

# Articles

## Synthesis and Cationic Polymerization of Vinyl Ethers Containing the NLO-chromophores Oxybenzylidenemalononitrile and Oxybenzylidenecyanoacetate in the Side Chain

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*o*-(2-Vinyloxyethoxy)benzylidenemalononitrile (**4a**), methyl *o*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**4b**), *m*-(2-vinyloxyethoxy)benzylidenemalononitrile (**5a**), methyl *m*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**5b**), *p*-(2-vinyloxyethoxy)benzylidenemalononitrile (**6a**), and methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**6b**) were prepared by the condensation of *o*-(2-vinyloxyethoxy)benzaldehyde (**1**), *m*-(2-vinyloxyethoxy)benzaldehyde (**2**), and *p*-(2-vinyloxyethoxy)benzaldehyde (**3**) with malononitrile or methyl cyanoacetate, respectively. Bifunctional vinyl ether monomers **4a-b** and **6a-b** polymerized readily with cationic initiators to give polymers with the NLO-chromophores *o*- and *p*-oxybenzylidenemalononitrile or *o*- and *p*-oxybenzylidenecyanoacetate in side chain at  $-60^{\circ}\text{C}$ , while meta-isomers **5a** and **5b** gave lower yields of polymers under the same conditions. The resulting polymers **7-9** were soluble in common organic solvents and the inherent viscosities of polymers were in the range of 0.20-0.30 dL/g in acetone. Solution-cast films were clear and brittle, showing  $T_g$  values in the range of  $40-70^{\circ}\text{C}$ .

### Introduction

Functional materials of nonlinear optical (NLO) activity based on organic compounds have long been the subject of curiosity and extensively studied because of their potential applications in the field of telecommunications, optical signal processing, optical switching, etc.<sup>1-6</sup> It is well known that organic and polymeric materials with highly dipolar electronic systems exhibit NLO properties. The organic materials seem to be superior because of their higher nonlinear optical activity and faster response time than the inorganic ones. Among the organic materials the NLO polymers are receiving great attention, mainly because they offer many advantages such as mechanical endurance, light weight, chemical resistance, and good processability to form optical devices.<sup>7</sup> A potential NLO polymer must contain a highly polarizable  $\pi$ -electronic systems and these polymers have to be mechanically very strong. There are tremendous challenges in designing and synthesis of polymers of large NLO effects. Polyesters,<sup>8-12</sup> polyurethanes,<sup>13</sup> polyamides,<sup>14,15</sup> and poly(phenyleneethylenes)<sup>16</sup> containing the chromophoric main chain were prepared. Various polymers with the NLO-chromophores in the side chain such as poly(meth)acrylates<sup>17-23</sup> and polystyrene<sup>24</sup> were also reported. Recently we have prepared poly(alkyl vinyl ethers)<sup>25-33</sup> containing various dipolar electronic groups, which is presumably effective chromophore for second-order nonlinear optical applications in the side chain. These polymers showed a thermal stability up to  $300^{\circ}\text{C}$  in TGA thermogram and the  $T_g$  was around  $61-87^{\circ}\text{C}$ . In this work we prepared six positional vinyl ether isomers containing NLO-chromophores in the side chain and polymerized them by cationic initiators. The present report describes the synthesis and cationic polymerization of

*o*-, *m*-, *p*-(2-vinyloxyethoxy)benzylidenemalononitrile (**4a**, **5a**, **6a**) and methyl *o*-, *m*-, *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**4b**, **5b**, **6b**).

