Product analysis. Naphthylethyl benzenesulfonate was reacted with excess aniline with stirring for more than 15 half-lives at 65.0 ℃ in methanol, and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was treated with column chromatography (silica gel, 10% ethyl acetate/n-hexane). Analysis of the product gave the following results.

1-naphthylethyl anilide. δ_H 3.42 (2H, t, -CH$_2$CH$_2$O-, J = 6.60 Hz), 3.57 (2H, t, -CH$_2$CH$_2$O-, J = 6.60 Hz), 3.74 (1H, br, s, NH), 6.60-8.10 (12H, m, aromatic ring).

1-naphthylethyl methyl ether. δ_H 3.41 (2H, t, -CH$_2$CH$_2$-, J = 7.33 Hz), 3.43 (3H, s, OMe), 3.77 (2H, t, -CH$_2$CH$_2$-, J = 7.33 Hz), 7.37-8.11 (7H, m, aromatic ring).

2-naphthylethyl anilide. δ_H 3.12 (2H, t, -CH$_2$CHO-, J = 6.59), 3.54 (2H, t, -CH$_2$CHO-, J = 6.60 Hz), 3.71 (1H, br, s, NH).

2-naphthylethyl methyl ether. δ_H 3.09 (2H, t, -CH$_2$CH$_2$-, J = 7.33 Hz), 3.41 (3H, s, OMe), 3.73 (2H, t, -CH$_2$CH$_2$-, J = 7.33 Hz), 7.39-7.85 (7H, m, aromatic ring).

C$_6$H$_5$NH$_3^+$-OSO$_2$C$_6$H$_4$CH$_3$. mp 226-228 ℃, δ_H 2.14 (3H, s, CH$_3$), 7.12-7.46 (9H, m, aromatic ring).

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A Novel Synthetic Route to Highly Cross-Linked Poly(alkylvinylether)s. Synthesis and Free Radical Polymerization of a Vinyl Ether Monomer Containing Electron Acceptors in Side Chain

Ju-Yeon Lee*, Hyun-Ju Lee, and Moo-Yong Kim

Department of Chemistry, Inje University, Aebang-dong, Kimhae 621-749, Korea
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p-(2-Vinyloxyethoxy)benzylidenemalononitrile **2** and methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate **3** was prepared by the condensation of *p*-(2-vinyloxyethoxy)benzaldehyde **1** with malononitrile or methyl cyanoacetate, respectively. Vinyl ether monomers **2** and **3** polymerized quantitatively with radical initiators in γ-butyrolactone solution at 65 ℃. The trisubstituted terminal double bond participated in the vinyl polymerization and radical polymerization of **2** and **3** led to swelling polymers **4** and **5** that were not soluble in common solvents due to cross-linking. Under the same polymerization conditions ethyl vinyl ether polymerized well with model compounds of *p*-methoxybenzylidenemalononitrile **6** and methyl *p*-methoxybenzylidenecyanoacetate **7**, respectively, to give 1 : 1 alternating copolymers **8** and **9** in high yields. Polymers **4** and **5** showed a thermal stability up to 300 ℃ without any characteristic T_g peaks in DSC thermograms. Alternating copolymers **8** and **9** were soluble in common solvents such as acetone and DMSO, and the inherent viscosities of the polymers were in the range of 0.36-0.74 dL/g. Films cast from acetone solution were cloudy and tough and T_g values obtained from DSC thermograms were in the range of 59-60 ℃.

Introduction

It is well known that electron-rich alkyl vinyl ethers do not radically homopolymerize, but copolymerize well with vinyl monomers of electron deficient character such as vinylidene cyanide,[1] 2-vinylcyclopropane-1,1-dicarbonitrile,[2] alkyl α-cyanoacrylates,[3~5] alkyl vinyl ketones,[6] maleic anhydride,[7,8] and others by radical initiation. Cycloadditions frequently accompanied these polymerizations and most of the cyclic adducts are cyclobutane compounds. For example, alkyl vinyl ethers readily form cyclobutane adducts with a variety of electron-poor olefins such as tetracyanoethylene[9] and tricyanoethylene.[10] 3,4-Dihydro-2H-pyrans are formed in the reactions of alkyl vinyl ethers with alkyl α-cyanoacrylates, dimethyl dicyanofumarate,[11] and alkyl vinyl ketones.[6] These facile reactions proceed through an electron donor-acceptor (EDA) complex, which generates zwitterion or diradical tetramethylenes as initiating species.[12] It has been reported that 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.[13~19] The question

