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Steric effect in the free radical polymerization of vinyl ethers containing electron-deficient olefin groups[*]

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Summary

o-(2-Vinyloxyethoxy)benzylidenemalononitrile (**3a**), methyl *o*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**3b**), 1,3-di-(2'-dicyanovinyl)-5-methyl-2-(2'-vinyloxyethoxy)benzene (**4a**), methyl 1,3-di-(2'-carbomethoxy-2'-cyanovinyl)-5-methyl-2-(2'-vinyloxyethoxy)benzene (**4b**), 2,3,4-tri-(2'-vinyloxyethoxy)benzylidenemalononitrile (**5a**), methyl 2,3,4-tri-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**5b**), 2,4,6-tri-(2'-vinyloxyethoxy)benzylidenemalononitrile (**6a**), and methyl 2,4,6-tri-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**6b**) were prepared by the condensation of *o*-(2-vinyloxyethoxy)benzaldehyde (**1a**), 2-(2'-vinyloxyethoxy)-5-methylisophthaldehyde (**1b**), 2,3,4-tri-(2'-vinyloxyethoxy)benzaldehyde (**2a**), 2,4,6-tri-(2'-vinyloxyethoxy)benzaldehyde (**2b**) with malononitrile or methyl cyanoacetate, respectively. Vinyl ether compounds **3a-b** and **5a-b** were polymerized readily by free radical initiators to give optically transparent swelling poly(vinyl ethers) **7a-b** and **9a-b**. Compounds **4a-b** and **6a-b** did not polymerize by radical initiators due to the steric hindrance. Polymers **7a-b** and **9a-b** were not soluble in common organic solvents such as acetone and DMSO due to crosslinking. Polymers **7a-b** and **9a-b** showed a thermal stability up to 300°C in TGA thermograms.

Introduction

Alkyl vinyl ethers do not radically homopolymerize, but copolymerize with electron-deficient monomers such as vinylidene cyanide (1), alkyl α-cyanoacrylate (2-4), alkyl vinyl ketone (5), maleic anhydride (6-7), and others by radical initiators. These facile reactions proceed through an electron donor-acceptor complex, which generates zwitterion or diradical tetramethylenes as initiating species (8). 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 (9-11). Recently we reported the free radical polymerization of alkyl vinyl ethers having an electron-poor olefin group. Bifunctional monomers containing both electron-rich alkyl vinyl ether and electron deficient trisubstituted olefin moieties such as *p*-(2-vinyloxyethoxy)benzylidenemalononitrile polymerize well by radical initiators (12). Trifunctional divinyl ethers containing an electron-poor trisubstituted olefin moieties such as 2,4-di-(2'-vinyloxyethoxy)benzylidenemalononitrile also polymerize readily with radical initiators to yield

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[*] Dedicated to Prof. Iwhan Cho on the occasion of his retirement from KAIST

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crosslinked poly(vinyl ethers) (13). 3,5-Dimethoxy-4-(2'-vinyloxyethoxy)benzylidene malononitrile do not polymerize radically due to the steric hindrance (14). In this report we investigated the steric effect in the free radical polymerization of vinyl ethers containing electron-deficient olefin groups. We prepared compounds **4** and **6** having vinyl ether group or electron deficient olefin group is located between two neighboring substituents, and compared their radical polymerizabilities with those of compounds **3** and **5** having free vinyl ether and/or electron deficient olefin group. We now report the interesting results of the work.

Experimental

Materials. The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2-Iodoethyl vinyl ether was prepared according to the procedure previously described (12).

