

Synthesis and Cationic Polymerization of Vinyl Ethers Containing Oxynitrobenzylidenemalononitrile and Oxynitrobenzylidenecyanoacetate as the NLO-phores in the Side Chain

Ju-Yeon Lee,* Moo-Yong Kim, and Mi-Ra Ahn

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

Received March 26, 1999

5-Nitro-2-(2'-vinylloxyethoxy)benzylidenemalononitrile (**2a**), methyl 5-nitro-2-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**2b**), 3-nitro-4-(2'-vinylloxyethoxy)benzylidenemalononitrile (**4a**), methyl 3-nitro-4-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**4b**), 2-nitro-5-(2'-vinylloxyethoxy)benzylidenemalononitrile (**6a**), and methyl 2-nitro-5-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**6b**) were prepared by the condensation of 5-nitro-2-(2'-vinylloxyethoxy)benzaldehyde (**1**), 3-nitro-4-(2'-vinylloxyethoxy)benzaldehyde (**3**), and 2-nitro-5-(2'-vinylloxyethoxy)benzaldehyde (**5**) with malononitrile or methyl cyanoacetate, respectively. Vinyl ether monomers **2a-b**, **4a-b**, and **6a-b** were polymerized with boron trifluoride etherate as a cationic initiator to yield poly(vinyl ethers) **7-9** having oxynitrobenzylidenemalononitrile and oxynitrobenzylidenecyanoacetate, which is effective chromophore for second-order nonlinear optical applications. Polymers **7-9** were soluble in common organic solvents such as acetone and DMSO. T_g values of the resulting polymers were in the range of 67-83 °C. Electrooptic coefficient (r_{33}) of the poled polymer films were in the range of 15-27 pm/V at 633 nm. Polymers **7-9** showed a thermal stability up to 300 °C in TGA thermograms, which is acceptable for NLO device applications.

Introduction

Materials of nonlinear optical (NLO) activity based on organic compounds have been extensively studied over the past decade because of their potential applications in the field of telecommunications, optical signal processing, optical switching, etc.¹⁻⁶ 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 make optical devices.⁷ A potential NLO polymer must contain a highly polarizable π -electronic systems and these polymers have to be mechanically very strong. There are tremendous challenges in designing and synthesis of polymers with large NLO effects. Polyesters,⁸⁻¹⁰ polyurethanes,¹¹ polyamides,¹²⁻¹³ and poly(phenyleneethylenes)¹⁴ containing the chromophoric main chain were prepared. Various polymers with the NLO-chromophores in the side chain such as poly(methacrylate)s¹⁹⁻²⁴ and polystyrene²⁵ were also reported. Recently we have prepared poly(alkyl vinyl ethers) containing *p*-oxybenzylidenemalononitrile or *p*-oxybenzylidenecyanoacetate as a NLO-phore.²⁶ These poly(vinyl ethers) showed a thermal stability up to 300 °C with a T_g of 40-70 °C, which is too low for electrooptic applications. In this work we prepared six isomeric poly(vinyl ethers) containing oxynitrobenzylidenemalononitrile or oxynitrobenzylidenecyanoacetate, which is presumably effective NLO-chromophore in the side chain. We

selected geminally substituted double bond as a NLO-phore because it is easy to synthesize and is more polar than monosubstituted one. We attached two electron-withdrawing nitro- and 1,1-dicyanovinyl- or 1-cyano-1-carbomethoxyvinyl groups onto the aromatic ring in the pendant substituent for enhancing T_g and thermal stability. Electrooptic (EO) coefficient, T_g , and thermal stability of the resulting poly(vinyl ethers) were compared with those of poly(vinyl ethers) without nitro group. All the thermal and EO properties were improved by introduction of nitro group. The present report describes the synthesis and cationic polymerization of 5-nitro-2-(2'-vinylloxyethoxy)benzylidenemalononitrile (**2a**), methyl 5-nitro-2-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**2b**), 3-nitro-4-(2'-vinylloxyethoxy)benzylidenemalononitrile (**4a**), and methyl 3-nitro-4-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**4b**).

Experimental Section

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. 2-Hydroxy-5-nitrobenzaldehyde, 4-hydroxy-3-nitrobenzaldehyde, and 5-hydroxy-2-nitrobenzaldehyde were used as received. 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 was prepared according to the procedure previously described.²⁶

Measurements. IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ¹H 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. The alignment of the NLO-phore of the polymers was carried out by corona poling method. As the temperature was raised to 80 °C, 6 kV of corona voltage was applied and kept 80 °C for 30 min. The polymer sample was then cooled to room temperature with the corona voltage applied. The electrooptic coefficient (*r*₃₃) of the corona poled film was measured by simple reflection technique.²⁷ Melting points were measured in Buchi 530 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

5-Nitro-2-(2'-vinylloxyethoxy)benzaldehyde (1). 2-Hydroxy-5-nitrobenzaldehyde (16.7 g, 0.10 mol), anhydrous potassium carbonate (41.5 g, 0.30 mol), and 2-iodoethyl vinyl ether (25.7 g, 0.13 mol) were dissolved in 100 mL of dry DMF under nitrogen. The mixture was heated in an oil bath at 80 °C for 20 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 recrystallization from *isopropyl alcohol* yielded 19.2 g (81% yield) of pure **1**. Mp: 37-38 °C. ¹H NMR (CDCl₃) δ 4.10-4.48 (m, 6H, CH₂=, -O-CH₂-CH₂-O-), 6.47-6.54 (q, 1H, =CH-O-), 7.13-7.16 (m, 1H, aromatic), 8.40-8.44 (m, 1H, aromatic), 10.47 (s, 1H, -CHO). IR (neat) 3114, 3070 (=C-H), 2962, 2939, 2882 (C-H), 1684 (C=O), 1611, 1572 (C=C), 1510, 1348 (N=O) cm⁻¹.