remains as to whether certain bifunctional monomers composed of both electron-rich alkyl vinyl ether and electron-poor trisubstituted olefin moieties can be polymerized by radical initiation. Thus, it is of intrest to prepare alkyl vinyl ethers containing electron acceptors in the side chain and polymerize by using radical initiators. In this work we prepared two ethyl vinyl ethers containing benzylidenemalononitrile and benzylidenecyanoacetate as electron acceptors in the side chain and investigated their polymerization behaviors. The present report describes the synthesis and radical polymerization of *p*-(2-vinyloxyethoxy)benzylidenemalononitrile **2** and methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate **3**.

Experimental

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 4h at 100 ℃ under vacuum. Acetone was purified by drying with anhydrous potassium carbonate, followed by distillation under reduced pressure. *p*-Hydroxybenzaldehyde was recrystallized from water and dried under vacuum. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. Methyl cyanoacetate was purified by drying with anhydrous sodium sulfate and distilled. Ethyl vinyl ether was dried over sodium metal and distilled, taking the middle fraction. *n*-Butanol was dried with anhydrous magnesium sulfate and distilled under nitrogen. γ-Butyrolactone was dried with anhydrous magnesium sulfate and distilled under nitrogen. Piperidine was dried with calcium hydride and fractionally distilled. α,α'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under reduced pressure at room temperature.

Measurements. IR spectra were taken on a Hitachi Model 260-30 infrared spectrophotometer. ^{1}H NMR spectra were obtained on a Varian EM 360L NMR spectrometer (60 MHz). 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 ℃/min up to 700 ℃ 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.

***p*-(2-Vinyloxyethoxy)benzaldehyde 1.** 4-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 acetone under nitrogen. The mixture was refluxed in an oil bath kept at 60 ℃ for 72 h under nitrogen. The resulting solution was cooled to room temperature, filtered, and the inorganic salts were washed with 50 mL of acetone. Rotary evaporation of acetone gave crude product, which on vacuum distillation yielded 16.3 g (85% yield) of pure product **2**. Bp: 72-74 ℃ (0.2 mmHg). Compound **1** was crystallized in the refrigerator (6 ℃). ^{1}H NMR (acetone-d$_6$) δ 9.89 (1H, s), 7.63-7.99 (2H, m), 6.87-7.28 (2H, m), 6.32-6.73 (1H, q), 4.18-4.48 (2h, m), 3.70-4.17 (4H, m). IR (neat) 3119, 3068, 2940, 2878, 2833 (C-H), 1694, 1603, 1579 (C=C) cm^{-1}.

***p*-(2-Vinyloxyethoxy)benzylidenemalononitrile 2.**
Piperidine (0.13 g, 1.5 mmol) was added to a solution of *p*-(2-vinyloxyethoxy)benzaldehyde **1** (5.38 g, 28 mmol) and malononitrile (1.98 g, 30 mmol) in 50 mL of n-butanol with stirring at 0 ℃ under nitrogen. After stirring for 1 h at 0 ℃, 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 **2**. Mp: 80-82 ℃. ^{1}H NMR (acetone-d$_6$) δ 7.75-8.13 (3H, m), 6.83-7.28 (2H, m), 6.30-6.73 (1H, q), 4.20-4.51 (2H, m), 3.76-4.21 (4H, m). IR (KBr) 3105, 3067, 2938, 2869 (C-H), 2230 (CN), 1628, 1603, 1579 (C=C) cm^{-1}. Anal. Calcd for C$_{14}$H$_{12}$N$_2$O$_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.90; H, 5.08; N, 11.58.

Methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate 3. Piperidine (0.17 g, 2.0 mmol) was added to a solution of *p*-(2-vinyloxyethoxy)benzaldehyde **1** (5.77 g, 30 mmol) and methyl cyanoacetate (2.98 g, 30 mmol) in 45 mL of *n*-butanol with stirring at 0 ℃ under nitrogen. The resulting solution was stirred for 1 h at 0 ℃ and 10 h at room temperature. After cooling in an ice bath, the product was filtered and washed successively with cold *n*-butanol (30 mL), water (50 mL), and cold *n*-butanol (20 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 5.90 g (72% yield) of **3**. Mp: 95-97 ℃. ^{1}H NMR (acetone-d$_6$) δ 7.84-8.25 (3H, m), 6.93-7.29 (2H, m), 6.32-6.75 (1H, q), 4.25-4.50 (2H, m), 3.87-4.24 (4H, m), 3.88 (3H, s). IR (KBr) 3103, 3016, 2957, 2930 (C-H), 2220 (CN), 1726 (C=O), 1618, 1588 (C=C) cm^{-1}. Anal. Calcd for C$_{15}$H$_{15}$NO$_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.85; H, 5.49; N, 5.18.

***p*-Methoxybenzylidenemalononitrile 6.** *p*-Methoxybenzylidenemalononitrile **6** was prepared according to the literature procedure[9] by condensing *p*-anisaldehyde with malononitrile in *n*-butanol in the presence of piperidine as catalyst. **6** : 95% yield. Mp: 114-115 ℃ [lit.[9] 114.5-115 ℃]. ^{1}H NMR (acetone-d$_6$) δ 7.86-8.17 (3H, m), 6.97-7.27 (2H, m), 3.93 (3H, s). IR (KBr) 2215 (CN), 1597, 1563, 1508 (C=C) cm^{-1}.

Methyl *p*-methoxybenzylidenecyanoacetate 7. Methyl *p*-methoxybenzylidenecyanoacetate **7** was prepared according to the literature procedure[9] by condensing *p*-anisaldehyde with methyl cyanoacetate in *n*-butanol in the presence of piperidine as catalyst. **7** : 88% yield. Mp: 98-99 ℃. ^{1}H NMR (acetone-d$_6$) δ 7.92-8.26 (3H, m), 6.95-7.25 (2H, m), 3.91 (3H, s), 3.86 (3H, s). IR (KBr) 2205 (CN), 1714 (C=O), 1574, 1552, 1504 (C=C) cm^{-1}.

Radical polymerization of 2 and 3. A representative radical polymerization procedure (the case of **2**) was as follows: In a polymerization tube were placed 0.48 g (2.0 mmol) of **2**, 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 ℃. After 2 h the polymerization tube was opened and the swelled polymer was poured into 400 mL of methanol. The precipitated polymer was collected and dried under vacum to give 0.48 g (100% yield) of polymer **4**. IR (KBr) 3021 (=C-H), 2928, 2872 (C-H), 2220 (CN), 1604, 1577, 1555, 1508 (C=C) cm^{-1}. Anal. Calcd for (C$_{14}$H$_{12}$N$_2$O$_2$)$_n$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.90; H, 5.12; N, 11.57. Polymer **5**: 100% yield. IR (KBr) 3025 (=C-H), 2950, 2873 (C-H), 2218 (CN), 1735 (C=O), 1605, 1591, 1511 (C=C) cm^{-1}. Anal. Calcd for (C$_{15}$H$_{15}$NO$_4$)$_n$: C, 65.92; H, 5.53; N, 5.13.

Found: C, 65.83; H, 5.45; N, 5.21.

