

## Steric Hindrance in the Free Radical Polymerization of Aryloxyethyl Vinyl Ethers Containing Electron-Deficient Olefin Groups<sup>†</sup>

Ju-Yeon Lee<sup>‡</sup> and Mi-Kyoung Jin

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

Received February 12, 2000

*p*-(2-Vinyloxyethoxy)benzylidenemalononitrile (**4a**), methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**4b**), 3,5-dimethoxy-4-(2'-vinyloxyethoxy)benzylidenemalononitrile (**5a**), methyl 3,5-dimethoxy-4-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**5b**), *o*-(2-vinyloxyethoxy)benzylidenemalononitrile (**6a**), methyl *o*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**6b**), 1,3-di-(2',2'-dicyanovinyl)-5-methyl-2-(2'-vinyloxyethoxy)benzene (**7a**), 1,3-di-(2'-carbomethoxy-2'-cyanovinyl)-5-methyl-2-(2'-vinyloxyethoxy)benzene (**7b**), 2,3,4-tri-(2'-vinyloxyethoxy)benzylidenemalononitrile (**8a**), methyl 2,3,4-tri-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**8b**), 2,4,6-tri-(2'-vinyloxyethoxy)benzylidenemalononitrile (**9a**), and methyl 2,4,6-tri-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**9b**) were prepared by the condensation of the corresponding benzaldehyde **1-3** with malononitrile or methyl cyanoacetate, respectively. Vinyl ether monomers **4**, **6**, and **8** polymerized readily with radical initiators to yield crosslinked polymers **10**, **12**, and **14**. However, compounds **5**, **7**, and **9** were inert to radical initiators due to the steric hindrance. The resulting polymers **10**, **12**, and **14** were not soluble in common solvents showing a thermal stability up to 300 °C.

### Introduction

It is well-known that vinyl ethers do not radically homopolymerize, but copolymerize readily with electron-deficient olefins such as vinylidene cyanide,<sup>1</sup> 2-vinylcyclopropane-1,1-dicarbonitrile,<sup>2</sup> alkyl cyanoacrylate,<sup>3-5</sup> and alkyl vinyl ketone<sup>6</sup> by radical initiators. These facile reactions proceed through an electron donor-acceptor (EDA) complex, which generates zwitterion or diradical tetramethylenes as initiating species.<sup>7</sup> 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.<sup>8-10</sup> Recently we have reported that vinyl ethers containing electron-deficient olefin groups polymerized readily by radical initiators to give crosslinked poly(vinyl ethers).<sup>11-13</sup> In this report we investigated the steric effect in the free radical polymerization of vinyl ethers containing electron deficient olefin groups. We prepared compounds **5**, **7**, and **9** having vinyl ether group or electron deficient olefin group is located between two neighboring substituents, and compared their radical polymerizabilities with those of compounds **4**, **6**, and **8** having free vinyl ether and/or electron deficient olefin group. The most important factor to the radical polymerization of those vinyl compounds was the steric hindrance, and experimental results showed that vinyl compounds having one of vinyl ether group or electron deficient olefin group is located between two substituents such as **5**, **7**, and **9** do not polymerize radically due to the steric hindrance. The present report describes the synthesis and radi-

cal polymerization of *p*-(2-vinyloxyethoxy)benzylidenemalononitrile (**4a**), methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**4b**), 3,5-dimethoxy-4-(2'-vinyloxyethoxy)benzylidenemalononitrile (**5a**), methyl 3,5-dimethoxy-4-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**5b**), *o*-(2-vinyloxyethoxy)benzylidenemalononitrile (**6a**), methyl *o*-(2-vinyloxyethoxy)benzylidenecyanoacetate (**6b**), 1,3-di-(2',2'-dicyanovinyl)-5-methyl-2-(2'-vinyloxyethoxy)benzene (**7a**), 1,3-di-(2'-carbomethoxy-2'-cyanovinyl)-5-methyl-2-(2'-vinyloxyethoxy)benzene (**7b**), 2,3,4-tri-(2'-vinyloxyethoxy)benzylidenemalononitrile (**8a**), methyl 2,3,4-tri-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**8b**), 2,4,6-tri-(2'-vinyloxyethoxy)benzylidenemalononitrile (**9a**), and methyl 2,4,6-tri-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**9b**).