5-Nitro-2-(2'-vinylloxyethoxy)benzylidenemalononitrile (2a). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 5-nitro-2-(2'-vinylloxyethoxy)benzaldehyde **1** (6.64 g, 28 mmol) and malononitrile (1.98 g, 30 mmol) in 40 mL of *isopropyl alcohol* with stirring at 0 °C under nitrogen. After stirring for 6 h at 0 °C, the reaction mixture was placed in refrigerator for crystallization. The product was filtered and washed with water (30 mL). The obtained pale yellow product was recrystallized from *isopropyl alcohol* to give 6.87 g (86% yield) of **2a**. Mp: 90-92 °C. ¹H NMR (CDCl₃) δ 4.13-4.47 (m, 6H, CH₂=, -O-CH₂-CH₂-O-), 6.47-6.54 (q, 1H, =CH-O-), 7.14-7.17 (d, 1H, aromatic), 8.22 (s, 1H, aromatic), 8.43-8.47 (m, 1H, aromatic), 9.04-9.05 (d, 1H, aromatic). IR (KBr) 3121, 3038 (=C-H), 2930 (C-H), 2237

(CN), 1628, 1611, 1585 (C=C), 1518, 1350 (N=O) cm⁻¹. UV/Vis (chloroform) λ_{max}=351 nm, ε=13650. Anal. Calcd for C₁₄H₁₁N₃O₄: C, 58.95; H, 3.88; N, 14.73. Found: C, 58.87; H, 3.82; N, 14.68.

Methyl 5-nitro-2-(2'-vinylloxyethoxy)benzylidenecyanoacetate (2b). Piperidine (0.17 g, 2.0 mmol) was added to a solution of 5-nitro-2-(2'-vinylloxyethoxy)benzaldehyde **1** (7.11 g, 30 mmol) and methyl cyanoacetate (2.98 g, 30 mmol) in 40 mL of *isopropyl alcohol* with stirring at 0 °C under nitrogen. The resulting solution was stirred for 6 h at 0 °C and 30 min at room temperature. After cooling in an ice bath, the product was filtered and washed successively with water (30 mL). The obtained pale yellow product was recrystallized from *isopropyl alcohol* to give 8.59 g (90% yield) of **2b**. Mp: 109-110 °C. ¹H NMR (acetone-d₆) δ 3.95 (s, 3H, CO₂CH₃), 4.10-4.45 (m, 6H, CH₂=, -O-CH₂-CH₂-O-), 6.46-6.53 (q, 1H, =CH-O-), 7.10-7.13 (d, 1H, aromatic), 8.37-8.41 (q, 1H, aromatic), 8.63 (s, 1H, aromatic), 9.07-9.09 (d, 1H, aromatic). IR (KBr) 3121, 3121, 3074, 3057 (=C-H), 2963, 2932 (C-H), 2230 (CN), 1720 (C=O), 1628, 1609 (C=C), 1518, 1317 (N=O) cm⁻¹. UV/Vis (chloroform) λ_{max}=346 nm, ε=25900. Anal. Calcd for C₁₅H₁₄N₂O₆: C, 56.61; H, 4.43; N, 8.80. Found: C, 56.53; H, 4.48; N, 8.87.

3-Nitro-4-(2'-vinylloxyethoxy)benzaldehyde (3). 4-Hydroxy-3-nitrobenzaldehyde (16.7 g, 0.10 mol), anhydrous potassium carbonate (41.5 g, 0.30 mol), and 2-iodoethyl vinyl ether (25.7 g, 0.13 mol) were dissolved in 120 mL of dry DMF under nitrogen. The mixture was heated in an oil bath at 80 °C for 18 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 recrystallization from *isopropyl alcohol* yielded 19.4 g (82% yield) of pure **3**. Mp: 75-76 °C. ¹H NMR (CDCl₃) δ 4.08-4.47 (m, 6H, CH₂=, -O-CH₂-CH₂-O-), 6.46-6.53 (q, 1H, =CH-O-), 7.28 (s, H, aromatic), 8.35 (s, 1H, aromatic), 9.94 (s, 1H, -CHO). IR (neat) 3074 (=C-H), 2936, 2882 (C-H), 1684 (C=O), 1611, 1589 (C=C), 1522, 1346 (N=O) cm⁻¹.

