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# Synthesis of highly crosslinked thermally stable poly(vinylethers) by free radical polymerization

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## Summary

2,4-Di-(2’-vinyloxyethoxy)benzylidenemalononitrile (**2a**), methyl 2,4-di-(2’-vinyloxyethoxy)benzylidenecyanoacetate (**2b**), 3,4-di-(2’-vinyloxyethoxy)benzylidenemalononitrile (**4a**), and methyl 3,4-di-(2’-vinyloxyethoxy)benzylidenecyanoacetate (**4b**) were prepared by the condensation of 2,4-di-(2’-vinyloxyethoxy)benzaldehyde (**1**) and 3,4-di-(2’-vinyloxyethoxy)benzaldehyde (**3**) with malononitrile or methyl cyanoacetate, respectively. Trifunctional vinyl ether monomers **2** and **4** were polymerized readily by free radical initiators to give optically transparent swelling poly(vinylethers) **5** and **6**. Polymers **5** and **6** were not soluble in common organic solvents such as acetone and DMSO due to crosslinking. Polymers **5** and **6** showed a thermal stability up to 300°C in DSC thermograms.

## Introduction

Alkyl vinyl ethers do not radically homopolymerize, but copolymerize with electron-deficient monomers such as vinylidene cyanide (1), 2-vinylcyclopropane-1,1-dicarbonitrile (2), alkyl α-cyanoacrylate (3-5), alkyl vinyl ketone (6), maleic anhydride (7-8), and others by radical initiators. These facile reactions proceed through an electron donor-acceptor complex, which generates zwitterion or diradical. tetramethylenes as initiating species (12). 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 captodative olefins with geminal electron-withdrawing and electron-donating groups have a strong tendency to polymerize if appropriate electron-donor and -acceptor combinations in the substituents are chosen (20-21). Bifunctional monomers containing both electron-rich alkyl vinyl ether and electron deficient trisubstituted olefin moieties such as *p*-(2-vinyloxyethoxy)benzylidenemalononitrile and methyl *p*-(2-vinyloxyethoxy)benzylidenecyanoacetate polymerize well by radical initiators (22). The question remains as to whether certain trifunctional monomers having two electron-rich alkyl vinyl ethers and a electron-poor trisubstituted olefin moieties can be polymerized by radical initiation. To explore these problems, we have prepared four trifunctional compounds 2,4-di-(2’-vinyloxy-ethoxy)benzylidenemalononitrile (**2a**), methyl 2,4-di-(2’-vinyloxyethoxy)benzylidene cyanoacetate

(**2b**), 3,4-di-(2'-vinyloxyethoxy)benzylidenemalononitrile (**4a**), and methyl 3,4-di-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**4b**), and investigated their radical polymerization behaviors. We now report the results of the initial phase of the work.

## 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 under vacuum. Sodium iodide was dried for 4h at 100°C under vacuum. 2,4-Dihydroxybenzaldehyde and 3,4-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*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure. Piperidine was dried with calcium hydride and fractionally distilled. $\alpha,\alpha'$-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under reduced pressure at room temperature. 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 (24).

*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.

*2,4-Di-(2'-vinyloxyethoxy)benzaldehyde* (**1**)

2,4-Dihydroxybenzaldehyde (13.8 g, 0.10 mol), anhydrous potassium carbonate (82.9 g, 0.60 mol), and 2-iodoethyl vinyl ether (49.5 g, 0.25 mol) were dissolved in 400 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80°C for 15 h 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 *n*-butanol yielded 25.0 g (90% yield) of pure product **1.** Mp=68-69°C. $^1$H NMR ($CDCl_3$) δ 4.03-4.35 (m, 12H, 2 $CH_2$=, 2 -O-$CH_2$-$CH_2$-O-), 6.50-6.62 (m, 4H, 2 =CH-O-, aromatic), 7.82-7.86 (d, 1H, aromatic), 10.35 (s, 1H, -CHO). IR (KBr) 3100, 3082 (w, =C-H), 2954, 2875 (m, C-H), 1674 (vs, C=O), 1615 (vs, C=C), 1575 (s, C=C) cm-1.

