

벤질리덴이미노페닐기를 포함하는 비닐 에테르의 합성 및 양이온 중합

李科淵* · 李賢珠 · 金京娥

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Synthesis and Cationic Polymerization of Vinyl Ethers Containing Benzylideneiminophenyl Groups

Ju-Yeon Lee*, Hyun-Ju Lee, and Kyoung-Ah Kim

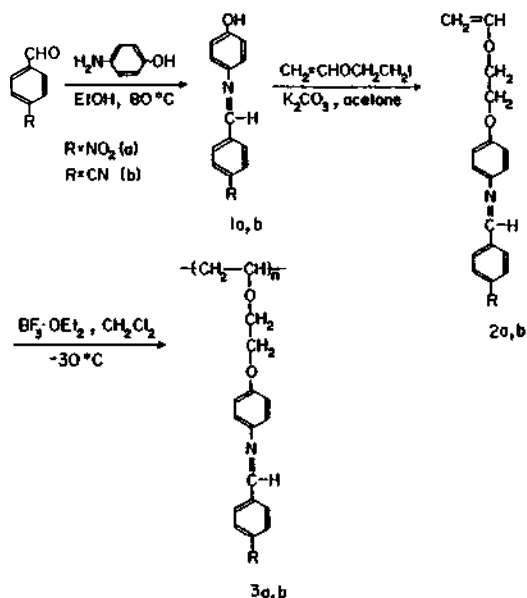
Department of Chemistry, Inje University, Kimhae 621-749, Korea

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Functional polymers with nonlinear optical (NLO) properties have long been the subject of curiosity and are currently receiving considerable interest.¹ It is well known that organic and polymeric materials with highly dipolar electronic systems exhibit NLO properties. Compared to them, NLO polymers offer many advantages such as high nonlinear optical activity, light weight, chemical resistance, and good processability. A potential 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)acrylates² and polystyrene³ were reported. Polyesters,⁴ polyurethanes,⁵ polyamides,⁶ and poly(phenyleneethynyls)⁷ containing the chromophoric main chain were also prepared. Campbell *et al.*⁸ prepared poly(ethyl vinyl ether) partly grafted with azo dyes by the reaction of poly(2-chloroethyl vinyl ether) with 4'-amino-4-nitroazobenzene. However, examples of polyalkyl vinyl ethers with the chromophoric side chain prepared directly by the polymerization of monomeric alkyl vinyl ethers are seldom found in the literature. Recently we have prepared poly(ethyl vinyl ethers) containing the NLO-phores *p*-oxybenzylidenemalononitrile,

methyl *p*-oxybenzylidenecyanoacetate,⁹ 3,5-dimethoxy-4-oxybenzylidenemalononitrile,¹⁰ 4'-oxy-4-nitrostilbene,^{11,12} or 3',5'-dimethoxy-4'-oxy-2,4-dinitrostilbene^{13,14} in the side chain by cationic polymerization of the corresponding monomers. This work is now extended with the synthesis and characterization of another poly(ethyl vinyl ethers) containing the NLO-phores *p*-oxy-*N*-(4-nitrobenzylidene)aniline and *p*-oxy-*N*-(4-cyanobenzylidene)aniline in the side chain. The present paper reports the synthesis and cationic polymerization of *p*-(2-vinyloxyethoxy)-*N*-(4-nitrobenzylidene)aniline **2a** and *p*-(2-vinyloxyethoxy)-*N*-(4-cyanobenzylidene)aniline **2b**.

p-Hydroxy-*N*-(4-nitrobenzylidene)aniline **1a** and *p*-hydroxy-*N*-(4-cyanobenzylidene)aniline **1b** were synthesized by the reactions of *p*-aminophenol with *p*-nitrobenzaldehyde and *p*-cyanobenzaldehyde respectively, according to the literature procedure.¹⁵ They also were recrystallized from ethanol. 2-Iodoethyl vinyl ether was prepared by the well known halogen exchange reaction¹⁶ from 2-chloroethyl vinyl ether and sodium iodide. It was reacted with *p*-hydroxy-*N*-(4-nitrobenzylidene)aniline **1a** and *p*-hydroxy-*N*-(4-cyanobenzylidene)aniline **1b** to yield *p*-(2-vinyloxyethoxy)-*N*-(4-nitrobenzylidene)aniline **2a** and *p*-(2-vinyloxyethoxy)-*N*-(4-cyanobenzylidene)aniline **2b**. Their



Scheme 1.

chemical structures were confirmed by ¹H NMR, IR, UV-Vis spectra, and elemental analyses. Compounds **2a** and **2b** showed strong UV absorption bands near 356~376 nm due to the chromophores such as *p*-oxy-*N*-(4-nitrobenzylidene)aniline and *p*-oxy-*N*-(4-cyanobenzylidene)aniline in the side chain. *p*-(2-Vinyloxyethoxy)-*N*-(4-nitrobenzylidene)aniline **2a** and *p*-(2-vinyloxyethoxy)-*N*-(4-cyanobenzylidene)aniline **2b** were polymerized in dichloromethane solution at -30 °C with boron trifluoride etherate as cationic initiator to obtain the polymers **3a** and **3b** (Scheme 1).