### Experimental Section

**Materials.** The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2-Chloroethyl vinyl ether, 4-hydroxybenzaldehyde, 3,5-dimethoxy-4-hydroxybenzaldehyde, 2-hydroxybenzaldehyde, 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde, 2,3,4-trihydroxybenzaldehyde, and 2,4,6-trihydroxybenzaldehyde 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.  $\alpha,\alpha'$ -Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under reduced pressure at room temperature.  $\gamma$ -Butyrolactone was dried with anhydrous magnesium sulfate and fractionally distilled under nitrogen. 2-Iodoethyl vinyl ether was prepared according to the procedure previously described.<sup>11</sup>

**Measurements.** IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. <sup>1</sup>H NMR spectra

<sup>‡</sup>Dedicated to Professor Iwhan Cho on the occasion of his retirement from KAIST.

<sup>†</sup>Corresponding author. Tel: +82-525-320-3221, Fax: +82-525-321-9718, e-mail: chemjy@ijnc.inje.ac.kr

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.

***p*-(2-Vinyloxyethoxy)benzaldehyde 1a.** Compound **1a** was prepared according to the literature procedure.<sup>11</sup>

**3,5-Dimethoxy-4-(2'-vinyloxyethoxy)benzaldehyde 1b.** Compound **1b** was prepared from 3,5-dimethoxy-4-hydroxybenzaldehyde and 2-iodoethyl vinyl ether according to the procedure similar to that of compound **1a**. Mp: 44–45 °C. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 9.78 (s, 1H, -CHO), 7.13 (s, 2H, aromatic), 6.18–6.67 (q, 1H, =CH-), 3.86–4.38 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 3.85 (s, 3H, 2 CH<sub>3</sub>O-). IR (neat) 3013 (m, =C-H), 2975, 2955, 2940, 2836 (s, C-H), 1677 (vs, C=O), 1627, 1578 (vs, C=C) cm<sup>-1</sup>.

***o*-(2-Vinyloxyethoxy)benzaldehyde 2a.** Compound **2a** was prepared according to the literature procedure<sup>12</sup> and recrystallized twice from chloroform.

**5-Methyl-2-(2'-vinyloxyethoxy)-1,3-benzenedicarboxaldehyde 2b.** 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) were dissolved in 160 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80 °C for 25 hr under nitrogen. The resulting solution was cooled to room temperature, diluted with 300 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 was recrystallized from 1-butanol yielded 21.5 g (92% yield) of pure product **2b**. Mp=46–47 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.43 (s, 3H, CH<sub>3</sub>), 4.05–4.38 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-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, 2860 (m, C-H), 1682 (vs, C=O), 1618 (vs, C=C), 1583 (s, C=C) cm<sup>-1</sup>.

**2,3,4-Tri-(2'-vinyloxyethoxy)benzaldehyde 3a.** 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) were dissolved in 90 mL of dry DMF under nitrogen. At 80 °C for 25 hr under nitrogen the mixture was refluxed in an oil bath. The resulting solution was cooled to room temperature, diluted with 300 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 a crude product, which was recrystallized from 1-butanol, yielding 5.83 g (80% yield) of pure **3a**. Mp=50–51 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.95–4.60 (m, 18H, 3 CH<sub>2</sub>=, 3 -O-CH<sub>2</sub>-CH<sub>2</sub>-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<sup>-1</sup>.

