

the mercury electrode.

**Acknowledgment.** Financial support from the Korea Science and Engineering Foundation is gratefully acknowledged.

### References

1. Garcia-Alvarez, O.; Gierst, L. *J. Electroanal. Chem.* **1979**, *100*, 819.
2. Boissonneau, J. F.; Repellin, M. J.; Eglim, A. *Analisis* **1980**, *8*, 230.
3. Yeo, I-H.; Choi, K-C.; Eom, T. Y. *Bull. Korean Chem. Soc.* **1991**, *12*, 10.
4. Lee, J. W.; Mho, S-i.; Pyun, C. H.; Yeo, I-H. *Bull. Korean Chem. Soc.* **1994**, *15*, 1038.
5. Neuburger, G. G.; Johnson, D. C. *Anal. Chem.* **1988**, *60*, 2288.
6. Johnson, D. C.; LaCourse, W. R. *Anal. Chem.* **1990**, *62*, 589A.
7. Vandeberg, P. J.; Kowagoe, J. L.; Johnson, D. C. *Anal. Chim. Acta.* **1992**, *260*, 1.
8. Johnson, D. C.; Polta, J. A.; Polta, T. Z.; Neuburger, G. G.; Johnson, J.; Tang, A. P-C.; Yeo, I-H.; Baur, J. J. *Chem. Soc., Faraday Trans. 1.* **1986**, *82*, 1081.
9. Reiley, C. N.; Schmid, R. W. *Anal. Chem.* **1958**, *30*, 947.

## A Novel Synthetic Route to Highly Cross-Linked Poly(vinyl ethers): III. Synthesis and Free Radical Polymerization of Aryloxyethyl Vinyl Ethers Having an Electron Acceptor in ortho- or meta-Position

Ju-Yeon Lee\*, Moo-Yong Kim, and Kwang-Duk Ahn<sup>†</sup>

Department of Chemistry, Inje University, 607 Aebang-dong, Kimhae 621-749, Korea

<sup>†</sup>Polymer Research Division, Korea Institute of Science and Technology,

P.O. Box 131, Cheongryang, Seoul 130-650, Korea

Received December 18, 1996

*o*-(2-Vinyloxyethoxy)benzylidenemalononitrile (**3a**) and methyl *o*-(2-vinyloxyethoxy)-benzylidenecyanoacetate (**3b**), *m*-(2-vinyloxyethoxy)benzylidenemalononitrile (**4a**), and methyl *m*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**4b**) were prepared by the condensation of *o*-(2-vinyloxyethoxy)benzaldehyde (**1**) and *m*-(2-vinyloxyethoxy)benzaldehyde (**2**) with malononitrile or methyl cyanoacetate, respectively. Bifunctional vinyl ether monomers **3a** and **3b** polymerized quantitatively with radical initiators in  $\gamma$ -butyrolactone solution at 65 °C, while meta-isomers **4a** and **4b** gave lower yields of polymers under the same conditions. The polymers **5-6** obtained from the monomers **3-4** were insoluble in common solvents due to cross-linking. Under the same polymerization conditions ethyl vinyl ether polymerized well with model compounds *o*-methoxybenzylidenemalononitrile **7a**, methyl *o*-methoxybenzylidenecyanoacetate **7b**, *m*-methoxybenzylidenemalononitrile **8a**, and methyl *m*-methoxybenzylidenecyanoacetate **8b**, respectively, to give 1:1 alternating copolymers **9-10** in high yields. Cross-linked polymers **5-6** showed a thermal stability up to 300 °C, and showed a double phase degradation pattern in their TGA thermograms. Polymers **5-6** showed broad endothermic bands around 75-110 °C without any characteristic  $T_g$  peaks in DSC thermograms. Alternating copolymers **9-10**, except copolymer **9b** were soluble in common organic solvents. The inherent viscosities of polymer **9-10** were in the range of 0.35-0.62 dL/g. Polymer films cast from acetone solution were cloudy and tough and  $T_g$  values obtained from DSC thermograms were in the range of 118-165 °C.

### Introduction

It is well known that electron-rich alkyl vinyl ethers do not radically homopolymerize, but copolymerize with vinyl monomers of electron deficient character such as vinylidene cyanide,<sup>1</sup> 2-vinylcyclopropane-1,1-dicarbonitrile,<sup>2</sup> alkyl  $\alpha$ -cyanoacrylates,<sup>3-5</sup> alkyl vinyl ketones,<sup>6</sup> maleic anhydride,<sup>7,8</sup> and others by radical initiation. Cycloadditions frequently accompanied these polymerizations and most of the cyclic adducts are cyclobutane compounds. For example, alkyl vinyl ethers readily form cyclobutane adducts with a variety of

electron-poor olefins such as tetracyanoethylene<sup>9</sup> and tricyanoethylene.<sup>10</sup> 3,4-Dihydro-2H-pyrans are formed in the reactions of alkyl vinyl ethers with alkyl  $\alpha$ -cyanoacrylates, dimethyl dicyanofumarate,<sup>11</sup> and alkyl vinyl ketones.<sup>6</sup> These facile reactions proceed through an electron donor-acceptor (EDA) complex, which generates zwitterion or diradical tetramethylenes as initiating species.<sup>12</sup> It has also been reported that trisubstituted electron-poor olefins such as benzylidenemalononitrile and ethyl benzylidenecyanoacetate do not homopolymerize, but copolymerize with vinyl acetate, styrene, acrylonitrile, or methyl acrylate by radical initiat-

