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Notes

Hydrogen-Transfer Polymerization of Vinylphosphonic Acid Monoethyl Ester

Shiro Kobayashi,* Jun-ichi Kadokawa, I-Fang Yen, Hiroshi Uyama, and Shin-ichiro Shoda

Department of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University, Aoba, Sendai 980, Japan

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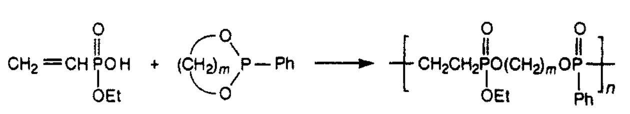
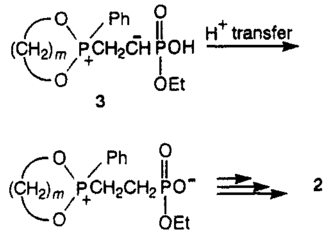
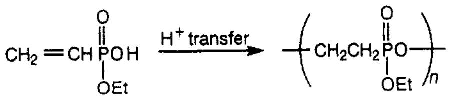
Introduction

Recently we have reported an alternating copolymerization of vinylphosphonic acid monoethyl ester (1) with a cyclic phosphonite to give copolymer 2 having a phosphinate–phosphonate structure.[1] In the copolymerization of 1 with the cyclic phosphonite the Michael-type adduct 3 is first formed, followed by a hydrogen transfer to give zwitterion 4. The propagation proceeds via the successive attack of 4 to produce the alternating copolymer 2. On the basis of these findings, we examined the possibility of the hydrogen-transfer process in the reaction of 1 and now we disclose a new mode of homopolymerization of 1 to produce poly(phosphonate) 5. Analogous hydrogen-transfer polymerizations of vinyl monomers such as acrylamide,[2] acrylic acid,[3] and hydroxyalkyl acrylate[4] with a base catalyst were previously reported.


1 (*m* = 2,3,4) 2





1 5

$$CH_2{=}CHP(O)(OH)(OEt) \xrightarrow{H^+\ \text{transfer}} \left(CH_2CH_2P(O)(OEt)O\right)_n$$

Results and Discussion

Polymerization of 1. Polymerization of 1 was carried out in *N,N*-dimethylformamide (DMF) by using triphenylphosphine as a base catalyst to give 5 (Table I). When other solvents such as acetonitrile and chloroform were used, the polymerization did not occur. Yield of 5 was not high because the monomer 1 did not disappear completely. The polymerization of 1 was also induced by other bases such as tri-*n*-butylphosphine (*n*-Bu_3P), potassium *tert*-butoxide (KOBu^t), and sodium acetate (NaOAc).

Table I
Hydrogen-Transfer Polymerization of 1 under Various Reaction Conditions[a]

entry	initiator (mol % for 1)	time, h	yield,[b] %	M_n[c]
1	Ph_3P (5.0)	69	27	1280 1350[d]
2	Ph_3P (1.0)	46	24	1180
3	*n*-Bu_3P (5.0)	43	24	1280
4	KOBu^t (5.0)	44	24	1170
5	NaOAc (5.0)	43	29	1220

[a] Monomer 1 (1.0 mmol); solvent DMF (0.3 mL); reaction temperature, 150 °C. [b] THF-insoluble part. [c] Determined by GPC. [d] Determined by ^1H NMR.

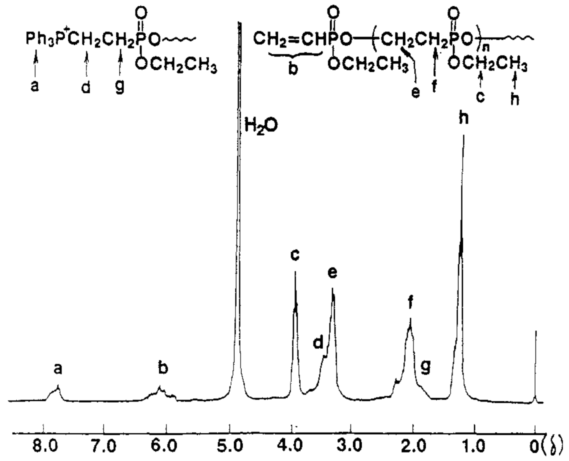
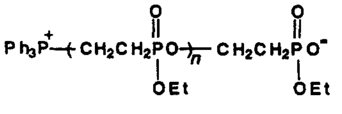


Figure 1. ^1H NMR spectrum of polymer 5 (entry 1) in D_2O (250 MHz).