**2,4,6-Tri-(2'-vinyloxyethoxy)benzaldehyde 3b.** Compound **3b** was prepared from 2,4,6-trihydroxybenzaldehyde and 2-iodoethyl vinyl ether according to the procedure similar to that of compound **3a**. Compound **3b** was purified by column chromatography (solvent: ethyl acetate/*n*-hexane=1/3) to give 4.52 g (62% yield) of pure **3b**. Mp=50–51 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.94–4.33 (m, 18H, 3 CH<sub>2</sub>=, 3 -O-CH<sub>2</sub>-CH<sub>2</sub>-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<sup>-1</sup>.

***p*-(2-Vinyloxyethoxy)benzylidenemalononitrile 4a.** Compound **4a** was prepared according to the literature procedure.<sup>11</sup>

**Methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate 4b.** Compound **4b** was prepared according to the literature procedure.<sup>11</sup>

**3,5-Dimethoxy-4-(2'-vinyloxyethoxy)benzylidenemalononitrile 5a.** Compound **5a** was prepared from 3,5-dimethoxy-4-(2'-vinyloxyethoxy)benzaldehyde **2a** and malononitrile according to the procedure previously described in compound **4a**.

Mp: 117–118 °C. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 8.08 (s, 1H, -Ph-CH=), 7.34 (s, 2H, aromatic), 6.23–6.71 (q, 1H, =CH-), 3.84–4.43 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 3.83 (s, 3H, 2 CH<sub>3</sub>O-). IR (neat) 3112, 3025 (w, =C-H), 2960, 2944, 2918 (m, C-H), 2228 (s, CN), 1655, 1614, 1585, 1573 (vs, C=C) cm<sup>-1</sup>. Anal. Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>:C, 63.99; H, 5.73; N, 9.33. Found: C, 69.92; H, 5.42; N, 9.38.

**Methyl 3,5-dimethoxy-4-(2'-vinyloxyethoxy)benzylidenecyanoacetate 5b.** Compound **5b** was prepared from 3,5-dimethoxy-4-(2'-vinyloxyethoxy)benzaldehyde **2a** and methyl cyanoacetate according to the procedure previously described in compound **4b**. Mp: 109–110 °C. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 8.10 (s, 1H, -Ph-CH=), 7.37 (s, 2H, aromatic), 6.19–6.63 (m, 1H, =CH-), 3.84–4.35 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 3.82 (s, 3H, 2 CH<sub>3</sub>O-). IR (neat) 3110, 3024 (m, =C-H), 2958, 2940 (m, C-H), 2220 (m, CN), 1642, 1604, 1577 (vs, C=C) cm<sup>-1</sup>. Anal. Calcd for C<sub>17</sub>H<sub>19</sub>NO<sub>6</sub>:C, 61.25; H, 5.75; N, 4.20. Found: C, 61.30; H, 5.72; N, 4.26.

***o*-(2-Vinyloxyethoxy)benzylidenemalononitrile 6a.** Compound **6a** was prepared according to the literature procedure.<sup>12</sup>

**Methyl *o*-(2-vinyloxyethoxy)benzylidenecyanoacetate 6b.** Compound **6a** was prepared according to the literature procedure.<sup>12</sup>

**1,3-Di-(2',2'-dicyanovinyl)-5-methyl-2-(2'-vinyloxyethoxy)benzene 7a.** Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2-(2'-vinyloxyethoxy)-5-methyl-1,3-benzenedicarboxaldehyde (**2b**) (4.69 g, 20 mmol) and malononitrile (1.45 g, 22 mmol) in 140 mL of 1-butanol with stirring at 0 °C under nitrogen. After stirring for 4 hr at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. The product was filtered and washed successively with cold 1-butanol (60 mL), water (20 mL), and cold 1-butanol (15 mL). The

obtained pale yellow product was recrystallized from 1-butanol to give 5.41 g (82% yield) of **7a**. Mp: 126-128 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.48 (s, 3H, CH<sub>3</sub>), 4.02-4.35 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-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<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>: C, 69.08; H, 4.27; N, 16.96. Found: C, 69.21; H, 4.36; N, 16.88.