ors.<sup>13-19</sup> The captodative olefins with geminal electron-withdrawing and electron-donating groups have a strong tendency to polymerize spontaneously due to the resonance stabilization of radical species.<sup>20,21</sup> The question remains as to whether certain bifunctional monomers composed of both electron-rich alkyl vinyl ether and electron-poor trisubstituted olefin moieties can be polymerized by radical initiation. Thus, it is of interest to prepare alkyl vinyl ethers containing electron acceptors in the side chain and polymerize by using radical initiators. Recently we have prepared *p*-(2-vinyloxyethoxy)benzylidenemalononitrile and methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate, and polymerized by radical initiators.<sup>22,23</sup> These bifunctional ethyl vinyl ethers polymerized quantitatively with radical initiators to give swelling polymers that were not soluble in organic solvents due to cross-linking. This work is now extended with the syntheses and radical polymerizations of another positional isomeric ethyl vinyl ethers containing electron acceptors. In this work we prepared four ethyl vinyl ethers containing electron acceptors in the side chain and investigated their polymerization behaviors toward radical initiators. The present report describes the synthesis and free radical polymerization of *o*-(2-vinyloxyethoxy)benzylidenemalononitrile (**3a**), methyl *o*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**3b**), *m*-(2-vinyloxyethoxy)benzylidenemalononitrile (**4a**), and methyl *m*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**4b**).

## Experimental

**Materials.** The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2-Chloroethyl vinyl ether was distilled. Sodium iodide was dried for 4 h at 100 °C under vacuum. Acetone was purified by drying with anhydrous potassium carbonate, followed by distillation under reduced pressure. *o*-Hydroxybenzaldehyde was dried with anhydrous magnesium sulfate under vacuum. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. Methyl cyanoacetate was purified by drying with anhydrous sodium sulfate and distilled. Ethyl vinyl ether (EVE) was dried over sodium metal and distilled, taking the middle fraction. *n*-Butanol was dried with anhydrous magnesium sulfate and distilled under nitrogen.  $\gamma$ -Butyrolactone was dried with anhydrous magnesium sulfate and distilled under nitrogen. Piperidine was dried with calcium hydride and fractionally distilled.  $\alpha,\alpha'$ -Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under reduced pressure at room temperature. 2-Iodoethyl vinyl ether was prepared according to the procedure previously described.<sup>21-23</sup>

**Measurements.** IR spectra were taken on a Hitachi Model 260-30 infrared spectrophotometer. <sup>1</sup>H NMR spectra were obtained on a Varian EM 360L NMR spectrometer (60 MHz). Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The glass transition temperatures ( $T_g$ ) were measured on a DuPont 910 differential scanning calorimeter in a nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of 10 °C/min up to 700 °C was used for the thermal degradation study of polymers under nitrogen. Melting points

were measured in Buchi 530 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

***o*-(2-Vinyloxyethoxy)benzaldehyde 1.** 2-Hydroxybenzaldehyde (12.2 g, 0.10 mol), anhydrous potassium carbonate (18.0 g, 0.13 mol), and 2-iodoethyl vinyl ether (25.7 g, 0.13 mol) were dissolved in 180 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath at 80 °C for 10 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 220 mL of water, and extracted with 300 mL of diethyl ether three times. The organic layer was washed with saturated aqueous sodium chloride solution, and dried with anhydrous magnesium sulfate. Rotary evaporation of acetone gave crude product, which on vacuum distillation yielded 16.3 g (85% yield) of pure product **1**. bp 73-75 °C (0.2 mmHg). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  3.89-4.53 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 6.24-6.69 (q, 1H, =CH-O-), 6.75-7.19 (m, 2H, aromatic), 7.28-7.89 (m, 2H, aromatic), 10.50 (s, 1H, -CHO). IR (neat) 3119, 3068, 2940, 2878, 2833 (C-H), 1694, 1603, 1579 (C=C) cm<sup>-1</sup>.

***m*-(2-Vinyloxyethoxy)benzaldehyde 2.** *m*-Hydroxybenzaldehyde (12.2 g, 0.10 mol), anhydrous potassium carbonate (18.0 g, 0.13 mol), and 2-iodoethyl vinyl ether (25.7 g, 0.13 mol) were dissolved in 180 mL of dry acetone under nitrogen. The mixture was refluxed in an oil bath kept at 60 °C for 72 h under nitrogen. The resulting solution was cooled to room temperature, and filtered, and the inorganic salts were washed with 50 mL of acetone. Rotary evaporation of acetone gave crude product, which on vacuum distillation yielded 16.3 g (85% yield) of pure product **2**. bp 75-77 °C (0.2 mmHg). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.88-4.44 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 6.28-6.71 (q, 1H, =CH-O-), 6.99-7.57 (m, 4H, aromatic), 9.88 (s, 1H, -CHO). IR (neat) 3052 (=C-H), 2928, 2864 (C-H), 1692 (C=O), 1617, 1594 (C=C) cm<sup>-1</sup>.

