Synthesis and Electro-Optic Properties of Novel X-Type Polyurethane Containing Nitrophenylazonitroresorcinoxy Group with Highly Enhanced Thermal Stability of Dipole Alignment

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ABSTRACT: Novel X-type polyurethane **4** containing 4-(4-nitrophenylazo)-6-nitroresorcinoxy groups as nonlinear optical (NLO) chromophores, which are parts of the polymer main chains, was prepared and characterized. Polyurethane **4** is soluble in common organic solvents such as acetone and *N*,*N*-dimethylformamide. It shows thermal stabilities up to 270 °C from thermogravimetric analysis with glass transition temperature obtained from differential scanning calorimetry of about 134 °C. The second harmonic generation (SHG) coefficient (*d*₃₃) of poled polymer film at 1064 nm fundamental wavelength is

 5.37×10^{-9} esu. Polymer **4** exhibits a thermal stability up to $T_{\rm g}$, and no significant SHG decay is observed below 135 °C, which is acceptable for NLO device applications. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 760–766

KEYWORDS: atomic force microscopy (AFM); differential scanning calorimetry (DSC); NLO; polyurethane; second harmonic generation (SHG); thermal stability; thermogravimetric analysis (TGA)

INTRODUCTION Nonlinear optical (NLO) materials have attracted much attention in the past two decades because of their vast applications in the field of electro-optic technology such as telecommunications, optical data storage, and optical information processing.^{1–9} Among them, the organic NLO polymers seem to be superior because of their higher NLO activity, faster response time, low cost, wide response wave band, high optical damage threshold, and good processability to form electro-optic devices. A potential NLO polymer must contain highly polarizable conjugated electronic systems and has to be mechanically very strong and thermally stable. In the manufacturing of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of the most challenging task; in this context, several approaches to minimize the randomization have been proposed such as the use of crosslinked systems,¹⁰⁻¹⁵ the utilization of polyimides¹⁶⁻²¹ with high glass transition temperature (T_{φ}) , and H-shape polymers.²² A polyurethane matrix forms strong hydrogen bonding between urethane linkages, which increases rigidity preventing the relaxation of induced dipoles.^{23,24} Polyurethanes functionalized with hemicyanine²⁵ and thiophene ring²⁶ in side chain show an enhanced thermal stability of aligned dipoles. Polyurethanes having dipole moments aligning transverse to the main chain

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exhibit large second-order nonlinearity with good thermal stability.^{27,28} Polymers with H-type NLO chromophores exhibit a thermal stability and large optical nonlinearity.²² Physically crosslinked systems via hydrogen bonds have the advantages such as homogeneity and good processability relative to chemically crosslinked systems, which suffer from significant optical loss and poor solubility. Recently, we prepared novel Y-type polyurethanes containing dioxynitrostilbene,²⁹ dioxynitroazobenzene,³⁰ and dioxybenzylidenemalononitrile as NLO chromophores.^{31,32} The resulting polymers exhibit enhanced thermal stability of second harmonic generation (SHG), which stems from the stabilization of dipole alignment of the NLO chromophore at high temperature.

In this work reported here, we have prepared novel polyurethane containing 4-(4-nitrophenylazo)-4-nitroresorcinoxy groups as NLO chromophores. We selected the latter as NLO chromophores because they are expected to have higher optical nonlinearities and thermal stability due to a quadruple conjugation and planarity of the dipole moments. Azobenzene groups have advantages to be aligned by an external electric field to obtain an asymmetric arrangement of chromophores required for the second-order nonlinearity.

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FIGURE 1 Main Chain NLO polymers (a), side chain NLO polymers (b), and X-type NLO polymers (c).

Furthermore, these 4-(4-nitrophenylazo)-6-nitroresorcinoxy groups can be incorporated into novel X-type NLO polyurthanes [see Fig. 1(c)]. The structure of NLO chromophores and these X-type NLO polyurethanes have not yet been described in the literature. Thus, we formulated new promising NLO polyurethane, in which the pendant NLO chromophores are components of the polymer backbone. This X-type NLO polymer is expected to have the merits of both main chain [Fig. 1(a)] and side chain [Fig. 1(b)] NLO polymers, namely stable dipole alignment and good solubility. After confirming the structure of the resulting polymer, we investigated its properties such as $T_{g'}$ thermal stability, surface morphology of polymer films, and SHG activity.