Measurements. IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ^{1}H NMR spectra were obtained on a Varian 300MHz 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. Viscosity values were obtained by using a Cannon-Fenske viscometer.

o-(2-Vinyloxyethoxy)benzaldehyde (**1a**)

2-Hydroxybenzaldehyde (12.2 g, 0.10 mol), anhydrous potassium carbonate (18.0 g, 0.13 mol), and 2-iodoethyl vinyl ether (25.7 g, 0.13 mol) were dissolved in 180 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath at 80°C for 10 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 220 mL of water, and extracted with 300 mL of diethyl ether three times. The organic layer was washed with saturated aqueous sodium chloride solution, and dried with anhydrous magnesium sulfate. Rotary evaporation of acetone gave crude product, which on vacuum distillation yielded 13.3 g (80% yield) of pure product **1a**. Bp 73-75°C (0.2 mm Hg). ^{1}H NMR (acetone-d_6) δ 3.89-4.53 (m, 6H, CH_2=, -O-CH_2-CH_2-O-), 6.24-6.69 (q, 1H, =CH-O-), 6.75-7.19 (m, 2H, aromatic), 7.28-7.89 (m, 2H, aromatic), 10.50 (s, 1H, -CHO). IR (neat) 3119, 3068, 2940, 2878, 2833 (C-H), 1694, 1603, 1579 (C=C) cm^{-1}.

2-(2'-Vinyloxyethoxy)-5-methyl-1,3-bezenedicarboxaldehyde (**1b**)

Compound **1b** was prepared from 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde (16.42 g, 0.1 mol), anhydrous potassium carbonate (20.73 g, 0.15 mol), and 2-iodoethyl vinyl ether (25.7 g, 0.13 mol) according to the procedure of compound **1a**. Mp=46-47°C. ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3H, CH_3), 4.05-4.38 (m, 6H, CH_2=, -O-CH_2-CH_2-O-), 6.46-6.51 (q, 1H, =CH-O-), 7.91 (s, 2H, aromatic), 10.41 (s, 1H, -CHO). IR (KBr) 3120 (w, =C-H), 2930 (m, C-H), 1682 (vs, C=O), 1618 (vs, C=C), 1583 (s, C=C) cm^{-1}.

2,3,4-Tri-(2'-vinyloxyethoxy)benzaldehyde (**2a**)

Compound **2a** was synthesized from 2,3,4-trihydroxybenzaldehyde (3.08 g, 0.02 mol), anhydrous potassium carbonate (24.9 g, 0.18 mol), and 2-iodoethyl vinyl ether (14.9 g, 0.075 mol) according to the procedure of compound **1a**. Mp=50-51°C. ^{1}H NMR ($CDCl_3$) δ 3.95-4.60 (m, 18H, 3 CH_2=, 3 -O-CH_2-CH_2-O-), 6.43-6.582 (m, 3H, 3 =CH-O-), 6.75-7.79 (m, 1H, aromatic), 7.58-7.62 (d, 1H, aromatic), 10.31 (s, 1H, -CHO). IR (KBr) 3110, 3042 (w, =C-H), 2955, 2906, 2885 (m, C-H), 1673 (vs, C=O), 1614 (vs, C=C), 1582 (s, C=C) cm^{-1}.

2,4,6-Tri-(2'-vinyloxyethoxy)benzaldehyde (**2b**)

Compound **2b** was synthesized from 2,3,4-trihydroxybenzaldehyde (3.08 g, 0.02 mol), anhydrous potassium carbonate (24.9 g, 0.18 mol), and 2-iodoethyl vinyl ether (14.9 g, 0.075 mol) according to the procedure of compound **2a**, and purified by column chromatography (solvent: ethyl acetate/*n*-hexane=1/3) yielded 4.52 g (62% yield) of pure product **2b**. Mp=50-51°C. ^1H NMR ($CDCl_3$) δ 3.94-4.33 (m, 18H, 3 CH_2=, 3 -O-CH_2-CH_2-O-), 6.17 (m, 2H, aromatic), 6.48-6.67 (q, 3H, 3 =CH-O-, 10.38 (s, 1H, -CHO). IR (KBr) 3115 (w, =C-H), 2939, 2875 (m, C-H), 1682 (s, C=O), 1622 (s, C=C), 1601 (vs, C=C) cm^{-1}.

o-(2'-Vinyloxyethoxy)benzylidenemalononitrile (**3a**)