The structure of the polymer was confirmed by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Figure 1 shows the ^1H NMR spectrum of 5 (entry 1). A triplet peak h at δ 1.26 is due to methyl protons of the ethyl group. Peaks f and e at δ 2.06 and 3.33 are assigned to methylene protons of PCH_2 and OCH_2 in the main chain, respectively. Peak c at δ 3.95 is due to methylene protons of the ethyl group. Besides these, small peaks are seen. Peak a at δ 7.76 is assigned to phenyl protons of the Ph_3P^+ species. A multiplet peak b at δ 5.8–6.4 is due to vinyl protons of alkyl phosphonate $CH_2{=}CHP(O)(OEt)$. In addition, broad peaks d and g overlapping with peaks e and f, respectively, are assigned respectively to α- and β-methylene protons of $P^+CH_2CH_2P(O)(OEt)$ in the phosphonium zwitterion species. In relation to the species 6, zwitterion 7 was prepared by the equimolar reaction of Ph_3P with 1. In the ^1H NMR spectrum of 7 the protons of P^+CH_2 and $CH_2P(O)(OEt)O^-$ appeared at δ 3.52 and 1.74, which are the same chemical shifts of peaks d and g, respectively.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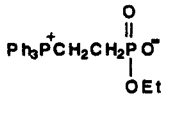
$$Ph_3P^+\!-\!\left(CH_2CH_2P(O)(OEt)O\right)_n\!-\!CH_2CH_2P(O)(OEt)O^-$$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$$Ph_3P^+CH_2CH_2P(O)(OEt)O^-$$

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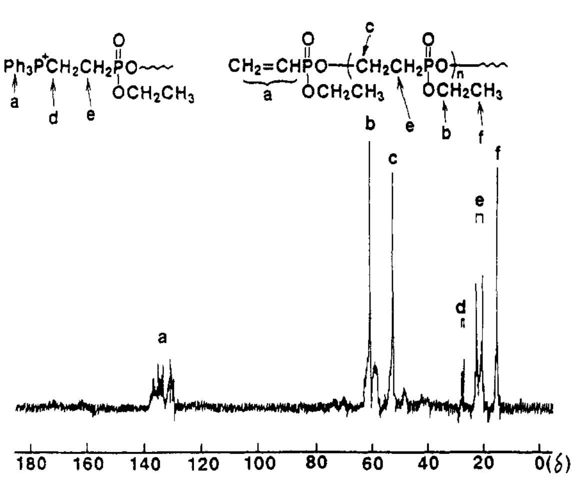
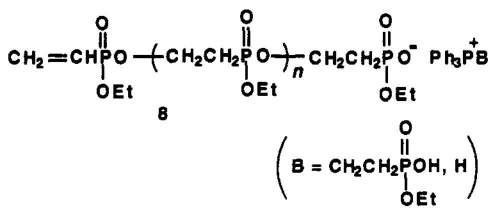


Figure 2. ^{13}C NMR spectrum of polymer **5** (entry 1) in D_2O (62.8 MHz).

The ^{13}C NMR spectrum (D_2O) of polymer **5** showed four peaks at δ 15.4 (CH_3), 21.6 (J_{cp} = 31.5 Hz, PCH_2), 52.5 (OCH_2CH_2P), and 60.5 (OCH_2CH_3) (Figure 2). A small doublet peak at δ 27.3 (J_{cp} = 5.4 Hz) is due to the α-carbon of the terminal triphenylphosphonium group. Furthermore, small multiplet peaks due to aromatic carbons of triphenylphosphonium and vinyl carbons of vinylphosphonate of the terminal groups were observed at δ 130–135. The ^{31}P NMR spectrum of the polymer in D_2O showed a main peak at δ +20.3 ascribed to the phosphorus atom of the phosphonate structure and small peaks at δ +15.8 and +25.8 assigned to the phosphorus atom of the vinyl phosphonate and of the terminal phosphonium group, respectively. A very small and broad peak at δ +4.6 was assigned as the phosphorus atom of the phosphonium phosphonate of **8** (B = H). These results strongly suggest that the polymer is of poly(phosphonate) structure and is a mixture of different terminal groups, phosphonium and vinyl phosphonate groups, respectively. Therefore, the two species **6** and **8** are probably responsible for the propagation. This was further confirmed by the following experiment; the polymer was dissolved in a 1 N Na_2CO_3 aqueous solution, and the solution was poured into a large amount of THF to precipitate the polymeric material. In the ^1H NMR spectrum of the precipitated polymer, the intensities of peaks a, d, and g (in Figure 1) decreased compared with that of peak b, indicating that the phosphonium part of **8** was removed by the above alkaline treatment and the phosphonium group chemically bound to the polymer chain in **6** was not removed.