3-Nitro-4-(2'-vinylloxyethoxy)benzylidenemalononitrile (4a). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 3-nitro-4-(2'-vinylloxyethoxy)benzaldehyde **3** (6.64 g, 28 mmol) and malononitrile (1.98 g, 30 mmol) in 40 mL of *isopropyl alcohol* with stirring at 0 °C under nitrogen. After stirring for 5 h at 0 °C and 1h at room temperature, the reaction mixture was placed in refrigerator for crystallization. The product was filtered and washed with water (30 mL). The obtained pale yellow product was recrystallized from *isopropyl alcohol* to give 6.63 g (83% yield) of **4a**. Mp: 100-102 °C. ¹H NMR (CDCl₃) δ 4.09-4.49 (m, 6H, CH₂=, -O-CH₂-CH₂-O-), 6.45-6.52 (q, 1H, =CH-O-), 7.28-7.31 (d, 1H, aromatic), 7.69 (s, 1H, aromatic), 8.24-8.28 (m, 2H, aromatic). IR (KBr) 3094, 3034 (=C-H), 2932, 2880 (C-H), 2232 (CN), 1616, 1585 (C=C), 1529, 1358 (N=O) cm⁻¹. Anal. Calcd for C₁₄H₁₁N₃O₄: C, 58.95; H, 3.88; N, 14.73. Found: C, 58.86;

H, 3.84; N, 14.78.

Methyl 3-nitro-4-(2'-vinylxyethoxy)benzylidenecyanoacetate (4b). Piperidine (0.17 g, 2.0 mmol) was added to a solution of 3-nitro-4-(2'-vinylxyethoxy)benzaldehyde **3** (7.11 g, 30 mmol) and methyl cyanoacetate (2.98 g, 30 mmol) in 40 mL of *isopropyl* alcohol with stirring at 0 °C under nitrogen. The resulting solution was stirred for 2 h at 0 °C and 5 h at room temperature. After cooling in an ice bath, the product was filtered and washed with 40 mL of water and 20 mL of cold *isopropyl* alcohol. The obtained pale yellow product was recrystallized from *isopropyl* alcohol to give 8.79 g (92% yield) of **4b**. Mp: 117-118 °C. ¹H NMR (acetone-d₆) δ 3.94 (s, 3H, CO₂CH₃), 4.08-4.47 (m, 6H, CH₂=, -O-CH₂-CH₂-O-), 6.45-6.52 (q, 1H, =CH-O-), 7.22-7.30 (m, 1H, aromatic), 8.15 (s, 1H, aromatic), 8.31-8.38 (m, 2H, aromatic). IR (KBr) 3122, 3076, 3041 (=C-H), 2953, 2882 (C-H), 2226 (CN), 1717 (C=O), 1628, 1614, 1599 (C=C), 1520, 1352 (N=O) cm⁻¹. Anal. Calcd for C₁₅H₁₄N₂O₆: C, 56.61; H, 4.43; N, 8.80. Found: C, 56.56; H, 4.49; N, 8.86.

2-Nitro-5-(2'-vinylxyethoxy)benzaldehyde (5). 5-Hydroxy-2-nitrobenzaldehyde (16.7 g, 0.10 mol), anhydrous potassium carbonate (41.5 g, 0.30 mol), and 2-iodoethyl vinyl ether (25.7 g, 0.13 mol) were dissolved in 150 mL of dry DMF under nitrogen. The mixture was heated in an oil bath at 80 °C for 20 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 recrystallization from *isopropyl* alcohol yielded 21.9 g (92% yield) of pure product **5**. Mp: 47-48 °C. ¹H NMR (CDCl₃) δ 4.07-4.37 (m, 6H, CH₂=, -O-CH₂-CH₂-O-), 6.47-6.55 (q, 1H, =CH-O-), 7.18-7.37 (m, 1H, aromatic), 8.14-8.17 (d, 2H, aromatic), 10.48 (s, 1H, -CHO). IR (neat) 3107 (=C-H), 2930, 2878 (C-H), 1697 (C=O), 1626, 1609 (C=C), 1512, 1331 (N=O) cm⁻¹.

2-Nitro-5-(2'-vinylxyethoxy)benzylidenemalononitrile (6a). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2-nitro-5-(2'-vinylxyethoxy)benzaldehyde **5** (6.64 g, 28 mmol) and malononitrile (1.98 g, 30 mmol) in 45 mL of *isopropyl* alcohol with stirring at 0 °C under nitrogen. After stirring for 5 h at 0 °C and 1 h at room temperature, the reaction mixture was placed in refrigerator for crystallization. The product was filtered and washed with 30 mL of water. The obtained pale yellow product was recrystallized from *isopropyl* alcohol to give 6.23 g (78% yield) of **6a**. Mp: 85-86 °C. ¹H NMR (CDCl₃) δ 4.08-4.39 (m, 6H, CH₂=, -O-CH₂-CH₂-O-), 6.47-6.55 (q, 1H, =CH-O-), 7.19-7.23 (m, 2H, aromatic), 8.32-8.35 (d, 1H, aromatic), 8.47 (s, 1H, aromatic). IR (KBr) 3132, 3098, 3043 (=C-H), 2930, 2875 (C-H), 2237 (CN), 1622, 1601 (C=C), 1514, 1302 (N=O) cm⁻¹. Anal. Calcd for C₁₄H₁₁N₃O₄: C, 58.95; H, 3.88; N, 14.73. Found: C, 58.89; H, 3.81; N, 14.76.