Piperidine (0.13 g, 1.5 mmol) was added to a solution of *o*-(2-vinyloxyethoxy)benzaldehyde **1a** (5.38 g, 28 mmol) and malononitrile (1.98 g, 30 mmol) in 50 mL of n-butanol with stirring at 0°C under nitrogen. After stirring for 1 h at 0°C, the product was filtered and washed successively with cold n-butanol (80 mL), water (30 mL), and cold n-butanol (20 mL). The obtained pale yellow product was recrystallized from n-butanol to give 5.38 g (80% yield) of **3a**. Mp: 69-70°C. ^1H NMR (acetone-d6) δ 3.94-4.57 (m, 6H, CH_2=, -O-CH_2-CH_2-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^{-1}. Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.91; H, 5.08; N, 11.62.

Methyl o-(2-vinyloxyethoxy)benzylidenecyanoacetate (**3b**)

Compound **3b** was prepared from *o*-(2-vinyloxyethoxy)benzaldehyde **1b** (5.77 g, 30 mmol) and methyl cyanoacetate (2.98 g, 30 mmol) according to the procedure of compound **3a**. Mp: 62-63°C. ^1H NMR (acetone-d_6) δ 3.86 (s, 3H, CO_2CH_3), 3.89-4.53 (m, 6H, CH_2=, -O-CH_2-CH_2-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^{-1}. Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.83; H, 5.58; N, 5.18.

1,3-Di-(2'-dicyanovinyl)-5-methyl-2-(2'-vinyloxyethoxy) benzene (**4a**)

Compound **4a** was prepared from 2-(2'-vinyloxyethoxy)-5-methyl-1,3-bezenedicarboxaldehyde (**1b**) (4.69 g, 20 mmol) and malononitrile (1.45 g, 22 mmol) according to the procedure of compound **3a**. Mp=126-128°C. ^1H NMR ($CDCl_3$) δ 2.48 (s, 3H, CH_3), 4.02-4.35 (m, 6H, CH_2=, -O-CH_2-CH_2-O-), 6.56-6.64 (q, 1H, =CH-O-), 8.21 (s, 1H, aromatic), 8.27 (s, 1H, aromatic). IR (KBr) 30473 (w, =C-H), 2926, 2882 (m, C-H), 2230 (s, CN), 1624, 1591 (s, C=C) cm^{-1}. Anal. Calcd for Calcd for $C_{19}H_{14}N_4O_2$: C, 69.08; H, 4.27; N, 16.96. Found: C, 69.02; H, 4.34; N, 16.88.

Methyl 1,3-di-(2'-carbomethoxy-2'-cyanovinyl)-5-methyl-2-(2'-vinyloxyethoxy)benzene **4b**)

Compound **4b** was prepared from 2-(2'-vinyloxyethoxy)-5-methyl-1,3-bezenedicarboxaldehyde (**1b**) (4.69 g, 20 mmol) and methyl cyanoacetate (2.18 g, 22 mmol) according to the procedure of compound **4a**. Mp=97-98°C. ^1H NMR ($CDCl_3$) δ 2.47 (s, 3H, CH_3), 3.95 (s, 3H, -CO_2CH_3), 3.97-4.24 (m, 6H, CH_2=, -O-CH_2-CH_2-O-), 6.52-6.56 (m, 2H, =CH-O-), 8.25 (s, 1H, aromatic), 8.68 (s, 1H, aromatic). IR (KBr) 3055 (w, =C-H), 2953 (m, C-H), 2228 (s, CN), 1732 (vs, C=O), 1620, 1597 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{21}H_{20}N_2O_6$: C, 63.63; H, 5.08; N, 7.07. Found: C, 63.72; H, 5.14; N, 7.16.

