

NOTES

**Synthesis of Poly(2-oxazoline) Ionene Polymer**

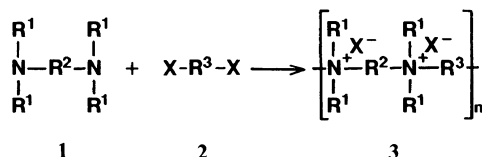
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Ionene polymers having ionic groups in the polymer main chain are well known. Among them, polymeric quaternary ammonium salts **3** have been prepared by the reaction of a tertiary diamine **1** with a dihalide **2** and shown to exhibit elastomeric properties.<sup>1,2</sup>



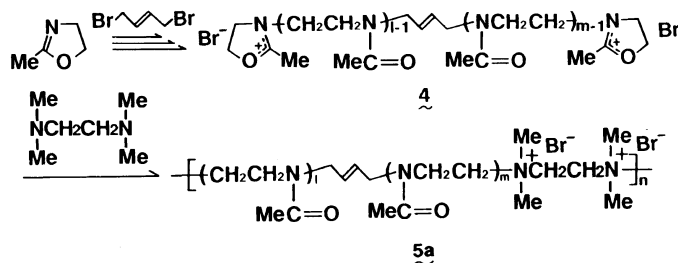
Electrophilic (cationic) ring-opening polymerization<sup>3</sup> of 2-alkyl-2-oxazoline (ROZO) is a versatile, convenient method to prepare linear poly(*N*-acylethylenimines) (PROZO).<sup>4</sup> The polymerization of ROZO proceeds *via* living propagating species and the living end reacts quantitatively with various nucleophiles

such as water and amines.<sup>5</sup> Very recently we found that allyl-type dihalides are effective bifunctional initiators for the polymerization of ROZO giving rise to a fast initiation system.<sup>6</sup> In using these initiators, PROZO having two living propagating species at both ends **4** can be readily obtained. This paper deals with the first synthesis of ionene polymers **5** by multicoupling reaction in one-pot between PROZO having two living ends **4** and a tertiary or aromatic diamine.

EXPERIMENTAL

Materials

Monomer, 2-methyl-2-oxazoline (MeOZO) was purified by distillation over potassium hydroxide. Other reagents and solvents were purified by distillation or recrystallization. All



Scheme 1.

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operations were carried out under argon.

*vacuo* to give 5.76 g (95% yield) of **5a**.

#### Preparation of Ionene Polymer 5 Containing PROZO

A typical run was as follows (entry 1). Under argon, a mixture of 1.07 g (5.02 mmol) of 1,4-dibromo-2-butene and 4.42 g (51.9 mmol) of MeOZO in 20 ml of DMF was heated at 80°C for 6 h. After cooling to room temperature, 0.581 g (5.00 mmol) of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was added to the mixture. The reaction mixture was then heated at 100°C for 2 h and poured into a large amount of diethyl ether. The polymeric materials were collected and dried *in*

#### Measurements

<sup>1</sup>H NMR spectra were recorded on a 60 MHz JEOL FX-60Q spectrometer or a 250 MHz Bruker AC250T spectrometer. The reduced viscosity of polymer solutions was measured with an Ubbelohde viscometer at 25°C.

## RESULTS AND DISCUSSION

The polymerization of MeOZO was carried out using allyl-type dihalide, 1,4-dibromo-2-butene as a bifunctional initiator at 80°C in

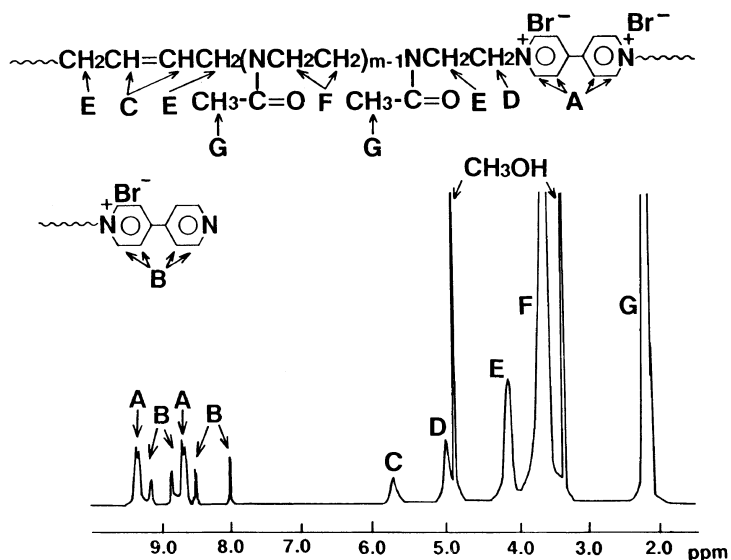
**Table I.** Synthesis of ionene polymer containing poly(MeOZO) **5**

Entry	Diamine <sup>a</sup>	Polymer <b>5</b>			
		Structure	<i>l</i> + <i>m</i> <sup>b</sup>	Yield/%	$\eta_{sp}/c^c$
1	TMEDA	<b>5a</b>	10.3	95	0.060
2	DABCO	<b>5b</b>	10.9	97	0.028
3	DPy	<b>5c</b>	10.2	88	0.040

<sup>a</sup> TMEDA = *N,N,N',N'*-tetramethylethylenediamine; DABCO = 1,4-diazabicyclo[2.2.2]octane; DPy = 4,4'-dipyridyl.