Methyl 2-nitro-5-(2'-vinylxyethoxy)benzylidenecyanoacetate (6b). Piperidine (0.17 g, 2.0 mmol) was added to a

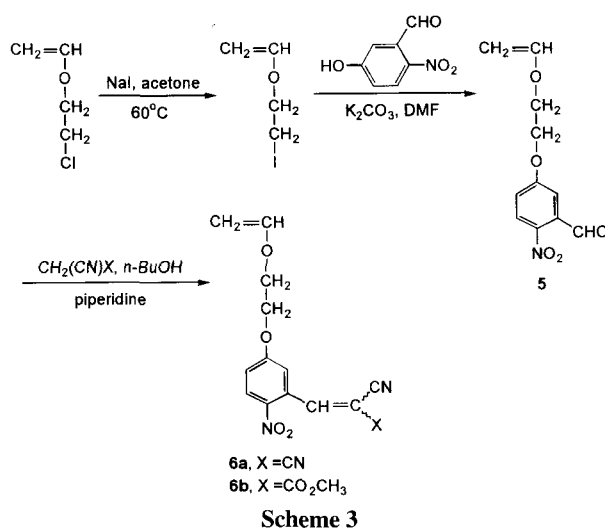
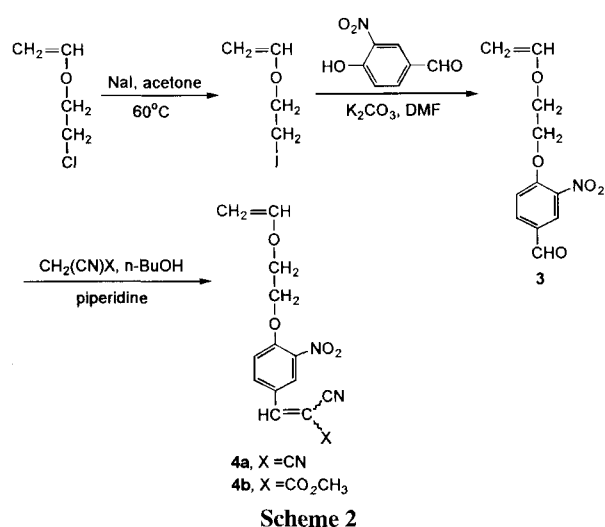
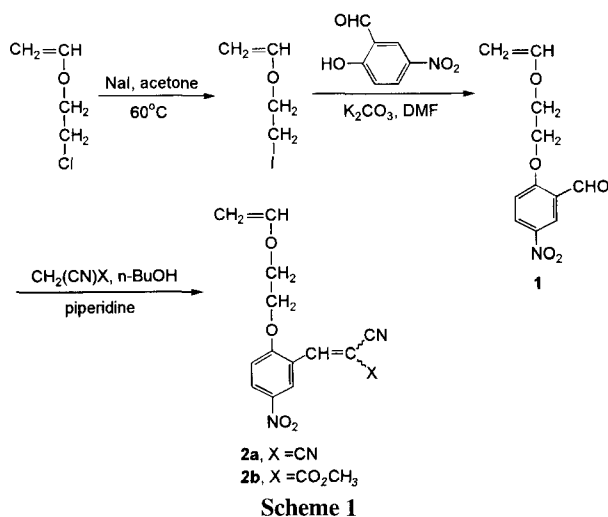
solution of 3-nitro-4-(2'-vinylxyethoxy)benzaldehyde **5** (7.11 g, 30 mmol) and methyl cyanoacetate (2.98 g, 30 mmol) in 40 mL of *isopropyl* alcohol with stirring at 0 °C under nitrogen. The resulting solution was stirred for 7 h at 0 °C and 30 min at room temperature. After cooling in an ice bath, the product was filtered and washed with 50 mL of water. The obtained pale yellow product was recrystallized from *isopropyl* alcohol to give 8.40 g (88% yield) of **6b**. Mp: 129-130 °C. ¹H NMR (acetone-d₆) δ 3.97 (s, 3H, CO₂CH₃), 4.07-4.38 (m, 6H, CH₂=, -O-CH₂-CH₂-O-), 6.48-6.55 (q, 1H, =CH-O-), 7.14-7.17 (d, 1H aromatic), 7.27 (s, 1H, aromatic), 8.28-8.31 (d, 1H, aromatic), 8.77 (s, 1H, aromatic). IR (KBr) 3115, 3053 (=C-H), 2955, 2930 (C-H), 2230 (CN), 1743 (C=O), 1624, 1603 (C=C), 1516, 1339 (N=O) cm⁻¹. Anal. Calcd for C₁₅H₁₄N₂O₆: C, 56.61; H, 4.43; N, 8.80. Found: C, 56.70; H, 4.48; N, 8.74.

