

Synthesis and Cationic Polymerization of Multifunctional Vinyl Ethers Containing Dipolar Electronic Systems

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2,4-Di-(2'-vinylloxyethoxy)benzylidenemalononitrile (**1a**), methyl 2,4-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**1b**), 3,4-di-(2'-vinylloxyethoxy)benzylidene malononitrile (**2a**), methyl 3,4-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**2b**), 2,5-di-(2'-vinylloxyethoxy)benzylidenemalononitrile (**3a**), methyl 2,5-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**3b**), 2,3-di-(2'-vinylloxyethoxy)benzylidenemalononitrile (**4a**), and methyl 2,3-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**4b**) were prepared by the condensation of 2,4-di-(2'-vinylloxyethoxy)benzaldehyde, 3,4-di-(2'-vinylloxyethoxy)benzaldehyde, 2,5-di-(2'-vinylloxyethoxy)benzaldehyde, and 2,3-di-(2'-vinylloxyethoxy)benzaldehyde with malononitrile or methyl cyanoacetate, respectively. Trifunctional divinyl ether monomers **1-4** were polymerized readily with boron trifluoride etherate as a cationic initiator to give optically transparent swelling poly(vinyl ethers) **5-8** having oxybenzylidenemalononitrile and oxycyanocinnamate, which is presumably effective chromophore for second-order nonlinear optical applications. Polymers **5-8** were not soluble in common organic solvents such as acetone and DMSO due to crosslinking. Polymers **5-8** showed a thermal stability up to 300 °C in TGA thermograms, which is acceptable for electrooptic device applications.

Introduction

Functional materials exhibiting 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.¹⁻² It is well known that organic and polymeric materials with highly dipolar electronic systems exhibit NLO properties.³ The organic materials seem to be superior to the inorganic ones because of their higher nonlinear optical activity and faster response time.⁴⁻⁶ Among organic materials, 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.⁷ Potential second-order NLO polymers must contain a highly polarizable dipolar electronic structure and these polymers have to be mechanically very strong with a high T_g . There are tremendous challenges in designing polymers of large NLO effects. Polyesters,⁸⁻¹² polyurethanes,¹³ polyamides,¹⁴⁻¹⁵ and poly(phenyleneethylenes)¹⁶ containing the chromophoric main chain were prepared. Various polymers with the NLO-chromophores in the side chain such as poly(meth)acrylates¹⁷⁻²⁵ and polystyrene²⁶ were also reported. Recently we have explored utilizing poly(vinyl ethers) as a new optical polymer system for second-order NLO applications. We prepared poly(alkyl vinyl ethers)²⁷⁻³² containing various NLO-chromophore in the side chain. These poly(vinyl ethers) exhibited a thermal stability up to 300 °C with a T_g of 60-90 °C, which is rather low for electrooptic applications. However, examples of crosslinked poly(vinyl ethers) containing a chromophoric side chain prepared directly by polymerization of monomeric vinyl ethers

are not shown in the literature. Thus, it is of interest to prepare crosslinked poly(vinyl ethers) having a NLO-phore in the side chain. To explore these problems, we have prepared a series of trifunctional divinyl ether compounds **1-4** containing oxybenzylidenemalononitrile and oxycyanocinnamate in the side chain, which is presumably effective chromophore for second-order nonlinear optical applications. These monomeric divinyl ethers were polymerized readily by cationic initiators to yield crosslinked poly(vinyl ethers) **5-8** having NLO-phore in the side chain with high yields. The present report describes the synthesis and their cationic polymerizations of 2,4-di-(2'-vinylloxyethoxy)benzylidenemalononitrile (**1a**), methyl 2,4-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**1b**), 3,4-di-(2'-vinylloxyethoxy)benzylidenemalononitrile (**2a**), methyl 3,4-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**2b**), 2,5-di-(2'-vinylloxyethoxy)benzylidenemalononitrile (**3a**), methyl 2,5-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**3b**), 2,3-di-(2'-vinylloxyethoxy)benzylidenemalononitrile (**4a**), and methyl 2,3-di-(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 under vacuum. Sodium iodide was dried for 4h at 100 °C under vacuum. 2,4-Dihydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, 2,5-dihydroxybenzaldehyde, and 2,3-dihydroxybenzaldehyde were used as received. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. *n*-Butanol was dried with anhydrous magnesium sulfate and distilled under nitrogen. *N,N*-Dimethylforma-