### 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  $100^{\circ}\text{C}$  under vacuum. *o*-Hydroxybenzaldehyde was dried with anhydrous magnesium sulfate under vacuum. *p*-Hydroxybenzaldehyde was recrystallized from water and dried under vacuum. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. Methyl cyanoacetate was purified by drying with anhydrous sodium sulfate and distilled. Piperidine was dried with calcium hydride and fractionally distilled. Acetone was purified by drying with anhydrous potassium carbonate, followed by distillation. *n*-Butanol was dried with anhydrous magnesium sulfate and distilled under nitrogen. Dichloromethane was dried with calcium chloride, distilled over anhydrous calcium sulfate, and stored in a brown bottle with 4A molecular sieves. 2-Iodoethyl vinyl ether (2-IEVE) was prepared according to the procedure previously described.<sup>34</sup>

**Measurements.** IR spectra were taken on a Hitachi Model 260-30 infrared spectrophotometer.  $^1\text{H}$  NMR spectra were obtained on a Varian EM 360L NMR (60 MHz) and Varian 300 MHz spectrometer. 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 under 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 (*o*-2-VOEBA)**

**1.** *o*-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 diethyl ether 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>) δ 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) 3065 (=C-H), 2940, 2870 (C-H), 1691 (C=O), 1623, 1604 (C=C) cm<sup>-1</sup>.

***m*-(2-Vinyloxyethoxy)benzaldehyde (*m*-2-VOEBA) **2.**** *m*-2-VOEBA was prepared from *m*-hydroxybenzaldehyde, anhydrous potassium carbonate, and 2-iodoethyl vinyl ether according to the procedure previously described in *o*-2-VOEBA. bp 75–77 °C (0.2 mmHg). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 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>.

***p*-(2-Vinyloxyethoxy)benzaldehyde (*p*-2-VOEBA) **3.**** *p*-2-VOEBA was prepared from *p*-Hydroxybenzaldehyde, anhydrous potassium carbonate, and 2-iodoethyl vinyl ether according to the procedure previously described in *o*-2-VOEBA. bp 72–74 °C (0.2 mmHg). Compound **3** was crystallized in the refrigerator (6 °C). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 9.89 (s, 1H, -CHO), 7.63–7.99 (m, 2H, aromatic), 6.87–7.28 (m, 2H, aromatic), 6.32–6.73 (q, 1H, =CH-O-), 4.18–4.48 (m, 2H, CH<sub>2</sub>=), 3.70–4.17 (m, 4H, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-). IR (neat) 3119, 3068 (=C-H), 2940, 2878, 2833 (C-H), 1684 (C=O), 1603, 1579 (C=C) cm<sup>-1</sup>.

***o*-(2-Vinyloxyethoxy)benzylidenemalononitrile (*o*-2-VOEBMN) **4a.**** 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 **4a**. mp 69–70 °C. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 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)benzylidenecyano-**

**acetate (*o*-2-VOEBCA) **4b.**** 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 **4b**. 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>13</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 (*m*-2-VOEBMN) **5a.**** Piperidine (0.13 g, 1.5 mmol) was added to a solution of *m*-(2-vinyloxyethoxy)benzaldehyde **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 **5a**. 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, H, 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 (*m*-2-VOEBCA) **5b.**** Piperidine (0.17 g, 2.0 mmol) was added to a solution of *m*-(2-vinyloxyethoxy)benzaldehyde **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 **5b**. 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.

***p*-(2-Vinyloxyethoxy)benzylidenemalononitrile **6a.**** Piperidine (0.13 g, 1.5 mmol) was added to a solution of *p*-(2-vinyloxyethoxy)benzaldehyde **3** (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 **6a**.

mp 80-82 °C.  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.76-4.21 (m, 4H, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 4.20-4.51 (m, 2H, CH<sub>2</sub>=), 6.30-6.73 (q, 1H, =CH-O-), 6.83-7.28 (m, 2H, aromatic), 7.75-8.13 (m, 3H, aromatic). IR (KBr) 3105, 3067, 2938, 2869 (C-H), 2230 (CN), 1628, 1603, 1579 (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, 69.90; H, 5.08; N, 11.58.

**Methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate 6b.** Piperidine (0.17 g, 2.0 mmol) was added to a solution of *p*-(2-vinyloxyethoxy)benzaldehyde **3** (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 with 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 **6b**. mp 95-97 °C.  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  7.84-8.25 (m, 3H, aromatic), 6.93-7.29 (m, 2H, aromatic), 6.32-6.75 (q, 1H, =CH-O-), 4.25-4.50 (m, 2H, CH<sub>2</sub>=), 3.87-4.24 (m, 4H, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 3.88 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>). IR (KBr) 3103, 3016, 2957, 2930 (C-H), 2220 (CN), 1726 (C=O), 1618, 1588 (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.

