

Synthesis and Free Radical Polymerization of Vinyl Ethers Containing Two Electron Acceptors

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Alkyl vinyl ethers do not radically homopolymerize, but copolymerize readily with electron-deficient olefins such as vinylidene cyanide,¹ 2-vinylcyclopropane-1,1-dicarbonitrile,² alkyl cyanoacrylate,³⁻⁵ and alkyl vinyl ketone⁶ by radical initiators. These facile reactions proceed through an electron donor-acceptor (EDA) complex, which generates zwitterion or diradical tetramethylenes as initiating species.⁷ 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 initiators.⁸⁻¹⁰ Recently we have explored utilizing free radical polymerization of vinyl ethers for obtaining crosslinked poly(vinyl ethers). Bifunctional monomers containing both electron-rich alkyl vinyl ether group and electron-deficient olefin moieties such as *p*-(2-vinyloxyethoxy)benzylidenemalononitrile polymerize well by radical initiators to yield highly crosslinked poly(vinyl ethers).¹¹ Trifunctional compounds having two electron-rich vinyl ether groups and an electron-poor olefin group also polymerize readily with radical initiators to give crosslinked polymers.¹² The question remains as to whether certain trifunctional compounds having one electron-rich alkyl vinyl ether group and two electron-deficient substituents can be polymerized by radical initiation. To explore these problems, we have prepared a series of trifunctional vinyl ethers containing benzylidenemalononitrile or benzylidenecyanoacetate and nitro groups. In this work we prepared four constitutional isomeric compounds 5-nitro-2-(2'-vinyloxyethoxy)benzylidenemalononitrile (**2a**), methyl 5-nitro-2-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**2b**), 3-nitro-4-(2'-vinyloxyethoxy)benzylidenemalononitrile (**4a**), and methyl 3-nitro-4-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**4b**), and investigated their radical polymerization behaviors. Polymerizabilities toward free radical initiators and properties of the resulting polymers are compared with those of bifunctional derivatives without nitro group.

Experimental Section

Materials. The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2-Hydroxy-5-nitrobenzaldehyde and 4-hydroxy-3-nitrobenzaldehyde were used as received. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure. γ -Butyrolactone was

dried with anhydrous magnesium sulfate and fractionally distilled under nitrogen. 2-Iodoethyl vinyl ether was prepared according to the procedure previously described.¹¹

Measurements. IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ¹H NMR spectra were obtained on a Varian 300 MHz NMR 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 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.

5-Nitro-2-(2'-vinyloxyethoxy)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 refluxed 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 product **1**. Mp: 37-38 °C. ¹H NMR (CDCl₃, δ , ppm) 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'-vinyloxyethoxy)benzylidenemalononitrile (2a). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 5-nitro-2-(2'-vinyloxyethoxy)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 (-15 °C) 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 , ppm) 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.

Anal. Calcd for $C_{14}H_{11}N_3O_4$: C, 58.95; H, 3.88; N, 14.73. Found: C, 58.87; H, 3.82; N, 14.68.

Methyl 5-nitro-2-(2'-vinylxyethoxy)benzylidenecyanoacetate (2b). Piperidine (0.17 g, 2.0 mmol) was added to a solution of 5-nitro-2-(2'-vinylxyethoxy)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- d_6 , δ , ppm) 3.95 (s, 3H, CO_2CH_3), 4.10-4.45 (m, 6H, CH_2 -, $-O-CH_2-CH_2-O-$), 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} . Anal. Calcd for $C_{15}H_{14}N_2O_6$: C, 56.61; H, 4.43; N, 8.80. Found: C, 56.53; H, 4.48; N, 8.87.

3-Nitro-4-(2'-vinylxyethoxy)benzaldehyde (3). Compound **3** was prepared from 4-hydroxy-3-nitrobenzaldehyde and 2-iodoethyl vinyl ether according to the procedure previously described in compound **1**. Mp: 75-76 °C. 1H NMR ($CDCl_3$, δ , ppm) 4.08-4.47 (m, 6H, CH_2 -, $-O-CH_2-CH_2-O-$), 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'-vinylxyethoxy)benzylidenemalononitrile (4a). Compound **4a** was prepared from 3-nitro-4-(2'-vinylxyethoxy)benzaldehyde (**3**) and malononitrile according to the procedure previously described in compound **2a**. Mp: 100-102 °C. 1H NMR ($CDCl_3$, δ , ppm) 4.09-4.49 (m, 6H, CH_2 -, $-O-CH_2-CH_2-O-$), 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 $C_{14}H_{11}N_3O_4$: 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). Compound **4b** was prepared from 3-nitro-4-(2'-vinylxyethoxy)benzaldehyde (**3**) and methyl cyanoacetate according to the procedure previously described in compound **2b**. Mp: 117-118 °C. 1H NMR (acetone- d_6 , δ , ppm) 3.94 (s, 3H, CO_2CH_3), 4.08-4.47 (m, 6H, CH_2 -, $-O-CH_2-CH_2-O-$), 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 $C_{15}H_{14}N_2O_6$: C, 56.61; H, 4.43; N, 8.80. Found: C, 56.56; H, 4.49; N, 8.86.

