Hydrogen–Transfer Alternating Copolymerization of *P*-Ethenyl-*N*-*n*-propylphosphonamidic Acid Ethyl Ester with Cyclic Phosphonites Involving Oxidation–Reduction Process

Shiro KOBAYASHI,* Jun-ichi KADOKAWA, Hiroshi UYAMA,
and Shin-ichiro SHODA

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

(Received January 25, 1991)

ABSTRACT: The present paper describes the alternating copolymerization of *P*-ethenyl-*N*-*n*-propylphosphonamidic acid ethyl ester (**1**) with cyclic phosphonites (**2**). The copolymerization took place without added catalyst to produce 1:1 alternating copolymer **3**. During the copolymerization the oxidation–reduction reaction of monomers occurred. Monomer **1** behaved as an oxidant monomer (M_{ox}) whereas **2** acted as a reductant monomer (M_{red}). The structure and composition of copolymers were determined by ^1H and ^{31}P NMR spectra as well as the hydrolysis experiments. The copolymerization is reasonably explained by a mechanism of propagation *via* zwitterion intermediates. The apparent monomer reactivity ratios determined in benzonitrile at 130°C were $r_1 = 0.00$ and $r_{2(\text{six-membered})} = 0.34$.

KEY WORDS Oxidation–Reduction Alternating Copolymerization / *P*-Ethenyl-*N*-*n*-propylphosphonamidic Acid Ethyl Ester / Cyclic Phosphonites / Oxidant Monomer / Reductant Monomer / Hydrogen–Transfer Process /

In a series of studies on alternating copolymerization involving zwitterion intermediates,¹ we have found various hydrogen–transfer copolymerization reactions between 2-phenyl-1,3,2-dioxaphospholane (**2a**) and vinyl monomers having an acidic hydrogen such as acrylic acid,² acrylamide,² and ethylene-sulfonamide.³ The copolymerizations occur spontaneously without any added catalyst involving a hydrogen–transfer process to produce 1:1 sequence-regulated alternating copolymers. Phosphorus atom in monomer **2a** is trivalent, whereas that is changed to pentavalent in the product copolymer. Thus, an oxidation of phosphorus atom takes place during the copolymerization. Concurrently, the vinyl monomer is reduced. Therefore, the copolymerization is termed as “oxidation–reduction copolymerization”.^{4,5} **2a** behaves as a reductant monomer (M_{red}) and vinyl monomers

behave as oxidant monomers (M_{ox}) during the copolymerization.

Very recently we have found an alternating copolymerization of vinylphosphonic acid monoethyl ester with **2a**,⁴ in which vinylphosphonic acid monoethyl ester behaved as an oxidant monomer. This paper reports a new hydrogen–transfer alternating copolymerization of *P*-ethenyl-*N*-*n*-propylphosphonamidic acid ethyl ester (**1**), *N*-*n*-propylamide derivative of vinylphosphonic acid monoethyl ester, with three monomers of five, six, and seven-membered cyclic phosphonites (**2**). This polymerization involves the reduction of monomer **1** and the oxidation of monomer **2**.

EXPERIMENTAL

Materials

Solvents, acetonitrile, benzonitrile, dimethylformamide (DMF) and diethyl ether were purified in a usual manner under argon. Monomers **2a–c** were prepared according to the literatures.^{6,7}

Preparation of *P*-Ethenyl-*N*-*n*-propylphosphonamidic Acid Ethyl Ester **1**

To phosphorus pentachloride (10.5 g, 0.05 mol) was added vinylphosphonic acid diethyl ester (8.2 g, 0.05 mol) with stirring at room temperature. After stirring for 1 h, phosphorus oxychloride was removed from the reaction mixture by evaporation. The residue was distilled to give vinylphosphonyl chloride monoethyl ester: bp 71–78°C (17 mmHg). To a mixture of *n*-propylamine (1.5 g, 0.025 mol) and triethylamine (3.0 g, 0.03 mol) in 10 ml of diethyl ether was added dropwise vinylphosphonyl chloride monoethyl ester (3.9 g, 0.025 mol) with stirring at –15°C. After stirring for 15 min, the precipitate triethylamine hydrochloride was removed by filtration. The filtrate was evaporated and the residue was distilled to give **1** (3.1 g, 71% yield): bp 95–100°C (0.8 mmHg); ¹H NMR (CDCl₃) δ 0.92 (t, *J* = 7.0 Hz, CH₂CH₂CH₃, 3H), 1.32 (m, CCH₂C and OCH₂CH₃, 5H), 2.90 (m, NCH₂C and NH, 3H), 4.07 (m, OCH₂C, 2H), 5.4–6.4 ppm (m, CH₂=CHP, 3H); ³¹P NMR (CDCl₃) δ +21.7.

