Synthesis and Properties of Novel Polyurethane Containing Nitrophenylazocatecholic Group as NLO Chromophore

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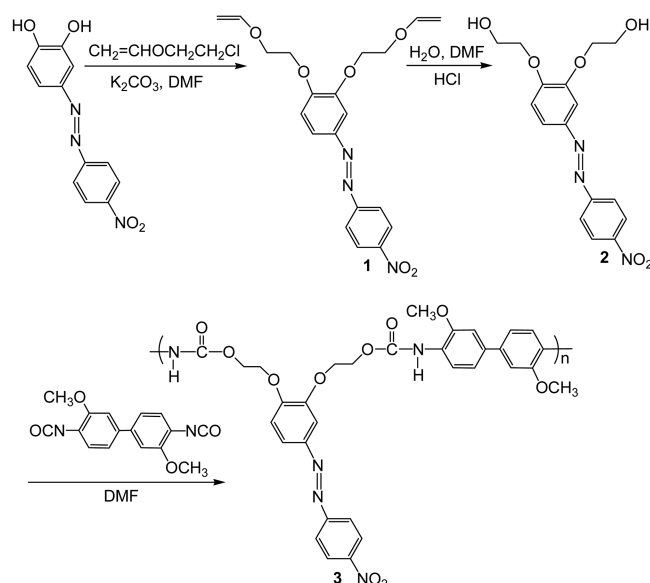*Received October 7, 2011, Accepted November 28, 2011*

Nonlinear optical (NLO) polymers have been identified as strong candidates for use in photonic devices, including high-speed optical modulators, ultrafast optical switches and high-density optical data storage media.[1-3] The promise of NLO polymers lies in their higher nonlinear optical activity, faster response time, and easy fabrication into electro-optic devices. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of important considerations; in this context, two approaches to minimize the randomization have been proposed, namely the use of cross-linked systems[4,5] and the utilization of polymers with high glass transition temperature (T_g) such as polyimides.[6,7] A polyurethane matrix forms extensive hydrogen bonding between urethane linkages, with increased rigidity preventing the relaxation of induced dipoles.[8,9] Polyurethanes functionalized with hemicyanine[10] and thiophene ring[11] in side chain show an enhanced thermal stability of aligned dipoles. Polyurethanes with NLO chromophores, whose dipole moments are aligned transverse to the main chains, show large second-order nonlinearity with good thermal stability.[12,13] Physically cross-linked systems *via* hydrogen bonds have the advantages such as homogenity and good processability relative to chemically cross-linked systems, which suffer from significant optical loss and poor solubility. Recently we prepared novel polyurethanes containing dioxynitrostilbene[14,15] and dioxybenzylidenemalononitrile as NLO chromophores.[16,17] The resulting polymers exhibit high thermal stability of second harmonic generation (SHG), which stems from the stabilization of dipole alignment of the NLO chromophore. In this work reported here, we have prepared novel polyurethane containing 4-(4-nitrophenylazo)catecholic groups as NLO chromophores. We selected the latter as NLO chromophores because they are expected to have high optical nonlinearities. Furthermore, these groups can be incorporated into novel Y-type NLO polyurthanes. The structure of NLO chromophores and these Y-type NLO polyurethanes have not yet been described in the literature. Thus we synthesized new type of NLO polyurethane, in which the pendant NLO chromophores are components of the polymer backbone. This Y-type NLO polymer is expected to have the merits of both main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility. After confirming the structure of the resulting polymer, we investigated its properties.