*2,4-Di-(2'-vinyloxyethoxy)benzylidenemalononitrile* (**2a**)

Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,4-di-(2'-vinyloxyethoxy)benzaldehyde **1** (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 9.01g (92% yield) of **2a**. Mp=80-81°C. $^1$H NMR ($CDCl_3$) δ 4.02-4.40 (m, 12H, 2 $CH_2$=, 2 -O-$CH_2$-$CH_2$-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) $cm^{-1}$. Anal. Calcd for $C_{18}H_{18}N_2O_4$: 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* (**2b**)

Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,4-di-(2'-vinyloxyethoxy)benzaldehyde **1** (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 9.49g (88% yield) of **2b**. Mp=96-97°C. $^1$H NMR ($CDCl_3$) δ 3.89 (s, 3H, -$CO_2CH_3$), 4.02-4.34 (m, 12H, 2 $CH_2$=, 2 -O-$CH_2$-$CH_2$-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) $cm^{-1}$. Anal. Calcd for $C_{19}H_{21}NO_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.62; H, 5.82; N, 3.83.

*3,4-Di-(2'-vinyloxyethoxy)benzaldehyde* (**3**)

3,4-Dihydroxybenzaldehyde (13.8 g, 0.10 mol), anhydrous potassium carbonate (82.9 g, 0.60 mol), and 2-iodoethyl vinyl ether (49.5 g, 0.25 mol) were dissolved in 400 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80°C for 15 h 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 *n*-butanol yielded 22.8 g (82% yield) of pure product **3.** Mp=56-57°C. $^1$H NMR ($CDCl_3$) δ 4.04-4.36 (m, 12H, 2 $CH_2$=, 2 -O-$CH_2$-$CH_2$-O-), 6.50-6.62 (q, 2H, 2 =CH-O-), 7.01-7.06 (d, 1H, aromatic), 7.45-7.52 (d, 2H, aromatic), 9.86 (s, 1H, -CHO). IR (KBr) 3099, 3080 (w, =C-H), 2952, 2872 (m, C-H), 1672 (vs, C=O), 1612 (vs, C=C), 1575 (s, C=C) $cm^{-1}$.

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

Piperidine (0.13 g, 1.5 mmol) was added to a solution of 3,4-di-(2'-vinyloxyethoxy)benzaldehyde **3** (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 5.55g (85% yield) of **4a**. Mp=64-65°C. $^1$H NMR ($CDCl_3$) δ 4.02-4.38 (m, 12H, 2 $CH_2$=, 2 -O-$CH_2$-$CH_2$-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) $cm^{-1}$. Anal. Calcd for $C_{18}H_{18}N_2O_4$: 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* (**4b**)

Piperidine (0.085 g, 1.0 mmol) was added to a solution of 3,4-di-(2'-vinyloxyethoxy)benzaldehyde **3** (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 6.18g (86% yield) of **4b**. Mp=86-87°C. $^1$H NMR ($CDCl_3$) $\delta$ 3.92 (s, 3H, $-CO_2CH_3$), 4.02-4.38 (m, 12H, 2 $CH_2$=, 2 $-O-CH_2-CH_2-O-$), 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) $cm^{-1}$. Anal. Calcd for $C_{19}H_{21}NO_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.62; H, 5.84; N, 3.82.

*Radical polymerizations of monomers* **2** *and* **4**

A representative radical polymerization procedure (the case of **2b**) was as follows: In a polymerization tube were placed 0.72 g (2.0 mmol) of **2b**, 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 0.68 g (94% yield) of polymer **5b**. IR (KBr) 2965, 2941, 2889 (m, C-H), 2224 (s, CN), 1616, 1561 (s, C=C), 1508 (vs, C=C) $cm^{-1}$. Anal. Calcd for $(C_{18}H_{18}N_2O_4)_n$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.35; H, 5.65; N, 8.51. **5a**: IR (KBr) 2956, 2934, 2881 (m, C-H), 2222 (w, CN), 1727 (vs, C=O), 1611, 1580, 1508 (vs, C=C) $cm^{-1}$. Anal. Calcd for $(C_{19}H_{21}NO_6)_n$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.61; H, 5.81; N, 3.83. **6a**: IR (KBr) 2936, 2887 (m, C-H), 2228 (s, CN), 1621, (s, C=C), 1583, 1517, 1508 (vs, C=C) $cm^{-1}$. Anal. Calcd for $(C_{18}H_{18}N_2O_4)_n$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.36; H, 5.66; N, 8.64. **6b**: IR (KBr) 2941, 2876 (m, C-H), 2222 (w, CN), 1730 (vs, C=O), 1620 (m, C=C), 1516, 1508 (vs, C=C) $cm^{-1}$. Anal. Calcd for $(C_{19}H_{21}NO_6)_n$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.62; H, 5.84; N, 3.97.