Copolymerization of **1** with **2**

A typical run was as follows (entry 6). A mixture of **1** (0.177 g, 1.0 mmol) and **2b** (0.182 g, 1.0 mmol) in 0.3 ml of DMF heated under

argon at 130°C. After 89 h the mixture was poured into a large amount of a mixture of diethyl ether and *n*-hexane (50:50 vol%) to precipitate the polymeric material. The material was isolated by decantation and dried *in vacuo* to give 0.21 g (59% yield) of **3b**.

Hydrolysis of Copolymer **3**

To 0.18 g of the copolymer **3b** (entry 6) in 0.3 ml of acetonitrile, 0.3 ml of 6*N* hydrochloric acid was added at room temperature. The mixture was kept at 150°C for 556 h. Then, 5 ml of water was added to the reaction mixture and the solution was poured into a large amount of acetonitrile to precipitate the solid material, followed by decantation to give **4** quantitatively. The supernatant was evaporated to give the mixture of **5** and **6**: ¹H NMR of **4** (D₂O) δ 1.5–2.0 (m, CH₂P, 4H), 7.55 and 7.74 (m, ArP, 5H); IR (neat) 1250 cm^{–1} (ν_{P=O}). ¹H NMR of the mixture of **5** and **6** (D₂O) δ 0.96 (t, *J* = 7.40 Hz, CH₃C, 3H), 1.68 (m, CCH₂CH₂N, 2H), 1.80 (m, OCH₂CH₂CH₂O, 2H), 2.95 (t, *J* = 6.94 Hz, CCH₂N, 2H), 3.67 ppm (t, *J* = 6.33 Hz, CCH₂O, 4H).

Determination of Monomer Reactivity Ratios

A general procedure is given as follows. Monomers **1** and **2b** of various feed ratios ([**1**] + [**2b**] = 1.0 mmol) were placed in 0.15 ml of PhCN under argon and kept at 130°C in a sealed tube. After 12 h, the reaction mixture was poured into a large amount of a diethyl ether–*n*-hexane (50:50 vol%) mixed solvent to precipitate the copolymer. The copolymer composition was determined by ¹H NMR spectroscopy. The monomer reactivity ratios were determined by using Mayo–Lewis meth-

Table I. Copolymerization of *P*-ethenyl-*N*-*n*-propylphosphonamidic acid ethyl ester (**1**) with cyclic phosphonites **2**^a

Entry	Cyclic phosphonite 2	Solvent	Temp.	Time	Yield ^b	Mol. wt. ^d
			°C	h	%	
1	2a	CD ₃ CN	130	242	56	900
2	2a	PhCN	130	176	56	890
3	2b	CD ₃ CN	130	214	52	990
4	2b	PhCN	130	70	56	940
5	2b	PhCN	150	70	62	1100
6	2b	DMF	130	89	59	1300
7	2c	CD ₃ CN	130	102	31 ^c	930
8	2c	PhCN	130	53	19 ^c	760

^a Copolymerization was carried out in the equimolar feed ratio of **1** and **2**.^b Diethyl ether—*n*-hexane (50:50 vol%), insoluble part.^c Diethyl ether, insoluble part.^d Determined by GPC with polystyrene standard.od.⁸

Measurements

¹H and ³¹P NMR spectra were recorded on a 250 MHz Bruker AC250T NMR spectrometer and 36.4 MHz JEOL FX-90Q NMR spectrometer, respectively. IR spectra were recorded on a Shimadzu IR-27G spectrometer. Gel permeation chromatographic (GPC) and high pressure liquid chromatographic (HPLC) analyses were performed by using a Hitachi 655A apparatus with UV and RI detectors under the following condition: GPC analysis, Gelpack GL-A130 and A120 columns with chloroform eluent at a flow rate of 1.0 ml min⁻¹; HPLC analysis, Gelpack GL-W520 column with water eluent at a flow rate of 1.0 ml min⁻¹.

