

3,5-디메톡시-4-옥시벤질리덴말로노니트릴과
3,5-디메톡시-4-옥시벤질리덴시아노아세테이트가 측쇄에 포함된
에틸 비닐 에테르의 합성 및 양이온 중합

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Synthesis and Cationic Polymerization of Ethyl Vinyl Ethers
Containing 3,5-Dimethoxy-4-oxybenzylidenemalononitrile and Methyl
3,5-Dimethoxy-4-oxybenzylidenecyanoacetate in the Side Chain

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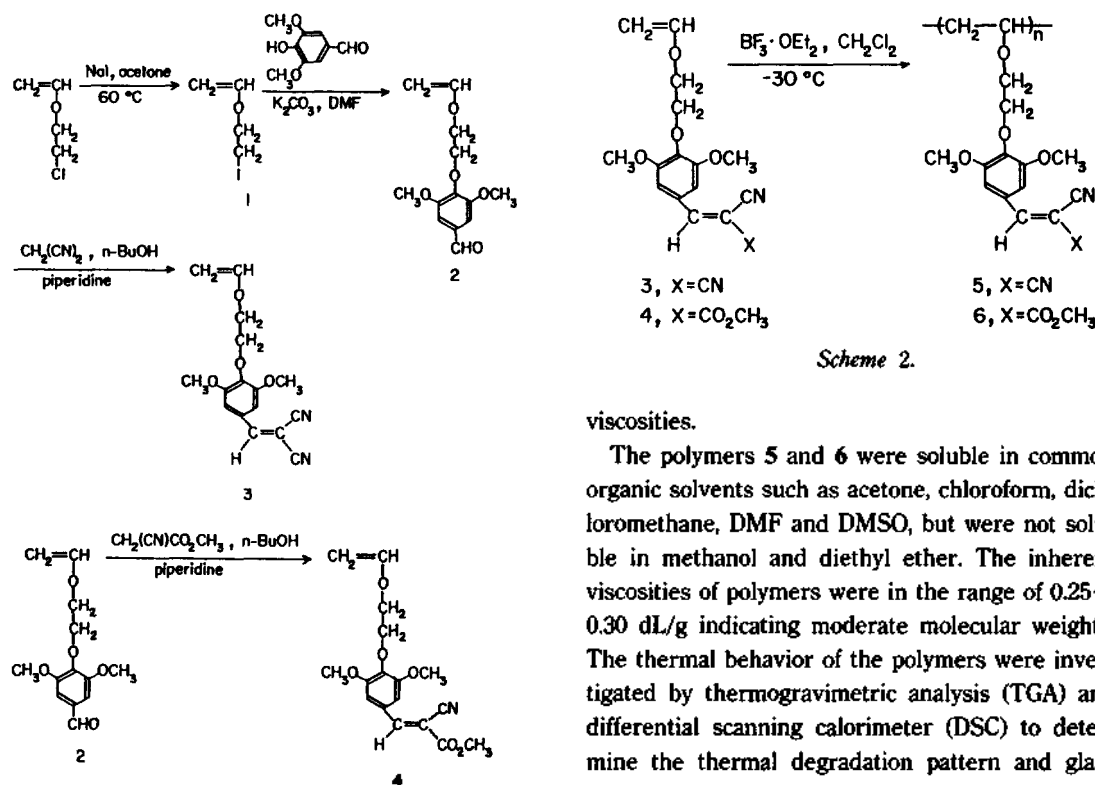
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Functional polymers of nonlinear optical (NLO) activity have long been the subject of curiosity and have caused recent interest.¹⁻⁵ It is well known that organic and polymeric materials with highly dipolar electronic systems exhibit NLO properties. Compared to other organic and inorganic substances, NLO polymers offer many advantages such as high nonlinear optical activity, light weight, chemical resistance, and good processability. A potentially NLO polymer must contain a highly polarizable π -electronic systems and these polymers have to be mechanically very strong. There are tremendous challenges in designing and synthesis of polymers of large NLO effects. Various polymers with the NLO-phores in the side chain such as poly(meth)acrylates⁶⁻¹² and polystyrene¹³ were reported. Polyesters,¹⁴⁻¹⁸ polyurethanes,¹⁹ polyamides,^{20,21} and poly(phenyleneethynyls)²² containing the chromophoric main chain were also prepared. Dix and his coworkers²³ prepared poly(ethyl vinyl ethers) partly grafted with pendant 4'-amino-4-nitroazobenzene by the reaction of poly(2-chloroethyl vinyl ether) with azo-dyes. However, examples of polyalkyl vinyl ethers with the chromophoric side chain prepared

directly by the polymerization of monomeric alkyl vinyl ethers are rare in the literature. Recently we have cleanly prepared²⁴ poly(vinyl ethers) containing the NLO-phore 4'-oxy-4-nitrostilbene in the side chain by cationic polymerization of the corresponding monomer.