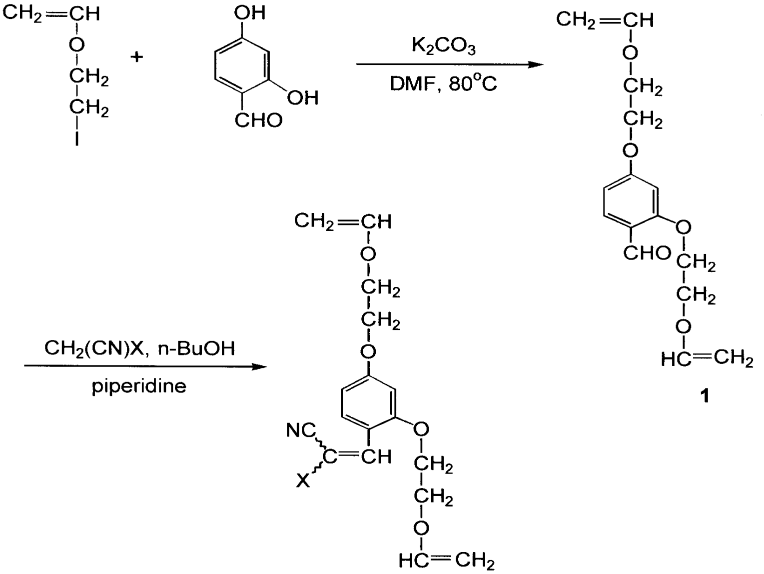
## Results and Discussion

*Synthesis of trifunctional monomers* **2** *and* **4**

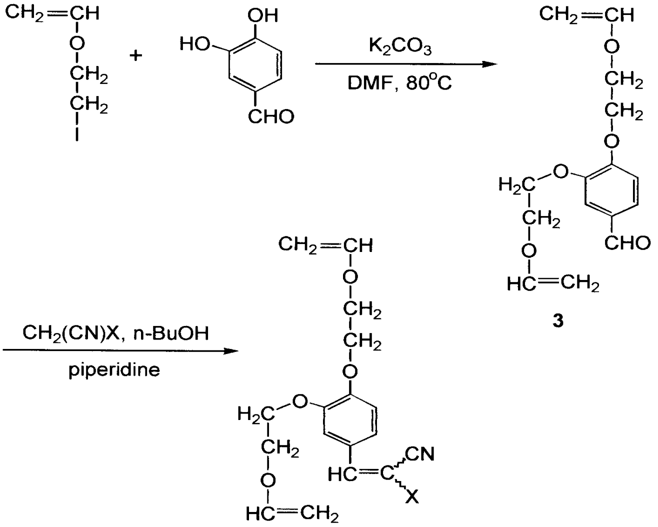
2,4-Di-(2’-vinyloxyethoxy)benzaldehyde (**1**) and 3,4-di-(2’-vinyloxyethoxy)benzaldehyde (**3**) were prepared by reaction of 2-iodoethyl vinyl ether with 2,4-dihydroxybenaldehyde and 3,4-dihydroxybenzaldehyde. Trifunctional monomers 2,4-di-(2’-vinyloxyethoxy)benzylidenemalononitrile (**2a**), methyl 2,4-di-(2’vinyloxyethoxy) benzylidenecyanoacetate (**2b**), 3,4-di-(2’-vinyloxyethoxy)benzylidenemalononitrile (**4a**), and methyl 3,4-di-(2’-vinyloxyethoxy)benzylidenecyanoacetate (**4b**) were prepared by the condensations of **1** and **3** with malononitrile or methyl cyanoacetate, respectively (25). The chemical structure of the compounds was identified by proton-NMR, IR spectra, and elemental analysis. All the analytical data confirmed the expected chemical structure.