***o*-(2-Vinyloxyethoxy)benzylidenemalononitrile 3a.** Piperidine (0.13 g, 1.5 mmol) was added to a solution of *o*-(2-vinyloxyethoxy)benzaldehyde **1** (5.38 g, 28 mmol) and malononitrile (1.98 g, 30 mmol) in 50 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 1 h at 0 °C, the product was filtered and washed successively with cold *n*-butanol (80 mL), water (30 mL), and cold *n*-butanol (20 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 5.38 g (80% yield) of **3a**. mp 69-70 °C. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  3.94-4.57 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 6.36-6.77 (q, 1H, =CH-O-), 6.99-7.38 (m, 2H, aromatic), 7.50-7.87 (m, 1H, aromatic), 8.03-8.29 (m, 1H, aromatic), 8.45 (s, 1H, aromatic). IR (KBr) 3110, 3035 (=C-H), 2950, 2880 (C-H), 2218 (CN), 1642, 1597, 1578 (C=C) cm<sup>-1</sup>. Anal. Calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.91; H, 5.08; N, 11.62.

**Methyl *o*-(2-vinyloxyethoxy)benzylidenecyanoacetate 3b.** Piperidine (0.17 g, 2.0 mmol) was added to a solution of *o*-(2-vinyloxyethoxy)benzaldehyde **1** (5.77 g, 30 mmol) and methyl cyanoacetate (2.98 g, 30 mmol) in 45 mL of *n*-butanol with stirring at 0 °C under nitrogen. The resulting solution was stirred for 1 h at 0 °C and 10 h at room temperature. After cooling in an ice bath, the product was filtered and washed successively with cold *n*-butanol (30 mL), water (50 mL), and cold *n*-butanol (20 mL). The

obtained pale yellow product was recrystallized from *n*-butanol to give 5.90 g (72% yield) of **3b**. mp 62–63 °C. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 3.86 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.89–4.53 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 6.32–6.73 (q, 1H, =CH-O-), 6.92–7.29 (m, 2H, aromatic), 7.39–7.73 (m, 1H, aromatic), 8.09–8.33 (m, 1H, aromatic), 8.68 (s, 1H, aromatic). IR (KBr) 3120, 3064 (=C-H), 2958, 2880 (C-H), 2225 (CN), 1733 (C=O), 1651, 1598 (C=C) cm<sup>-1</sup>. Anal. Calcd for C<sub>15</sub>H<sub>15</sub>NO<sub>4</sub>: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.83; H, 5.58; N, 5.18.

***m*-(2-Vinyloxyethoxy)benzylidenemalononitrile 4a.** Piperidine (0.13 g, 1.5 mmol) was added to a solution of **2** (5.38 g, 28 mmol) and malononitrile (1.98 g, 30 mmol) in 50 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 1 h at 0 °C, the product was filtered and washed successively with cold *n*-butanol (80 mL), water (30 mL), and cold *n*-butanol (20 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 5.38 g (80% yield) of **4a**. mp 63–64 °C. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 3.87–4.55 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 6.31–6.77 (q, 1H, =CH-O-), 7.08–7.45 (m, 1H, aromatic), 7.46–7.73 (m, 3H, aromatic), 8.21 (s, 1H, aromatic). IR (KBr) 3068, 3026 (=C-H), 2933, 2858 (C-H), 2220 (CN), 1618, 1600, 1585, 1569 (C=C) cm<sup>-1</sup>. Anal. Calcd for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.89; H, 5.09; N, 11.72.

**Methyl *m*-(2-vinyloxyethoxy)benzylidenecyanoacetate 4b.** Piperidine (0.17 g, 2.0 mmol) was added to a solution of **2** (5.77 g, 30 mmol) and methyl cyanoacetate (2.98 g, 30 mmol) in 45 mL of *n*-butanol with stirring at 0 °C under nitrogen. The resulting solution was stirred for 1 h at 0 °C and 10 h at room temperature. After cooling in an ice bath, the product was filtered and washed successively with cold *n*-butanol (30 mL), water (50 mL), and cold *n*-butanol (20 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 5.90 g (72% yield) of **4b**. mp 100–101 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.88 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.89–4.37 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 6.24–6.64 (q, 1H, =CH-O-), 6.88–7.57 (m, 4H, aromatic), 8.08 (s, 1H, aromatic). IR (KBr) 3118, 3060, 3026 (=C-H), 2938, 2865 (C-H), 2224 (CN), 1725 (C=O), 1626, 1608 (C=C) cm<sup>-1</sup>. Anal. Calcd for C<sub>15</sub>H<sub>15</sub>NO<sub>4</sub>: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.85; H, 5.49; N, 5.18.

***o*-Methoxybenzylidenemalononitrile 7a.** *o*-Methoxybenzylidenemalononitrile **7a** was prepared according to the literature procedure<sup>9</sup> by condensing *o*-anisaldehyde with malononitrile in *n*-butanol in the presence of piperidine as catalyst. **7a**: 95% yield. mp 83–84 °C. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 3.95 (s, 3H, -OCH<sub>3</sub>), 6.94–7.33 (m, 2H, aromatic), 7.49–7.84 (m, 1H, aromatic), 7.98–8.22 (m, 1H, aromatic), 8.38 (s, 1H, aromatic). IR (KBr) 3034 (=C-H), 2962, 2933, 2874, 2836 (C-H), 2218 (CN), 1599, 1578, 1560 (C=C) cm<sup>-1</sup>.