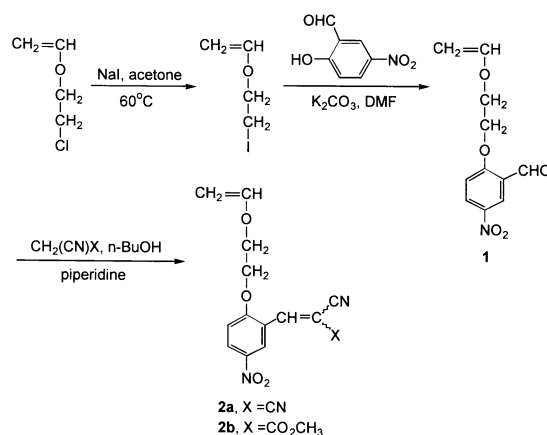
Radical polymerizations of monomers 2 and 4. A representative radical polymerization procedure (the case of **2a**) was as follows: In a polymerization tube were placed 0.86 g (3.0 mmol) of **2a**, 4.4 mg (0.03 mmol) of DTBP, and 3.0 mL of γ -butyrolactone under nitrogen. The resulting solution

was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 120 °C. After 24 h the polymerization tube was opened and the swelling polymer was poured into 300 mL of methanol. The precipitated polymer was collected and dried under vacuum to give 0.56 g (65% yield) of polymer **5a**. IR (KBr) 3025 ($-C-H$), 2914, 2850 (C-H), 2230 (CN), 1622, 1590 (C=C), 1520, 1338 (N-O) cm^{-1} . Anal. Calcd for $(C_{14}H_{11}N_3O_4)_n$: C, 58.95; H, 3.88; N, 14.73. Found: C, 58.87; H, 3.82; N, 14.78. **5b**: IR (KBr) 3124 ($-C-H$), 2941, 2855 (C-H), 2230 (CN), 1725 (C=O), 1611, 1597 (C=C), 1510, 1339 (N-O) cm^{-1} . Anal. Calcd for $(C_{15}H_{14}N_2O_6)_n$: C, 56.61; H, 4.43; N, 8.80. Found: C, 56.56; H, 4.45; N, 8.85. **6a**: IR (KBr) 3025 ($-C-H$), 2946, 2836 (C-H), 2236 (CN), 1614 (C=C), 1533 (N-O) cm^{-1} . Anal. Calcd for $(C_{14}H_{11}N_3O_4)_n$: C, 58.95; H, 3.88; N, 14.73. Found: C, 58.90; H, 3.92; N, 14.80. **6b**: IR (KBr) 2960, 2835 (C-H), 2231 (CN), 1728 (C=O), 1614 (C=C), 1530 (N-O) cm^{-1} . Anal. Calcd for $(C_{15}H_{14}N_2O_6)_n$: C, 56.61; H, 4.43; N, 8.80. Found: C, 56.68; H, 4.48; N, 8.87.

Results and Discussion

Synthesis of trifunctional monomers 2 and 4. 5-Nitro-2-(2'-vinylxyethoxy)benzaldehyde (**1**) and 3-nitro-4-(2'-vinylxyethoxy)benzaldehyde (**3**) were prepared by reaction of 2-iodoethyl vinyl ether with the corresponding 2-hydroxy-5-nitrobenzaldehyde and 4-hydroxy-3-nitrobenzaldehyde, respectively. 5-Nitro-2-(2'-vinylxyethoxy)benzylidenemalononitrile (**2a**), methyl 5-nitro-2-(2'-vinylxyethoxy)benzylidenecyanoacetate (**2b**), 3-nitro-4-(2'-vinylxyethoxy)benzylidenemalononitrile (**4a**), and methyl 3-nitro-4-(2'-vinylxyethoxy)benzylidenecyanoacetate (**4b**) were prepared by the condensations of **1** and **3** with malononitrile or methyl cyanoacetate, respectively.¹³ Compounds **2** and **4** were obtained in high yield and were purified by recrystallization in *isopropyl* alcohol. The chemical structure of the compounds was identified by 1H NMR, IR spectra, and elemental analysis. All the analytical data were matched well with the expected chemical structure.