Cationic Polymerization of Monomers 2, 4 and 6. A representative cationic polymerization procedure (the case of **2a**) was as follows: A solution of **2a** (0.86 g, 3.0 mmol) in 3.0 mL of dichloromethane 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 14 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 0.74 g (86% yield) of polymer **7a**; $\eta_{inh} = 0.26$ dL/g (0.5 g/dL in acetone at 25 °C). **7a**: ¹H NMR (acetone-d₆) δ 1.50-2.14 (m, 2H, -CH₂-), 3.67-4.16 (m, 3H, -CH₂-O-CH-), 4.32-4.60 (m, 2H, -Ph-O-CH₂-), 7.23-7.54 (m, 1H, aromatic), 8.28-8.57 (m, 2H, aromatic), 8.82-9.02 (m, 1H, aromatic). IR (KBr) 3049 (=C-H), 2934, 2874 (C-H), 2231 (CN), 1612, 1593 (C=C), 1522, 1346 (N=O) cm⁻¹. UV/Vis (chloroform) $\lambda_{max} = 350$ nm. Anal. Calcd for (C₁₄H₁₁N₃O₄)_n: C, 58.95; H, 3.88; N, 14.73. Found: C, 58.88; H, 3.94; N, 14.81. **7b**: ¹H NMR (acetone-d₆) δ 1.51-2.15 (m, 2H, -CH₂-), 3.92 (s, 3H, -OCH₃), 3.67-4.16 (m, 3H, -CH₂-O-CH-), 4.32-4.57 (m, 2H, -Ph-CH₂-O-), 7.26-7.52 (m, 1H, aromatic), 8.26-8.72 (m, 2H, aromatic), 8.96-9.14 (m, 1H, aromatic). IR (KBr) 3050 (=C-H), 2955, 2876 (C-H), 2226 (CN), 1736 (C=O), 1611, 1582 (C=C), 1522, 1346 (N=O) cm⁻¹. UV/Vis (chloroform) $\lambda_{max} = 345$ nm. Anal. Calcd for (C₁₅H₁₄N₂O₆)_n: C, 56.61; H, 4.43; N, 8.80. Found: C, 56.70; H, 4.49; N, 8.85. **8a**: ¹H NMR (acetone-d₆) δ 1.50-2.08 (m, 2H, -CH₂-), 3.67-4.09 (m, 3H, -CH₂-O-CH-), 4.35-4.58 (m, 2H, -Ph-O-CH₂-), 7.40-7.61 (m, 1H, aromatic), 8.14-8.38 (m, 2H, aromatic), 8.39-8.55 (m, 1H, aromatic). IR (KBr) 3040 (=C-H), 2934, 2878 (C-H), 2230 (CN), 1616, 1591 (C=C), 1533, 1356 (N=O) cm⁻¹. Anal. Calcd for (C₁₄H₁₁N₃O₄)_n: C, 58.95; H, 3.88; N, 14.73. Found: C, 58.90; H, 3.93; N, 14.79. **8b**: ¹H NMR (acetone-d₆) δ 1.45-2.08 (m, 2H, -CH₂-), 3.89 (s, 3H, -OCH₃), 3.60-4.06 (m, 3H, -CH₂-O-CH-), 4.32-4.56 (m, 2H, -Ph-CH₂-O-), 7.32-7.59 (m, 1H, aromatic), 8.12-8.40 (m, 2H, aromatic), 8.40-8.59 (m, 1H, aromatic). IR (KBr) 3040 (=C-H), 2934, 2876 (C-H), 2224 (CN), 1732 (C=O), 1603

(C=C), 1535, 1354 (N=O) cm^{-1} . Anal. Calcd for $(\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_6)_n$: C, 56.61; H, 4.43; N, 8.80. Found: C, 56.56; H, 4.48; N, 8.86. **9a**: ^1H NMR (acetone- d_6) δ 1.60-2.05 (m, 2H, $-\text{CH}_2-$), 3.6-4.20 (m, 3H, $-\text{CH}_2-\text{O}-\text{CH}-$), 4.25-4.45 (m, 2H, $-\text{Ph}-\text{O}-\text{CH}_2-$), 7.24-7.51 (m, 2H, aromatic), 8.18-8.35 (m, 1H, aromatic), 8.71-8.84 (m, 1H, aromatic). IR (KBr) 3042 ($=\text{C}-\text{H}$), 2873 (C-H), 2235 (CN), 1597, 1577 (C=C), 1514, 1327 (N=O) cm^{-1} . Anal. Calcd for $(\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_4)_n$: C, 58.95; H, 3.88; N, 14.73. Found: C, 58.88; H, 3.95; N, 14.78. **9b**: ^1H NMR (acetone- d_6) δ 1.46-2.08 (m, 2H, $-\text{CH}_2-$), 3.93 (s, 3H, $-\text{OCH}_3$), 3.60-4.10 (m, 3H, $-\text{CH}_2-\text{O}-\text{CH}-$), 4.24-4.46 (m, 2H, $-\text{Ph}-\text{CH}_2-\text{O}-$), 7.22-7.52 (m, 2H, aromatic), 8.17-8.38 (m, 1H, aromatic), 8.70-8.86 (m, 1H, aromatic). IR (KBr) 3042 ($=\text{C}-\text{H}$), 2936, 2879 (C-H), 2232 (CN), 1736 (C=O), 1603, 1577 (C=C), 1514, 1340 (N=O) cm^{-1} . Anal. Calcd for $(\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_6)_n$: C, 56.61; H, 4.43; N, 8.80. Found: C, 56.66; H, 4.49; N, 8.87.