2,3,4-Tri-(2'-vinyloxyethoxy)benzylidenemalononitrile (**5a**)

Piperidine (0.04 g, 0.5 mmol) was added to a solution of 2,3,4-tri-(2'-vinyloxyethoxy)-

benzaldehyde **2a** (3.64 g, 10 mmol) and malononitrile (0.73 g, 11 mmol) in 50 mL of isopropyl alcohol with stirring at 0°C under nitrogen. After stirring for 6 h at 0°C, the reaction mixture was cooled to -10°C for crystallization. The product was filtered and washed successively with cold isopropyl alcohol (20 mL), water (10 mL), and cold isopropyl alcohol (10 mL). The obtained pale yellow product was recrystallized from isopropyl alcohol to give 3.13g (76% yield) of **5a**. Mp=56-57°C. ^{1}H NMR ($CDCl_3$) δ 3.90-4.48 (m, 18H, 3 CH_2=, 3 -O-CH_2-CH_2-O-), 6.45-6.58 (m, 3H, 3 =CH-O-), 6.78-6.82 (d, 1H, benzylic), 8.08-8.11 (d, 1H, aromatic), 8.32 (s, 1H, aromatic). IR (KBr) 3120, 3056 (w, =C-H), 2936, 2882 (m, C-H), 2223 (s, CN), 1624 (s, C=C), 1571 (vs, C=C) cm^{-1}. UV/Vis (chloroform) λ_{max}=354 nm, ε=25,810. Anal. Calcd for $C_{22}H_{24}N_2O_6$: C, 64.06; H, 5.87; N, 6.79. Found: C, 64.14; H, 5.85; N, 6.86.

Methyl 2,3,4-tri-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**5b**)

Compound **5b** was synthesized from 2,3,4-tri-(2'-vinyloxyethoxy)benzaldehyde **2a** (3.64 g, 10 mmol) and methyl cyanoacetate (1.09 g, 11 mmol) according to the procedure of compound **5a**. Mp=60-62°C. ^{1}H NMR ($CDCl_3$) δ3.89 (s, 3H, -CO_2CH_3), 3.91-4.44 (m, 18H, 3 CH_2=, 3 -O-CH_2-CH_2-O-), 6.46-6.58 (m, 3H, 3 =CH-O-), 6.77-6.82 (d, 1H, benzylic), 8.17-8.21 (d, 1H, aromatic), 8.78 (s, 1H, aromatic). IR (KBr) 3134, 3078 (w, =C-H), 2933, 2852 (m, C-H), 2222 (s, CN), 1720 (vs, C=O), 1632, 1611 (s, C=C), 1582 (vs, C=C) cm^{-1}. UV/Vis (chloroform) λ_{max}=345 nm, ε=25,230. Anal. Calcd for $C_{23}H_{27}NO_8$: C, 62.02; H, 6.11; N, 3.14. Found: C, 62.10; H, 6.15; N, 3.18.

2,4,6-Tri-(2'-vinyloxyethoxy)benzylidenemalononitrile (**6a**)

Compound 6a was prepared from 2,4,6-tri-(2'-vinyloxyethoxy)benzaldehyde **2b** (3.64 g, 10 mmol) and malononitrile (0.73 g, 11 mmol) according to the procedure of compound **5a**. The obtained pale yellow product was recrystallized from isopropyl alcohol to give 3.13g (76% yield) of **6a**. Mp=72-73°C. ^{1}H NMR ($CDCl_3$) δ 3.96-4.33 (m, 18H, 3 CH_2=,3 -O-CH_2-CH_2-O-), 6.19 (s, 2H, aromatic), 6.44-6.58 (m, 3H, 3 =CH-O-), 7.91 (s, 1H, aromatic). IR (KBr) 3117, 3036 (w, =C-H), 2947, 2880 (m, C-H), 2222 (s, CN), 1609 (s, C=C), 1587 (s, C=C) cm^{-1}. UV/Vis (chloroform) λ_{max}=361 nm, ε=23,700 Anal. Calcd for $C_{22}H_{24}N_2O_6$: C, 64.06; H, 5.87; N, 6.79. Found: C, 64.16; H, 5.88; N, 6.75.