Monomers **2a** and **2b** were quite reactive toward cationic initiator and polymerized readily at low temperature. The chemical structures of the resulting polymers were confirmed by ¹H NMR, IR, and elemental analyses. Spectral data indicated that the internal double bond of imine moiety partly hydrolyzed during the polymerization. Proton resonance peaks due to amino groups appeared at 5.13~6.14 and 4.37~5.33 ppm, respectively, in the ¹H NMR spectra of the polymer **3a** and **3b**. Broad absorption bands due to the presence of amino functional groups were also shown at 3365 and 3380 cm⁻¹ in each IR spectrum of the polymers **3a** and **3b**. In most cases, conversions were

quite high, but the molecular weights were rather low, which was indicated by the inherent viscosities. The polymers **3a** and **3b** were soluble in DMF and DMSO, but were not soluble in methanol and diethyl ether. The inherent viscosities of the polymers were in the range of 0.20~0.30 dL/g indicating moderate molecular weights. The thermal behavior was investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (*T*_g). TGA thermograms showed double phase degradation patterns, probably due to the presence of two benzene rings in the pendant group. The *T*_g values of the polymers obtained from DSC thermograms were around 52 °C. They have higher *T*_g than poly(ethyl vinyl ether) (-43 °C). This is, probably, due to the presence of polar and bulky 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. Copolymerization with other monomers to increase the *T*_g values and measurements of NLO activity are in progress, and the results will be reported later.

EXPERIMENTAL

Materials. 2-Chloroethyl vinyl ether, 4-nitrobenzaldehyde, 4-cyanobenzaldehyde, 4-aminophenol (Aldrich) were used as received. Sodium iodide was dried for 4 h at 100 °C under vacuum. Acetone was purified by drying with anhydrous potassium carbonate, followed by distillation under nitrogen. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure. 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 pentoxide, and distilled. Boron trifluoride etherate was trea-

ted with a small amount of diethyl ether and distilled under reduced pressure.

Measurements. IR spectra were taken on a Hitachi Model 260-30 infrared spectrophotometer. ^1H NMR spectra were obtained on a Varian EM 360L NMR spectrometer (60 MHz). UV-VIS spectra were obtained on a Kontron UVikon 860 spectrophotometer. 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 $10\text{ }^\circ\text{C}/\text{min}$ up to $700\text{ }^\circ\text{C}$ 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.

Preparation of 2-iodoethyl vinyl ether. Anhydrous sodium iodide (45.0 g, 0.30 mol) was dissolved in 320 mL of dry acetone contained in a 500 mL round-bottom flask fitted with a reflux condenser protected by a calcium chloride tube, and heated on a heating mantle for 1 h with stirring. 2-Chloroethyl vinyl ether (25.0 g, 0.23 mol) was added to the mixture, and refluxed for an additional 25 h with stirring to complete the reaction. The resulting solution was cooled to room temperature and filtered with suction. The sodium chloride on the filter was washed with 55 mL of acetone and the filtrate was concentrated by distillation of about 260 mL of the solvent. The residue was poured into 260 mL of water contained in a separate funnel, which was shaken. The lower layer was 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: $50\sim 52\text{ }^\circ\text{C}$ (20 mmHg). ^1H NMR (CDCl_3) 6.22~6.57 (q, =CH-O-), 3.50~4.37 (m, $\text{CH}_2=$ and -O- CH_2-), 2.82~3.47 (t, - CH_2 -I). IR (neat): 3105, 3034, 2960, 2922, 2845 (m, C-H), 1635, 1612 (vs, C=C) cm^{-1} .

Preparation of *p*-hydroxy-*N*-(4-nitrobenzylidene)aniline (1a). Compound 1a was prepared by a known method¹⁵ from 4-nitrobenzaldehyde and 4-aminophenol in absolute ethanol, and recrystallized from ethanol. Yield=92%; mp $171\sim 172\text{ }^\circ\text{C}$; ^1H NMR (acetone- d_6) δ 6.67~7.43 (m, aromatic 4H), 7.88~8.40 (m, aromatic 4H), 8.67 (s, -N=CH-); IR (KBr) 3445 (O-H), 1625, 1594, 1575 (C=C) cm^{-1} . Compound 1a: Yield=90%; mp $184\sim 185\text{ }^\circ\text{C}$; ^1H NMR (acetone- d_6) δ 6.71~7.40 (m, aromatic 4H), 7.67~8.17 (q, aromatic 4H), 8.63 (s, -N=CH-); IR (KBr) 3405 (O-H), 2225 (CN), 1618, 1584 (C=C) cm^{-1} .