Results and Discussion

Compound **1** was prepared by the reaction of 2-chloroethyl vinyl ether with 4-(4-nitrophenylazo)catechol. Compound **2** was prepared by acid-catalyzed hydrolysis of **1** in DMF. Diol **2** was condensed with 3,3'-dimethoxy-4,4'-biphenylenediisocyanate in a dry DMF solvent to yield novel polyurethane **3** containing 4-(4-nitrophenylazo)catecholic group as NLO chromophore. The synthetic route for polymer **3** is presented in Scheme 1. The resulting polymer was purified by Soxhlet extraction for two days with methanol as a solvent. The polymerization yield was 88%. The chemical structure of the polymer was identified using ^{1}H NMR, IR spectra, and elemental analysis. ^{1}H NMR spectrum of the polymer **3** has a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The signal at 8.92-9.18 ppm of [1]N NMR spectrum of polymer **3** assigned to the amine proton indicates the formation of urethane linkage. The IR spectrum of polymer **3** shows strong carbonyl peaks near
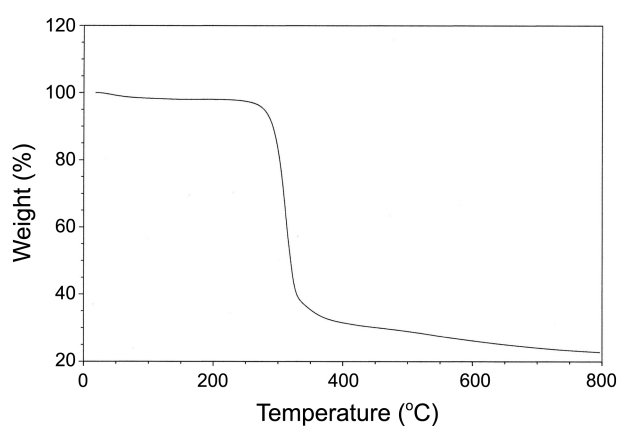

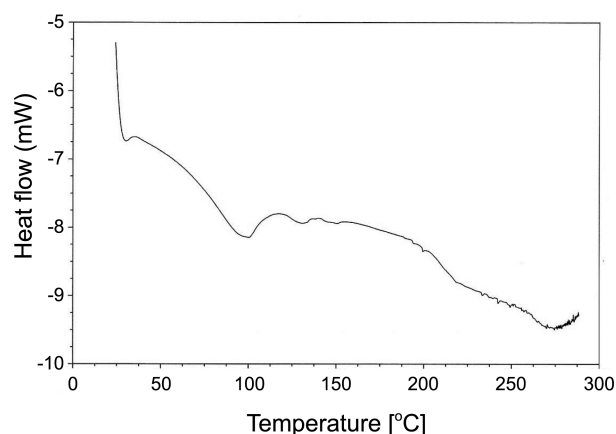**Scheme 1.** Synthetic scheme and structure of polymer **3**.

1729 cm^{-1} indicating the presence of urethane bond. The spectrum also shows strong absorption peak near 1589 cm^{-1} due to azo group and absorptions at 1516 and 1341 cm^{-1} due to nitro group indicating the presence of nitroazobenzene unit. These results are consistent with the proposed structure, indicating that the NLO chromophores remained intact during the polymerization. The molecular weights were determined using GPC with polystyrene as the standard and THF as the eluent. M_n of the polymer **3**, determined using GPC, is 14,200 g mol^{-1} ($M_w/M_n = 1.98$). The polymer **3** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity is 0.31 dL g^{-1}. Polymer **3** shows strong absorption near 384 nm due to the 4-(4-nitrophenylazo)-catecholic group NLO chromophore. The striking feature of this polymerization system is that it gives unprecedented Y-type NLO polymers, in which the pendant NLO chromophores are part of the polymer backbone. These Y-type NLO polymers are expected to have the advantages of both main-chain and side-chain NLO polymers. Thus, we obtained a new type of NLO polyurethane with side-chain and main-chain characteristics. Having obtained the well defined Y-type polyurethane **3**, we investigated its properties.

The thermal behavior of the polymer was investigated using TGA and DSC to determine the thermal degradation pattern and glass transition temperature. The results are summarized in Table 1. The TGA and DSC thermograms of the polymer **3** are shown in Figure 1 and Figure 2, respectively. Polymer **3** has a thermal stability up to 270 °C according to its TGA thermogram. The T_g value of the polymer **3** measured using DSC is near 96 °C. This T_g value is lower than those of the polyurethanes containing dioxynitrostilbene, which are in the range 143-150 °C[14,15] or dioxybenzyl-idenemalononitrile, which are in the range 135-159 °C.[16,17] The lower T_g value is probably due to the easy *cis-trans* isomerization of diazo linkage.