mide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure. Piperidine was dried with calcium hydride and fractionally distilled. 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.³³ 2,4-Di-(2'-vinyloxyethoxy)benzaldehyde, 3,4-di-(2'-vinyloxyethoxy)benzaldehyde, 2,5-di-(2'-vinyloxyethoxy)benzaldehyde, and 2,3-di-(2'-vinyloxyethoxy)benzaldehyde were prepared by the reaction of 2-iodoethyl vinyl ether with the corresponding dihydroxybenzaldehydes, respectively.

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

2,4-Di-(2'-vinyloxyethoxy)benzylidenemalononitrile (1a). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,4-di-(2'-vinyloxyethoxy)benzaldehyde (8.35 g, 30 mmol) and malononitrile (2.18 g, 33 mmol) in 170 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. 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 9.01 g (92% yield) of **1a**. Mp=80-81 °C. ¹H NMR (CDCl₃) δ 4.02-4.40 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.45-6.71 (m, 4H, 2 =CH-O-, aromatic), 8.17-8.34 (t, 2H, aromatic). IR (KBr) 3117, 3037 (w, =C-H), 2943, 2887 (m, C-H), 2222 (s, CN), 1611 (s, C=C), 1566 (vs, C=C) cm⁻¹. UV/Vis (chloroform) λ_{max}=369 nm, ε=26960. Anal. Calcd for C₁₈H₁₈N₂O₄: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.38; H, 5.65; N, 8.46.

Methyl 2,4-di-(2'-vinyloxyethoxy)benzylidenecyanoacetate (1b). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,4-di-(2'-vinyloxyethoxy)benzaldehyde (8.35 g, 30 mmol) and methyl cyanoacetate (3.27 g, 33 mmol) in 200 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 3 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. 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 9.49 g (88% yield) of **1b**. Mp=96-97 °C. ¹H NMR (CDCl₃) δ 3.89 (s, 3H, -CO₂CH₃), 4.02-4.34 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.46-6.65 (m, 4H, 2 =CH-O-, aromatic), 8.36-8.428 (d, 1H, aromatic), 8.70 (s, 1H, aromatic). IR (KBr) 3044 (w, =C-H),

2954, 2943 (m, C-H), 2222 (s, CN), 1705 (vs, C=O), 1622, 1611, 1594, 1583 (vs, C=C) cm⁻¹. UV/Vis (chloroform) λ_{max}=363 nm, ε=26410. Anal. Calcd for C₁₉H₂₁N₂O₆: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.62; H, 5.82; N, 3.85.

3,4-Di-(2'-vinyloxyethoxy)benzylidenemalononitrile (2a). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 3,4-di-(2'-vinyloxyethoxy)benzaldehyde (5.57 g, 20 mmol) and malononitrile (1.45 g, 22 mmol) in 140 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. The product was filtered and washed successively with cold *n*-butanol (60 mL), water (20 mL), and cold *n*-butanol (15 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 5.55 g (85% yield) of **2a**. Mp=64-65 °C. ¹H NMR (CDCl₃) δ 4.02-4.38 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.47-6.58 (m, 2H, 2 =CH-O-), 6.95-7.02 (d, 1H, aromatic), 7.38-7.44 (d, 1H, aromatic), 7.60-7.69 (d, 2H, aromatic). IR (KBr) 3033 (w, =C-H), 2943, 2876 (m, C-H), 2233 (s, CN), 1637, 1614 (s, C=C), 1583, 1566, 1510 (vs, C=C) cm⁻¹. UV/Vis (chloroform) λ_{max}=369 nm, ε=25020. Anal. Calcd for C₁₈H₁₈N₂O₄: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.36; H, 5.66; N, 8.67.