Preparation of *p*-hydroxy-*N*-(4-cyanobenzylidene)aniline (1b). Compound 1b was prepared by a known method¹⁵ from 4-cyanobenzaldehyde and 4-aminophenol in absolute ethanol, and recrystallized from ethanol. 1b: Yield=90%; mp $184\sim 185\text{ }^\circ\text{C}$; ^1H NMR (acetone- d_6) δ 6.71~7.40 (m, aromatic 4H), 7.67~8.17 (q, aromatic 4H), 8.63 (s, -N=CH-); IR (KBr) 3405 (O-H), 2225 (CN), 1618, 1584 (C=C) cm^{-1} .

Preparation of *p*-(2-vinylloxyethoxy)-*N*-(4-nitrobenzylidene)aniline (2a). *p*-hydroxy-*N*-(4-nitrobenzylidene)aniline (2.91 g, 0.012 mol), anhydrous potassium carbonate (2.22 g, 0.016 mol), and 2-iodoethyl vinyl ether (3.16 g, 0.016 mol) were dissolved in 60 mL of dry acetone under nitrogen. The mixture was refluxed in an oil bath kept at $60\text{ }^\circ\text{C}$ for 40 h under nitrogen. The resulting solution was cooled to room temperature, filtered, and the inorganic salts were washed with 80 mL of acetone. Rotary evaporation of the solvent under reduced pressure gave crude product, which was washed with water completely to remove the residue salts. Thus obtained product was recrystallized from acetone yielded 3.30 g (88% yield) of pure product 2a. mp $138\sim 139\text{ }^\circ\text{C}$. ^1H NMR 3.80~4.41 (m, - $\text{CH}_2=$ and -O- CH_2 - CH_2 -O-), 6.31~6.76 (q, =CH-O-), 6.83~7.56 (m, aromatic 4H), 7.88~8.46 (m, aromatic 4H), 8.79 (s, -N=CH-); IR (KBr) 3078 (=C-H), 2935, 2870 (C-H), 1625, 1596, 1579 (C=C) cm^{-1} . UV/Vis (chloroform) $\lambda_{\text{max}}=376$, $\epsilon=5760$. Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_4$: C, 65.38; H, 5.16; N, 8.97. Found: C, 65.45; H, 5.10; N, 8.90.

Preparation of *p*-(2-vinyloxyethoxy)-*N*-(4-cyanobenzylidene)aniline (2b). *p*-hydroxy-*N*-(4-cyanobenzylidene)aniline (2.67 g, 0.012 mol), anhydrous potassium carbonate (2.22 g, 0.016 mol), and 2-iodoethyl vinyl ether (3.16 g, 0.016 mol) were dissolved in 60 mL of dry acetone under nitrogen. The mixture was refluxed in an oil bath kept at 60 °C for 40 h under nitrogen. The resulting solution was cooled to room temperature, filtered, and the inorganic salts were washed with 80 mL of acetone. Rotary evaporation of the solvent under reduced pressure gave crude product, which was washed with water completely to remove the residue salts. Thus obtained product was recrystallized from acetone yielded 3.02 g (86% yield) of pure product 2b. mp 136~137 °C. ¹H NMR (acetone-*d*₆) δ 3.83~4.45 (m, -CH₂= and -O-CH₂-CH₂-O-), 6.40~6.82 (q, =CH-O-), 6.89~7.56 (m, aromatic 4H), 7.82~8.28 (m, aromatic 4H), 8.83 (s, -N=CH-); IR (KBr) 3028 (=C-H), 2935, 2864 (C-H), 2215 (CN), 1623, 1586, 1575 (C=C) cm⁻¹. UV/Vis (chloroform) λ_{max}=356, ε=12740. Anal. Calcd for C₁₈H₁₆N₂O₂: C, 73.95; H, 5.52; N, 9.58. Found: C, 74.04; H, 5.56; N, 9.66.

Cationic polymerization of 2a and 2b. A representative cationic polymerization procedure (the case of 2a) was as follows: A solution of 2a (0.94 g, 3.0 mmol) in dichloromethane (6.0 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 0.0051 mL (0.045 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 500 mL of methanol. The precipitated polymer was collected and reprecipitated from DMSO into methanol to give 0.80 g (85% yield) of polymer 3a; η_{inh}=0.25 dL/g (c 0.5 g/dL in DMSO at 25 °C). 3a: ¹H NMR (DMSO-*d*₆) δ 1.47~2.83 (m, -CH₂-), 3.33~4.37 (m, -CH-O-CH₂-CH₂-O-), 5.13~6.14 (m, Ph-NH₂-), 6.47~8.57 (m, aromatic 9H); IR (KBr) 3365 (N-H), 3060 (=C-H), 2920, 2858 (C-H), 1612, 1594 (C=C) cm⁻¹. Polymer 3b: Yield=88%; η_{inh}=

0.28 dL/g; ¹H NMR (DMSO-*d*₆) δ 1.27~2.53 (m, -CH₂-), 3.42~4.37 (m, -CH-O-CH₂-CH₂-O-), 4.37~5.33 (m, Ph-NH₂-), 6.30~8.47 (m, aromatic 9H); IR (KBr) 3380 (N-H), 2922, 2855 (C-H), 2225 (CN), 1617, 1604 (C=C) cm⁻¹.

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