**Methyl *o*-methoxybenzylidenecyanoacetate 7b.** Methyl *o*-methoxybenzylidenecyanoacetate **7b** was prepared according to the literature procedure<sup>9</sup> by condensing *o*-anisaldehyde with methyl cyanoacetate in *n*-butanol in the presence of piperidine as catalyst. **7b**: 88% yield. mp 107–108 °C. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 3.87 (s, 3H, -CO<sub>2</sub>CH<sub>3</sub>), 3.93 (s, 3H, -OCH<sub>3</sub>), 6.90–7.27 (m, 2H, aromatic), 7.41–7.75 (m, 1H, aromatic), 8.07–8.30 (m, 1H, aromatic), 8.62 (s, 1H, aromatic). IR (KBr) 3044, 3004 (=C-H), 2978, 2948 (C-H), 2215 (CN), 1720 (C=O), 1587 (C=C) cm<sup>-1</sup>.

***m*-Methoxybenzylidenemalononitrile 8a.** *m*-Methoxybenzylidenemalononitrile **8a** was prepared according to the literature procedure<sup>9</sup> by condensing *m*-anisaldehyde with malononitrile in *n*-butanol in the presence of piperidine as catalyst. **8a**: 90% yield. mp 105–106 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.82 (s, 3H, -OCH<sub>3</sub>), 6.87–7.45 (m, 4H, aromatic), 7.66 (s, 1H, aromatic). IR (KBr) 3075, 3028 (=C-H), 2925, 2836 (C-H), 2226 (CN), 1596, 1570 (C=C) cm<sup>-1</sup>.

**Methyl *m*-methoxybenzylidenecyanoacetate 8b.** Methyl *m*-methoxybenzylidenecyanoacetate **8b** was prepared according to the literature procedure<sup>9</sup> by condensing *m*-anisaldehyde with methyl cyanoacetate in *n*-butanol in the presence of piperidine as catalyst. **8b**: 86% yield. mp 68–69 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.83 (s, 3H, -CO<sub>2</sub>CH<sub>3</sub>), 3.90 (s, 3H, -OCH<sub>3</sub>), 6.92–7.28 (m, 1H, aromatic), 7.30–7.65 (m, 3H, aromatic), 8.17 (s, 1H, aromatic). IR (KBr) 3026, 3004 (=C-H), 2950, 2828 (C-H), 2215 (CN), 1723 (C=O), 1603, 1570 (C=C) cm<sup>-1</sup>.

**Radical polymerization of 3 and 4.** A representative radical polymerization procedure (the case of **3a**) is as follows: In a polymerization tube were placed 0.48 g (2.0 mmol) of **3a**, 1.97 mg (0.012 mmol) of AIBN, and 2.0 mL of  $\gamma$ -butyrolactone under nitrogen. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 65 °C. After 4 h the polymerization tube was opened and the swelled polymer was poured into 400 mL of methanol. The precipitated polymer was collected and dried under vacuum to give 0.48 g (100% yield) of polymer **5a**. IR (KBr) 3058 (=C-H), 2928, 2860 (C-H), 2228 (CN), 1601, 1586 (C=C) cm<sup>-1</sup>. Anal. Calcd for (C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>)<sub>n</sub>: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.92; H, 5.11; N, 11.58. Polymer **5b**: 100% yield. IR (KBr) 3060 (=C-H), 2936, 2860 (C-H), 2236 (CN), 1735 (C=O), 1598 (C=C) cm<sup>-1</sup>. Anal. Calcd for (C<sub>15</sub>H<sub>15</sub>NO<sub>4</sub>)<sub>n</sub>: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.85; H, 5.46; N, 5.18. Polymer **6a**: 62% yield. IR (KBr) 3020 (=C-H), 2922, 2860 (C-H), 2224 (CN), 1585, 1576 (C=C) cm<sup>-1</sup>. Anal. Calcd for (C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>)<sub>n</sub>: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.88; H, 5.08; N, 11.60. Polymer **6b**: 60% yield. IR (KBr) 3025 (=C-H), 2930, 2852 (C-H), 2220 (CN), 1725 (C=O), 1620, 1592, 1588 (C=C) cm<sup>-1</sup>. Anal. Calcd for (C<sub>15</sub>H<sub>15</sub>NO<sub>4</sub>)<sub>n</sub>: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.84; H, 5.60; N, 5.19.

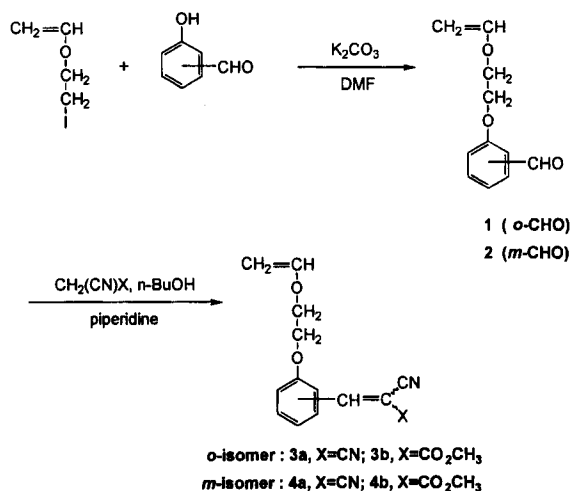
**Radical copolymerization of model compounds 7–8 with ethyl vinyl ether.** A representative radical polymerization procedure is as follows: In a polymerization tube were placed 0.27 g (1.5 mmol) of **7a**, 0.54 g (7.5 mmol) of ethyl vinyl ether, 4.9 mg (0.030 mmol) of AIBN, and 2.4 mL of  $\gamma$ -butyrolactone under nitrogen. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 65 °C. After 5 h the polymerization tube was opened and the viscous polymer solution was poured into 400 mL of methanol. The precipitated polymer was collected and reprecipitated from acetone into methanol. Thus obtained white polymer was dried under vacuum to give 0.36 g (94% yield) of copolymer **9a**;  $\eta_{inh}$  = 0.54 dL/g (c 0.5 g/dL in acetone at 25 °C). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 0.88–1.97 (m, 5H, -CH<sub>3</sub>, -CH<sub>2</sub>-), 2.96–3.74 (m, 7H, -CH-Ph, -OCH<sub>3</sub>, -CH-O-CH<sub>2</sub>-), 6.37–7.93 (m, 4H, aromatic). IR (KBr) 3058 (=C-H), 2973, 2935, 2897, 2838 (C-H), 2238 (CN), 1602, 1588 (C=C) cm<sup>-1</sup>. Anal. Calcd for (C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>)<sub>n</sub>:

C, 70.29; H, 6.29; N, 10.93. Found: C, 70.22; H, 6.24; N, 10.98. Copolymer **9b**: IR (KBr) 3074 (=C-H), 2976, 2955, 2896, 2840 (C-H), 2238 (CN), 1740 (C=C), 1598, 1586 (C=C)  $\text{cm}^{-1}$ . Anal. Calcd for  $(\text{C}_{16}\text{H}_{19}\text{NO}_4)_n$ : C, 66.42; H, 6.62; N, 4.84. Found: C, 66.50; H, 6.56; N, 4.90. Copolymer **10a**:  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  0.89-1.94 (m, 5H,  $-\text{CH}_3$ ,  $-\text{CH}_2-$ ), 2.87-4.65 (m, 7H,  $-\text{CH-Ph}$ ,  $-\text{OCH}_3$ ,  $-\text{CH-O-CH}_2-$ ), 6.23-7.08 (m, 4H, aromatic). IR (KBr) 3078 (=C-H), 2970, 2928, 2827 (C-H), 2230 (CN), 1596, 1582 (C=C)  $\text{cm}^{-1}$ . Anal. Calcd for  $(\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2)_n$ : C, 70.29; H, 6.29; N, 10.93. Found: C, 70.35; H, 6.34; N, 10.85. Copolymer **10b**:  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  0.72-1.97 (m, 5H,  $-\text{CH}_3$ ,  $-\text{CH}_2-$ ), 2.83-4.12 (m, 10H,  $-\text{CH-Ph}$ ,  $-\text{OCH}_3$ ,  $-\text{CH-O-CH}_2-$ ,  $-\text{COOCH}_3$ ), 6.22-7.27 (m, 4H, aromatic). IR (KBr) 3075, 3048 (=C-H), 2970, 2952, 2890, 2826 (C-H), 2232 (CN), 1745 (C=C), 1596, 1584 (C=C)  $\text{cm}^{-1}$ . Anal. Calcd for  $(\text{C}_{16}\text{H}_{19}\text{NO}_4)_n$ : C, 66.42; H, 6.62; N, 4.84. Found: C, 66.48; H, 6.55; N, 4.92.

## Results and Discussion

**Syntheses of Monomers 3 and 4.** 2-Iodoethyl vinyl ether was prepared by the well known halogen exchange reaction<sup>25</sup> from 2-chloroethyl vinyl ether and sodium iodide, and reacted with *o*-hydroxybenzaldehyde and *m*-hydroxybenzaldehyde to yield *o*-(2-vinyl-oxyethoxy)benzaldehyde (**1**) and *m*-(2-vinyl-oxyethoxy)benzaldehyde (**2**).<sup>26</sup> *o*-(2-vinyl-oxyethoxy)benzylidenemalononitrile (**3a**), methyl *o*-(2-vinyl-oxyethoxy)benzylidenecyanoacetate (**3b**), *m*-(2-vinyl-oxyethoxy)benzylidenemalononitrile (**4a**), and methyl *m*-(2-vinyl-oxyethoxy)benzylidenecyanoacetate (**4b**) were synthesized by the condensation of **1** and **2** with malononitrile or methyl cyanoacetate, respectively.<sup>24</sup> The chemical structure of the compounds was identified by proton-NMR, and IR spectra, and elemental analysis. Monomer **3** and **4** show olefinic protons at  $\delta$ =6.36-6.77 (q, 1H, vinylic) and  $\delta$ =6.32-6.73 (q, 1H, vinylic) in their  $^1\text{H}$  NMR spectra, respectively. IR analysis of the monomer **3b** showed strong absorption bands at 2220, 1726, and 1618  $\text{cm}^{-1}$  indicating the presence of nitrile, carbonyl, and olefinic groups, respectively. Spectral data indicated that compounds **3b** and **4b** were a mixtures of the *cis*- and *trans*-isomers.

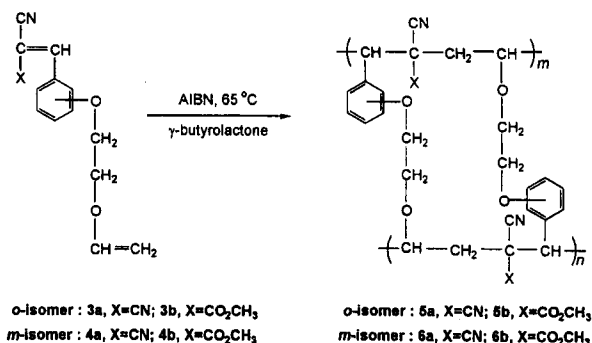
### Radical Polymerizations of Monomers 3 and 4.



