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Synthesis and Characterization of Polyurethanes Containing the NLO-phore Dioxynitrostilbene[†]

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Abstract : 3,4-Di-(2'-hydroxyethoxy)-4-nitrostilbene (**2**) was prepared by the reaction of 2-iodoethanol with 3,4-dihydroxy-4-nitrostilbene (**1**). Diol **2** was condensed with 2,4-toluenediisocyanate, 3,3-dimethoxy-4,4'-biphenylenediisocyanate, and 1,6-hexamethylenediisocyanate to yield polyurethanes **3**, **4**, and **5** containing the NLO-chromophore. Polymers **3-5** were soluble in common organic solvents such as acetone and DMSO. The glass transition temperatures (T_g) of the resulting polymers **3-5** were observed around 100-114°C. Electrooptic coefficients (r_{33}) of the poled polymer films were in the range of 18-25 pm/V at 633 nm. Polymers **3-5** began to decompose around 250°C in TGA thermograms.

Introduction

Nonlinear optical (NLO) materials based on organic compounds have been extensively studied over the past decade because of their potential applications in the field of telecommunications, optical signal processing, optical switching, etc.¹⁻³ Among the organic materials the NLO polymers are considered candidate materials, mainly because they offer many advantages such as mechanical endurance, light weight, chemical resistance, and good processability to form optical devices.⁴⁻⁷ One of the current challenges is to design novel NLO polymers with optimized properties. In the developments of NLO polymers for electrooptic applications, stabilization of electrically induced dipole alignment is important considerations. Two approaches to minimize the randomization of dipole alignment have been proposed. One is to use crosslinking method⁸⁻¹¹ and the other is to use a high T_g polymers such as a polyimide.^{12,13} However, these two methods present some drawbacks. Polyurethane matrix forms extensive hydrogen

bond between urethane linkage and increased rigidity prevents the relaxation of oriented dipoles. Shim and coworkers prepared polyurethanes functionalized with hemicyanine¹⁴ and thiophene chromophore¹⁵ in the side chain. Physically crosslinked systems via hydrogen bonds have the advantages such as homogeneity and good processibility relative to the chemically crosslinked systems, which suffer from significant optical loss and poor processibility. In this work we prepared three new polyurethanes containing oxynitrostilbene unit, which is presumably effective NLO-chromophore. After confirming the structure of the resulting polymers we investigated the properties such as T_g , thermal stability, and electrooptic (EO) coefficient. 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. 4-Nitrophenylacetic acid, 2,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, and 2-iodoethanol were used as received. 2,4-Toluenediisocyanate (TDI) and 1,6-hexamethylenediisocyanate (HDI) were

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[†]Dedicated to Professor Iwhan Cho on the occasion of his retirement from KAIST.

purified by distillation under reduced pressure. 3,3'-Dimethoxy-4,4'-biphenylenediisocyanate was recrystallized from ethyl acetate. Piperidine was dried with calcium hydride and fractionally distilled. Acetone was purified by drying with anhydrous potassium carbonate, followed by distillation. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure.

Measurements. IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ^1H NMR spectra were obtained on a Varian EM 360L NMR (60 MHz) and Varian 300 MHz 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 under nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of $10^\circ\text{C}/\text{min}$ up to 700°C was used for the thermal degradation study of polymers under nitrogen. The electrooptic coefficient (r_{33}) of the corona poled film was measured by simple reflection technique.¹⁶ Melting points were measured in Buchi 530 melting point apparatus and are corrected. Viscosities of polymers were obtained by using a Cannon-Fenske viscometer.

3,4-Dihydroxy-4'-nitrostilbene(1). Compound **1** was prepared by a known method¹⁷ from 3,4-dihydroxybenzaldehyde and p-nitrophenylacetic acid, and recrystallized from 80% aqueous ethanol. Mp: $196\text{--}197^\circ\text{C}$. ^1H NMR (CDCl_3) 6.89-6.92 (d, 2H, aromatic), 7.06-7.24 (m, 3H, aromatic), 7.40-7.46 (d, 1H, aromatic), 7.83-7.86 (d, 2H, aromatic), 8.24-8.27 (d, 2H, aromatic). IR (KBr) 3439 (s, O-H), 3031 (w, =C-H), 2875 (w, C-H), 16703, 1589(vs, C=C) cm^{-1} .