Radical copolymerization of p-methoxybenzylide-nemalononitrile 6 and methyl p-methoxybenzylide-necyanoacetate 7. A representative radical polymeriza-tion procedure was as follows: In a polymerization tube were placed 0.27 g (1.5 mmol) of **6**, 0.11 g (1.5 mmol) of ethyl vinyl ether, 3.0 mg (0.018 mmol) of AIBN, and 1.8 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 viscous polymer solution was pou-red into 400 mL of methanol. The precipitated polymer was collected and reprecipitated from acetone into methanol. Thus obtained white polymer was dried under vacum to give 0.36 g (96% yield) of copolymer **8**; $\eta_{inh}=0.74$ dL/g (c 0.5 g/dL in acetone at 25 °C). ^{1}H NMR (acetone-d$_6$) δ 6.18-7.33 (4H, m), 3.40-4.63 (6H, m), 2.83-3.37 (1H, m), 1.50-2.27 (2H, m), 0.72-1.47 (3H, m). IR (KBr) 2972, 2930, 2895, 2833 (C-H), 2235 (CN), 1610, 1577, 1512 (C=C) cm^{-1}. Anal. Calcd for (C$_{15}$H$_{16}$N$_2$O$_2$)$_n$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70. 20; H, 6.21; N, 11.02. Copolymer **9** : ^{1}H NMR (acetone-d$_6$) δ 6.11-7.50 (4H, m), 2.88-4.17 (9H, m), 2.12-2.85 (1H, m), 1.30-1.93 (2H, m), 0.51-1.27 (3H, m). IR (KBr) 2972, 2950, 2895, 2832 (C-H), 2233 (CN), 1738 (C=O), 1606, 1575, 1508 (C=C) cm^{-1}. Anal. Calcd for (C$_{16}$H$_{19}$NO$_4$)$_n$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.48; H, 6.55; N, 4.92.

Results and Discussion

Syntheses of Monomers 2 and 3. 2-Iodoethyl vinyl ether was prepared by the well known halogen exchange reaction[20] from 2-chloroethyl vinyl ether and sodium iodide, and reacted with 4-hydroxybenaldehyde to yield *p*-(2-vinylo-xyethoxy)benzaldehyde **1**.[21] *p*-(2-Vinyloxyethoxy)benzylidene-malononitrile **2** and methyl *p*-(2-vinyloxyethoxy)benzylidene-cyanoacetate **3** were synthesized by the condensation of **1** with malononitrile or methyl cyanoacetate, respectively.[22,23] The chemical structure of the compounds was confirmed by ^{1}H NMR (Figure 1a), IR (Figure 2a) spectra, and elemental analysis. Monomer **2** and **3** show olefinic protons at δ=6.30-6.73 (q, 1H, vinylic) and δ=6.32-6.75 (q, 1H, vinylic) in their ^{1}H NMR spectra, respectively (Figure 1a). The same mono-mer **3** sample showed strong absorption bands at 2220, 1726, and 1618 cm^{-1} indicating the presence of nitrile, carbonyl, and olefinic groups, respectively as shown in Figure 2(a).