This work is now extended with the synthesis and characterization of another poly(ethyl vinyl ethers) containing the NLO-phores 3,5-dimethoxy-4-oxybenzylidenemalononitrile and methyl 3,5-dimethoxy-4-oxybenzylidenecyanoacetate in the side chain. The present report describes the synthesis and cationic polymerization of 3,5-dimethoxy-4-(2'-vinylxyethoxy)benzylidenemalononitrile **3** and methyl 3,5-dimethoxy-4-(2'-vinylxyethoxy)benzylidenecyanoacetate **4**.

2-Iodoethyl vinyl ether **1** was prepared by the well known halogen exchange reaction²⁵ from 2-chloroethyl vinyl ether and sodium iodide, and reacted¹⁸ with 3,5-dimethoxy-4-hydroxybenzaldehyde to yield 3,5-dimethoxy-4-(2'-vinylxyethoxy)benzaldehyde **2**. 3,5-Dimethoxy-4-(2'-vinylxyethoxy)benzylidenemalononitrile **3** and methyl 3,5-dimethoxy-4-(2'-vinylxyethoxy)benzylidenecyanoacetate **4** were synthesized by the condensation



Scheme 2.

viscosities.

The polymers **5** and **6** were soluble in common organic solvents such as acetone, chloroform, dichloromethane, DMF and DMSO, but were not soluble in methanol and diethyl ether. The inherent viscosities of polymers were in the range of 0.25~0.30 dL/g indicating moderate molecular weights. 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. Polymer **6** showed a good thermal stability and was not decomposed below 280 °C, which is acceptable for NLO device application. T_g values of the polymers by DSC thermograms were around 53~59 °C. These T_g values are higher than those for poly(ethyl vinyl ether) (-43 °C), probably due to the presence of polar pendant group. Solution-cast films were clear and brittle, which could be due to the rather low molecular weight and/or high concentration of dipole moment.

In summary, we prepared clean poly(ethyl vinyl ethers) **5** and **6** containing the NLO phores 3,5-dimethoxy-4-oxybenzylidenemalononitrile or methyl 3,5-dimethoxy-4-oxybenzylidenecyanoacetate in the side chain by the cationic polymerization of the vinyl monomers **3** and **4**, respectively. The resulting substituted poly(ethyl vinyl ethers) **5** and **6** were soluble in common organic solvents except methanol and diethyl ether. Polymer **6** showed a good thermal stability, which is acceptable for electrooptic device application. Polymers **5** and **6** sho-

of **2** with malononitrile and methyl cyanoacetate, respectively.²⁶ The chemical structure of the compounds was confirmed by ¹H NMR, IR spectra, and elemental analyses. Spectral data indicated that **4** was a mixture of the *cis*- and *trans*-isomer.

3,5-Dimethoxy-4-(2'-vinylxyethoxy)benzylidenemalononitrile **3** and methyl 3,5-dimethoxy-4-(2'-vinylxyethoxy)benzylidenecyanoacetate **4** were polymerized in solution at -30 °C with boron trifluoride etherate as cationic initiator to obtain the polymers **5** and **6**. The polymerization results are summarized in Table 1.

Monomers **3** and **4** were quite reactive toward cationic initiator and polymerized readily at low temperature. The chemical structures of the polymers were identified by ¹H NMR, IR spectra, and elemental analyses. All the spectral data confirmed the expected polymer structure. In most cases, conversions were quite high, but the molecular weights were rather low as indicated by the inherent

Table 1. Cationic polymerization of 3 and 4 under various conditions^a

Monomer	Solvent	M/S ^b (mol/L)	Initiator ^c (mol-%)	Temp. (°C)	Time (h)	Conversion (%)	η_{inh}^d (dL/g)
3	CH ₂ Cl ₂	0.67	1.0	-30	20	88	0.25
3	CH ₂ Cl ₂	0.57	1.2	-60	16	85	0.26
3	C ₆ H ₅ CH ₃	0.67	1.0	-30	20	90	0.30
3	C ₆ H ₅ CH ₃	0.80	1.2	-60	12	86	0.28
4	CH ₂ Cl ₂	0.67	1.0	-30	24	88	0.30
4	CH ₂ Cl ₂	0.57	1.5	-60	20	90	0.24
4	C ₆ H ₅ CH ₃	0.67	1.0	-30	20	86	0.28
4	C ₆ H ₅ CH ₃	0.80	1.5	-60	24	90	0.25

^a3 = 3,5-dimethoxy-4-(2'-vinylxyethoxy)benzylidenemalononitrile. 4 = methyl 3,5-dimethoxy-4-(2'-vinylxyethoxy)benzylidenecyanoacetate. ^bM/S as a ratio of monomer to solvent by mol/L. ^cMol-% of boron trifluoride etherate to monomer. ^dInherent viscosity of a polymer with concentration of 0.5 g/dL in acetone at 25 °C.