Scheme 1.

*o*-(2-Vinyl-oxyethoxy)benzylidenemalononitrile (**3a**), methyl *o*-(2-vinyl-oxyethoxy)benzylidenecyanoacetate (**3b**) *m*-(2-vinyl-oxyethoxy)benzylidenemalononitrile (**4a**), and methyl *m*-(2-vinyl-oxyethoxy)benzylidenecyanoacetate (**4b**) were polymerized in  $\gamma$ -butyrolactone solution at 65 °C with AIBN as radical initiator. The polymerization results are summarized in Table 1. The monomers **3a** and **3b** were readily polymerized to yield the polymers **5a** and **5b** quantitatively within 4 h under the above reaction condition. However, polymerizabilities of meta-isomers **4a** and **4b** toward radical initiators are rather low and gave moderate polymer yields under the same polymerization conditions, as shown in Table 1. According to our experimental results, polymerizabilities of *ortho*-monomers toward radical initiators are similar as those of *para*-isomers. These experimental results are probably reasonable in view of the fact that terminal electron-deficient benzylidenyl groups of *o*- and *p*-isomers are conjugated with nonbonding electrons on the oxygen of electron-releasing ethoxy groups. The chemical structures of the polymers were identified by IR spectra and elemental analyses. The IR spectra confirmed the chemical structures, exhibiting all the absorption bands attributable to the functional groups comprising the polymers.

Recently we have reported the vinyl polymerization of *p*-isomers of monomers **3a** and **3b** by cationic initiators without cross-linking.<sup>26</sup> In contrast to that report, the trisubstituted terminal double bond participated in the vinyl polymerization, and radical polymerization of **3** and **4** led only to optically transparent swelling polymers **5-6**. Polymers **5-6** were not soluble in any organic solvents due to cross-link-



Scheme 2.

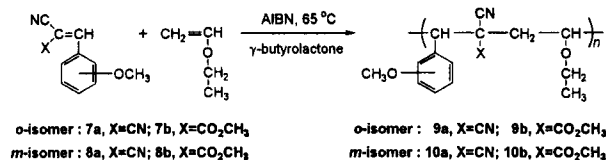
Table 1. Free Radical Polymerizations of Vinyl Ethers in  $\gamma$ -Butyrolactone at 65 °C

| Monomer   | Monomer/<br>Solvent<br>(mol/L) | Initiator to<br>Monomer<br>(mol%) | Time<br>(h) | Yield<br>(%) |
|-----------|--------------------------------|-----------------------------------|-------------|--------------|
| <b>3a</b> | 1.00                           | 0.6                               | 4           | 100          |
| <b>3a</b> | 0.67                           | 0.8                               | 4           | 100          |
| <b>3a</b> | 0.33                           | 1.0                               | 5           | 100          |
| <b>3b</b> | 1.00                           | 0.6                               | 3           | 100          |
| <b>3b</b> | 0.67                           | 0.8                               | 4           | 100          |
| <b>3b</b> | 0.33                           | 1.0                               | 4           | 100          |
| <b>4a</b> | 1.00                           | 0.6                               | 10          | 64           |
| <b>4a</b> | 0.67                           | 1.0                               | 18          | 72           |
| <b>4b</b> | 1.00                           | 0.8                               | 12          | 60           |
| <b>4b</b> | 0.67                           | 1.0                               | 20          | 65           |

ing. Thus, we have found a unique polymerization system that lead to highly cross-linked poly(alkylvinylether)s by radical initiators. Furthermore, the striking feature of this particular polymerization system is that it provides an unprecedented radical polymerization of alkyl vinyl ethers which do not polymerize radically.

**Synthesis and Radical Copolymerization of Model Compounds 7-8 with Ethyl Vinyl Ether.** *o*-Methoxybenzylidenemalononitrile **7a**, methyl *o*-methoxybenzylidenecyanoacetate **7b**, *m*-methoxybenzylidenemalononitrile **8a**, and methyl *m*-methoxybenzylidenecyanoacetate **8b** were prepared according to the literature procedure<sup>9</sup> by condensing *o*-anisaldehyde and *m*-anisaldehyde with malononitrile or methyl cyanoacetate, respectively, in the presence of piperidine. To investigate if the cross-linking was due to the terminal double bond, ethyl vinyl ether was copolymerized by AIBN at 65 °C in the presence of model compounds **7-8**. The resulting copolymers were isolated by reprecipitation from acetone solution into methanol and identified by <sup>1</sup>H NMR, IR spectral, and elemental analyses. The copolymerization results are summarized in Table 2.

As shown in Table 2, the monomers **7-8** copolymerized well with ethyl vinyl ether with AIBN as a free radical initiator to give high molecular weight ( $\eta_{inh}=0.62$  dL/g) copolymers **9-10** in high yields. The yields were calculated based on 1:1 alternating compositions of the resulting copolymers. Elemental analyses and spectral data indicated



Scheme 3.

