signals centered at δ 1.81 and 1.98 are due to the methylene protons of CCH_2C and PCH_2, respectively, and the signal at δ 4.00 is due to those of OCH_2. The signal at δ 7.52 is ascribed to the phenyl protons. The small signal at δ 3.65 may be assigned to the terminal methylene group ($HOCH_2$). By comparison of the integral value of the phenyl protons and the methyl protons, the content of vinylphosphonic acid unit and cyclic phosphonite unit in the copolymer was calculated to be 50%. The ^{31}P NMR spectrum of the copolymer in CD_3OD showed two main peaks at δ +35.3 and +51.2 (relative to 85% H_3PO_4 external standard), which are assignable to two kinds of phosphorus atoms indicated as A and B, respectively (Figure 1). These peaks are accompanied by a small peak at δ +23.3, which is due to the terminal phosphorus atom of the phosphonate type.

The hydrolysis of the copolymer was carried out to confirm the structure of copolymer **3**. An acetonitrile solution of **3b** was treated with 6 N hydrochloric acid at 150 °C for 98 h in a sealed tube to give **4a**, trimethylene glycol (**5**) and ethanol (**6**). The product **4a** was unstable and could not be isolated probably because dehydration reaction of **4a** occurred readily to produce a polymeric compound. After treating the reaction mixture with sodium hydroxide, the solvent and volatile products **5** and **6** were removed to dryness and the residue was analyzed by ^{1}H and ^{31}P NMR. The ^{1}H NMR spectrum showed two peaks at δ 1.60 and 7.24, which are assigned to the methylene protons and phenyl protons of the product **4b**. The ^{31}P NMR also supported the structure **4b**; signals derived from two phosphorus atoms, $NaO(\mathit{P}{=}O)PhCH_2$ and $CH_2(\mathit{P}{=}O)(ONa)_2$, were observed at δ +38.8 and +31.2, respectively. The GPC analysis of the hydrolyzed mixture indicated quantitative formation of **5** and **6** as well as the complete disappearance of the copolymer **3b**.



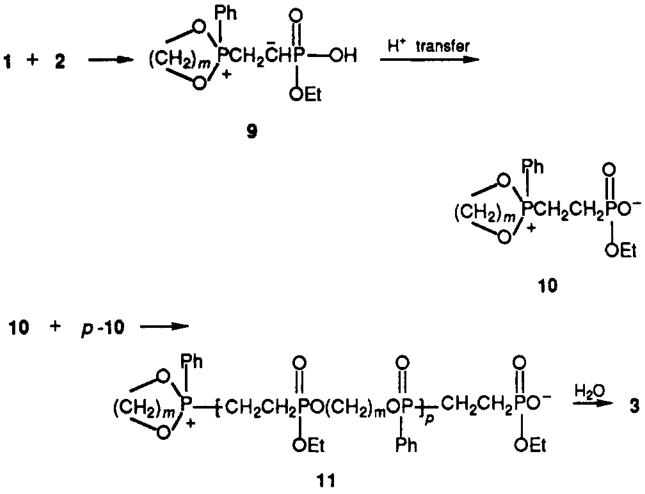
$$\mathbf{3b} \xrightarrow{H_3O^+} HO\underset{Ph}{\overset{O}{\overset{\|}{P}}}CH_2CH_2\underset{OH}{\overset{O}{\overset{\|}{P}}}OH + HOCH_2CH_2CH_2OH + EtOH$$

4a **5** **6**

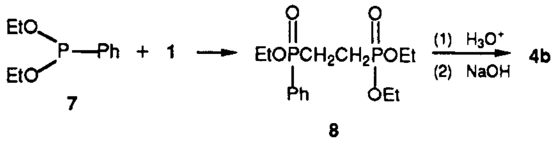
$$\xrightarrow{NaOH} NaO\underset{Ph}{\overset{O}{\overset{\|}{P}}}CH_2CH_2\underset{ONa}{\overset{O}{\overset{\|}{P}}}ONa$$

4b

Scheme I



In order to obtain information about the reaction mechanism and to confirm the structure of the hydrolyzed product **4**, the following model reaction was carried out. When a mixture of diethyl phenylphosphonate (**7**) and **1** in benzonitrile was heated at 150 °C for 51 h, the adduct **8** was quantitatively formed. The hydrolysis of **8** and successive neutralization afforded the product, which is identical with **4b**.



$$(EtO)_2P{-}Ph + \mathbf{1} \longrightarrow EtO\underset{Ph}{\overset{O}{\overset{\|}{P}}}CH_2CH_2\underset{OEt}{\overset{O}{\overset{\|}{P}}}OEt \xrightarrow[(2)\ NaOH]{(1)\ H_3O^+} \mathbf{4b}$$

7 **8**

On the basis of the above data, the following copolymerization mechanism may be proposed (Scheme I). The first step is the formation of zwitterion **9** by the Michael-type addition of vinylphosphonic acid monoethyl ester (**1**) with a cyclic phosphonite **2** followed by a hydrogen-transfer process to give a genetic zwitterion **10**.

Then, the reaction between two molecules of genetic zwitterion occurs, in which the phosphonium ring of one molecule is opened by a nucleophilic attack of the anion of the other molecule according to the mode of the Arbuzov reaction involving an oxidation–reduction. The propagation proceeds via the successive attack of the genetic zwitterion **10** onto dimeric zwitterion **11** ($p = 1$) to form a macrozwitterion of an alternating copolymer **3**.