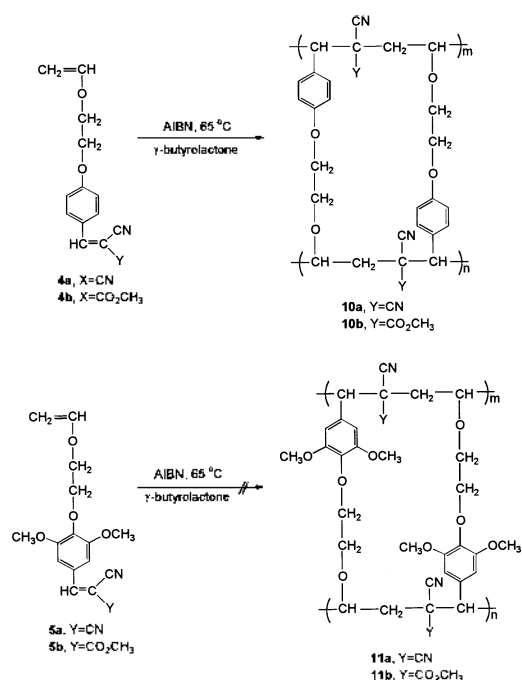
**1,3-Di-(2'-carbomethoxy-2'-cyanovinyl)-5-methyl-2-(2'-vinylxyethoxy)benzene 7b**. Piperidine (0.085 g, 1.0 mmol) was added to a solution of 2-(2'-vinylxyethoxy)-5-methyl-1,3-benzenedicarboxaldehyde (**1b**) (4.69 g, 20 mmol) and methyl cyanoacetate (2.18 g, 22 mmol) in 140 ml. of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 4 hr at 0 °C, the reaction mixture was cooled to -10 °C for crystallization. The product was filtered and washed successively with cold 1-butanol (60 ml.), water (20 ml.), and cold 1-butanol (15 ml.). The obtained pale yellow product was recrystallized from 1-butanol to give 6.89 g (87% yield) of **4b**. Mp: 97-98 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.47 (s, 3H, CH<sub>3</sub>), 3.95 (s, 3H, -CO<sub>2</sub>CH<sub>3</sub>), 3.97-4.24 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-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<sup>-1</sup>. Anal. Calcd for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>: C, 63.63; H, 5.08; N, 7.07. Found: C, 63.72; H, 5.14; N, 5.16.

**Radical polymerizations of monomers 4-9**. Free radical polymerizations of monomers **4-9** were carried out according to the literature procedure.<sup>11,12</sup> **14a**: IR (KBr) 3121 (w, =C-H), 2939, 2878 (m, C-H), 2226 (w, CN), 1638, 1622 (s, C=C) cm<sup>-1</sup>. Anal. Calcd for (C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub>)<sub>n</sub>: C, 64.06; H, 5.87; N, 6.79. Found: C, 64.14; H, 5.81; N, 6.85. Polymer **14b**: IR (KBr) 3117 (w, =C-H), 2957, 2876 (m, C-H), 2225 (w, CN), 1744 (vs, C=O), 1636, 1622 (vs, C=C) cm<sup>-1</sup>. Anal. Calcd for (C<sub>23</sub>H<sub>27</sub>NO<sub>8</sub>)<sub>n</sub>: C, 62.02; H, 6.11; N, 3.14. Found: C, 62.10; H, 6.18; N, 3.19.