Radical Polymerizations of Monomers 2 and 3. *p*-(2-Vinyloxyethoxy)benzylidenemalononitrile **2** and methyl *p*-
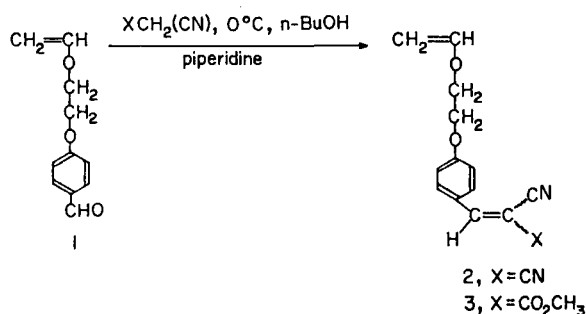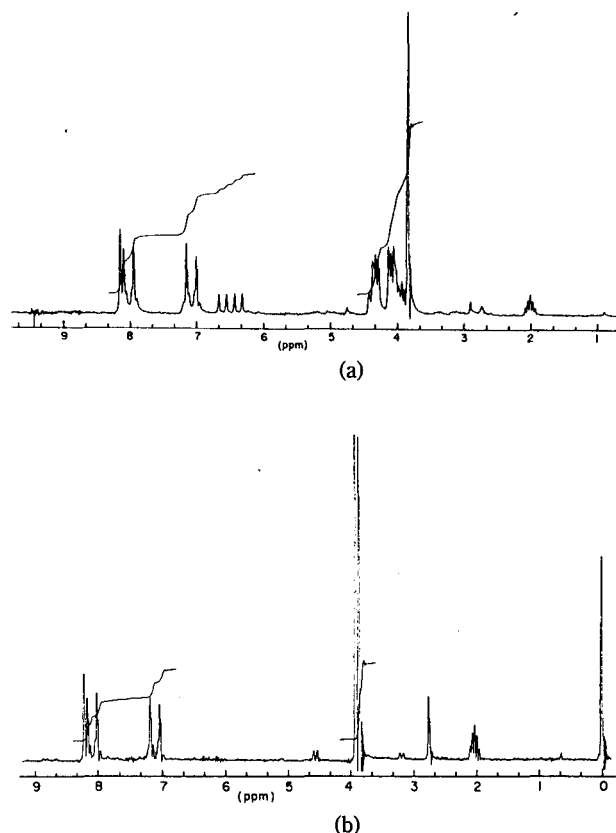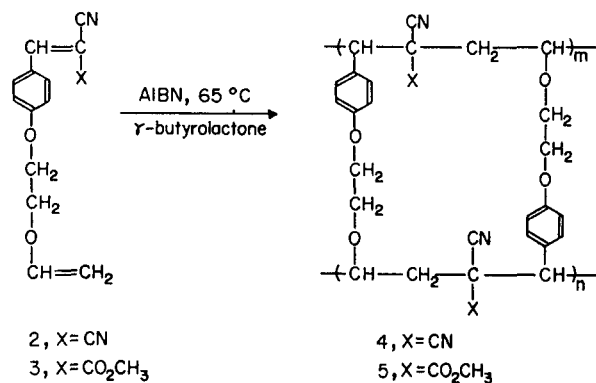

Figure 1. ^{1}H NMR spectra of methyl *p*-(2-vinyloxyethoxy)benzy-lidenecyanoacetate **3** (b) and methyl *p*-methoxybenzylidenecya-noacetate **7** (b) taken in acetone-d$_6$ at room temperature.


Scheme 2.

(2-vinyloxyethoxy)benzylidenecyanoacetate **3** were polymeri-zed in γ-butyrolactone solution at 65 °C with AIBN as a radi-cal initiator to give the polymers **4** and **5**. The polymerization results are summarized in Table 1. Monomers **2** and **3** were quite reactive toward radical initiator and readily polymeri-zed. The polymerizabilities of the monomers toward the ra-dical initiator were very high and in all cases, **2** and **3** poly-merized quantitatively within 3 h. The chemical structures of the polymers were identified by IR spectra (Figure 2b) and elemental analyses. The IR spectra confirmed the che-mical structures, exhibiting all the absorption bands attribu-table to the functional groups comprising the polymers. The

Scheme 1.

Table 1. Free radical polymerizations of **2** and **3** by AIBN in γ-butyrolactone at 65 ℃

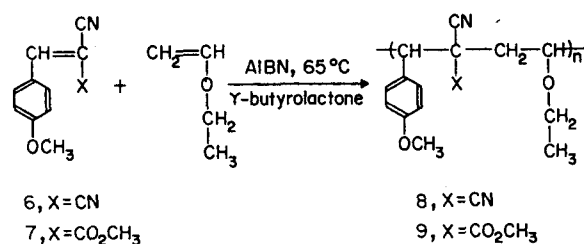| Monomer[a]	Monomer/Solvent (mol/L)	Initiator to Monomer (mol%)	Time (h)	Yield (%)
2	1.00	0.6	2	100
2	0.67	0.8	3	100
2	0.33	1.0	4	100
2	0.25	3.0	4	100
3	1.00	0.6	2	100
3	0.67	0.8	3	100
3	0.33	1.0	4	100
3	0.25	3.0	5	100