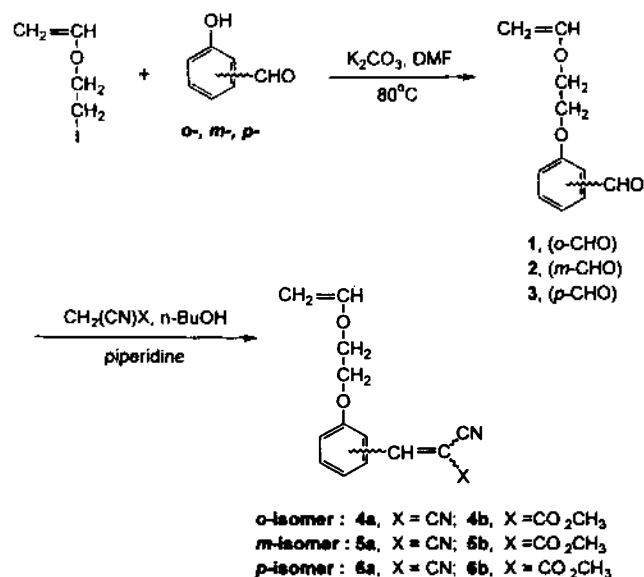
**Cationic polymerization of monomers 4-6.** A representative cationic polymerization procedure (the case of **4a**) was as follows: A solution of **4a** (0.72 g, 3.0 mmol) in dichloromethane (2.5 mL) was placed in a rubber septum stopper capped glass ampule under nitrogen. The resulting solution was flushed with nitrogen for 20 min. The ampule was then placed in an ethanol-acetone bath kept at -60 °C under nitrogen, and 0.0034 mL (0.03 mmol) of boron trifluoride etherate was added to the solution. After 16 h the ampule was taken out and the polymerization mixture was poured into 500 mL of methanol. The precipitated polymer was collected and reprecipitated from acetone into methanol to give 0.65 g (90% yield) of polymer **7a**;  $\eta_{inh}$  = 0.26 dL/g (c 0.5 g/dL in acetone at 25 °C).  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  1.43-2.05 (m, 2H, -CH<sub>2</sub>-), 3.65-4.33 (m, 5H, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-CH-), 6.88-7.20 (m, 2H, aromatic), 7.44-7.69 (m, 1H, aromatic), 7.96-8.15 (m, 1H, aromatic), 8.27-8.48 (m, 1H, aromatic). IR (KBr) 3023 (=C-H), 2920, 2860 (C-H), 2220 (CN), 1594, 1579 (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, 11.75. **7b**:  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  1.42-2.06 (m, 2H, -CH<sub>2</sub>-), 3.59-4.29 (m, 5H, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-CH-), 6.85-7.17 (m, 2H, aromatic), 7.30-7.58 (m, 1H, aromatic), 8.12-8.22 (m, 1H, aromatic), 8.58-8.77 (m, 1H, aromatic). IR (KBr) 3030 (=C-H), 2945, 2865 (C-H), 2220 (CN), 1724 (C=O), 1590 (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, 5.58; N, 5.22. **8a**:  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  1.40-2.06 (m, 2H, -CH<sub>2</sub>-), 3.67-4.21 (m, 5H, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-CH-), 7.12-7.30 (m, 1H, aromatic), 7.34-7.58 (m, 3H, aromatic), 8.02-8.21 (m, 1H, aromatic). IR (KBr) 3028 (=C-H), 2930, 2860 (C-H), 2230 (CN), 1595, 1574 (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, 69.93; H, 5.09; N, 11.58. **8b**:  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  1.53-2.09 (m, 2H, -CH<sub>2</sub>-), 3.66-4.21 (m, 5H, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-CH-), 7.05-7.21 (m, 1H, aromatic), 7.29-7.64 (m, 3H, aromatic), 8.06-8.27. IR (KBr) 3030 (=C-H), 2950,