Table 2. Thermal properties of polymer 5 and 6

Polymer	T_g^a , °C	Degradation temp, °C ^b			Residue ^b at 700 °C, %
		5% -loss	20% -loss	40% -loss	
5	53	244	297	330	0.6
6	59	286	340	370	2.0

^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.

wed sharp T_g peaks around 53~59 °C in their DSC thermograms. Copolymerization with other monomers to elevate the T_g values and measurements of NLO activity are in progress, and the results will be reported later.

EXPERIMENTAL

Materials. The reagent grade chemicals were purified by distillation or recrystallization before use. Dichloromethane washed with concentrated sulfuric acid and then with water, dried with anhydrous calcium chloride, refluxed with calcium hydride, and distilled under nitrogen before use. Toluene was washed with cold concentrated sulfuric acid and then with water, aqueous 5% sodium bicarbonate, again with water, dried with anhydrous calcium sulfate, refluxed with phosphorus pento-

xide, and distilled. Boron trifluoride etherate was treated with a small amount of diethyl ether and distilled under reduced pressure.

2-Iodoethyl vinyl ether (1). Anhydrous sodium iodide (45 g, 0.30 mol) was dissolved in 320 mL of dry acetone for 1 h with stirring. 2-Chloroethyl vinyl ether (25.0 g, 0.23 mol) was added to the mixture, and refluxed for 25 h with stirring. Sodium chloride was filtered off and the filtrate was concentrated by distillation of the solvent. The residue was poured into 260 mL of water and washed successively with 55 mL of 10% sodium bisulfite solution, 55 mL of 5% sodium bicarbonate, and 30 mL of water. It was dried with anhydrous magnesium sulfate (1.8 g) and fractionated under reduced pressure to give 32.8 g (72%, yield) of 1. bp 50~52 °C (20 mmHg). ¹H NMR (CDCl₂) δ 6.22~6.57 (q, 1H, =CH-O-), 3.50~4.37(m, 4H, CH₂= and -O-CH₂-), 2.82~3.47 (t, 2H, -CH₂-I). IR (neat) 3105, 3034, 2960, 2922, 2845 (s, C-H), 1635, 1612 (vs, C=C) cm⁻¹.

3,5-Dimethoxy-4-(2'-vinylxyethoxy)benzaldehyde (2). 3,5-Dimethoxy-4-hydroxybenzaldehyde (7.29 g, 0.04 mol), anhydrous potassium carbonate (16.59 g, 0.12 mol), and 2-iodoethyl vinyl ether (11.88 g, 0.06 mol) were dissolved in 70 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80 °C for 6 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 the solvent under reduced pressure gave crude product, which was recrystallized from *n*-butanol yielded 9.59 g (95% yield) of pure product **2**. mp 44–45 °C. ¹H NMR (acetone-*d*₆) δ 3.85 (s, 2 CH₃O-), 3.86~4.38(m, CH₂= and -O-CH₂-CH₂-O-), 6.18~6.67 (q, =CH-O-), 7.13 (s, aromatic), 9.78 (s, -CH₂=O). IR(KBr) 3013 (m, =C-H), 2975, 2955, 2940, 2836 (s, C-H), 1677, 1677 (vs, C=O), 1627, 1578 (vs, C=C) cm⁻¹. Anal. Calcd for C₁₃H₁₆O₅: C, 61.90; H, 6.39. Found: C, 61.84; H, 6.36.