[a] **2**=p-(2-Vinyloxyethoxy)benzylidenemalononitrile; **3**=methyl p-(2-vinyloxyethoxy)benzylidenecyanoacetate.
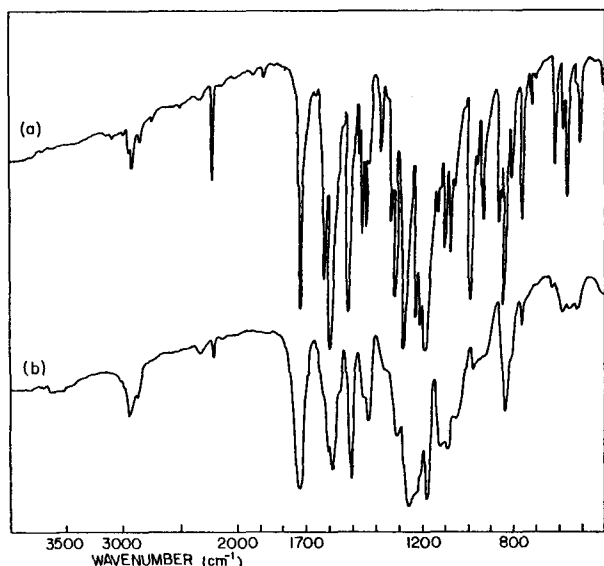
Figure 2. IR specta of monomer **3** (a) and polymer **5** (b).

polymer **5** showed strong absorption bands at 2218, 1735, and 1605 cm^{-1} in its IR spectrum indicating the presence of nitrile, carbonyl, and olefinic groups, respectively as shown in Figure 2(b).

Recently we have reported the vinyl poymerization of the monomers **2** and **3** by cationic initiators without cross-linking.[23] In contrast to that report, the terminal trisubstituted double bond participated in the vinyl polymerization, and radical polymerization of **2** and **3** led only to optically trasparent swelling polymers **4** and **5**. Polymers **4** and **5** were not soluble in any organic solvents due to cross-linking. Thus, we have found a unique polymerization system that lead to highly cross-linked poly(alkyl vinyl ether)s by radical initiators. Furthermore, the striking feature of this particular polymerization system is that it provides an unprecedented radical polymerization of alkyl vinyl ethers which do not homopolymerize radically.

Syntheses and Radical Copolymerizations of Model Compounds 6 and 7. p-Methoxybenzylidenemalono-

Scheme 3.

Table 2. Free radical copolymerizations[a] of **6** and **7** with ethyl vinyl ether by AIBN in γ-butyrolactone at 65 ℃

Monomer[b]	Monomer/Solvent (mol/L)	Initiator to Monomer (mol%)	Time (h)	Yield[c] (%)	η_{inh}[d] (dL/g)
6/EVE, 1/1	1.67	0.6	3	96	0.74
6/EVE, 1/2	1.20	0.8	3	98	0.68
6/EVE, 1/2	1.00	1.0	4	98	0.56
6/EVE, 1/3	1.00	3.0	4	97	0.48
7/EVE, 1/1	1.67	0.6	3	94	0.66
7/EVE, 1/2	1.20	0.8	3	98	0.60
7/EVE, 1/2	1.00	1.0	4	96	0.52
7/EVE, 1/3	1.00	3.0	5	96	0.36

[a] The copolymer compositions were estimated to be 1 : 1 by ^{1}H NMR spectra and elemental analyses. [b] **6**=p-Mthoxybenzylidenemalononitrile; EVE=ethyl vinyl ether; **7**=methyl p-methoxybenzylidenecyanoacetate; [c] The yields were calculated based on 1 : 1 alternating compositions of the resulting copolymers. [d] Inherent viscosity of polymer: 0.5 g/dL in acetone at 25 ℃.

nitrile **6** and methyl p-methoxybenzylidenecyanoacetate **7** were prepared according to the literature procedure[9] by condensing p-anisaldehyde with malononitrile or methyl cyanoacetate in n-butanol in the presence of piperidine. To investigate if the cross-linking was due to the terminal double bond, ethyl vinyl ether was copolymerized by AIBN at 65 ℃ in the presence of p-methoxybenzylidenemalononitrile **6** and methyl p-methoxybenzylidenecyanoacetate **7**, respectively. The resulting copolymers were isolated by reprecipitation from acetone solution into methanol and identified by ^{1}H NMR, IR spectral, and elemental analyses. The copolymerization results are summarized in Table 2.