RESULTS AND DISCUSSION

Alternating Copolymerization of **1** with Cyclic Phosphonites **2**

Copolymerizations of **1** with three monomers of cyclic phosphonites **2** were carried out without any added catalyst to produce the respective alternating copolymers **3a**—**c** (Table I). Three solvents, acetonitrile, benzonitrile,

and DMF, were used for the copolymerization. In all cases the copolymerization occurred, but the molecular weight of the copolymers was not high. In our previous results on copolymerization of vinylphosphonic acid monoethyl ester with cyclic phosphonites, the molecular weight of the resulting copolymer was relatively high. This difference is probably due to the reactivity difference of the anionic site of zwitterion species: the phosphonate anion was more reactive than the phosphonamide anion. A similar tendency has been reported in the copolymerization of cyclic phosphonites with acrylic acid and with acrylamide.² In the present copolymerization, the conversion of the monomers **1** and **2** was quantitative; the yield of **3**, however, was not high. This is probably because the lower molecular weight portion was lost with dissolving in a non-solvent during the work-up procedure.

The structure of the alternating copolymers was confirmed by ¹H and ³¹P NMR spectroscopy. Figure 1 shows the ¹H NMR spectrum of the copolymer **3b** (in CDCl₃) (entry 6 in Table I). Peaks' assignment is as follows: triplet-like peak at δ 0.91 ppm due to methyl protons of *n*-propyl group, triplet-like peak *b* centered at δ 1.29 ppm due to methyl protons

Figure 1. 250 MHz ^1H NMR spectrum of copolymer **3b** (entry 6) in CDCl_3 .

of ethyl group, broad peak c at δ 1.48 ppm due to methylene protons of $\text{NCH}_2\text{CH}_2\text{CH}_3$, multiplet peak d at δ 1.99 ppm due to methylene protons of $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ and $\text{PCH}_2\text{CH}_2\text{P}$, broad peak e at δ 2.47 ppm due to the terminal amide proton of $\text{P}(=\text{O})\text{NH}$ and hydroxyl proton of CH_2OH , broad peak f at δ 2.82 ppm due to methylene protons of NCH_2C , broad peak g at δ 3.30 ppm due to the terminal methylene protons of CCH_2OH , multiplet peak h centered at δ 4.05 ppm due to methylene protons of OCH_2C , and multiplet peak i at δ 7.50 and 7.75 ppm due to phenyl protons of PPh . The peak e disappeared in measuring in D_2O . From the areas of the respective peaks, the molar ratio in copolymer **3b** was found to be 1 : 1. The molecular weight, calculated from the integrated area of the peak g and the peak i, was 1560, which agreed well with that obtained by gel permeation chromatographic (GPC) analysis. ^{31}P NMR spectrum of copolymer in CDCl_3 showed main two peaks at +44.5 and +32.1 ppm (relative to H_3PO_4 external standard), which were ascribed to two kinds of phosphorus atoms A and B as indicated in Figure 1. A small peak at +33.9 ppm was assigned to the terminal phosphorus atom C derived from monomer **1**. The equimolar ratio of two monomers **1** and **2** was also confirmed from the ratio of

integrated area of signals A and (B + C).

In order to confirm further the structure of copolymer **3**, the hydrolysis of copolymer **3b** was carried out. **3b** in acetonitrile was treated with 6*N* hydrochloric acid at 150°C for 556 h. An acid hydrolysis of **3b** is expected to give **4**, trimethylene glycol **5**, *n*-propylamine hydrochloride **6**, and ethyl alcohol **7**.

The hydrolysis products **4**–**7** were analyzed by high pressure liquid chromatography (HPLC) of the reaction mixture and of the corresponding authentic samples. Furthermore, **4** was isolated by the separation of an acetonitrile-insoluble part from the reaction mixture and confirmed to be **4** by ^1H NMR and IR analyses.⁴ The acetonitrile-soluble part was analyzed by ^1H NMR to identify the mixture of **5** and **6**.