**Table 2.** Free Radical Copolymerizations of **7-8** with Ethyl Vinyl Ether by AIBN in  $\gamma$ -Butyrolactone at 65 °C<sup>a</sup>

| Monomer to EVE <sup>b</sup><br>(mol ratio) | Monomer /Solvent<br>(mol/L) | Initiator to Monomer<br>(mol%) | Time<br>(h) | Yield <sup>c</sup><br>(%) | $\eta_{inh}^d$<br>(dL/g) |
|--------------------------------------------|-----------------------------|--------------------------------|-------------|---------------------------|--------------------------|
| <b>7a</b> /EVE, 1/1                        | 1.67                        | 0.6                            | 6           | 88                        | 0.62                     |
| <b>7a</b> /EVE, 1/2                        | 1.20                        | 0.8                            | 6           | 86                        | 0.58                     |
| <b>7a</b> /EVE, 1/5                        | 1.00                        | 1.0                            | 5           | 90                        | 0.54                     |
| <b>7b</b> /EVE, 1/1                        | 1.67                        | 0.6                            | 5           | 92                        | - <sup>e</sup>           |
| <b>7b</b> /EVE, 1/2                        | 1.20                        | 0.8                            | 5           | 88                        | - <sup>e</sup>           |
| <b>7b</b> /EVE, 1/5                        | 1.00                        | 1.0                            | 4           | 90                        | - <sup>e</sup>           |
| <b>8a</b> /EVE, 1/1                        | 1.67                        | 0.6                            | 10          | 86                        | 0.40                     |
| <b>8a</b> /EVE, 1/2                        | 1.20                        | 0.8                            | 9           | 82                        | 0.36                     |
| <b>8a</b> /EVE, 1/5                        | 1.00                        | 1.0                            | 10          | 85                        | 0.35                     |
| <b>8b</b> /EVE, 1/1                        | 1.67                        | 0.6                            | 9           | 86                        | 0.52                     |
| <b>8b</b> /EVE, 1/2                        | 1.20                        | 0.8                            | 10          | 84                        | 0.47                     |
| <b>8b</b> /EVE, 1/5                        | 1.00                        | 1.0                            | 10          | 87                        | 0.44                     |

<sup>a</sup>The copolymer compositions were estimated to be 1:1 by <sup>1</sup>H NMR spectra and elemental analyses. <sup>b</sup>EVE=ethyl vinyl ether.

<sup>c</sup>The yields were calculated based on 1:1 alternating compositions of the resulting copolymers. <sup>d</sup>Inherent viscosities measured in a concentration 0.5 g/dL in acetone at 25 °C.

<sup>e</sup>Insoluble in acetone.

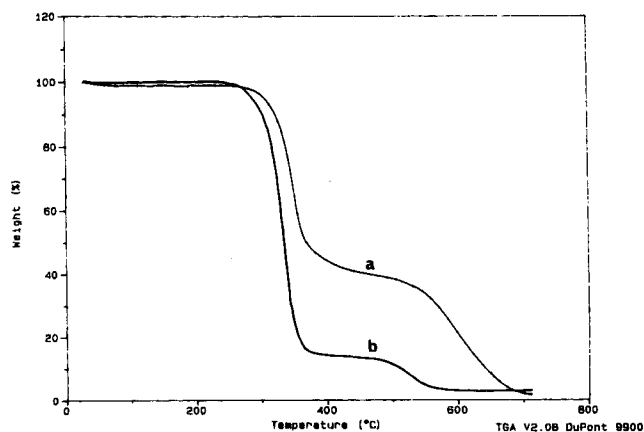
that the polymer obtained in each case was 1:1 alternating copolymer of both monomers regardless of the monomer feed ratio. Excess ethyl vinyl ether did not participate in the radical copolymerization as expected. These experimental results are reasonable in view of the fact that methoxybenzylidenemalononitrile and methyl methoxybenzylidenecyanoacetate are strong electron-acceptor olefins and ethyl vinyl ether is a strong electron-donor monomer, which does not homopolymerize by radical initiators.

**Properties of Polymers.** The swelling polymers **5-6** were not soluble in any organic solvents including DMF and DMSO due to cross-linking. The 1:1 alternating copolymers **9-10** were white amorphous materials. Copolymers **9a**, **10a**, **10b** were soluble in acetone and DMSO, but copolymer **9b** was not soluble in common organic solvents. The inherent viscosities of polymer **9-10** were in the range of 0.35-0.62 dL/g. Polymers **9-10** have good film-forming properties and films cast from acetone solution were cloudy and quite tough. The thermal behaviors of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature ( $T_g$ ). Polymers **5-6** showed a good thermal stability and did not decompose below 300 °C as shown in Table 3. The polymers show a double phase degradation pattern in their TGA thermograms (Figure 1), probably due to cross-linking. Cross-linked polymers **5-6** showed broad endothermic bands around 75-110 °C without any charac-

**Table 3.** Thermal Properties of Polymers\*

| Polymer    | $T_g$ , °C | Degradation temp, °C |          |          | Residue at 700 °C, % |
|------------|------------|----------------------|----------|----------|----------------------|
|            |            | 5%-loss              | 20%-loss | 40%-loss |                      |
| <b>5a</b>  | -          | 310                  | 340      | 360      | 2.0                  |
| <b>5b</b>  | -          | 300                  | 320      | 370      | 1.3                  |
| <b>6a</b>  | -          | 310                  | 350      | 410      | 2.0                  |
| <b>6b</b>  | -          | 290                  | 340      | 370      | 3.3                  |
| <b>9a</b>  | 165        | 280                  | 320      | 330      | 2.7                  |
| <b>9b</b>  | -          | 270                  | 300      | 330      | 4.9                  |
| <b>10a</b> | 118        | 270                  | 310      | 330      | 2.7                  |
| <b>10b</b> | -          | 260                  | 310      | 330      | 2.4                  |

\*Thermal analysis data obtained from DSC and TGA curves with a heating rate of 10 °C/min under nitrogen atmosphere.



