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# Preparation of Ring-Opening Polymerizable Macromer and Its Copolymerization Leading to Graft Copolymer

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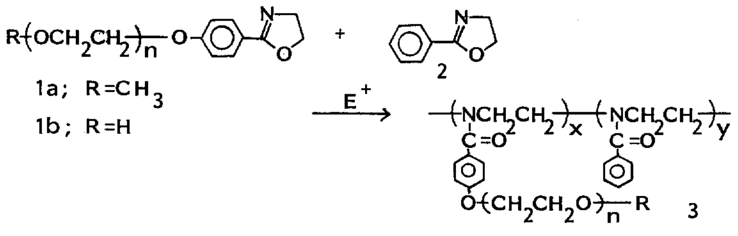
## SUMMARY

A poly(ethylene oxide) macromer(1) having a ring-opening polymerizable 2-oxazoline group at the end has been prepared starting with 2-(*p*-hydroxyphenyl)-2-oxazoline(4). Cationic ring-opening homo-polymerization of 1 took place to give a comb-like polymer having poly(ethylene oxide) branches. Cationic copolymerization of 1 with 2-phenyl-2-oxazoline(2) produced graft copolymer of poly[(2-phenyl-2-oxazoline)-*g*-(ethylene oxide)](3). From the results of fractional reprecipitation of 3 the polymerizability of 1 is considered to be less due at least partly to the electronic effect of *p*-alkoxy group in 1 than that of monomer 2.

## INTRODUCTION

Very recently much attention has been paid on macromers which are macromolecular monomers having a polymerizable group at the end. They are very useful to prepare well-defined graft copolymers with special functionalities and this concept of macromer was first patented as a registered name (1). Normally, the polymerizable group in macromer is referred to a vinyl group. For these few years a number of papers in this direction have been published in which macromers were prepared and employed to synthesize various graft copolymers of special functions (e.g., 2-10).

The polymerizable group, in a broader sense, may include a group capable of ring-opening polymerization. The present paper deals with synthesis of poly(ethylene oxide) macromers(1) having a ring-opening polymerizable 2-oxazoline group and with cationic ring-opening copolymerization of 1 with 2-phenyl-2-oxazoline(2) to give graft copolymers of poly[(2-phenyl-2-oxazoline)-*g*-(ethylene oxide)](3). To our knowledge 1 is the first instance of macromer which polymerized via ring-opening.



1a; $R=CH_3$

1b; $R=H$

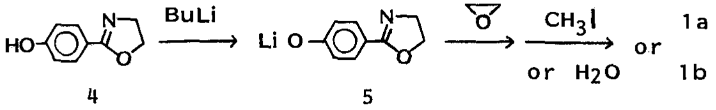
2

3

## RESULTS AND DISCUSSION

### Synthesis of Macromer 1

First, 2-(*p*-hydroxyphenyl)-2-oxazoline(4) was prepared. Then, 4 was lithiated with butyllithium to yield a phenoxyl type anion(5). The anionic polymerization of ethylene oxide with **5** followed by treatment with methyl iodide or water gave a white powdery material of macromer **1a** having a methoxy terminal group or that of **1b** with a hydroxyl terminal group.



Molecular weights of **1a** determined by vapor pressure osmometry (VPO) were 1010(n=18.9) for **1a** and 1930(n=40.2) for **1b**, respectively.

### Homo-polymerization of Macromer 1

First, ring-opening homo-polymerization of macromers **1a** and **1b** was examined with $BF_3 \cdot OEt_2$ catalyst, and produced the so-called "comb-like" polymers having poly(ethylene oxide) branches (No 1 and 4 in Table 1). The degree of polymerization was not high; about five in both cases under these reaction conditions. These polymers showed similar solubilities as starting macromers, e.g., being readily soluble in water.

### Copolymerization of Macromer 1 with 2-Phenyl-2-oxazoline 2

The cationic ring-opening copolymerization of **1** with **2** was carried out by $BF_3 \cdot OEt_2$ catalyst at 80°C in $CH_3CN$ under nitrogen (Table 1). In all cases a white powdery polymeric material was obtained.