<sup>b</sup> Calculated from the monomer to initiator ratio.

<sup>c</sup> Measured in 1.0 M NaBr aqueous solution at 25°C; *c* = 0.6 g dl<sup>-1</sup>.



**Figure 1.** <sup>1</sup>H NMR spectrum of **5c** in CD<sub>3</sub>OD.

DMF. The living propagating species of the polymer **4** was reacted with an equimolar amount of a tertiary or aromatic diamine at 100°C to produce ionene polymer containing PROZO **5**. The tertiary and aromatic diamines used were TMEDA, 1,4-diazabicyclo[2.2.2]octane (DABCO), and 4,4'-dipyridyl (DPy). Polymerization results are shown in Table I. In all cases, polymer yields were very high.

Figure 1 shows the  $^1\text{H}$  NMR spectrum of **5c** (from DPy) (entry 3). In order to assign multiplet peaks at  $\delta$  8.0–9.3, two model reactions were carried out: a reaction of DPy with a five molar excess amount of methyl iodide (MeI) and an equimolar reaction between DPy and MeI.  $^1\text{H}$  NMR analyses of the products obtained by the model reactions revealed that diquaternalized DPy shows two doublet peaks due to aromatic protons and monoquaternalized DPy exhibits four doublet peaks due to aromatic protons. From these observation, the multiplet peaks were assigned; the two doublet peaks A are due to the diquaternalized aromatic protons and the four doublet peaks B are due to the monoquaternalized aromatic protons of DPy. The ratio of integrated area of peaks A and B is 3 : 2, which indicates that the degree of multicoupling reaction ( $n$  value) is 2.5. The ratio of integrated area of the peaks A + B and C due to  $\text{CH}=\text{CH}$  protons derived from initiator is 4 : 1. This means that polymer **5c** contains an equimolar amount of DPy and the initiator. Other signal assignments are given in Figure 1.

All polymers were very soluble in water, methanol and DMF, but slightly soluble in chloroform and insoluble in acetonitrile and diethyl ether. On the other hand, the homopolymer of MeOZO was soluble in acetonitrile and chloroform.

The viscosity behavior of solutions of **5a** (TMEDA) (entry 1) is shown in Figure 2. The polymer **5a** in water showed typical polyelectrolyte behavior; the reduced viscosity,  $\eta_{sp}/c$  increased remarkably with decreasing concentration of polymer (Figure 2(A)). It is known

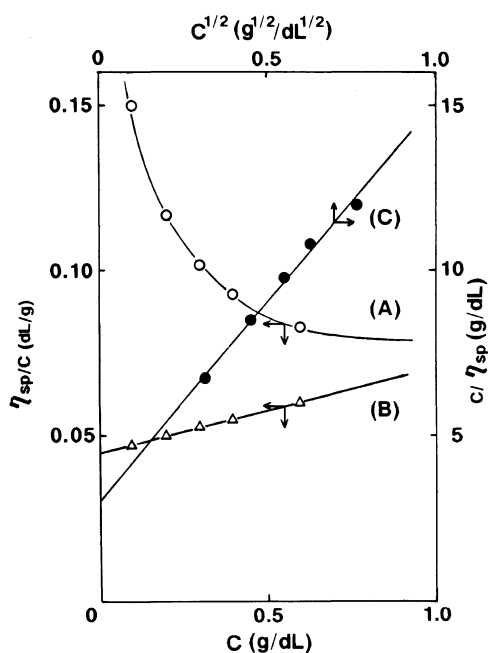


Figure 2. Reduced viscosity–polymer concentration relationships of **5a** (A) in water and (B) in  $1.0 \text{ mol l}^{-1}$  NaBr aqueous solution. (C) Fuoss–Strauss plots of **5a** in water.

that various ionomers behave in a similar manner. Fuoss and Strauss proposed eq 1 for the reduced viscosity of polyelectrolyte solutions<sup>7</sup>

$$\eta_{sp}/c = A/(1 + BC^{1/2}) \quad (1)$$

where  $A$  and  $B$  are characteristic constants of polymer. The plots according to eq 1 show a linear relationship (Figure 2(C)), indicating the dissociation of **5a** in water.  $A$  value is  $0.32 \text{ dl g}^{-1}$  and  $B$  value is  $3.86 \text{ dl}^{1/2} \text{ g}^{-1/2}$ . On the other hand, plots of the reduced viscosity of **5a** in water containing an electrolyte (NaBr) against the polymer concentration showed linearity (Figure 2(b)). The added electrolyte suppressed the dissociation, and hence, viscosity behavior of **5a** is similar to that of nonionic polymers.

Polymers **5** have quaternary ammonium groups and poly( $N$ -acetylenimine) (P-MeOZO) segment in the main chain. Poly-

mers containing quaternary ammonium groups have various applications such as disinfection and antibacterial agents.<sup>8,9</sup> On the other hand, PMeOZO is a polymeric analogue of *N,N*-dimethylacetamide (DMAc). DMAc is well known as an aprotic polar solvent, and hence, shows high hydrophilicity and ability to solubilize various organic polymers and inorganic compounds. Accordingly, PMeOZO has unique properties: high hydrophilicity<sup>10-13</sup> and miscibility with commodity polymers such as poly(vinyl chloride) and poly(vinylidene fluoride).<sup>14</sup> PMeOZO does not show acute toxicity.<sup>10</sup> Therefore polymer **5** may be used as a pharmacological active agent and compatibilizer with highly polar polymers.

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