Methyl 3,4-di-(2'-vinyloxyethoxy)benzylidenecyanoacetate (2b). Piperidine (0.085 g, 1.0 mmol) was added to a solution of 3,4-di-(2'-vinyloxyethoxy)benzaldehyde (5.57 g, 20 mmol) and methyl cyanoacetate (2.18 g, 22 mmol) in 140 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. The product was filtered and washed successively with cold *n*-butanol (60 mL), water (20 mL), and cold *n*-butanol (15 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 6.18 g (86% yield) of **2b**. Mp=86-87 °C. ¹H NMR (CDCl₃) δ 3.92 (s, 3H, -CO₂CH₃), 4.02-4.38 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.48-6.60 (m, 2H, 2 =CH-O-), 6.95-7.02 (d, 1H, aromatic), 7.47-7.54 (m, 1H, aromatic), 7.75-7.79 (m, 1H, aromatic), 8.11-8.16 (m, 1H, aromatic). IR (KBr) 3113 (w, =C-H), 2954, 2934, 2876 (m, C-H), 2222 (s, CN), 1720 (vs, C=O), 1638 (s, C=C), 1591, 1519 (vs, C=C) cm⁻¹. UV/Vis (chloroform) λ_{max}=359 nm, ε=24550. Anal. Calcd for C₁₉H₂₁N₂O₆: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.62; H, 5.84; N, 3.82.

2,5-Di-(2'-vinyloxyethoxy)benzylidenemalononitrile (3a). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,5-di-(2'-vinyloxyethoxy)benzaldehyde (9.74 g, 35 mmol) and malononitrile (2.58 g, 39 mmol) in 150 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. 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 9.37 g (82% yield) of **3a**. Mp=64-65 °C. ¹H NMR (CDCl₃) δ 3.95-4.34 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.47-6.58 (m, 2H, 2 =CH-O-), 6.92-6.98 (d, 1H, aromatic), 7.17-7.23 (m, 1H, aromatic), 7.74 (s, 1H, aromatic), 8.28 (s, 1H, aromatic). IR (KBr) 3039 (w, =C-H), 2938, 2867 (m, C-H), 2222 (s, CN), 1623 (s,

C=C), 1583 (vs. C=C) cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.36; H, 5.64; N, 8.48.

Methyl 2,5-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (3b). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,5-di-(2'-vinylloxyethoxy)benzaldehyde (8.35 g, 30 mmol) and methyl cyanoacetate (3.27 g, 33 mmol) in 170 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. 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 9.27 g (86% yield) of **3b**. Mp=65-66 °C. ^1H NMR (CDCl_3) δ 3.88 (s, 3H, $-\text{CO}_2\text{CH}_3$), 4.01-4.33 (m, 12H, 2 $\text{CH}_2=$, 2 $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$), 6.46-6.58 (m, 2H, 2 $=\text{CH}-\text{O}-$), 6.93-6.98 (d, 1H, aromatic), 7.12-7.18 (m, 1H, aromatic), 7.85 (s, 1H, aromatic), 8.73 (s, 1H, aromatic). IR (KBr) 3043 (w, $=\text{C}-\text{H}$), 2930, 2862 (m, C-H), 2220 (m, CN), 1735 (vs. C=O), 1625, 1617, 1594 (vs. C=C) cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.61; H, 5.84; N, 3.96.

2,3-Di-(2'-vinylloxyethoxy)benzylidenemalononitrile (4a). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,3-di-(2'-vinylloxyethoxy)benzaldehyde (9.74 g, 35 mmol) and malononitrile (2.58 g, 39 mmol) in 150 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. 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 8.00 g (70% yield) of **4a**. Mp=61-62 °C. ^1H NMR (CDCl_3) δ 3.87-4.42 (m, 12H, 2 $\text{CH}_2=$, 2 $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$), 6.44-6.57 (m, 2H, 2 $=\text{CH}-\text{O}-$), 7.15-7.21 (m, 2H, aromatic), 7.78-7.89 (m, 1H, aromatic), 8.46 (s, 1H, aromatic). IR (KBr) 3038 (w, $=\text{C}-\text{H}$), 2937, 2881 (m, C-H), 2225 (s, CN), 1618 (vs. C=C), 1571 (s, C=C) cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.36; H, 5.64; N, 8.48.