3,4-Di-(2'-hydroxyethoxy)-4'-nitrostilbene (2). 3,4-Dihydroxy-4'-nitrostilbene (7.71 g, 0.03 mol), anhydrous potassium carbonate (24.9 g, 0.18 mol), and 2-iodoethanol (23.8 g, 0.12 mol) were dissolved in 100 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80°C for 12 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 200 mL of water, stirred, filtered, and the obtained product was washed with 100 mL of water. Thus obtained product was recrystallized

from ethanol to give 9.22 g (89% yield) of **2**. Mp: $150\text{--}154^\circ\text{C}$. ^1H NMR ($\text{DMSO-}d_6$) 3.72-3.80 (m, 4H, -O-CH₂-CH₂-O-), 3.96-4.11 (m, 4H, -O-CH₂-CH₂-O-), 6.93-7.47 (m, 5H, aromatic), 7.78-7.83 (m, 2H, aromatic), 8.17-8.23 (m, 2H, aromatic). IR (KBr) 3501 (s, O-H), 2926 (m, C-H), 1589 (s, C=C) cm^{-1} . UV/Vis (chloroform) $\lambda_{\text{max}}=392\text{ nm}$, $\epsilon=21140$. Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_6$: C, 62.60; H, 5.54; N, 4.06. Found: C, 62.52; H, 5.48; N, 4.11.

Synthesis of Polyurethanes 3-5. A representative polymerization procedure (the case of **3**) is as follows: 2,4-Toluenediisocyanate (1.74 g, 0.01 mol) was added slowly to a solution of 3.45 g of diol **2** (0.01 mol) in 50 mL of dry DMF. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 80°C . After heating 6 h with stirring the polymerization tube was opened and the viscous polymer solution was poured into 400 mL of cold water. The precipitated polymer was collected and reprecipitated from DMSO into methanol. Thus the obtained polymer was dried under vacuum to give 4.15 g (80% yield) of polymer **3**; $\eta_{\text{inh}}=0.21\text{ dL/g}$ (c 0.5 g/dL in acetone at 25°C). ^1H NMR ($\text{DMSO-}d_6$) 1.90-2.25 (m, 3H, -CH₃), 3.64-4.83 (m, 4H, 2 -O-CH₂-CH₂-O-), 6.77-8.32 (m, 12H, aromatic), 8.48-8.95 (m, 2H, N-H). IR (KBr) 3377 (s, N-H), 2927, 2885 (m, C-H), 1709 (s, C=O), 1591 (vs, C=C) cm^{-1} . UV/Vis (chloroform) $\lambda_{\text{max}}=391\text{ nm}$, $\epsilon=14360$. Anal. Calcd for $(\text{C}_{27}\text{H}_{25}\text{N}_3\text{O}_8)_n$: C, 62.42; H, 4.85; N, 8.09. Found: C, 62.55; H, 4.98; N, 8.17. Polymer **4**: $\eta_{\text{inh}}=0.23\text{ dL/g}$ (c 0.5 g/dL in acetone at 25°C). ^1H NMR ($\text{DMSO-}d_6$) 3.26-3.35 (m, 6H, -OCH₃), 3.74-4.85 (m, 4H, 2 -O-CH₂-CH₂-O-), 6.98-8.21 (m, 15H, aromatic), 8.55-9.14 (m, 2H, N-H). IR (KBr) 3398 (m, N-H), 2939, 2837 (m, C-H), 1728 (s, C=O), 1589 (s, C=C) cm^{-1} . UV/Vis (DMSO) $\lambda_{\text{max}}=393\text{ nm}$, $\epsilon=12660$. Anal. Calcd for $(\text{C}_{34}\text{H}_{31}\text{N}_3\text{O}_{10})_n$: C, 63.64; H, 4.87; N, 6.55. Found: C, 63.78; H, 4.95; N, 6.46. Polymer **5**: $\eta_{\text{inh}}=0.21\text{ dL/g}$ (c 0.5 g/dL in acetone at 25°C). ^1H NMR ($\text{DMSO-}d_6$) 0.98-1.42 (m, 8H, -(CH₂)₃-), 2.80-3.02 (m, 4H, 2 -NH-CH₂-), 3.63-4.83 (m, 4H, 2 -O-CH₂-CH₂-O-), 5.67 (s, 2H, 2 N-H), 6.77-8.32 (m, 12H, aromatic), 6.88-8.30 (m, 9H, aromatic). IR (KBr) 3325 (s, N-H), 2934, 2856 (s, C-H),