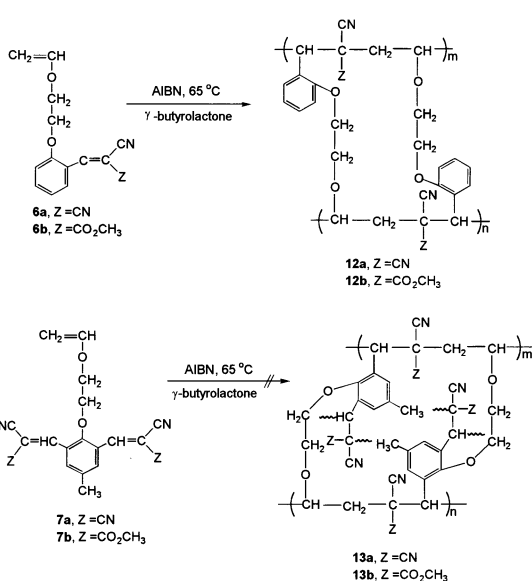
## Results and Discussion

**Synthesis of monomers 4-9**. Monomers **4-9** were prepared by the condensation of the corresponding benzaldehyde **1-3** with malononitrile or methyl cyanoacetate, according to the literature procedure.<sup>11,12</sup> Compounds **4-9** were obtained in high yield and were purified by recrystallization in 1-butanol for polymerization. The chemical structure of the compounds was identified by <sup>1</sup>H NMR, IR spectra, and elemental analysis. All the analytical data were matched well with the expected chemical structure.

**Radical polymerizations of monomers 4-9**. Monomers **4-9** were polymerized in  $\gamma$ -butyrolactone solution at 65 °C with AIBN as radical initiator. The polymerization results are summarized in Table 1. Monomers **4**, **6**, and **8** 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 com-

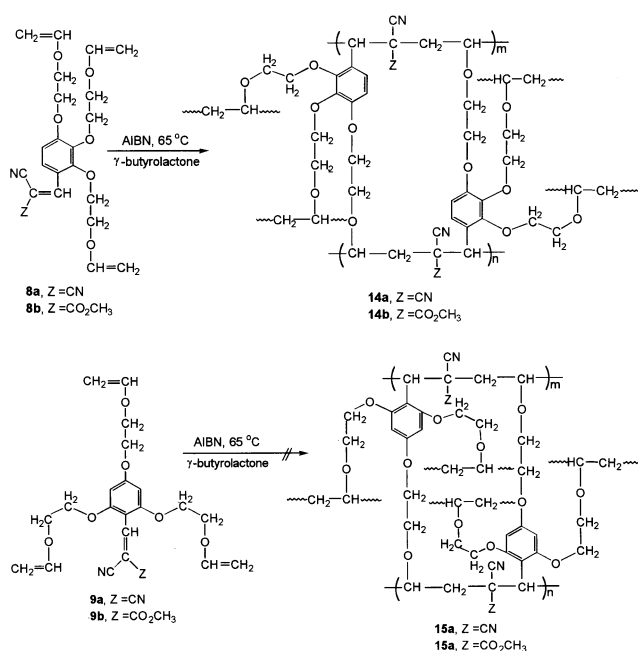


Scheme 1



Scheme 2

prising the polymers. The trisubstituted terminal double bond participated in the vinyl polymerization, and radical polymerization of **4**, **6**, and **8** led only to optically transparent swelling polymers **10**, **12**, and **14**. The resulting polymers **10**, **12**, and **14** were not soluble in any organic solvents due to cross-linking. However, compounds **5**, **7**, and **9** did not polymerize by radical initiators such as AIBN and DTBP (di-*tert*-butylperoxide), probably due to the steric hindrance. All the attempts to secure a polymer sample failed so far. Our experimental results show that vinyl compounds having one of vinyl ether group or electron deficient olefin group is located between two neighboring substituents such as **5**, **7**, and **9** do not polymerize with radical initiators due to the steric hindrance. These experimental results mean that steric



Scheme 3

**Table 1.** Free radical polymerizations of 4-9 by AIBN in  $\gamma$ -butyrolactone at 65 °C

Monomer	Monomer/ Solvent (mol/l L)	Initiator to Monomer (mol%)	Time (hr)	Yield (%)
4a	1.00	0.6	2	100
4a	0.67	0.8	3	100
4b	1.00	0.6	2	100
4b	0.67	0.8	3	100
5a	1.00	0.6	12	nil
5a	0.67	0.8	24	nil
5b	1.00	0.6	12	nil
5b	0.67	0.8	24	nil
6a	1.00	0.6	4	100
6a	0.67	0.8	4	100
6b	1.00	0.6, 3	100	
6b	0.67	0.8	4	100
7a	1.00	0.8	12	nil
7a	0.67	1.0	24	nil
7b	1.00	0.8	12	nil
7b	0.67	1.0	24	nil
8a	1.00	0.6	3	86
8a	0.67	0.8	8	88
8b	1.00	0.6	3	87
8b	0.67	0.8	8	86
9a	1.00	0.8	12	nil
9a	0.67	1.0	24	nil
9b	1.00	0.8	12	nil
9b	0.67	1.0	24	nil