Table 1

Ring-opening Copolymerization of Macromer **1** with **2**[a]

| No | Macromers (0.14 mmol) | **2** (mmol) | $BF_3 \cdot OEt_2$ (mmol) | Copolymer yields(%) | Compositions of copolymers **3**[b] x:y | Mol.wt.[c] |
|---|---|---|---|---|---|---|
| 1 | **1a** | 0 | 0.014 | 63 | 1 : 0 | 5100 |
| 2 | **1a** | 1.4 | 0.035 | 60 | 1 : 8.5 | 6800 |
| 3 | **1a** | 2.8 | 0.070 | 65 | 1 :17 | 7850 |
| 4 | **1b** | 0 | 0.014 | 83 | 1 : 0 | 10410 |
| 5 | **1b** | 1.4 | 0.035 | 79 | 1 :11 | 13700 |
| 6 | **1b** | 2.8 | 0.070 | 65 | 1 :20 | 7880 |

a) [**1**]=0.14 mmol in 0.3 ml of $CH_3CN$ for No 1 and 4, and in 3.0 ml of $CH_3CN$ for No 2,3,5 and 6, at 80°C for 50 hr under nitrogen. The amounts of **2** and of $BF_3 \cdot OEt_2$ were varied.

b) Determined by $^1H$ NMR of copolymer **3**.

c) Determined by vapor pressure osmometry at 40°C in $CHCl_3$.

The $^1H$ NMR of the copolymer in $CDCl_3$ showed three kinds of signals at $\delta 6.5$-$7.8$ due to phenyl protons, at $\delta 2.3$-$4.1$ (broad) assignable to *N*-methylene protons, and at $\delta 3.7$ (sharp) ascribable to *O*-methylene protons. From the ratio of peak areas the molar ratio of **1** to **2** (x:y in **3**) was calculated. The IR spectrum of the copolymer showed strong characteristic bond of $\nu(C{=}O)$ at 1630 $cm^{-1}$ and of $\nu(C{-}O{-}C)$ at 1100 $cm^{-1}$.

The analysis of gel permeation chromatography (GPC) of the copolymer (sample No 2) showed that the copolymer does not contain starting macromer **1a**. It was established that two peaks due to copolymer and macromer **1a** were well separated if both had been present (Figure 1). From the GPC chart of (a) in Figure 1, $M_w/M_n=1.90$ was obtained, showing that the molecular weight distribution of the copolymer is not narrow.

To examine the copolymer composition, fractional reprecipitation was made using $CHCl_3$ as solvent and diethyl ether as non-solvent (Table 2).

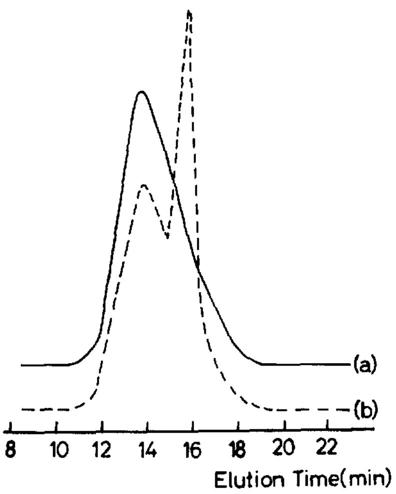


Figure 1. GPC charts of (a) product copolymer (sample No 2) and (b) copolymer + macromer(1a); flow rate=1.0 ml of $CHCl_3$/min.

Sample polymer (No 2) was fractionated into three parts (F-1, F-2 and F-3). From these results the followings can be pointed out. (i) Copolymerization between 1 and 2 actually took place since all fractions contain both units. (ii) Copolymer was fractionated by reprecipitation according to the difference of molecular weight as well as that of composition. (iii) The reason for (ii) is due to the different polymerizability between macromer 1 and monomer 2. 1 showed a reduced reactivity compared with 2 due at least partly to the electronic effect of a *p*-alkoxy group in 1(11). The elucidation of the quantitative reactivity of 1, however, must await further studies.

The present graft copolymers are composed of *N*-benzoylethylenimine main chain and poly(ethylene oxide) graft chain, and hence, are expected to be an efficient antistatics for Nylon 6 fibers.

Table 2

Fractional Reprecipitation of Graft Copolymer[a]

| No | Weight (g) | Monomer content, unit ratio x:y in 3[b] | Mol.wt.[c] |
|---|---|---|---|
| F-1 | 0.086 | 1 : 16.9 | 9900 |
| F-2 | 0.058 | 1 : 9.0 | 5910 |
| F-3 | 0.065 | 1 : 3.9 | 2190 |

a) 0.209 g of sample polymer No 2 was used for the experiment.

b) Determined by $^1H$ NMR.

c) Obtained by VPO.