The ^{31}P NMR spectrum of the reaction mixture at the early stage of copolymerization showed signals at δ +61.9 and +20.1, which may be ascribed to the phosphorus atoms of the terminal phosphonium ion and phosphonate anion of intermediates **10** and/or **11**.

The more detailed studies including kinetics and mechanism of the present copolymerization are now in progress.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Area of "New Functionality Materials Design, Preparation, and Control" from the Ministry of Education, Science and Culture, Japan (Nos. 62604004 and 63604004).

Registry No. 1, 4546-13-8; (1)(**2a**) (alternating copolymer), 123168-40-1; (1)(**2b**) (alternating copolymer), 123168-39-8; (1)(**2c**) (alternating copolymer), 123168-41-2; **4b**, 123183-65-3; **7**, 1638-86-4; **8**, 123168-38-7.

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Received March 1, 1989

A Holoenzyme Model of Thiamine Dependent Enzymes: Polymer Catalyst Supported Thiazolium Salt

Intense attention has been focused on studies of enzyme and coenzyme model reactions. A coenzyme, the most important site of a holoenzyme, acts as the active catalytic site of enzymic reaction by using its own functional group. Therefore, in a few cases, a coenzyme has catalytic activity even without an apoenzyme, and a biomimic compound, which has a functional group similar to that of a coenzyme, has catalytic activity comparable to that of a coenzyme. From this viewpoint, many chemists have studied the model reaction of coenzyme-dependent enzymes in detail,[1] and it has become evident that the apoenzyme not only plays a role in the support of the coenzyme but also participates actively in the stereospecificity and substrate specificity of enzymic reaction. In the heme protein, the heme, which is isolated from the supporting protein, loses its activity in vivo;[2] i.e., the apoenzyme plays a role as a protector of the active site.

Table I
Results of Acyloin Condensations[a]

cat.	yield, %	cat.	yield, %
MPTI	4.5	PTS$^+$(14)-DVB(5)	29.9
PTS$^+$(14)	21.0	PTS$^+$(9)-NVP(89)	4.7
PTS$^+$(69)	13.7		

[a] [cat.] = 0.036 mmol and [furfural] = 3.6 mmol; in phosphate buffer, 3.3 mL (pH 8.0), at 60 °C for 40 h.

Since Breslow[3] reported that the thiazolium salt unit is an active site of thiamine pyrophosphate, which is the coenzyme for a number of important biochemical reactions including decarboxylation and acyloin condensation, many chemists have investigated the catalytic activity of thiazolium salt in various reactions.[4] It was reported that in an aqueous system a thiazolium salt changed into an open-chain compound and lost its activity because of an attack by hydroxide ions, even though naturally occurring thiamine-dependent enzymes are known to be active in a hydrophilic environment.[5] In vivo an apoenzyme may protect an active site, i.e., a thiazolium salt unit, from the attack of hydroxide ions. Therefore, many model reactions have been performed in a nonaqueous system. Concerning the aqueous system, Tagaki et al.[6] obtained a highly active thiazolium salt catalyst when acyloin condensation was carried out in the micellar system. Recently, Breslow et al.[7] synthesized a thiazolium salt with a γ-cyclodextrin and reported that the catalyst had high catalytic activity in the dimethyl sulfoxide/H_2O mixed solvent. They emphasized the importance of the incorporation of a substrate for this reaction.

To the best of our knowledge, no study has investigated the role of synthetic polymer catalysts, which are used as a model compound of a holoenzyme by considering the protection of an active site. In the present study, we conducted acyloin condensation of furfural in buffer solution using a thiazolium salt polymer whose synthesis was reported in our previous investigation.[8] It became clear that the hydrophobic environment generated by the polymer main chain around the active site was important in maintaining the catalytic activity in the aqueous system.

The thiazolium salt polymer catalysts were synthesized by quaternization of homopoly(4-(4-vinylphenyl)thiazole) (VPT) and abbreviated as PTS$^+$(x%) in which x stands for the mol % of quaternized thiazole units. The acyloin condensation of furfural was done in phosphate buffer (pH 8.0, $\mu = 0.194$) at 60 °C. An excess of substrates (100 times the amount of catalyst) was reacted in a sealed, degassed tube, in which the system was heterogeneous throughout the reaction.

After the reaction, the reaction mixture was poured into MeOH. The precipitated polymer catalyst was filtered and the filtrate was analyzed and quantified by high-performance liquid chromatography (JASCO TriRoter-V chromatograph) with benzophenone as an internal standard. The results are shown in Table I. A low molecular weight analogue, *N*-methyl-4-phenylthiazolium iodide (MPTI), which gave a quantitative yield in MeOH,[8] had very low activity in the aqueous system. However, a polymeric catalyst, PTS$^+$(14), had a higher catalytic activity than MPTI in the aqueous system. Moreover, the insoluble cross-linked polymer catalyst PTS$^+$(14)–DVB(5) (containing 5 mol % of divinylbenzene) had the highest catalytic activity. It is thought that the hydrophobic environment formed by polymer main chains protects the active site from an attack by hydroxide ions. This assumption is supported by the fact that the more hydrophilic polymer catalysts PTS$^+$(69) and PTS$^+$(9)–NVP(89), which were synthesized by quaternization of the copolymer

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