Methyl 2,4,6-tri-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**6b**)

Compound **6b** was prepared from according to the procedure of compound **4a**. Mp=77-78°C. ^{1}H NMR ($CDCl_3$) δ 3.89 (s, 3H, -CO_2CH_3), 4.02-4.32 (m, 18H, 3 CH_2=, 3 -O-CH_2-CH_2-O-), 6.20 (s, 2H, aromatic), 6.43-6.57 (m, 3H, 3 =CH-O-), 8.43 (s, 1H, aromatic). IR (KBr) 3115, 3040 (w, =C-H), 2955, 2893 (m, C-H), 2226 (s, CN), 1715 (vs, C=O), 1607, (vs, C=C), 1578 (s, C=C) cm^{-1}. UV/Vis (chloroform) λ_{max}=352 nm, ε=19,590. Anal. Calcd for $C_{23}H_{27}NO_8$: C, 62.02; H, 6.11; N, 3.14. Found: C, 62.09; H, 6.16; N, 3.20.

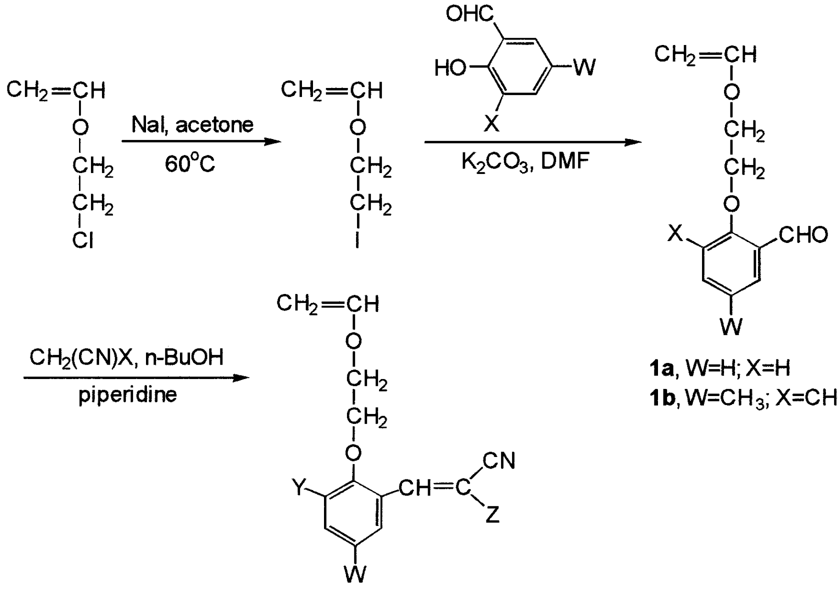
Radical polymerizations of monomers **3-6**

A representative radical polymerization procedure (the case of **3a**) was as follows: In a polymerization tube were placed 0.48 g (2.0 mmol) of **3a**, 1.97 mg (0.012 mmol) of AIBN, and 2.0 mL of γ-butyrolactone under nitrogen. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 65°C. After 3 h the polymerization tube was opened and the swelling polymer was poured into 300 mL of diethyl ether. The precipitated polymer was collected and dried under vacum to give 0.48g (100% yield) of polymer **7a**. IR (KBr) 3058 (w, =C-H), 2928, 2860 (m, C-H), 2228 (m, CN), 1601, 1586 (s, C=C) cm^{-1}. Anal. Calcd for $(C_{14}H_{12}N_2O_2)_n$: C, 69.99; H, 5.03; N, 11.66.Found: C, 69.92; H, 5.11; N, 11.58. Polymer **7b**: 100% yield. IR (KBr) 3060 (w, =C-H), 2936, 2860 (m, C-H), 2236 (m, CN), 1735 (s, C=O), 1598 (s, C=C) cm^{-1}. Anal. Aalcd for $(C_{15}H_{15}NO_4)_n$: C, 65.92; H, 5.53; N, 5.13.Found: C, 65.85; H, 5.46; N, 5.18. **9a**. IR (KBr) 2925, 2887 (m, C-H), 2224 (s, CN), 1620 (s, C=C) cm^{-1}. Anal. Calcd for $(C_{22}H_{24}N_2O_6)_n$: C, 64.06; H, 5.87; N, 6.79. Found: C, 64.15; H, 5.85; N, 6.86. **9b**: IR (KBr) 2936, 2866 (m, C-H), 2222 (w, CN), 1728 (vs, C=O), 1620 (vs, C=C) cm^{-1}. Anal. Calcd for $(C_{23}H_{27}NO_8)_n$: C, 62.02; H, 6.11; N, 3.14. Found: C, 62.11; H, 6.03; N, 3.18.