The NLO properties of polymers were studied using the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. The refractive index of the sample was measured using the optical transmission technique.[23] The transmittance of thin film gives information on the thickness, refractive index and extinction coefficient. Thus, we could determine these para-

Table 1. Thermal Properties of Polymer **3**

Polymer	T_g^a, °C	Degradation temp, °C^b			M_n^c	M_w^c
		5 wt %-Loss	20 wt %-Loss	40 wt %-Loss		
3	96	278	302	314	14,200	28,100
4^d	143	316	341	362	13,600	27,200

^{a}Determined from DSC curves measured with a TA 2920 differential scanning calorimeter with a heating rate of 10 °C/min under nitrogen atmosphere. ^{b}Determined from TGA curves measured with a TA Q50 thermogravimetric analyzer with a heating rate of 10 °C/min under nitrogen atmosphere. ^{c}Measured by gel permeation chromatography (GPC) in THF using polystyrene standard. ^{d}Polyurethane containing 3,4-dioxynitrostilbene.[14]

Figure 1. TGA thermogram of polymer **3** obtained at a heating rate of 10 °C/min under nitrogen.

Figure 2. DSC thermogram of polymer **3** obtained at a heating rate of 10 °C/min under nitrogen.

meters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of 1064 nm with a mode locked Nd-YAG laser and OPO. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Figure 3 shows the angular dependence of SHG signal for a poled sample of polymer **3**. The SHG values were compared with those obtained from a Y-cut quartz plate. To calculate the d_{31} and d_{33} values, both *s*-polarized and *p*-polarized IR laser were directed at the samples. The NLO properties of polymer **3** are summarized in Table 2. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure.[24] The values of d_{31} and d_{33} for polymer **3** are 1.45 × 10^{-9} and 4.58 × 10^{-9} esu, respectively. These SHG values are smaller than those of the polyurethanes containing 3,4-dioxynitrostilbene (3.64 × 10^{-8} esu).[14] Since the second harmonic wavelength is at 532 nm, which is not in the absorptive region of the resulting polyurethane, there is little resonant contribution to this d_{33} value. In the isotropic model, the ratio of d_{33}/d_{31} is predicted to be about 3. Our d_{33}/d_{31} value of 3.16 is in good agreement with the predicted value. To evaluate the high-temperature stability of the polymer, we studied the temporal stability of the SHG signal.

Table 2. Nonlinear Optical Properties of Polymer **3**

Polymer	$\lambda_{max}{}^a$ (nm)	$d_{33}{}^b$ (esu)	Φ^c	$d_{31}{}^b$ (esu)	film thickness^d (μm)	n
3	384	4.58×10^{-9}	0.14	1.45×10^{-9}	0.50	n_1=1.72
4^e	383	3.64×10^{-8}	0.17	1.28×10^{-8}	0.45	n_1=1.70

^{a}Polymer film after corona poling. ^{b}SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.[19] ^{c}Order parameter Φ=1-A_1/A_0, where A_0 and A_1 are the absorbances of the polymer film before and after corona poling, respectively. ^{d}Film thickness was determined using the optical transmission technique.[18] ^{e}Polyurethane containing 3,4-dioxynitrostilbene.[14]
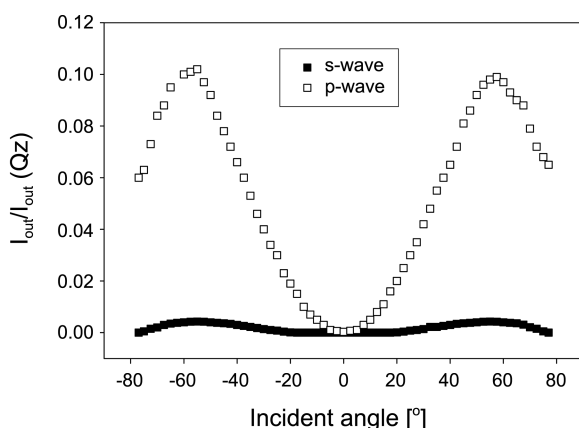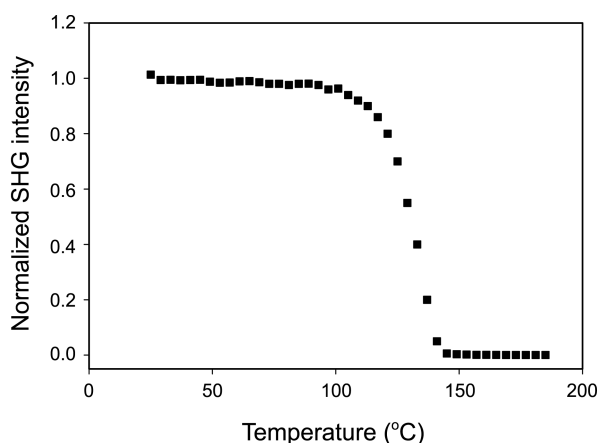

Figure 3. Angular dependence of SHG signal for a poled film of polymer **3**.