From the data shown in Table 2 it was found that compounds **6** and **7** copolymerized well with ethyl vinyl ether by AIBN as a free radical initiator to give high molecular weight (η_{inh}=0.74 dL.g) copolymers **8** and **9** in high yields. The yields were calculated based on 1 : 1 alternating compositions of the resulting copolymers. Elemental analyses and spectral data indicated that the polymer obtained in each case was 1 : 1 alternating copolymer of both monomers regardless of the monomer feed ratio. Excess ethyl vinyl ether did not participate in the radical copolymerization as expected. These experimental results are reasonable in view of the fact that p-methoxybenzylidenemalononitrile and methyl p-methoxybenzylidenecyanoacetate are strong electron-acceptor olefins and ethyl vinyl ether is a strong electron-donor momoner,

Free Radical Polymerization of a Vinyl Ether Monomer

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Table 3. Thermal properties of polymers

Polymer	$T_g{}^a$, ℃	Degradation temp, ℃[b]			Residue[b] at
		5%-loss	20%-loss	40%-loss	700 ℃, %
4	—	310	338	430	6.67
5	—	305	340	384	4.62
8	60	271	303	332	8.24
9	59	265	297	335	2.92

[a] Determined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10 ℃/min under nitrogen atmosphere. [b] Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10 ℃/min under nitrogen atmosphere.
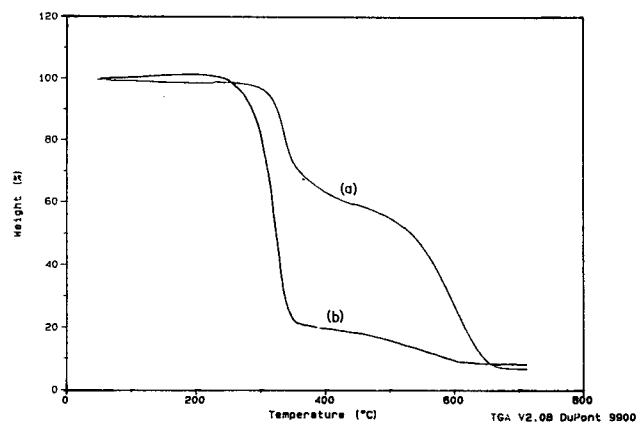
Figure 3. TGA thermograms of cross-linked polymer **4** (a) and 1 : 1 alternating copolymer **8** (b) (10 ℃/min, N₂).

which does not homopolymerize by radical initiators.

Properties of Polymers. The swelling polymers **4** and **5** were not soluble in any organic solvents including DMF and DMSO due to cross-linking. The 1 : 1 alternating copolymers **8** and **9** were white amorphous materials that were soluble in acetone and DMSO, but insoluble in methanol and diethyl ether. The inherent viscosities of polymers **8** and **9** were in the range of 0.36-0.74 dL/g. The polymers **8** and **9** have good film-forming properties and films cast from acetone solution were cloudy and quite tough. The thermal behaviors 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 3. Polymers **4** and **5** showed a good thermal stability and did not decompose below 300 ℃ as shown in Table 3. The polymers show a double phase degradation pattern in their TGA thermograms (Figure 3a), probably due to cross-linking. Cross-linked polymers **4** and **5** showed broad endothermic bands around 75-110 ℃ without any characteristic T_g peaks in DSC thermograms (Figure 4a). Alternating copolymers **8** and **9** showed a thermal stability up to 270 ℃ in TGA thermograms (Figure 3b) and the T_g values of the polymers obtained from DSC thermograms (Figure 4b) were around 59-60 ℃. These T_g values are higher than those for poly(ethyl vinyl ether) (−43 ℃), probably due to the presence of polar pendant group.
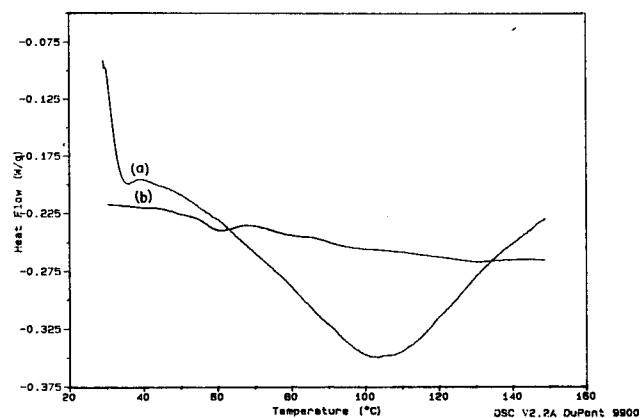
Figure 4. DSC thermograms of cross-linked polymer **4** (a) and 1 : 1 alternating copolymer **8** (b) (10 ℃/min, N₂).