Results and Discussion

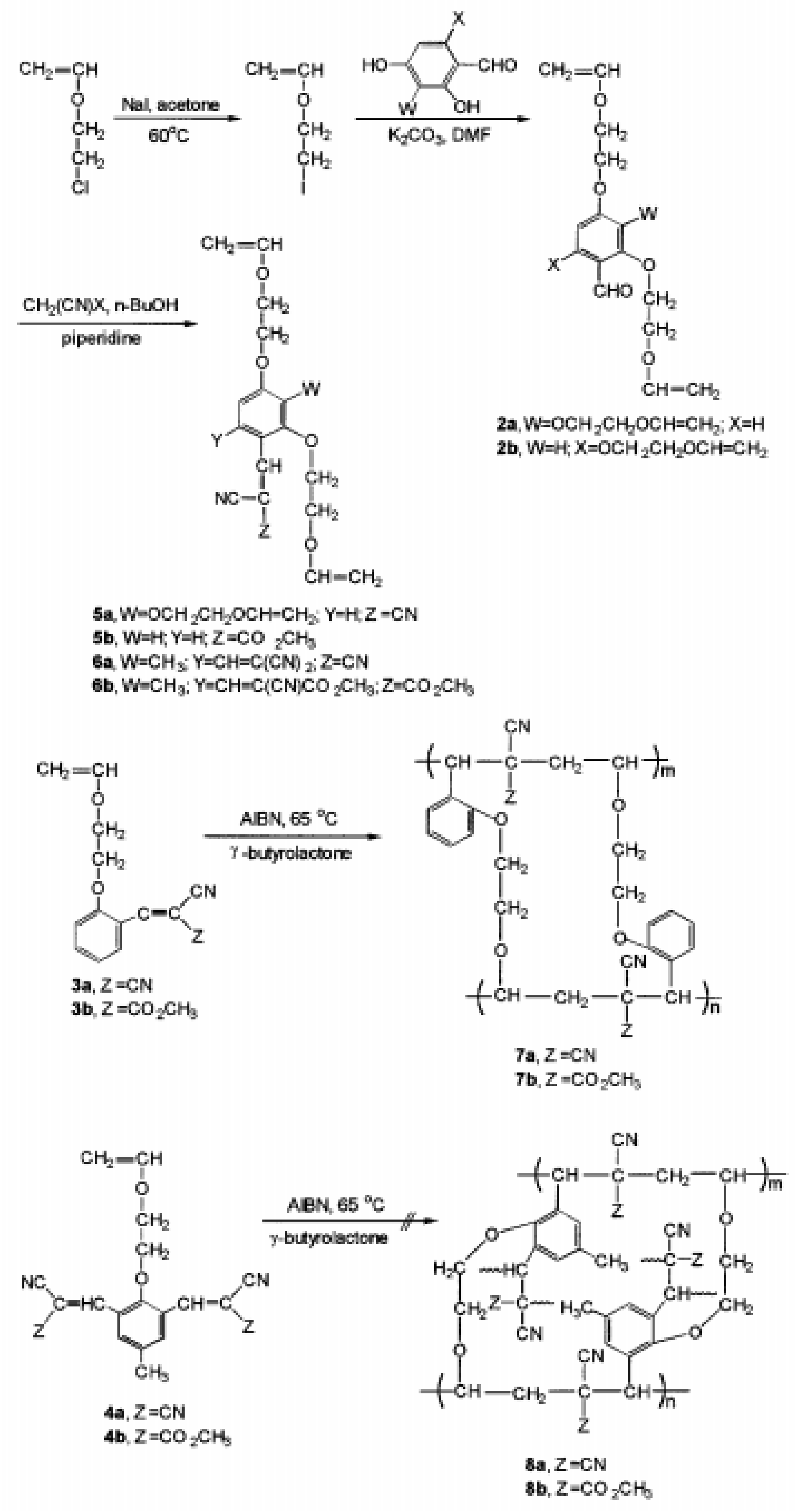
Synthesis and free radical polymerizations of monomers **3-6**