1707 (s, C=O), 1618, 1578 (vs, C=C) cm^{-1} . UV/Vis (DMSO) $\lambda_{\text{max}}=390$ nm, $\epsilon=10840$. Anal. Calcd for $(\text{C}_{26}\text{H}_{31}\text{N}_3\text{O}_8)_n$: C, 60.81; H, 6.08; N, 8.18. Found: C, 60.72; H, 6.16; N, 8.25.

Results and Discussion

Synthesis and Characterization of Polymers 3-5. 3,4-Dihydroxy-4'-nitrostilbene (**1**) was prepared by the condensation of 4-nitrophenylacetic acid with 3,4-dihydroxybenzaldehyde according to a literature procedure.¹⁷ 3,4-Di-(2'-hydroxyethoxy)-4'-nitrostilbene (**2**) was prepared by the reaction of 2-iodoethanol with **1**. The chemical structures of the compounds were identified by proton-NMR, IR spectra, and elemental analyses. All the analytical data confirmed the expected chemical structure. Spectral data indicated that stilbene compounds **1** and **2** were isolated as the trans-isomers. Compound **2** showed strong UV absorption band around 392 nm measured in chloroform. Polymers **3**, **4**, and **5** were prepared by polyaddition between a diol **2** and 2,4-toluenediisocyanate (TDI), 3,3'-dimethoxy-4,4'-biphenylenediisocyanate, and 1,6-hexamethylenediisocyanate (HDI) in DMF (Scheme I, II). The results of polymerization are tabulated in

Table I. The yield of polymerization was 75-88%. ^1H NMR spectra of the polymers showed a signal broadening due to polymerization, but the chemical shifts are well consistent with the proposed polymer structures. The signal at 8.5-9.0 ppm assigned to the aromatic amine proton in the ^1H NMR spectra of polymers **3** and **4** indicates the formation of urethane linkage. The IR spectra of the same polymer samples also show a strong carbonyl peak around 1707 cm^{-1} indicating the presence of urethane bond. We now have well

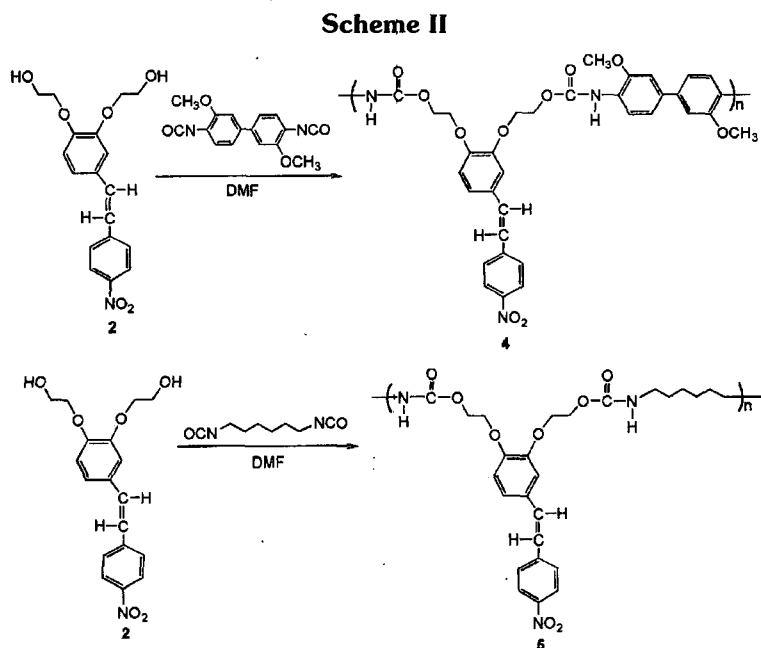
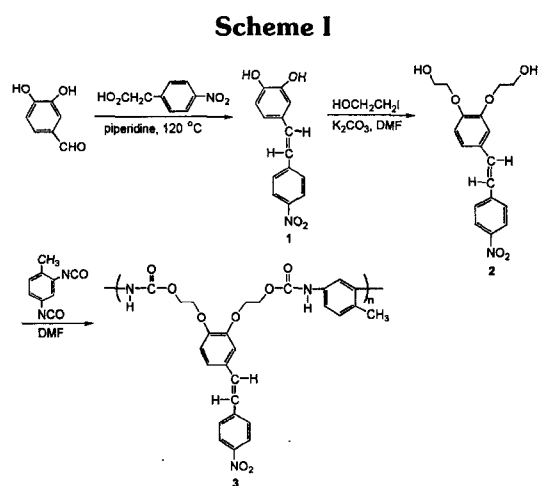