effect is one of the conclusive factor to the free radical polymerization of the present polymer systems.

**Properties of polymers.** The polymers 10, 12, and 14 were not soluble in common solvents such as methanol, eth-

**Table 2.** Thermal properties of polymers 10-14

Polymer	$T_g^a$ , °C	Degradation temp. °C <sup>b</sup>			Residue <sup>b</sup> at 700 °C, %
		5%-loss	20%-loss	40%-loss	
10a	—	310	338	430	6.7
10b	—	305	340	384	4.6
12a	—	310	340	360	2.0
12b	—	300	320	370	1.3
14a	—	308	347	387	2.7
14b	—	302	350	372	2.0

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

anol, diethyl ether, benzene, toluene, acetone, methyl ethyl ketone, cyclohexanone, dichloromethane, chloroform, DMF, and DMSO due to crosslinking. Polymers 10, 12, and 14 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 10, 12, and 14 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 10, 12, and 14 showed broad endothermic bands around 80-200 °C without any characteristic  $T_g$  peaks in DSC thermograms as expected.

## Conclusions

We prepared twelve vinyl ether compounds 4-9 having electron-deficient benzylidenemalononitrile or benzylidene-cyanoacetate group, and compared their radical polymerizabilities. Vinyl compounds 4, 6, and 8 with free vinyl ether and/or electron deficient olefin group polymerized well with free radical initiators. The trisubstituted terminal double bond participated in the vinyl polymerization and radical polymerization of 4, 6, and 8 led to crosslinked polymers 10, 12, and 14 in high yields. However, compounds having vinyl ether group or electron deficient olefin group is located between two neighboring substituents such as 5, 7, and 9 did not polymerize by radical initiators due to the steric hindrance. These experimental results show that the most important factor to the radical polymerization of these vinyl compounds is the steric effect. We are now exploring further the polymerization of other donor-acceptor systems and the results will be reported elsewhere.

**Acknowledgment.** This study was supported by the academic research fund (BK21, HEKSIM D0024) of Ministry of Education, Republic of Korea.

## References

1. Stille, J. K.; Chung, D. C. *Macromolecules* 1975, 8, 114.

2. Cho, I.; Lee, J.-Y. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 639.
  3. Cho, I.; Lee, J.-Y. *Macromolecules* **1983**, *16*, 150.
  4. Cho, I.; Lee, J.-Y. *Macromolecules* **1983**, *16*, 1245.
  5. Lee, J.-Y.; Cho, I. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1987**, *25*, 3089.
  6. Cho, I.; Lee, J.-Y. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 389.
  7. Hall, Jr. H. K.; Padias, A. B. *Acc. Chem. Res.* **1990**, *23*, 3.
  8. Kharas, G.; Kohn, D. H. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1457.
  9. Kharas, G.; Kohn, D. H. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 583.
  10. Angelorici, M. M.; Kohn, D. H. *J. Appl. Polym. Sci.* **1990**, *40*, 485.
  11. Lee, J.-Y.; Lee, H.-J.; Kim, M.-Y. *Bull. Korean Chem. Soc.* **1996**, *17*, 257.
  12. Lee, J.-Y.; Kim, M.-Y.; Ahn, K.-D. *Bull. Korean Chem. Soc.* **1997**, *18*, 318.
  13. Lee, J.-Y.; Kim, J.-H. *Bull. Korean Chem. Soc.* **1998**, *19*, 851.
-