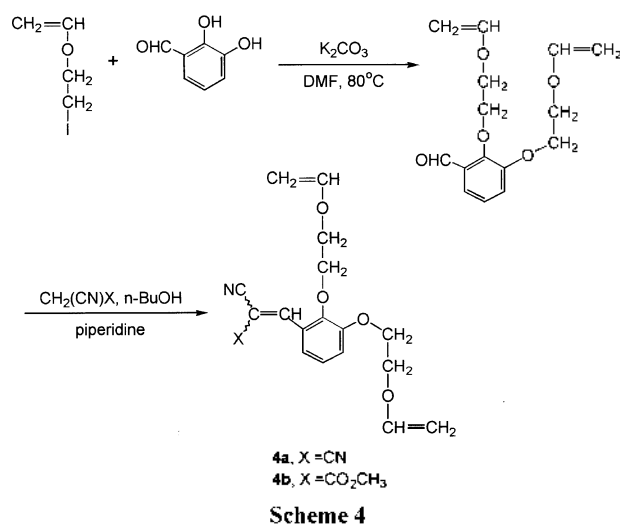
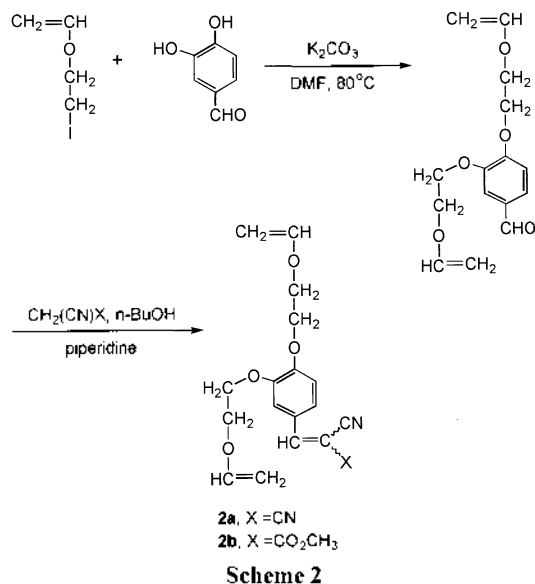
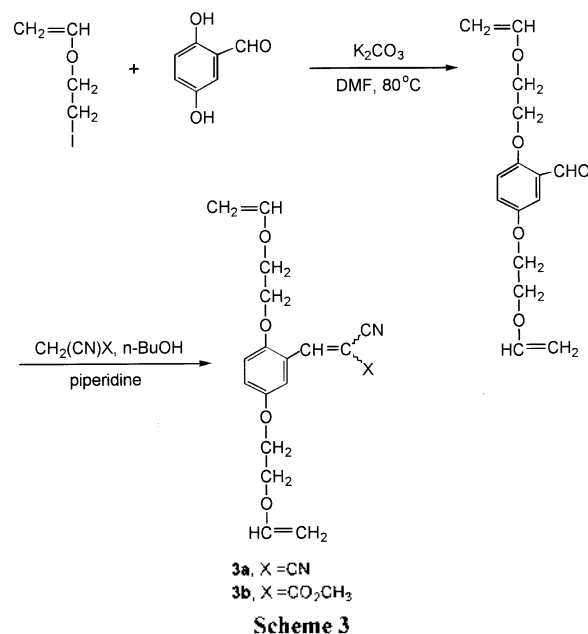
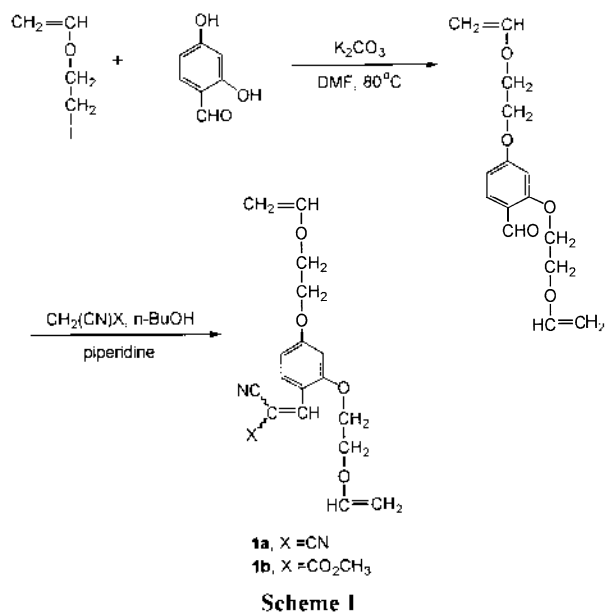
Methyl 2,3-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (4b). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,3-di-(2'-vinylloxyethoxy)benzaldehyde (8.35 g, 30 mmol) and methyl cyanoacetate (3.27 g, 33 mmol) in 170 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. 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 8.19 g (77% yield) of **4b**. Mp=52-54 °C. ^1H NMR (CDCl_3) δ 3.88 (s, 3H, $-\text{CO}_2\text{CH}_3$), 4.01-4.38 (m, 12H, 2 $\text{CH}_2=$, 2 $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$), 6.47-6.57 (m, 2H, 2 $=\text{CH}-\text{O}-$), 7.10-7.19 (m, 2H, aromatic), 7.89-7.97 (m, 1H, aromatic), 8.84 (s, 1H, aromatic). IR (KBr) 3041 (w, $=\text{C}-\text{H}$), 2934, 2872 (m, C-H), 2223 (m, CN), 1735 (vs. C=O), 1624, 1615, 1591 (vs. C=C) cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.61; H, 5.84; N, 3.96.