Free radical polymerizations of monomers 2 and 4. Trifunctional monomers **2a-b** and **4a-b** were polymerized in γ -butyrolactone solution at 120 °C with DTBP as radical initi-



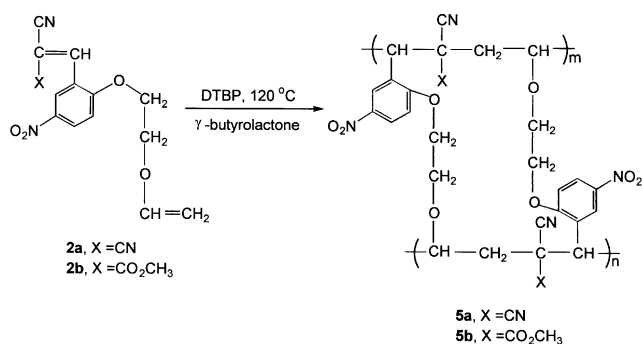
Scheme 1

ator to give polymers **5-6**. The polymerization results are summarized in Table 1. Monomers **2** and **4** were not reactive toward AIBN as a free radical initiator. 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. The trisubstituted electron-deficient benzylidenyl group participated in the vinyl polymerization, and radical polymerization of **2** and **4** led to polymers **5-6**. Polymers **5-6** were not soluble in common organic solvents such as chloroform and benzene due to crosslinking. Therefore, we have found another poly-

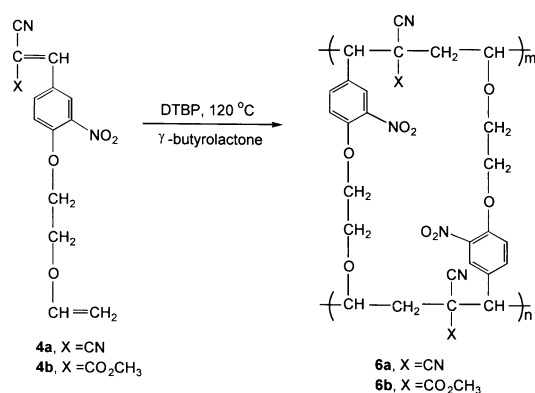
Table 1. Free Radical Polymerizations of **2**^a and **4**^b by DTBP^c at 120 °C

Monomer	Monomer/Solvent ^d (mol/l L)	Initiator to Monomer (mol%)	Time (h)	Yield (%)
2a	1.00	1.0	24	65
2a	1.50	1.2	36	70
2b	1.00	1.0	24	68
2b	1.50	1.2	36	73
4a	1.00	1.0	24	66
4a	1.50	1.2	36	75
4b	1.00	1.0	24	68
4b	1.50	1.0	36	70

^a**2a** = 5-Nitro-2-(2'-vinylloxyethoxy)benzylidenemalononitrile; **2b** = Methyl 5-nitro-2-(2'-vinylloxyethoxy)benzylidenecyanoacetate. ^b**4a** = 3-Nitro-4-(2'-vinylloxyethoxy)benzylidenemalononitrile; **4b** = Methyl 3-nitro-4-(2'-vinylloxyethoxy)benzylidenecyanoacetate. ^cDTBP=Di-tert-butyl peroxide. ^dSolvent: γ -Butyrolactone.



Scheme 2



Scheme 3

Table 2. Thermal Properties of Polymers **5-6**

Polymer	T_g^a , °C	Degradation temp. °C ^b			Residue ^b at 700°C, %
		5%-loss	20%-loss	40%-loss	
5a	-	296	327	467	0.6
5b	-	298	326	388	0.5
6a	-	300	349	475	1.1
6b	-	293	325	373	0.4

^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.

merization system that lead to crosslinked poly(alkyl vinyl ethers) by free radical initiators. Polymerizabilities of compounds **2** and **4** toward radical initiators were much lower than those of bifunctional derivatives without nitro group,¹¹ probably due to the inhibition effect of nitro group.

Properties of polymers 5-6. The polymers **5-6** were not soluble in methanol, ethanol, diethyl ether, benzene, dichloromethane, and chloroform. Polymers **5-6** 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 temperature (T_g). The results are summarized in Table 2. Polymers **5-6** showed a thermal stability and did not decompose below 300 °C. Thermal stability of polymers **5-6** were similar to those of the poly(vinyl ethers) without nitro group. The polymers show a double phase degradation pattern in their TGA thermograms. Crosslinked polymers **5-6** showed broad endothermic bands around 100-200 °C without any characteristic T_g peaks in DSC thermograms.

In summary, we prepared four trifunctional monomers **2a-b** and **4a-b** having an electron-rich vinyl ether group and electron-poor benzylidenemalononitrile or benzylidenecyanoacetate moiety and nitro group. The electron-deficient terminal double bond participated in the vinyl ether polymerization and radical polymerization of **2** and **4** led to cross-linked polymers **5-6**. Polymerizabilities of compounds **2** and **4** toward radical initiators were lower than those of bifunctional derivatives without nitro group due to the inhibition effect of nitro group. Polymers **5-6** were not soluble in common organic solvents due to crosslinking. We are now exploring further the polymerization of other donor-acceptor systems and the results will be reported elsewhere.

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