Figure 4 shows the dynamic thermal stability study of the NLO activity of a film of polymer **3**. To investigate the real time NLO decay of the SHG signal of the poled polymer film as a function of temperature, *in situ* SHG measurement was performed at a heating rate of 4 ^{o}C min^{-1} from 30 to 200 ^{o}C. The polymer film exhibits a high thermal stability even at 4 ^{o}C higher than T_g, and no significant SHG decay is observed below 100 ^{o}C. This SHG thermal stability is lower than those of the polyurethanes containing dioxynitrostilbene, which are in the range 160-175 ^{o}C[14,15] or dioxybenzylidenemalononitrile, which are in the range 145-155 ^{o}C.[16,17] The lower SHG thermal stability is probably due to the lower T_g value of the polymer. In general, side-chain NLO polymers lose the thermal stability of dipole alignment

below T_g. Stabilization of dipole alignment is a characteristic of main-chain NLO polymers. The enhanced thermal stability of second harmonic generation of polymer **3** is due to the stabilization of dipole alignment of NLO chromophores, which stems from the partial main-chain character of the polymer structure. Thus, we obtained a new NLO polyurethane having the advantages of both main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility.

Experimental Section

Materials. Reagent-grade chemicals were purchased from Aldrich or AlfaAesar and purified by either distillation or recrystallization before use. 4-(4-Nitrophenylazo)catechol and 2-chloroethyl vinyl ether were used as received. 3,3'-Dimethoxy-4,4'-biphenylenediisocyanate (DMBPI) was recrystallized from ethyl acetate. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure.

Measurements. Infrared (IR) spectra were obtained with a Varian FT IR-1000 IR spectrophotometer. ^{1}H NMR NMR spectra were obtained with a Varian 300 MHz NMR spectrometer. UV-visible absorption spectra were obtained with a SECOMAM Model UVIKON XS 99-90289 spectrophotometer. T_g values were measured using a TA 2920 differential scanning calorimeter (DSC) in a nitrogen atmosphere. A TA Q50 thermogravimetric analyzer (TGA) with a heating rate of 10 ^{o}C min^{-1} up to 800 ^{o}C was used for the thermal degradation of polymers under nitrogen. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymers were estimated using gel permeation chromatography (GPC; styragel HR5E4E columns; tetrahydrofuran (THF) solvent). The alignment of the NLO chromophore of the polymers was carried out using a corona poling method. As the temperature was raised gradually to 5-10 ^{o}C higher than T_g, a corona voltage of 6.5 kV was applied and the temperature was maintained for 30 min. The films were cooled to room temperature in the presence of the electric field. Finally, the electric field was removed. The refractive index of the sample was measured using the optical transmission technique.[18] A continuum PY61 mode-locked Nd:YAG laser (λ = 1064 nm) with pulse width of 40 ps and repetition rate of 10 Hz was used as the fundamental light source and Y-cut quartz was used as reference. The Maker Fringe pattern was obtained by measuring the SHG signal at 0.5^o intervals using a rotation stage. SHG coefficients (d_{33}) were derived from the analysis of measured

Figure 4. Normalized SHG signal of polymer **3** as a function of temperature at a heating rate of 4 ^{o}C/min.