3,5-Dimethoxy-4-(2'-vinylxyethoxy)benzylidenemalononitrile (3). Piperidine (0.05 g, 0.6 mmol) was added to a solution of 3,5-dimethoxy-4-(2'-vinylxyethoxy)benzaldehyde **2** (2.52 g, 0.010 mol) and malononitrile (0.79 g, 0.012 mol) in 30 mL of *n*-butanol with stirring at 0 °C under nitrogen. After stirring for 3 h at 0 °C, the product was filtered and washed with successively with cold *n*-butanol (30 mL), water (150 mL), and cold *n*-butanol (20 mL). The obtained pale yellow product was recrystallized from ethanol to give 2.76 g (92% yield) of pure product **3**. mp 117~118 °C. ¹H NMR (acetone-*d*₆) δ 3.83 (s, 2 CH₃O-), 3.84~4.43 (m, CH₂= and -O-CH₂-CH₂-O-), 6.23~6.71 (q, =CH-O-), 7.34 (s, aromatic), 8.08 (s, Ph-CH=). IR (KBr) 3112, 3025 (w, =C-H), 2960, 2944, 2918 (m, C-H), 2228 (s, CN), 1655, 1614, 1585, 1573 (vs, C=C) cm⁻¹. Anal. Calcd for C₁₆H₁₆N₂O₄: C, 63.99; H, 5.37; N, 9.33. Found: C, 69.92; H 5.42; N, 9.38.

Methyl 3,5-dimethoxy-4-(2'-vinylxyethoxy)benzylidenecyanoacetate (4). Piperidine (0.10 g, 1.2 mmol) was added to a solution of 3,5-dimethoxy-4-(2'-vinylxyethoxy)benzaldehyde **2** (5.05 g, 0.020 mol) and methyl cyanoacetate (2.38 g, 0.024 mol) in 35 mL of *n*-butanol with stirring at 0 °C under nitrogen. The resulting solution was stirred for 3 h at 0 °C under nitrogen. After cooling in an ice bath, the product was filtered and washed with successively with cold *n*-butanol (30 mL), water (150 mL), and cold *n*-butanol (20 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 3.00 g (90% yield) of pure pro-

duct **4**. mp 109~110 °C. ¹H NMR (acetone-*d*₆) δ 3.82 (s, 3 CH₃O-), 3.84~4.35(m, CH₂= and -O-CH₂-CH₂-O-), 6.19~6.63 (m, =CH-O-) 7.37 (s, aromatic), 8.10 (s, Ph-CH=). IR (KBr) 3110, 3024 (m, =C-H), 2958, 2940 (m, C-H), 2220 (s, CN), 1724 (vs, C=O), 1642, 1604, 1577 (vs, C=C) cm⁻¹. Anal. Calcd for C₁₇H₁₉NO₆: C, 61.25; H, 5.75; N, 4.20. Found: C, 61.30; H, 5.72; N, 4.26.

Cationic polymerization of 3 and 4. A representative cationic polymerization procedure (the case of **3**) was as follows: A solution of **3** (0.60 g, 2.0 mmol) in dichloromethane (3.0 mL) was placed in a rubber septum stopper capped glass ampule under nitrogen. The resulting solution was flushed with nitrogen for 20 min. The ampule was then placed in an ethanol-acetone bath kept at -30 °C under nitrogen, and 0.0023 mL (0.020 mmol) of boron trifluoride etherate was added to the solution. After 10 h the ampule was taken out and the polymerization mixture was poured into 300 mL of diethyl ether. The precipitated polymer was collected and reprecipitated from acetone into diethyl ether to give 0.53 g (88% conversion) of polymer **5**; η_{inh} = 0.25 dL/g (c 0.5 g/dL in acetone at 25 °C). ¹H NMR (acetone-*d*₆) δ 0.90~2.03 (m, -CH₂-), 3.37~4.37 (m, -CH-O-CH₂-CH₂-O- and 2 CH₃O-), 7.08~7.41 (m, aromatic), 7.83~8.10 (m, Ph-CH=). IR (KBr) 3010 (m, =C-H), 2970, 2942 (m, C-H), 2230 (s, CN), 1588, 1575 (vs, C=C) cm⁻¹. Anal. Calcd for (C₁₆H₁₆N₂O₄)_n: C, 63.99; H, 5.37; N, 9. Found: C, 63.92; H, 5.33; N, 9.38. **6**: ¹H NMR (acetone-*d*₆) δ 0.90~2.04 (m, -CH₂-), 3.42~4.39 (m, -CH-O-CH₂-O-) and 3 CH₃O-), 7.08~7.41 (m, aromatic), 7.83~8.10 (m, Ph-CH=). IR (KBr) 3010 (m, =C-H), 2950, (s, C-H), 2223 (m, CN), 1728 (s, C=O), 1607, 1581 (vs, C=C) cm⁻¹. Anal. Calcd for (C₁₇H₁₉NO₆)_n: C, 61.25; H, 5.75; N, 4.20. Found: C, 61.33; H, 5.71; N, 4.24.

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