2875 (C-H), 2223 (CN), 1725 (C=O), 1604, 1580 (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, 65.95; H, 5.60; N, 5.18. **9a**: IR (KBr) 3013 (=C-H), 2925, 2857 (C-H), 2220 (CN), 1598, 1576, 1553 (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, 69.90; H, 5.12; N, 11.57. **9b**:  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  7.47-8.18 (3H, m), 6.58-7.33 (2H, m), 3.22-4.54 (8H, s), 1.33-2.20 (2H, m). IR (KBr) 3032, 2942, 2938, 2848 (C-H), 2218 (CN), 1720 (C=O), 1584, 1556 (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, 65.83; H, 5.45; N, 5.21.

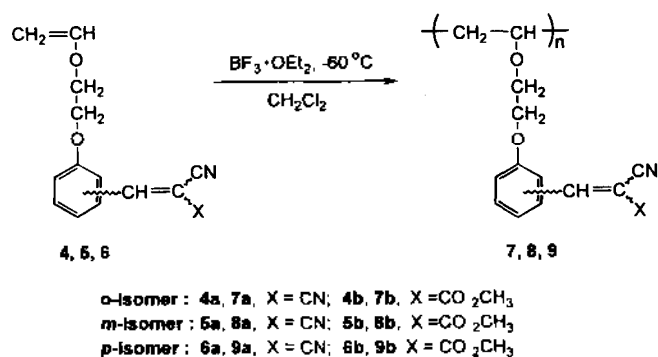
## Results and Discussion

**Syntheses of monomers 4-6.** 2-IEVE was prepared by the well known halogen exchange reaction<sup>34</sup> from 2-chloroethyl vinyl ether and sodium iodide, and reacted with *o*-hydroxybenzaldehyde, *m*-hydroxybenzaldehyde, and *p*-hydroxybenzaldehyde to yield *o*-(2-vinyloxyethoxy)benzaldehyde (**1**), *m*-(2-vinyloxyethoxy)benzaldehyde (**2**), *p*-(2-vinyloxyethoxy)benzaldehyde (**3**).<sup>35</sup> *o*-2-VOEBMN (**4a**), *o*-(2-VOEBCA (**4b**)), *m*-2-VOEBMN (**5a**), *m*-2-VOEBCA (**5b**), *p*-2-VOEBMN (**6a**), and *p*-2-VOEBCA (**6b**) were synthesized by the condensation of **1**, **2**, and **3** with malononitrile or methyl cyanoacetate, respectively.<sup>36</sup> The chemical structure of the compounds was identified by  $^1\text{H}$  NMR, and IR spectra, and elemental analysis. Monomers **4-6** show olefinic protons at  $\delta$  = 6.24-6.77 (q, 1H, vinylic) in their  $^1\text{H}$  NMR spectra, respectively. The same monomers showed strong absorption bands at 2218-2230, 1725-1733, and 1569-1642 cm<sup>-1</sup> indicating the presence of nitrile, carbonyl, and olefinic groups, respectively. Spectral data indicated that compounds **4b**, **5b**, and **6b** were a mixtures of the *cis*- and *trans*-isomers.

**Cationic polymerization of monomers 4-6.** Isomeric vinyl ether monomers **4-6** were polymerized in solution at -60 °C with boron trifluoride etherate as cationic initiator to obtain the polymers **7-9**. The polymerization results are summarized in Table 1. The *ortho*- and *para*-isomeric



Scheme 1.



Scheme 2.

Table 1. Cationic polymerization of 4-6<sup>a</sup> under various conditions

Monomer	Monomer/ Solvent <sup>b</sup> (mol/l L)	Initiator to Monomer (mol%)	Temp. (°C)	Time (h)	Yield (%)	$\eta_{\text{inh}}^c$ (dL/g)
4a	1.20	1.0	-60	16	90	0.26
4a	1.00	0.8	-30	12	88	0.28
4b	1.20	1.0	60	18	86	0.25
4b	1.00	0.8	-30	15	85	0.24
5a	1.20	1.0	-60	20	68	0.17
5a	1.00	0.8	-30	24	72	0.15
5b	1.20	1.0	-60	24	70	0.16
5b	1.00	0.8	-30	24	65	0.14
6a	1.05	1.0	-60	10	100	-
6a	0.92	0.8	-60	16	100	-
6b	1.18	1.0	-60	10	86	0.22
6b	0.95	0.8	-60	20	88	0.26