Maker-fringes.[19]

Preparation of 3,4-Di-(2'-vinyloxyethoxy)-4'-nitroazobenzene (1). 4-(4-Nitrophenylazo)catechol (25.9 g, 0.10 mol), anhydrous potassium carbonate (82.9 g, 0.60 mol) and 2-chloroethyl vinyl ether (32.0 g, 0.30 mol) were dissolved in 400 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 90 °C for 24 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 purified by column chromatography (ethyl acetate/hexane = 1/2 by volume). Thus obtained product was washed with 10% aqueous ethanol and dried in a vacuum oven yielded 29.9 g (75% yield) of pure product **1**. ^{1}H NMR (CDCl$_3$) δ 3.99-4.23 (m, 6H, 2 CH$_2$=, -O-CH$_2$-CH$_2$-O-), 4.29-4.46 (m, 62H, CH$_2$=, -O-CH$_2$-CH$_2$-O-), 6.58-6.72 (q, 2H, 2 =CH-O-), 7.32-7.38 (d, 1H, aromatic), 7.62 (s, 1H, aromatic), 7.76-7.84 (m, 1H, aromatic), 8.07-8.14 (d, 2H, aromatic), 8.28-8.38 (m, 1H, aromatic), 8.45-8.53 (d, 1H, aromatic). IR (KBr) 3081 (w, =C-H), 2946 (m, C-H), 1622 (s, N=N), 1584 (s, C=C), 1511, 1344 (vs, N=O), 1196 (vs, N=N) cm^{-1}. Anal. Calcd for C$_{20}$H$_{21}$N$_3$O$_6$: C, 60.15; H, 5.30; N, 10.52. Found: C, 60.23; H, 5.38; N, 10.61.

Preparation of 2,4-Di-(2'-hydroxyethoxy)-4'-nitroazobenzene (2). Aqueous hydrochloric acid (1.5 mol L^{-1}, 30 mL) was slowly added to a solution of compound **1** (3.99 g, 10 mmol) in 50 mL of dry DMF with stirring under nitrogen at room temperature. The mixture was stirred at 50 °C for 6 h under nitrogen. The resulting solution was cooled to room temperature and poured into 100 mL of ice water, stirred, separated by suction, and washed with 50 mL of water. The obtained product was dried in a vacuum oven to give 2.98 g (86% yield) of pure **2**. ^{1}H NMR (DMSO-d_6) δ 3.77-3.88 (m, 4H, 2 -O-CH$_2$-), 4.11-4.24 (m, 4H, 2 Ph-O-CH$_2$-), 4.92-5.03 (m, 2H, 2 -OH), 7.32 (d, 1H, aromatic), 7.58 (d, 1H, aromatic), 7.75 (d, 1H, aromatic), 8.11 (d, 2H, aromatic), 8.48 (d, 2H, aromatic). IR (KBr) 3336 (s, O-H), 2936 (m, C-H), 1586 (s, N=N), 1507, 1337 (vs, N=O), 1261 (vs, N=N) cm^{-1}. Anal. Calcd for C$_{16}$H$_{17}$N$_3$O$_6$: C, 55.33; H, 4.93; N, 12.10. Found: C, 55.42; H, 4.99; N, 12.18.

Synthesis of Polymer 3. A representative polyaddition reaction procedure was as follows. DMBPI (2.96 g, 0.01 mol) was added slowly to a solution of 3.47 g of diol **2** (0.01 mol) in 25 mL of anhydrous 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 16 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 re-precipitated from dimethylsulfoxide (DMSO) into methanol. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum to give 5.66 g (88% yield) of polymer **3**. Inherent viscosity (η$_{inh}$): 0.31 dL g^{-1} (c, 0.5 g dL^{-1} in DMSO at 25 °C). ^{1}H NMR (DMSO-d_6) δ 3.48 (s 6H, -OCH$_3$), 3.86-4.06 (m, 4H, 2 -O-CH$_2$-), 4.12-4.63 (m, 4H, 2 Ph-O-CH$_2$-), 7.18-7.51 (m, 4H, aromatic), 7.58-7.7.78 (m, 3H, aromatic), 7.82-8.13 (m, 2H, aromatic), 8.17-8.34 (m, 2H, aromatic), 8.39-8.51 (m, 1H, aromatic), 8.61-8.79 (t, 1H, aromatic), 8.92-9.18 (s, 2H, N-H). IR (KBr) 3348 (m, N-H), 2883 (m, C-H), 1729 (s, C=O), 1589 (s, N=N), 1516, 1341 (vs, N=O) cm^{-1}. Anal. Calcd for (C$_{32}$H$_{29}$N$_5$O$_{10}$)$_n$: C, 59.72; H, 4.54; N, 10.88. Found: C, 59.61; H, 4.46; N, 10.81.

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