Cationic Polymerization of Monomers 1-4. A representative cationic polymerization procedure (the case of **1a**) was

as follows: A solution of **1a** (0.98 g, 3.0 mmol) in dichloromethane (4.0 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 by immersion cooler under nitrogen, and 0.0034 mL (0.03 mmol) of boron trifluoride etherate was added to the solution. After 2 h the ampule was taken out and the polymerization mixture was poured into 500 mL of methanol and stirred. The precipitated polymer was collected and dried under vacuum to give 0.96 g (98% yield) of polymer **5a**. IR (KBr) 2962, 2940 (m, C-H), 2223 (s, CN), 1617, 1565 (vs. C=C), 1498 (s, C=C) cm^{-1} . Anal. Calcd for $(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4)_n$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.35; H, 5.65; N, 8.51. **5b**: IR (KBr) 2946, 2882 (m, C-H), 2222 (m, CN), 1722 (s, C=O), 1612, 1572, 1560, 1510 (vs. C=C) cm^{-1} . Anal. Calcd for $(\text{C}_{19}\text{H}_{21}\text{NO}_6)_n$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.61; H, 5.81; N, 3.83. **6a**: IR (KBr) 2932, 2883 (m, C-H), 2224 (s, CN), 1583, 1563 (s, C=C), 1510 (vs. C=C) cm^{-1} . Anal. Calcd for $(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4)_n$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.36; H, 5.66; N, 8.64. **6b**: IR (KBr) 2934, 2875 (m, C-H), 2222 (m, CN), 1722 (vs. C=O), 1581, 1512 (vs. C=C) cm^{-1} . Anal. Calcd for $(\text{C}_{19}\text{H}_{21}\text{NO}_6)_n$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.62; H, 5.84; N, 3.97. **7a**: IR (KBr) 2924, 2863 (m, C-H), 2218 (s, CN), 1582, (s, C=C), 1496 (vs. C=C) cm^{-1} . Anal. Calcd for $(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4)_n$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.35; H, 5.63; N, 8.66. **7b**: IR (KBr) 2935, 2868 (m, C-H), 2218 (m, CN), 1730 (vs. C=O), 1595 (s, C=C), 1498 (vs. C=C) cm^{-1} . Anal. Calcd for $(\text{C}_{19}\text{H}_{21}\text{NO}_6)_n$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.60; H, 5.82; N, 3.96. **8a**: IR (KBr) 2924, 2870 (m, C-H), 2224 (m, CN), 1572, (s, C=C) cm^{-1} . Anal. Calcd for $(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4)_n$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.35; H, 5.63; N, 8.66. **8b**: IR (KBr) 2934, 2872 (m, C-H), 2220 (w, CN), 1726 (vs. C=O), 1604 (m, C=C), 1572 (vs. C=C) cm^{-1} . Anal. Calcd for $(\text{C}_{19}\text{H}_{21}\text{NO}_6)_n$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.60; H, 5.82; N, 3.96.