*Free radical polymerizations of monomers* **2** *and* **4**

Monomers **2** and **4** were polymerized in γ-butyrolactone solution at 65°C with AIBN as radical initiator to give polymers **5** and **6**. The polymerization results are summarized in Table 1. Monomers **2** and **4b** were quite reactive toward radical initiator and polymerized readily with high yields, except **4a**. Monomer **4a** gave rather lower polymer yield. The chemical structures of the polymers were identified by IR

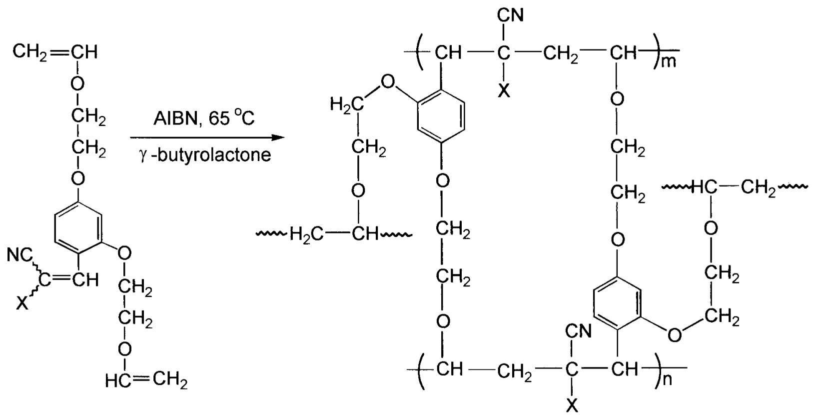


**2a**, X =CN
**2b**, X =CO$_2$CH$_3$



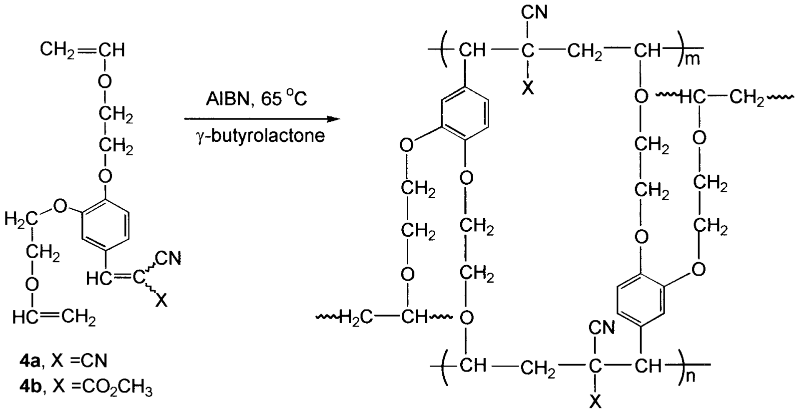
**4a**, X =CN
**4b**, X =CO$_2$CH$_3$

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 **2** and **4** led only to optically trasparent swelling polymers **5** and **6**. Polymers **5** and **6** were not soluble in any organic solvents due to cross-linking. Thus, we have found a another polymerization system that lead to highly cross-linked poly(alkylvinylether)s by free radical initiators.



**2a**, X =CN
**2b**, X =CO$_2$CH$_3$

**5a**, X =CN
**5b**, X =CO$_2$CH$_3$



**4a**, X =CN
**4b**, X =CO$_2$CH$_3$

**6a**, X =CN
**6b**, X =CO$_2$CH$_3$

Table 1. Free radical polymerizations of **2** and **4** by AIBN in γ-butyrolactone at 65°C

| Monomer | Monomer/Solvent (mol/1 L) | Initiator to Monomer (mol%) | Time (h) | Yield (%) |
|---|---|---|---|---|
| **2a** | 1.00 | 0.6 | 3 | 75 |
| **2a** | 0.67 | 1.0 | 8 | 86 |
| **2b** | 1.00 | 0.6 | 3 | 94 |
| **2b** | 0.67 | 0.8 | 6 | 96 |
| **4a** | 1.00 | 0.6 | 10 | 56 |
| **4a** | 0.67 | 1.0 | 12 | 65 |
| **4b** | 1.00 | 0.6 | 5 | 88 |
| **4b** | 0.67 | 0.8 | 10 | 90 |

Previously we have prepared p-substituted bifunctional vinyl ethers containing electron acceptors and polymerized them with radical initiators to give highly cross-linked poly(vinyl ethers) quantitatively (22). Sterically hindered 3,5-dimethoxy-4-(2-vinyloxyethoxy)benzylidenemalononitrile did not homopolymerized by radical initiators (23), but it copolymerized radically with ethyl vinyl ether to give cross-linked copolymers. Radical polymerizabilities of trifunctional vinyl ether compounds **2** and **4** are rather lower than those of p-substituted bifunctional vinyl ether compounds, probably due to the steric hindrance. Compounds **2** and **4** also polymerized well by cationic initiators such as boron trifluoride to give crosslinked poly(vinylether)s having benzylidenemalononitrile and benzylidenecyanoacetate in the side chain, which is presumably effective NLO-chromophore for second order nonlinear optical applications.