Compounds **3-6** were prepared by the condensations of **1** and **2** with malononitrile or methyl cyanoacetate, respectively (15). The chemical structure of the compounds was identified by ^{1}H NMR, IR spectra, and elemental analysis. All the analytical data confirmed the expected chemical structure. Monomers **3-6** were polymerized in γ-butyrolactone solution at 65°C with AIBN as radical initiator. The polymerization results are summarized in Table 1. Monomers **3** and **5** were quite reactive toward radical initiator 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 the polymers. The trisubstituted terminal double bond participated in the vinyl polymerization, and radical polymerization of **3** and **5** led only to optically trasparent swelling polymers **7** and **9**. Polymers **7** and **9** were not soluble in any organic solvents due to cross-linking. However, compounds **4** and **6** did not polymerize by radical initiators such as AIBN and DTBP (di-tert-butylperoxide), probably due to the steric hindrance. Previously we have reported that sterically hindered 3,5-dimethoxy-4-(2'-vinyloxyethoxy)benzylidenemalononitrile did not homopolymerized by radical initiators (14). According to our experimental results, vinyl compounds having one of vinyl ether group or electron deficient olefin group is located between two neighboring substituents such as **4** and **6** do not polymerize radically due to the steric hindrance.



1a, W=H; X=H
1b, W=CH$_3$; X=CHO

3a, W=H; Y=H; Z =CN
3b, W=H; Y=H; Z =CO $_2$CH$_3$
4a, W=CH$_3$; Y=CH=C(CN)$_2$; Z=CN
4b, W=CH$_3$; Y=CH=C(CN)CO$_2$CH$_3$; Z=CO$_2$CH$_3$



2a, W=OCH$_2$CH$_2$OCH=CH$_2$; X=H
2b, W=H; X=OCH$_2$CH$_2$OCH=CH$_2$

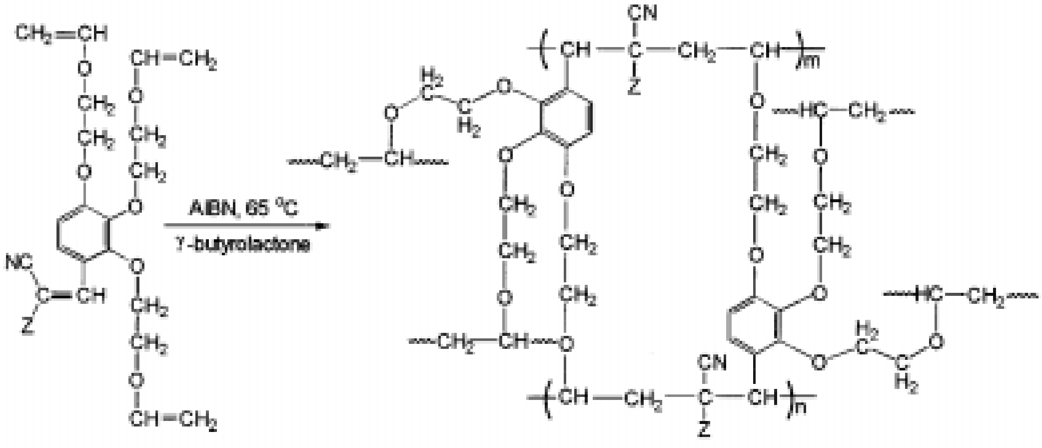
5a, W=OCH$_2$CH$_2$OCH=CH$_2$; Y=H; Z=CN
5b, W=H; Y=H; Z=CO$_2$CH$_3$
6a, W=CH$_3$; Y=CH=C(CN)$_2$; Z=CN
6b, W=CH$_3$; Y=CH=C(CN)CO$_2$CH$_3$; Z=CO$_2$CH$_3$