Results and Discussion

Synthesis of trifunctional monomers 1-4. 2,4-Di-(2'-vinylloxyethoxy)benzaldehyde, 3,4-di-(2'-vinylloxyethoxy)benzaldehyde, 2,5-di-(2'-vinylloxyethoxy)benzaldehyde, and 2,3-di-(2'-vinylloxyethoxy)benzaldehyde were prepared from 2-iodoethyl vinyl ether and 2,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, 2,5-dihydroxybenzaldehyde, and 2,3-dihydroxybenzaldehyde, respectively, and were reacted with malononitrile or methyl cyanoacetate to give trifunctional monomers 2,4-di-(2'-vinylloxyethoxy)benzylidenemalononitrile (**1a**), methyl 2,4-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**1b**), 3,4-di-(2'-vinylloxyethoxy)benzylidenemalononitrile (**2a**), methyl 3,4-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**2b**), 2,5-di-(2'-vinylloxyethoxy)benzylidenemalononitrile (**3a**), methyl 2,5-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**3b**), 2,3-di-(2'-vinylloxyethoxy)benzylidenemalononitrile (**4a**), and methyl 2,3-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**4b**). Compounds **1-4** were obtain-



ed in high yield and were purified by recrystallization in *n*-butanol for polymerization. The chemical structure of the compounds was identified by proton-NMR (Figure 1), IR spectra, and elemental analysis. All the analytical data confirmed the expected chemical structure. Compounds **1-4** showed strong uv absorption bands near 360-370 nm by the chromophore oxybenzylidenemalononitrile or oxycyanocinnamate in the side chain measured in chloroform.

Cationic Polymerization of Monomers 1-4. Isomeric divinyl ether compounds **1-4** were polymerized in solution at -60 °C with boron trifluoride etherate as cationic initiator to obtain the polymers **5-8**. The polymerization results are summarized in Table 1. Monomers **1-4** were quite reactive toward cationic initiators and polymerized readily with high yields. 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

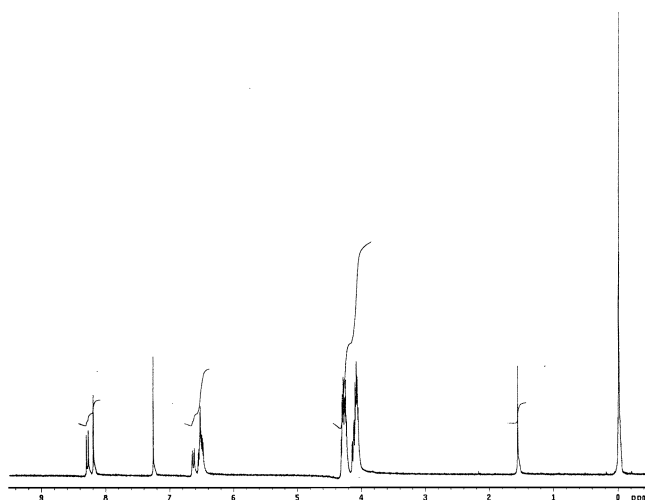
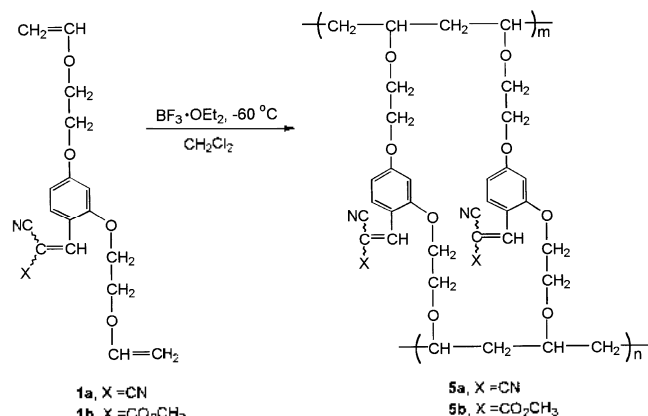
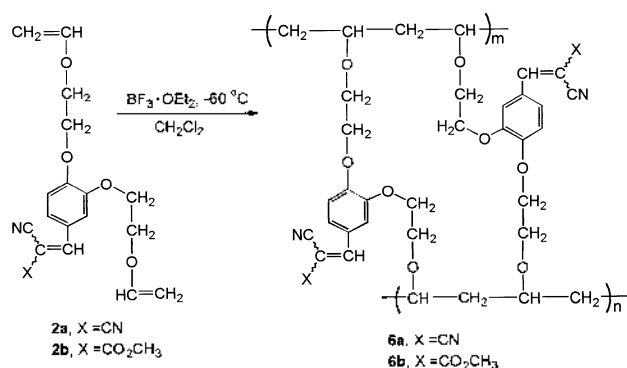