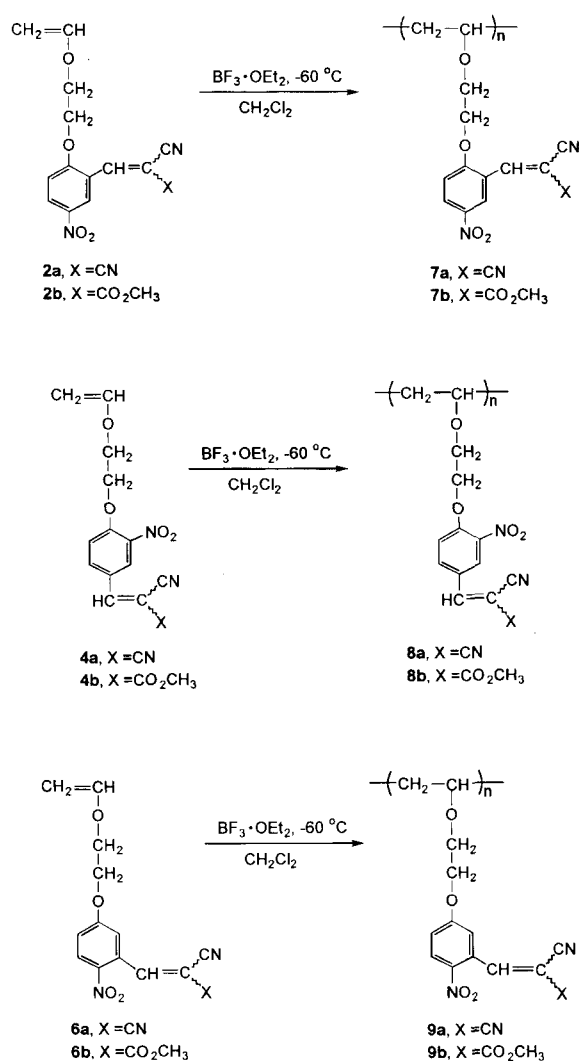
Results and Discussion

Syntheses of Monomers 2 and 4. 5-Nitro-2-(2'-vinylxyethoxy)benzaldehyde (**1**) 3-nitro-4-(2'-vinylxyethoxy)benzaldehyde (**3**) and 2-nitro-5-(2'-vinylxyethoxy)benzaldehyde (**5**) were prepared by the reaction of 2-iodoethyl vinyl ether with the corresponding 2-hydroxy-5-nitrobenzaldehyde, 4-hydroxy-3-nitrobenzaldehyde, and 5-hydroxy-2-nitrobenzaldehyde. 5-Nitro-2-(2'-vinylxyethoxy)benzylidenemalononitrile (**2a**), methyl 5-nitro-2-(2'-vinylxyethoxy)benzylidenecyanoacetate (**2b**), 3-nitro-4-(2'-vinylxyethoxy)benzylidenemalononitrile (**4a**), methyl 3-nitro-4-(2'-vinylxyethoxy)benzylidenecyanoacetate (**4b**), 2-nitro-5-(2'-vinylxyethoxy)benzylidenemalononitrile (**6a**), and methyl 2-nitro-5-(2'-vinylxyethoxy)benzylidenecyanoacetate (**6b**) were prepared by the condensations of **1**, **3**, and **5** with malononitrile or methyl cyanoacetate, respectively.²⁸ Compounds **2**, **4**, and **6** were obtained in high yield and were purified by recrystallization from isopropyl alcohol for polymerization. The chemical structure of the compounds was identified by ^1H NMR, and IR spectra, and elemental analysis. Monomers **2**, **4**, and **6** show olefinic protons at $\delta = 6.45-$



6.55 (q, 1H, vinylic) in their ^1H NMR spectra, respectively. The same monomers showed strong absorption bands at 2226-2237, 1717-1743, 1585-1628, and 1512-1529 cm^{-1} indicating the presence of nitrile, carbonyl, olefin, and nitro groups, respectively. Spectral data indicated that compounds **2b**, **4b**, and **6b** were a mixtures of the *Z*- and *E*-isomers. Compounds **2**, **4**, and **6** showed strong UV absorption bands near 350 nm by the chromophore oxynitrobenzylidenemalononitrile or oxynitrocyanocinnamate in the side chain measured in chloroform.

Cationic Polymerization of Monomers 2, 4, and 6. Isomeric vinyl ether monomers **2** and **4** were polymerized in solution at -60 °C with boron trifluoride etherate as cationic initiator to yield the polymers **5-6**. The polymerization results are summarized in Table 1. Isomeric monomers **2** and **4** were readily polymerized to yield the polymers **5** and **6** in high yield. Polymerizabilities of monomers **2** and **4** toward cationic initiators were lower than those of vinyl ethers without nitro group, probably due to the electron-withdrawing inductive effect by nitro group. The chemical structure of the polymers were confirmed by ^1H NMR, IR spectra, and elemental analyses. Spectral data indicated that the terminal



Scheme 4

benzylidene group did not participate in the vinyl polymerization.