### *Properties of polymers* **5** *and* **6**

The polymers **5** and **6** 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** and **6** 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 **5** and **6** showed a good thermal stability and did not decompose below 300°C as shown in Table 3. The polymers show a double phase degradation pattern in their TGA thermograms, probably due to cross-linking. Cross-linked polymers **5** and **6** showed broad endothermic bands around 80-200°C without any characteristic $T_g$ peaks in DSC thermograms.

Table 2. Thermal properties of polymers **5** and **6**

| Polymer | $T_g^a$, °C | Degradation temp, °C$^b$ | | | Residue$^b$ at 700 °C, % |
|---|---|---|---|---|---|
| | | 5%-loss | 20%-loss | 40%-loss | |
| **5a** | - | 285 | 341 | 375 | 8.0 |
| **5b** | - | 324 | 356 | 381 | 9.9 |
| **6a** | - | 333 | 356 | 387 | 26.7 |
| **6b** | - | 291 | 335 | 358 | 3.8 |

[a] Determined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10°C/min under nitrogen atmosphere.

[b] Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

### *Conclusion*

We prepared four trifunctional monomers **2** and **4** having two electron-rich vinyl ether groups and a electron-poor benzylidenemalononitrile and benzylidenecyanoacetate. The trisubstituted terminal double bond participated in the vinyl polymerization and radical polymerization of **2** and **4** led to optically trasparent swelling polymers **5** and **6** in high yields. Polymerizabilities of trifunctional vinyl ether compounds **2** and **4** toward radical initiators were rather lower than those of p-disubstituted bifunctional derivatives due to the steric hindrance. Polymers **5** and **6** were not soluble in any organic solvents due to cross-linking. We are now exploring further the polymerization of other donor-acceptor systems and the results will be reported elsewhere.

## Acknowledgement

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## References

1. Stille JK, Chung, DC (1975) Macromolecules 8: 114
2. Cho I, Lee JY (1980) J Polym Sci Polym Lett Ed 18: 639
3. Cho I, Lee JY (1983) Macromolecules 16: 150
4. Cho I, Lee JY (1983) Macromolecules 16: 1245
5. Lee JY, Cho I (1987) J Polym Sci Part A Polym Chem Ed 25: 3089
6. Cho I, Lee JY (1983) J Polym Sci Polym Lett Ed 21: 389
7. Florianczyk T, Sullivan C, Janovic Z, Vogl O (1981) Polym Bull 5: 521
8. Xi F, Bassett W, Vogl O (1983) J Polym Sci Polym Chem Ed 21: 891
9. Williams JK, Wiley DW, McKusick BC (1962) J Am Chem Soc 84: 2210
10. Hall Jr HK, Ykman P (1975) J Am Chem Soc 97: 800
11. Hall Jr HK, Rasoul HAA, Gillard M, Abdelkader M, Nogues P, Sentman RC (1982) Tetrahedron Lett 23: 603
12. Hall Jr HK, Padias AB (1990) Acc Chem Res 23: 3
13. Kresel M, Garbratski U, Kohn DH (1964) J Polym Sci A 2: 105
14. Gilath A, Ronel SH, Shmueli M, Kohn DH (1970) J Appl Polym Sci 14: 1491
15. Ronel SH, Shmueli M, Kohn DH (1969) J Polym Sci A-1 7: 2209
16. Lieberson A, Kohn DH (1974) J Polym Sci Polym Chem Ed 12: 2435
17. Kharas G, Kohn DH (1983) J Polym Sci Polym Chem Ed 21: 1457
18. Kharas G, Kohn DH (1984) J Polym Sci Polym Chem Ed 22: 583
19. Angelorici MM, Kohn DH (1990) J Appl Polym Sci 40: 485
20. Tanaka H (1993) Trends Polym Sci 32: 361
21. Tanaka H (1996) Trends Polym Sci 4: 106
22. Lee JY (1996) Polym Bull 36: 525
23. Lee JY, Lee HJ, Kim MY (1997) Polym Bull 38: 27
24. Moore AHF (1963) Org Syn Coll Vol 4: 84
25. Corson BB, Stoughton RW (1928) J Am Chem Soc 50: 2825