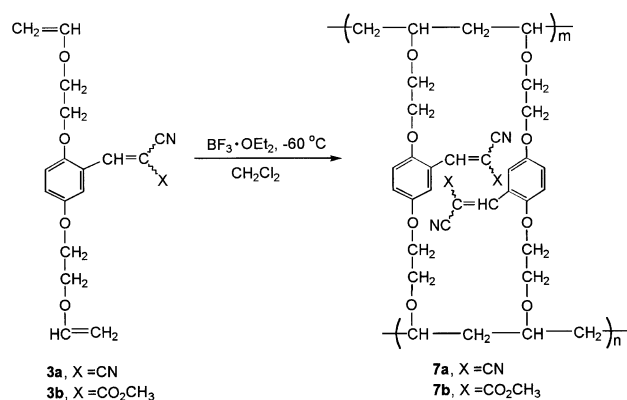
Figure 1. ¹H NMR spectrum of 2,4-Di-(2'-vinylxyethoxy)benzylidenemalononitrile (**1a**) taken in CDCl₃ at room temperature.



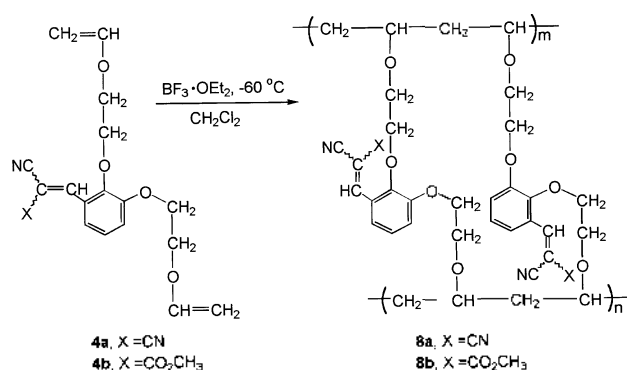
Scheme 5



Scheme 6



Scheme 7



Scheme 8

Table 1. Cationic polymerizations of 1-4^a by BF₃ in CH₂Cl₂ at 60 °C

Monomer	Monomer/Solvent (mol/l l.)	Initiator to Monomer (mol%)	Time (h)	Yield (%)
1a	1.00	0.6	1	95
1a	0.75	1.0	2	98
1b	1.00	0.6	1	97
1b	0.75	0.8	2	98
2a	1.00	0.8	2	92
2a	0.75	1.0	2	94
2b	1.00	0.8	1	91
2b	0.75	1.0	1	92
3a	1.00	0.6	2	97
3a	0.75	0.8	2	99
3b	1.00	0.6	1	97
3b	0.75	0.8	1	98
4a	1.00	0.8	2	93
4a	0.75	1.0	2	95
4b	1.00	0.8	2	90
4b	0.75	1.0	2	93

^a**1a** = 2,4-Di-(2'-vinyl-oxyethoxy)benzylidenemalononitrile; **1b** = Methyl 2,4-di-(2'-vinyl-oxyethoxy)benzylidencyanoacetate; **2a** = 3,4-Di-(2'-vinyl-oxyethoxy)benzylidenemalononitrile; **2b** = Methyl 3,4-di-(2'-vinyl-oxyethoxy)benzylidencyanoacetate; **3a** = 2,5-Di-(2'-vinyl-oxyethoxy)benzylidenemalononitrile; **3b** = Methyl 2,5-di-(2'-vinyl-oxyethoxy)benzylidencyanoacetate; **4a** = 2,3-Di-(2'-vinyl-oxyethoxy)benzylidenemalononitrile; **4b** = Methyl 2,3-di-(2'-vinyl-oxyethoxy)benzylidencyanoacetate.