Properties of Polymers. The resulting polymers **7-9** were soluble in common solvents such as acetone, chloroform, dichloromethane, DMF and DMSO, but was not soluble in methanol and diethyl ether. The inherent viscosities of polymers were in the range of 0.20-0.30 dL/g indicating moderate molecular weights. Polymers **7-9** showed strong uv absorption bands near 350 nm by the chromophore oxynitrobenzylidenemalononitrile or oxynitrobenzylidenecyanoacetate in the side chain as in the monomers. The thermal behavior of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and T_g . The results are summarized in Table 2. The polymers showed a double phase degradation pattern and did not decompose up to 300 °C in TGA thermograms. The T_g of the polymers measured by DSC thermograms were around 67-83 °C. These T_g values are higher than those for poly(ethyl vinyl ethers) without nitro group (60-70 °C),²⁹ probably due to the presence of polar nitro group. T_g values of benzylidenemalononitrile derivatives **7a**, **8a**, and **9a** were always

Table 1. Cationic Polymerization of **2**, **4**, and **6**^a Under Various Conditions

Monomer	Monomer/ Solvent ^b (mol/l L)	Initiator to Monomer (mol%)	Temp (°C)	Time (h)	Yield (%)	η_{inh}^c (dL/g)
2a	1.0	1.0	-60	14	86	0.26
2a	0.8	0.8	-30	15	84	0.28
2b	1.0	1.0	-60	16	78	0.25
2b	0.8	0.8	-30	15	75	0.24
4a	1.0	1.0	-60	15	71	0.20
4a	0.8	0.8	-30	15	68	0.25
4b	1.0	1.0	-60	19	75	0.24
4b	0.8	0.8	-30	15	72	0.23
6a	1.0	1.0	-60	12	85	0.28
6a	0.8	0.8	-30	12	84	0.26
6b	1.0	1.0	-60	15	77	0.25
6b	0.8	0.8	-30	15	75	0.25

^a**2a** = 5-Nitro-2-(2'-vinylxyethoxy)benzylidenemalononitrile; **2b** = Methyl 5-nitro-2-(2'-vinylxyethoxy)benzylidenecyanoacetate; **4a** = 3-Nitro-4-(2'-vinylxyethoxy)benzylidenemalononitrile; **4b** = Methyl 3-nitro-4-(2'-vinylxyethoxy)benzylidenecyanoacetate; **6a** = 2-Nitro-5-(2'-vinylxyethoxy)benzylidenemalononitrile; **6b** = Methyl 2-nitro-5-(2'-vinylxyethoxy)benzylidenecyanoacetate. ^bSolvent: Dichloro-methane. ^cInherent viscosity of polymer: Concentration of 0.5 g/dL in acetone at 25 °C.

Table 2. Thermal Properties of Polymer **7-9**

Polymer	T_g^a , °C	Degradation temp, °C ^b			Residue ^b at 700°C, %	r_{33}^c
		5%-loss	20%-loss	40%-loss		
7a	78	302	359	523	1.7	22
7b	75	318	368	456	14.0	19
8a	83	306	348	543	3.3	27
8b	72	309	353	452	6.7	23
9a	68	288	323	439	1.3	16
9b	67	283	367	529	2.0	15
P(o-VEBM) ^d	59	307	350	389	21.4	13
P(o-VEBCA) ^d	60	314	351	370	9.3	11
P(p-VEBM) ^d	70	254	316	365	29.5	16
P(p-VEBCA) ^d	61	330	367	394	27.4	14

^aDetermined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10 °C/min under nitrogen atmosphere. ^bDetermined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10 °C/min under nitrogen atmosphere. ^cEO coefficients were measured by simple reflection technique.²⁷ ^d**P(o-VEBM)** = Poly[o-(2-vinylxyethoxy)benzylidenemalononitrile]; **P(o-VEBCA)** = Poly [methyl o-(2-vinylxyethoxy)benzylidenecyanoacetate]; **P(p-VEBM)** = Poly [p-(2-vinylxyethoxy)benzylidenemalononitrile]; **P(p-VEBCA)** = Poly [methyl p-(2-vinylxyethoxy)benzylidenecyanoacetate].

higher than those of benzylidenecyanoacetate derivatives **7b**, **8b**, and **9b**. Among three constitutional isomers **7-9**, T_g values increased in order of **8** > **7** > **9** (Figure 1). The electrooptic coefficient (r_{33}) of the corona poled polymer films **7-9** measured by simple reflection technique²⁷ was in the range of 15-27 pm/V at 633 nm, which was improved by introducing of nitro group, as shown in Table 2.

Among three constitutional isomers **7-9**, the EO coefficients values increased in order of **8** > **7** > **9**. The EO coeffi-

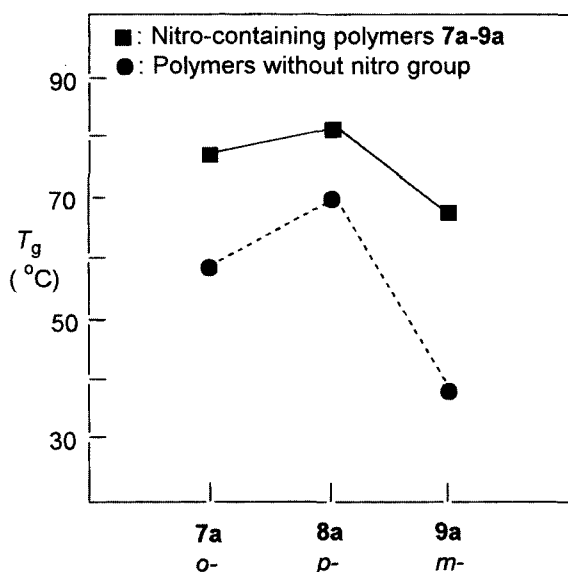


Figure 1. Glass transition temperatures (T_g) of constitutional isomers 7a-9a.

icients were higher when the electron-withdrawing 1,1-dicyanovinyl, 1-cyano-1-carbomethoxyvinyl, and nitro groups are attached in *ortho*- or *para*-position than in *meta*-position. These are reasonable in view of the fact that only when the electron-withdrawing vinyl and nitro groups are attached in *ortho*- or *para*-position, the polymer molecules have a resonance effect, thereby having a large dipole moment.