3a, Z=CN
3b, Z=CO$_2$CH$_3$

7a, Z=CN
7b, Z=CO$_2$CH$_3$

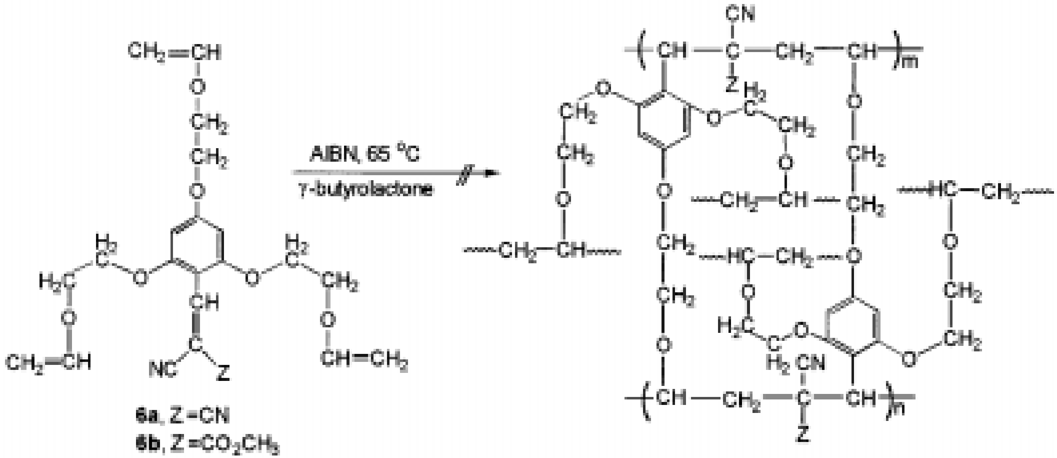
4a, Z=CN
4b, Z=CO$_2$CH$_3$

8a, Z=CN
8b, Z=CO$_2$CH$_3$



5a, Z=CN
5b, Z=CO$_2$CH$_3$

9a, Z=CN
9b, Z=CO$_2$CH$_3$



6a, Z=CN
6b, Z=CO$_2$CH$_3$

10a, Z=CN
10a, Z=CO$_2$CH$_3$

Table 1. Free radical polymerizations of **3-6** by AIBN in γ-butyrolactone at 65°C

Monomer	Monomer/Solvent (mol/1 L)	Initiator to Monomer (mol%)	Time (h)	Yield (%)
3a	1.00	0.6	4	100
3a	0.67	0.8	4	100
3b	1.00	0.6	3	100
3b	0.67	0.8	4	100
4a	1.00	0.8	12	nil
4b	1.00	0.8	12	nil
5a	1.00	0.6	3	86
5a	0.67	0.8	8	88
5b	1.00	0.6	3	87
5b	0.67	0.8	8	86
6a	1.00	0.8	12	nil
6b	1.00	0.8	12	nil

Properties of polymers **7** *and* **9**

The polymers **7** and **9** 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 **7** and **9** isolated from methanol were white colored 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 **7** and **9** 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, probably due to crosslinking. Crosslinked polymers **7** and **9** showed broad endothermic bands around 80-200°C without any characteristic T_g peaks in DSC thermograms. We are now exploring further the polymerization of these donor-acceptor systems and the full account of the work will be reported later.

Table 2. Thermal properties of polymers **7** and **9**

Polymer	T_g, °C	Degradation temp, °C			Residue at 700 °C, %
		5%-loss	20%-loss	40%-loss	
7a	-	310	340	360	2.0
7b	-	300	320	370	1.3
9a	-	308	347	387	2.7
9b	-	302	350	372	2.0

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