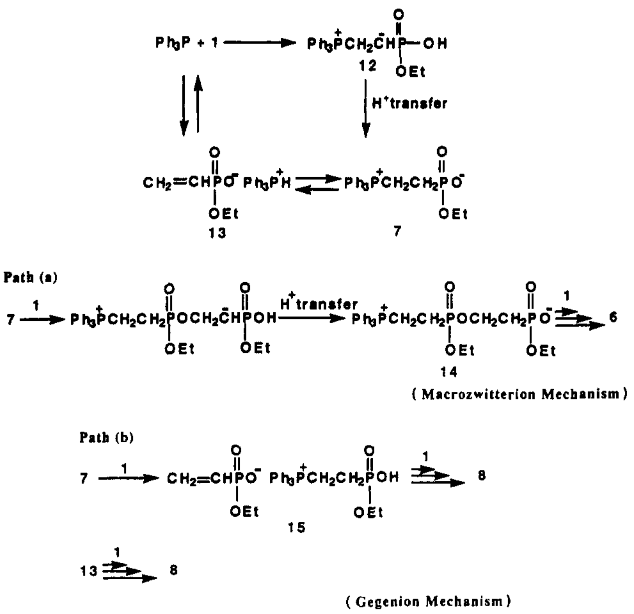


$$CH_2{=}CHP(O)(OEt)O{-}\!\left(CH_2CH_2P(O)(OEt)O\right)_n\!{-}CH_2CH_2P(O)(OEt)O^-\ Ph_3\overset{+}{P}B \quad \left(B = CH_2CH_2P(O)(OEt)OH,\ H\right)$$

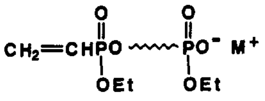
8

The molar ratio from the integrated area of peak a (15 H) and peak b (3 H) was 1.0:5.8. On the basis of the assumption that 1 mol equiv of Ph_3P^+ and $CH_2{=}CHP(O)(OEt)O$ groups is attached at the polymer end, the molecular weight of the polymer was calculated to be 1350. The molecular weight determined by gel permeation chromatography (GPC) was 1280. Both data obtained by these two methods agreed well with each other. The molecular weight of the polymer after alkaline treatment obtained by the ^1H NMR spectrum was also calculated as 1010 by the integrated ratio in the ^1H NMR spectrum on the basis that the molar ratio of **6** and **8** was 1.0:5.8. The decrease of the molecular weight was due to the loss of the phosphonium species in polymer **8**.

Scheme I

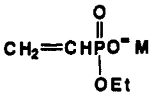


The n-Bu_3P-initiated system also contained two types of propagation species corresponding to **6** and **8**. In the system using $KOBu^t$ or NaOAc as an initiator, however, the terminal vinyl group was observed and the phosphonium species was not detected in the ^1H NMR spectrum, indicating that the propagation species was only gegenion species **9** which was initiated by **10**.



$$CH_2{=}CHP(O)(OEt)O\sim\sim P(O)(OEt)O^-\ M^+$$

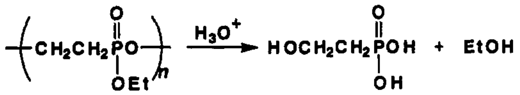
9 (M = K, Na)



$$CH_2{=}CHP(O)(OEt)O^-\ M^+$$

10

Hydrolysis of 5. The hydrolysis of polymer **5** was carried out to confirm further the structure of **5**.



$$\left(CH_2CH_2P(O)(OEt)O\right)_n \xrightarrow{H_3O^+} HOCH_2CH_2P(O)(OH)OH + EtOH$$

5 11

The polymer was hydrolyzed in a 1 N HCl aqueous solution at 150 °C for 97 h. The resulting product was an equimolar mixture of (2-hydroxyethyl)phosphonic acid (**11**) and ethyl alcohol, confirmed by ^1H NMR analysis in D_2O; peaks at δ 3.57 (m, 4 H), 2.00 (br, 2 H), and 1.06 (t, 3 H) were assigned to the protons of CCH_2O, CCH_2P, and CH_3C, respectively. Furthermore, the assignment was supported by comparing the authentic samples (**11** and ethyl alcohol).