Conclusions

We prepared six isomeric vinyl ether monomers **2a-b**, **4a-b**, and **6a-b** having two highly dipolar electronic system. The vinyl ether compounds were polymerized by cationic initiator to give poly(ethyl vinyl ethers) **7-9** containing oxynitrobenzylidenemalononitrile or oxynitrobenzylidene-cyanoacetate, which is 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 67-83 °C in their DSC thermograms, which is rather low for electrooptic device applications. The electrooptic coefficient (r_{33}) of the corona poled polymer films **7-9** was in the range of 15-27 pm/V, which is acceptable for NLO 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 elsewhere.

Acknowledgement. This work was supported by GRANT No. 971-0301-006-2 from the Korea Science and Engineering Foundation.

References

- Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690.
- Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1984.
- Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Plenum Press: New York, 1987.
- Nonlinear Optical Properties of Organic Molecules and Crystals*, vol. 1, 2; Chemla, D. S., Zys, J., Eds.; Academic Press: New York, 1987.
- Nonlinear Optical Properties of Polymers*, Mater. Res. Soc. Symp. Proc. Vol. 109; Heeger, A. J., Orestein, J., Ulrich, D. R., Eds.; Mat. Res. Soc.: Pittsburg, 1988.
- Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Prasad, P. N., Williams, D. J., Eds.; John Wiley & Sons: New York, 1991.
- Nonlinear Optical Effects in Organic Polymers*; Lytel, R., Libscomb, G. F., Stiller, M., Thackara, J. I., Ticknor, A. J., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989.
- Stenger-Smith, J. D.; Fisher, J. W.; Henry, R. A.; Hoover, J. M.; Lindsay, G. A.; Hayden, L. M. *Makromol. Chem. Rapid Commun.* **1990**, *11*, 141.
- Fuso, F.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1991**, *24*, 1710.
- Wright, M. E.; Mullick, S.; Lackritz, H. S.; Liu, L.-Y. *Macromolecules* **1994**, *27*, 3009.
- Boogers, J. A. F.; Klaase, P. T. A.; Vlieger, J. J. D.; Tinne-mans, A. H. A. *Macromolecules* **1994**, *27*, 205.
- Lindsay, G. A.; Stenger-Smith, J. D.; Henry, R. A.; Hoover, J. M.; Nissan, R. A. *Macromolecules* **1992**, *25*, 6075.
- Xu, C.; Wu, B.; Dalton, L. R.; Ranon, P. M.; Shi, Y.; Steier, W. H. *Macromolecules* **1992**, *25*, 6716.
- Kondo, K.; Okuda, M.; Fugitani, T. *Macromolecules* **1993**, *26*, 7382.
- Shim, H.-K.; Hwang, D.-H. *Makromol. Chem.* **1993**, *194*, 1115.
- Jin, J.-I.; Lee, Y.-H.; Park, C.-K.; Man, B.-K. *Macromolecules* **1994**, *27*, 5239.
- Hwang, D.-H.; Lee, J.-I.; Shim, H.-K.; Hwang, W.-Y.; Kim, J.-J.; Jin, J.-I. *ibid* **1994**, *27*, 6000.
- Shim, H.-K.; Yoon, C.-B.; Lee, J.-I.; Hwang, D.-H. *Polym. Bull.* **1995**, *34*, 161.
- Robello, D. R. *J. Polym. Sci.: Part A: Polym. Chem.* **1990**, *28*, 1.
- Ni, Z.; Leslie, T. M.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1991**, *24*, 2100.
- S'heeren, G.; Persoons, A.; Rondou, P.; Wiersma, J.; Bey-len, M. V.; Samyn, C. *Makromol. Chem.* **1993**, *194*, 1733.
- McCulloch, I. A. *Macromolecules* **1994**, *27*, 1697.
- Baehr, C.; Glusen, B.; Wendorff, J. H.; Staring, E. G. *Makromol. Chem. Rapid Commun.* **1994**, *15*, 327.
- Lee, J.-Y. *Polym. Bull.* **1996**, *36*, 533.
- Vanermen, G.; Samyn, C.; S'heeren, G.; Persoons, A. *Makromol. Chem.* **1992**, *193*, 3057.
- Lee, J.-Y. *Polym. Bull.* **1994**, *33*, 635.
- Teng, C. C.; Mann, H. T. *Appl. Phys. Lett.* **1990**, *56*, 30.
- Corson, B. B.; Stoughton, R. W. *J. Am. Chem. Soc.* **1928**, *50*, 2825.
- Lee, J.-Y.; Kim, M.-Y.; Kim, J.-H. *Bull. Korean Chem. Soc.* **1998**, *19*, 155.