Conclusion

We prepared two vinyl ether monomers **2** and **3** containing strong electron-acceptors in the side chain, and polymerized radically. The terminal trisubstituted double bond participated in the vinyl polymerization and radical polymerization of **2** and **3** led to highly cross-linked polymers quantitatively. This particular polymerization system provides an unprecedented, unique route to highly cross-linked poly(alkyl vinyl ether)s by radical initiators. Model compounds **6** and **7** readily copolymerized with ethyl vinyl ether under the polymerization conditions by radical initiators to give 1 : 1 alternating copolymers **8** and **9** in high yields, which support the high polymerizabilities of monomers **2** and **3** toward radical initiators. We are now exploring further the polymerization of other donor-acceptor systems and the results will be reported later.

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The Equilibrium between Dilatant and Thixotropic Flow Units

Jeong-Hwan Bang, Nam-Jeong Kim[†], Sang-Won Choi[‡], Eung-Ryul Kim[§], and Sang-Joon Hahn[§]

Department of Chemistry, Seonam University, Namwon, Chonbuk 590-170, Korea

[†]*Department of Chemistry, Sahmyook University, Seoul 139-742, Korea*

[§]*Department of Chemical Engineering, Yosu National Fisheries University, Yosu, Chonnam 550-749, Korea*

[§]*Department of Chemistry, Hanyang University, Seoul 133-791, Korea*

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Flow properties of all suspensions are controlled by their flow units. The factors effecting on the flow units are the characteristics of the particle itself (surface properties, particle sizes, particle shapes and etc.), the electrostatic interactions among the particles and the influences of the medium in the suspensions. Here, we studied the transition between the flow units with shear rate which can be added to the above factors. For the concentrated starch-water suspensions, by using the Couette type rotational viscometer, we confirmed that at low shear rate, dilatancy is appeared, but it is transformed to thixotropy with increasing shear rate. In order to explain this fact, we derived the following flow equation, representing the transition from dilatancy to thixotropy with shear rate, by assuming the equilibrium between the flow units.

$$f = \frac{X_1 \beta_1}{\alpha_1} \dot{s}$$

$$+ \frac{1}{1+K \ \exp(c_0\dot{s}^2/RT)} \frac{1-X_1}{\alpha_2} \sinh^{-1}\{(\beta_2)_0 \ \dot{s} \ \exp(c_2\dot{s}^2/RT)\}$$

$$+ \frac{K \ \exp(c_0\dot{s}^2/RT)}{1+K \ \exp(c_0\dot{s}^2/RT)} \frac{1-X_1}{\alpha_3} \sinh^{-1}\{(\beta_3)_0 \ \dot{s} \ \exp(-c_3\dot{s}^2/RT)\}$$

By applying this flow equation to the experimental flow curves for the concentrated starch-water suspensions, the flow parameters were obtained. And, by substituting the obtained flow parameters to the flow equation, the theoretical flow curves were reproduced. Also, Ostwald curve was represented by applying the flow equation, and the applicability for stress relaxation was discussed.

Introduction

Most of the suspensions exhibit complicated non-Newtonian flow, such as thixotropy and dilatancy, by the process of the structural change among the particles with applied shear. These phenomena have been studied by many rheolo-

gists with the interests in views of the industrial applicability and the pure science. Here, the investigations for these phenomena will be reviewed and the objectives in this paper will also be given.

Thixotropy is a common phenomenon, and is important in the paint, cosmetic and food industries. Recently, thixotropy is found in the fields of biochemistry and material science.

[†]All correspondence should be addressed here.