We have already prepared ABA type block copolymers where A and B denote poly(*N*-acylethylenimine) and poly(ethylene oxide) chains, respectively (12). These block copolymers showed good compatibility and antistatic properties toward Nylon 6 fibers.

## EXPERIMENTAL

### Materials

All solvents and $BF_3 \cdot OEt_2$ were purified by distillation under nitrogen. 2-Phenyl-2-oxazoline(2) was prepared by the reaction of benzonitrile with monoethanolamine with $ZnCl_2$ catalyst (13). Ethylene oxide was purified by distillation.

### Synthesis of Macromer 1

2-(*p*-Hydroxyphenyl)-2-oxazoline(4) was obtained by the cyclization of *N*-(2-hydroxyethyl)-*p*-hydroxybenzamide with $SOCl_2$ in 92% yield, mp 194-195 °C. Into a pressure tube containing 4 (1.5 mmol) dissolved in 1.3 ml of DMSO, hexane solution (0.9 ml) of BuLi (1.5 mmol) was added with stirring at room temperature, and then ethylene oxide (30 mmol) was added at 0°C.

The tube was sealed and kept at 35°C for 3 days. The tube was opened and $CH_3I$ (1.5 mmol) was added to the reaction mixture. After the mixture was stirred overnight at room temperature, 7 ml of water was added and the polymeric material was extracted with $CHCl_3$ three times. The combined $CHCl_3$ solution was dried over $Na_2SO_4$ for 1 day, concentrated and poured into a large amount of diethyl ether to precipitate macromer **1a** in 50% yield. The molecular weight of **1a** was 1010 determined by VPO(n=18.9). The $^1$H NMR spectrum of **1a**($CDCl_3$) showed a big peak at $\delta$3.7 due to methylene protons of $OCH_2$, a small singlet at $\delta$3.4 due to methoxy protons, a $A_2B_2$ type quartet ($\delta$6.85, 7.00, 7.80 and 7.95) due to aromatic protons, and a multiplet at $\delta$3.4-4.4 due to the oxazoline ring methylene protons. From the peak area ratio of $OCH_2$ and aromatic protons, n value in **1a** was obtained as 20. *Anal*. Calcd for $C_{48}H_{87}NO_{21}$(n=19): C, 56.85; H, 8.65; N, 1.38. Found: C, 55.99; H, 8.69; N, 1.02.

For the preparation of **1b** analogous procedures were undertaken except that more ethylene oxide (60 mmol) was used and that after the polymerization the system was treated with water instead of $CH_3I$. The molecular weight of **1b** was 1930 determined by VPO. The chain length of ethylene oxide of **1b** is 40.2.

### Copolymerization of Macromer **1** with 2

A typical run (No 2) was as follows. Into a tube containing 0.14 mmol of **1a** and 2.8 mmol of 2 in 3.0 ml of $CH_3CN$, 0.72 mmol of $BF_3 \cdot OEt_2$ was introduced with a micro-syringe at room temperature under nitrogen. The tube was shaken, sealed, and kept at 80°C for 50 hr. The tube was then opened and the mixture was poured into 100 ml of diethyl ether to precipitate the polymeric material. The reprecipitation procedure was repeated three times using $CHCl_3$ as a good solvent and diethyl ether as a poor solvent. After drying *in vacuo* 0.31 g (60% yield) of the polymer was obtained.

### Fractional Reprecipitation

Sample polymer No 2 (0.209 g) was dissolved in 25 ml of $CHCl_3$ and 40 ml of diethyl ether was added to the solution slowly with stirring. The mixture was kept standing at room temperature for 5 hr. Then, the solution became clear. The precipitates were separated by decantation and dried *in vacuo* to give 86 mg of polymer (fraction F-1). To the decanted solution 60 ml of diethyl ether was added. After standing overnight the polymeric material precipitated and the supernatant solution became clear. The polymer was separated and dried *in vacuo* to give 58 mg (fraction F-2). Solvents of the supernatant were evaporated *in vacuo* to give 65 mg of polymer (fraction F-3).

### Measurements

$^1$H NMR spectra were recorded on HITACHI R-20B (60 MHz) spectrometer. Molecular weight data were obtained by vapor pressure osmometry using CORONA 117 molecular weight apparatus. Gel permeation chromatography was performed on JASCO Tri Rotar liquid chromatography apparatus using Shodex 803 column (8 mm $\phi$ X 500 mm) with $CHCl_3$ eluent.

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