As a possible alternative of **3b**, copolymer structure **8** is conceivable. An acid hydrolysis of **8** is expected to give **4**, **7**, and **9**. No detection of **9** by HPLC analysis of the reaction mixture, however, is taken to exclude the possibility of structure **8**.

Apparent monomer reactivity ratios between **1** and **2b** were determined. Copolymerization experiments were carried out in benzonitrile at 130°C for 12 h, which resulted in a low conversion. The copolymer **3b** was isolated and the copolymer composition was determined by ^{31}P NMR analysis. Figure 2 indicates a copolymer composition curve with varying

Figure 2. Copolymerization of **1** with **2b** at 130°C in PhCN for 12 h. Polymer compositions at various comonomer feeds: $[1] + [2b] = 1$ mmol in 0.15 ml of PhCN.

monomer feed ratio. The monomer reactivity ratios are thus obtained as $r_1 = 0.00 \pm 0.03$ and $r_{2b} = 0.34 \pm 0.08$.⁸

Copolymerization Mechanism

On the basis of the above data, the following mechanism may be proposed. The first step is

the formation of zwitterion **10** by the Michael-type addition of **1** with **2** followed by a hydrogen-transfer to give a genetic zwitterion **11**. Then, the reaction between two molecules of the genetic zwitterions occurs, where the phosphonium ring of one molecule **11** is opened by a nucleophilic attack of the anion of the other molecule according to the mode of the Arbuzov reaction. In this process oxidation of phosphorus atom of **2** and reduction of carbon atom of **1** take place. The propagation proceeds *via* the successive attack of the genetic zwitterion **11** onto dimeric zwitterion **12** ($p=1$) to lead to a macrozwitterion of an alternating copolymer **3**. The terminal groups of the isolated copolymer are of phosphonamidic acid monoethyl ester and alcohol structures as shown in Figure 1. These groups were probably formed by the hydrolysis of anion and cation sites of macrozwitterions during the isolation process.

The ³¹P NMR spectrum (in dimethylformamide-*d*⁷ (DMF-*d*⁷)) of the reaction mixture of copolymerization *in situ* showed signals at +60.9 and +25.5 ppm besides main two peaks. These peaks are ascribed to the phosphorus atoms of the terminal phosphonium ion and ambident anion of **11** and/or **12**, respectively.

In the copolymerization of **1** with **2**, the anions in **11** and **12** are of an ambident nature

having an anionic site at nitrogen **13a** and at oxygen **13b**. The copolymerization took place

exclusively through **13b** to give **3** in a regiospecific manner. This should be compared with the copolymerization of **2a** with acrylamide² and with ethylenesulfonamide.³ In these copolymerizations zwitterions having an

ambident anion site **14** and **15** are considered. In the ambident anion site, nitrogen atom reacted in **14** whereas oxygen atom reacted in **15** regiospecifically.

Acknowledgment. This work was partly supported by Grants-in-Aid for Scientific

Research on Priority Area of "New Functionality Materials-Design, Preparation, and Control" (No. 01604004 and 02205010) from the Ministry of Education, Science, and Culture of Japan.

REFERENCES

1. S. Kobayashi and T. Saegusa, "Alternating Copolymers," T. M. G. Cowie, Ed., Plenum Publishing Co., New York, N. Y., 1985, pp 189—238.
2. T. Saegusa, Y. Kimura, N. Ishikawa, and S. Kobayashi, *Macromolecules*, **9**, 724 (1976).
3. T. Saegusa, S. Kobayashi, and J. Furukawa, *Macromolecules*, **11**, 1027 (1978).
4. S. Kobayashi, J. Kadokawa, I. F. Yen, and S. Shoda, *Macromolecules*, **22**, 4390 (1989).
5. S. Kobayashi, S. Iwata, M. Abe, and S. Shoda, *J. Am. Chem. Soc.*, **112**, 1625 (1990).
6. T. Mukaiyama, T. Fujisawa, Y. Tamura, and Y. Yokota, *J. Org. Chem.*, **29**, 2572 (1964).
7. S. Kobayashi, M. Tokunoh, and T. Saegusa, *Macromolecules*, **19**, 466 (1986).
8. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).