Model Reaction. In order to confirm the polymerization mechanism, the following model reaction was carried out. The equimolar mixture of **1** and triphenylphosphine was heated at 150 °C for 92 h in CD_3CN. By reprecipitation (acetonitrile–diethyl ether), a hygroscopic white powder was obtained. The product was found to be zwitterion **7** by ^1H and ^{31}P NMR analysis. Furthermore, the polymerization of **1** by using **7** as the initiator in DMF was induced to produce polymer **5** consisting of the two species **6** and **8**. These results are taken to support that the first step of the polymerization is the formation of **7**, which is responsible for the polymerization of **1**.

Polymerization Mechanism. Based on the above data, the following mechanism is proposed for the triphenylphosphine-initiated system (Scheme I). The first step is the formation of zwitterion **12** by the Michael-type addition of **1** with triphenylphosphine followed by a hydrogen-transfer process to give a zwitterion species **7**. Zwitterion **7** is in equilibrium with a phosphonium phosphonate **13** under the polymerization condition. **13** may be partly formed by protonation of triphenylphosphine with **1**. Then, the Michael-type addition of **7** onto **1** involving the hydrogen-transfer process occurs to produce the dimeric zwitterion **14**. **7** and/or **14** induce(s) the polymerization of **1** to give **6** (path (a), "macrozwitterion mechanism"). On the other hand, protonation of **7** with **1** gives **15**, leading to the formation of polymer **8**. The polymerization of **1** by **13** as an initiator also produces **8** (path (b), "gegenion mechanism"). The polymerization initiated by n-Bu_3P is explained by a mechanism similar to that of Scheme I. In using $KOBu^t$ or NaOAc as an initiator, the polymerization proceeded extensively by a gegenion mechanism.

Experimental Section

Materials. Solvents DMF and acetonitrile were purified by distillation over CaH_2. All initiators were purified in the usual manner. Monomer **1** and (2-hydroxyethyl)phosphonic acid (**11**) were prepared according to the literature.[1a,5] All operations were carried out under argon.

Polymerization of 1. A typical procedure is as follows (entry 1): Monomer **1** (1.0 mmol) and triphenylphosphine (0.05 mmol) as the initiator in 0.3 mL of DMF were heated at 150 °C for 69 h. The reaction mixture was poured into a large amount of diethyl ether. The precipitate was collected by decantation and dissolved in a small amount of water. The aqueous solution was poured into a large amount of THF to precipitate the polymeric material. The polymer was dried in vacuo to give 0.033 g (22% yield based on **1** and triphenylphosphine) of pale yellow solid material **5**.

Model Reaction of 1 with Triphenylphosphine. An equimolar amount of **1** and triphenylphosphine (1.0 mmol) in 0.3 mL of acetonitrile was heated at 150 °C for 92 h under argon. The product was purified by repeated reprecipitation from acetonitrile to diethyl ether until the product became powdery. After drying in vacuo, 0.074 g (19% yield) of **7** was obtained: ^1H NMR (CD_3CN) δ 1.12 (t, CH_3, 3 H), 1.74 (m, $P(O)CH_2$, 2 H), 3.52 (m, P^+CH_2, 2 H), 3.79 (m, OCH_2, 2 H), and 7.73 (br, Ar, 15 H); ^{31}P NMR ($CDCl_3$) δ 28.8 (phosphonium) and 21.9 (phosphonate).

Measurements. ^1H (250 MHz), ^{13}C (62.6 MHz), and ^{31}P (100 MHz) NMR spectra were recorded on a Bruker AC250T NMR spectrometer. Gel permeation chromatographic (GPC) analysis was performed by using a Hitachi 665 A with an RI detector under the following conditions: Gelpack GL-W520 columns with water eluent at a flow rate of 1.0 mL/min.

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References and Notes

(1) (a) Kobayashi, S.; Kadokawa, J.; Yen, I. F.; Shoda, S. *Macromolecules* **1989**, *22*, 4390. (b) Kadokawa, J.; Yen, I. F.; Shoda, S.; Uyama, H.; Kobayashi, S. *Polym. J.*, in press.

(2) Breslow, D. S.; Hulle, G. E.; Mallach, A. S. *J. Am. Chem. Soc.* **1957**, *79*, 3760.

(3) Saegusa, T.; Kobayashi, S.; Kimura, Y. *Macromolecules* **1974**, *7*, 256.

(4) Saegusa, T.; Kobayashi, S.; Kimura, Y. *Macromolecules* **1975**, *8*, 950.

(5) Sommer, K.; Raab, G. German Offen. 2252684, 1974; *Chem. Abstr.* **1974**, *81*, 37651m.

Registry No. 1, 4546-13-8; 5, 41302-90-3; 7, 143843-68-9; $P(O)(OH)_2(CH_2)_2OH$, 22987-21-9; Et_3P, 603-35-0.