**Figure 1.** TGA thermograms of cross-linked polymer **5a** (a) and 1:1 alternating copolymer **9a** (b) (10 °C/min, N<sub>2</sub>).

teristic  $T_g$  peaks in DSC thermograms. Alternating copolymers **9-10** showed a thermal stability up to 270 °C in TGA thermograms and the  $T_g$  values of the polymers **9-10** obtained from DSC thermograms were in the range of 118-165 °C. These  $T_g$  values are higher than those for poly(ethyl vinyl ether) (-43 °C), probably due to the presence of polar pendant group.

### Conclusions

We prepared four ethyl vinyl ethers **3** and **4** containing electron acceptors, benzylidenemalononitrile and benzylidenecyanoacetate, and investigated their polymerization behaviors. Monomers **3a** and **3b** were very reactive toward radical initiators, and polymerized quantitatively by AIBN at 65 °C within 4 h. However, polymerizabilities of meta-isomers **4a** and **4b** toward radical initiators are rather low and gave moderate polymer yields under the same polymerization conditions. The trisubstituted terminal double bond participated in the vinyl polymerization and radical polymerizations of **3** and **4** led to highly cross-linked poly(alkylvinylether)s. This particular polymerization system provides an unprecedented, unique route to highly cross-linked poly(alkylvinylether)s by radical initiators. Model compounds **7-8** readily copolymerized with ethyl vinyl ether under the polymerization conditions by radical initiators to give 1:1 alternating copolymers **9-10** in high yields, which support the high polymerizabilities of monomers **3** and **4** toward radical initiators. We are now exploring further the polymerization of other donor-acceptor systems and the results will be reported later. We are now exploring further the radical polymerization of other donor-acceptor systems and the results will be reported later.

**Acknowledgment.** This paper was supported by NON-DIRECTED RESEARCH FUND, Korea Research Foundation, 1996.

### References

1. Stille, J. K.; Chung, D. C. *Macromolecules* **1975**, *8*, 114.
2. Cho, I.; Lee, J.-Y. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 639.
3. Cho, I.; Lee, J.-Y. *Macromolecules* **1983**, *16*, 150.
4. Cho, I.; Lee, J.-Y. *Macromolecules* **1983**, *16*, 1245.
5. Lee, J.-Y.; Cho, I. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1987**, *25*, 3089.
6. Cho, I.; Lee, J.-Y. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 389.
7. Florianczyk, T.; Sullivan, C.; Janovic, Z.; Vogl, O. *Polym. Bull.* **1981**, *5*, 521.
8. Xi, F.; Bassett, W.; Vogl, O. *J. Polym. Sci.: Polym. Chem. Ed.* **1983**, *21*, 891.
9. Williams, J. K.; Wiley, D. W.; McKusick, B. C. *J. Am. Chem. Soc.* **1962**, *84*, 2210.
10. Hall, Jr. H. K.; Ykman, P. *J. Am. Chem. Soc.* **1975**, *97*, 800.
11. Hall, Jr. H. K.; Rasoul, H. A. A.; Gillard, M.; Abdelkader, M.; Nogue, P.; Sentman, R. C. *Tetrahedron Lett.* **1982**, *23*, 603.
12. Hall, Jr. H. K.; Padias, A. B. *Acc. Chem. Res.* **1990**, *23*, 3.
13. Kresel, M.; Garbratski, U.; Kohn, D. H. *J. Polym. Sci., Part A* **1964**, *2*, 105.
14. Gilath, A.; Ronel, S. H.; Shmueli, M.; Kohn, D. H. *J. Appl. Polym. Sci.* **1970**, *14*, 1491.
15. Ronel, S. H.; Shmueli, M.; Kohn, D. H. *J. Polym. Sci., A-1* **1969**, *7*, 2209.
16. Lieberman, A.; Kohn, D. H. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2435.
17. Kharas, G.; Kohn, D. H. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1457.
18. Kharas, G.; Kohn, D. H. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 583.
19. Angelorici, M. M.; Kohn, D. H. *J. Appl. Polym. Sci.* **1990**, *40*, 485.
20. Tanaka, H. *Trends Polym. Sci.* **1993**, *1*, 361.
21. Tanaka, H. *Trends Polym. Sci.* **1996**, *4*, 106.
22. Lee, J.-Y. *Polym. Bull.* **1996**, *36*, 525.
23. Lee, J.-Y.; Lee, H.-J.; Kim, M.-Y. *Bull. Korean Chem. Soc.* **1996**, *17*, 257.
24. Moore, A. H. F. *Org. Syn. Coll. Vol.* **4** **1963**, 84.
25. Griffin, A. C.; Bhatti, A. M.; Hung, R. S. in Prasad, P. N.; Ulrich, D. R. Eds. *Nonlinear Optical and Electroactive Polymers*; Plenum Press: New York, 1987, pp 375-391.
26. Corson, B. B.; Stoughton, R. W. *J. Am. Chem. Soc.* **1928**, *50*, 2825.
27. Lee, J.-Y. *Polym. Bull.* **1994**, *33*, 635.