<sup>a</sup>4a = *o*-(2-Vinylxyethoxy)benzylidenemalononitrile; 4b = Methyl *o*-(2-Vinylxyethoxy)benzylidenecyanoacetate; 5a = *m*-(2-Vinylxyethoxy)benzylidenemalononitrile; 5b = Methyl *m*-(2-Vinylxyethoxy)benzylidenecyanoacetate; 6a = *p*-(2-Vinylxyethoxy)benzylidenemalononitrile; 6b = Methyl *p*-(2-Vinylxyethoxy)benzylidenecyanoacetate. <sup>b</sup>Solvent: Dichloromethane. <sup>c</sup>Inherent viscosity of polymer: Concentration of 0.5 g/dL in acetone at 25 °C.

monomers 4 and 6 were readily polymerized to yield the polymers 7 and 9 in high yield. However, polymerizabilities of *meta*-isomers 5a and 5b toward cationic initiators are rather low and gave low polymer yields under the same polymerization conditions, as shown in Table 1. According to our experimental results, polymerizabilities of *ortho*-monomers toward cationic 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 structure of the polymers were confirmed by <sup>1</sup>H NMR, IR spectra, and elemental analyses. Spectral data indicated that the terminal benzylidenyl group did not participate in the vinyl polymerization. In most cases, conversions were quite high, but the molecular weights were rather low as indicated by the inherent viscosities.

**Properties of polymers.** The resulting polymers were soluble in common solvents such as acetone, chloro-

Table 2. Thermal properties of polymer 7-9

Polymer	$T_g^a$ , °C	Degradation temp, °C <sup>b</sup>			Residue <sup>b</sup> at 700 °C, %
		5%-loss	20%-loss	40%-loss	
7a	59	307	350	389	21.4
7b	60	314	351	370	9.3
8a	39	278	333	370	2.0
8b	44	291	348	376	2.0
9a	70	254	316	365	29.5
9b	61	330	367	394	27.4

<sup>a</sup>Determined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10 °C/min under nitrogen atmosphere. <sup>b</sup>Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10 °C/min under nitrogen atmosphere.

form and DMSO, but was not soluble in methanol and diethyl ether. Polymer 9a was not soluble in common organic solvents, probably due to the high molecular weight and/or the high crystallinity by the presence of polar symmetric dicyano substituents in the side chain. The inherent viscosities of polymers were in the range of 0.20-0.30 dL/g indicating moderate molecular weights. The thermal behavior of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature ( $T_g$ ). The results are summarized in Table 2. The polymers showed a thermal stability up to 300 °C in TGA thermograms. The glass transition temperature ( $T_g$ ) of the polymers measured by DSC thermograms were around 40-70 °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. Solution-cast films were clear and brittle, which could be due to the rather low molecular weight and/or high concentration of dipole moment, and therefore the nonlinear optical behavior has not been measured yet.

## Conclusions

We prepared six isomeric vinyl ether monomers 4-6 having highly dipolar electronic system. The vinyl ether compounds were polymerized by cationic initiator to obtain poly(ethyl vinyl ethers) 7-9 containing *o*-, *m*-, and *p*-oxybenzylidenemalononitrile or *o*-, *m*-, and *p*-oxybenzylidenecyanoacetate, which is presumably effect NLO-chromophore for second-order nonlinear optical applications in the side chain. The resulting substituted poly(ethyl vinyl ethers) were soluble in common organic solvents. The polymers showed a thermal stability up to 300 °C in TGA thermograms. These polymers showed characteristic  $T_g$  peaks around 40-70 °C in their DSC thermograms, which is rather low for electrooptic device applications. We are now in the process of extending the polymerization system to the synthesis of other type of NLO polymers, and the results will be reported at a later date.

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