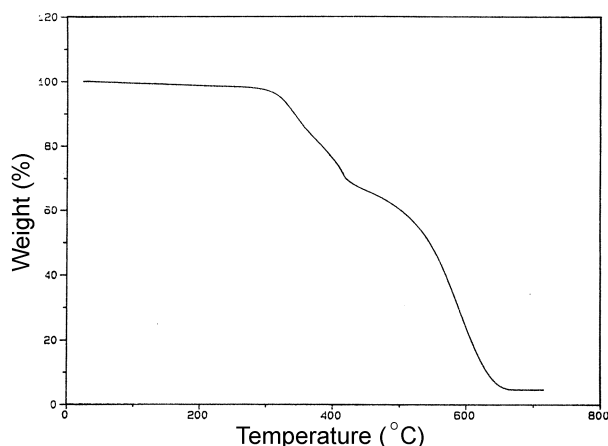
the polymers. The two vinyl ether group participated in the vinyl polymerization, and cationic polymerization of 1-4 led only to optically transparent swelling poly(vinyl ethers) 5-8 containing oxybenzylidenemalononitrile and oxycyanocinnamate in the side chain, which is presumably effective chromophore for second-order nonlinear optical applications. The trisubstituted electron-poor terminal olefin did not participate in the cationic vinyl polymerization. Polymers 5-8 were not soluble in any organic solvents due to cross-linking. Thus, we have found a unique polymerization system that leads to cross-linked poly(alkyl vinyl ethers) having NLO-phore in the side chain by cationic initiators. These polymerization systems can be applied to the synthesis of new crosslinked NLO polymers. Previously we have prepared bifunctional vinyl ethers containing p-oxybenzylidenemalononitrile and p-oxycyanocinnamate and polymerized them with cationic initiators to give poly(vinyl ethers).²⁷ Cationic polymerizabilities of trifunctional divinyl ether compounds 1-4 are higher than those of p-substituted bifunctional vinyl ether compounds.

Properties of Polymers. The polymers 5-8 were not soluble in common solvents such as methanol, ethanol, diethyl ether, benzene, toluene, acetone, methyl ethyl ketone, cyclohexanone, dichloromethane, chloroform, DMF, and DMSO due to crosslinking. Polymers 5-8 isolated from methanol were amorphous materials. 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

Table 2. Thermal Properties of Polymer 5-8

Polymer	T_g^a , °C	Degradation temp. °C ^b			Residuc ^b at 700 °C, %
		5%-loss	20%-loss	40%-loss	
5a	-	329	389	497	1.3
5b	-	332	367	415	4.3
6a	-	300	343	385	2.3
6b	-	299	342	364	2.0
7a	-	327	386	488	1.7
7b	-	328	367	414	2.3
8a	-	299	366	444	4.0
8b	-	291	357	376	2.0

^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.

**Figure 2.** TGA thermogram of cross-linked polymer 5a (10 °C/min, N₂).

temperature (T_g). The results are summarized in Table 2. Polymers 5-8 showed a good thermal stability and did not decompose below 300 °C as shown in Table 2. The polymers show a double phase degradation pattern in their TGA thermograms (Figure 2), probably due to cross-linking. Cross-linked polymers 5-8 showed broad endothermic bands around 100-200 °C without any characteristic T_g peaks in DSC thermograms.

Conclusions

We prepared eight isomeric divinyl ether compounds 1-4 having highly polarizable π -conjugated dipolar electronic system. The divinyl ether compounds were polymerized by cationic initiator to obtain crosslinked poly(vinyl ethers) 5-8 containing oxybenzylidenemalononitrile or oxycyanocinnamate, which was potential effective NLO-chromophore for second-order nonlinear optical applications in the side chain. Monomers 1-4 were quite reactive toward cationic initiators and polymerized readily in high yields within 3 hr. Cationic polymerizabilities of trifunctional divinyl ether compounds were higher than those of *p*-disubstituted bifunctional derivatives. Polymers 5-8 were not soluble in any

organic solvents due to cross-linking. The polymers showed a thermal stability up to 300 °C in TGA thermograms, which is acceptable for electrooptic device applications. We are now in the process of extending the polymerization system to the synthesis of other type of crosslinked NLO polymers, and the results will be reported at a later date.

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