Table I. Polymerization of **2^a with TDI^b, DMBPI^c, and HDI^d in DMF**

Monomer	Monomer/Solvent (mol/L)	Diol 2 to Diisocyanate (mole ratio)	Time(h)	Yield(%)	η_{inh}^e (dL/g)
2 , TDI	0.40	1.0	6	80	0.21
2 , TDI	0.80	1.0	10	82	0.23
2 , DMBPI	0.40	1.0	6	85	0.23
2 , DMBPI	0.80	1.0	10	88	0.26
2 , HDI	0.40	1.0	6	75	0.21
2 , HDI	0.80	1.0	10	77	0.24

^a**2**: 3,4-Di-(2-hydroxyethoxy)-4'-nitrostilbene. ^bTDI: 2,4-Toluendiisocyanate.

^cDMBPI: 3,3'-Dimethoxy-4,4'-biphenylenediisocyanate.

^dHDI: 1,6-Hexamethylenediisocyanate.

^eInherent viscosity of polymer: Concentration of 0.5 g/dL in DMSO at 25 °C.

Table II. Thermal Properties of Polymers 3-5

Polymer	T_g^a , °C	Degradation Temp., °C ^b			Residue ^b at 700°C, %	r_{33}^c (pm/V)
		5%-loss	20%-loss	40%-loss		
3	109	298	330	385	2.7	20
4	114	297	339	411	3.3	25
5	100	291	331	419	3.3	18

^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.

^cEO coefficients were measured by simple reflection technique.¹⁶

defined polyurethanes (**3-5**) and investigate their properties.

Properties of Polymers. The polymers **3**, **4**, and **5** were soluble in common solvents such as acetone, methyl ethyl ketone, cyclohexanone, DMF, and DMSO, but were not soluble in methanol and diethyl ether. Polymers **3**, **4**, and **5** isolated from methanol were yellow colored amorphous powder. The inherent viscosities were measured in the range of 0.21-0.26 dL/g. They showed strong absorption near 390 nm by the chromophore oxynitrostilbene. 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 II. Polymers **3**, **4**, and **5** began to decompose around 250 °C, and 5% of polymer sample was

decomposed at 300 °C as shown in Table II. The polymers show a double phase degradation pattern in their TGA thermograms. T_g values of the polymers **3**, **4**, and **5** measured by DSC were around 100-114 °C, which is acceptable for electrooptic device applications. The electrooptic coefficient (r_{33}) of corona poled polymer films measured by simple reflection technique¹⁶ was in the range of 18-25 pm/V at 633 nm.

In summary, we prepared polyurethanes **3**, **4**, and **5** having 3,4-dioxy-4'-nitrostilbene as a NLO-chromophore. Polymers **3**, **4**, and **5** were soluble in common organic solvents. The resulting polymers began to decompose around 250 °C with a T_g of 100-114 °C. The electrooptic coefficient (r_{33}) of poled polymer films was in the range of 18-25 pm/V at 633 nm. We are now in the process of extending the polymerization system to the synthesis of other type of NLO polymers and the

results will be reported elsewhere.

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