EXPERIMENTAL

Materials

Reagent-grade chemicals were purchased from Aldrich or AlfaAesar and purified by either distillation or recrystallization before use. All glassware was thoroughly dried under vacuum with a hot air gun before use. 4-(4-Nitrophenylazo) resorcinol, 2-chloroethyl vinyl ether, and bismuth(III) tri-fluoromethanesulfonate were used as supplied. 3,3'-Dime-thoxy-4,4'-biphenylenediisocyanate was recrystallized from ethyl acetate. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure.

Instrumentation

Infrared (IR) spectra were obtained with a Varian FTIR-1000 IR spectrophotometer. ¹H NMR spectra were obtained with a Varian VNMRS 500-MHz NMR spectrometer. UV-visible absorption spectra were obtained with a SECOMAM Model UVIKON XS 99-90289 spectrophotometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. $T_{\rm g}$ values were measured using a TA 2920 differen-

tial scanning calorimeter DSC in a nitrogen atmosphere. A TA Q50 thermogravimetric analyzer with a heating rate of 10 °C min⁻¹ up to 800 °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). AFM images were recorded with a Park Science Instrument Autoprobe CP, operated in a contact mode, which measures topography. Viscosity values were obtained using a Cannon-Fenske viscometer.

Film Preparation and SHG Measurements

Polymer films were prepared from a 10-wt % polymer solution in DMF deposited on an indium-tin oxide (ITO) covered glass. Before film casting, the polymer solution was filtered through 0.45-µm Teflon® membrane filter. The films were spin-cast at room temperature in the range 1000-1200 rpm. The films were dried for 12 h under vacuum at 60 °C. The alignment of the NLO chromophore of the polymers was carried out using a corona poling method. The poling was performed in a wire-to plane geometry under in situ conditions. The discharging wire to plane distance was 10 mm. As the temperature was raised gradually to 5–10 °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.³³ The transmittance of thin film gives information on the thickness, refractive index, and extinction coefficient of the film. Thus, we can determine these parameters by analyzing the transmittance. SHG measurement was carried out 1 day after poling. A continuum PY61 mode-locked Nd:YAG laser ($\lambda = 1064$ 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. A poled polymer film was mounted on the rotator coupled to a step motor. The output signals from the photodiode and photomultiplier tube (PMT) were detected as a function of the incident angle. A 3-mm-thick Y-cut quartz crystal (a piece of quartz plate whose plane is perpendicular to the crystalline y-axis and the thickness of the plate is 3 mm and $d_{11} = 0.3$ pm V^{-1}) was used as a reference for determining the relative intensities of the SH signals generated from the samples. The Maker Fringe pattern was obtained by measuring the SHG signal at 0.5° intervals using a rotation stage. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.³⁴

Preparation of 2,4-Di-(2'-vinyloxyethoxy)-4'nitroazobenzene (1)

4-(4-Nitrophenylazo)resorcinol (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 $^{\circ}$ 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 30.3 g (76% yield) of pure product 1.

¹H NMR (DMSO-*d*₆) δ 4.02–4.49 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.56–6.63 (m, 2H, 2 =CH-O-), 6.70– 6.74 (m, 1H, aromatic), 6.89–6.91 (m, 1H, aromatic), 7.71– 7.74 (d, 1H, aromatic), 7.95–7.98 (d, 2H, aromatic), 8.40– 8.43 (d, 2H, aromatic). IR (KBr) 3082 (w, =C-H), 2934 (m, C-H), 1600 (vs, N=N), 1583 (s, C=C), 1515, 1332 (vs, N=O), 1180 (m, N=N) cm⁻¹. Anal. Calcd for C₂₀H₂₁N₃O₆: C, 60.15; H, 5.30; N, 10.52. Found: C, 60.24; H, 5.26; N, 10.45.

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 2.78 g (80% yield) of pure **2**.

¹H NMR (DMSO-*d*₆) δ 3.74–3.78 (t, 2H, $-0-CH_2-$), 3.79– 3.83 (t, 2H, $-0-CH_2-$), 4.12–4.16 (t, 2H, Ph- $0-CH_2-$), 4.24–4.28 (t, 2H, Ph- $0-CH_2-$), 4.92–4.96 (t, 2H, 2 –0H), 6.65–6.69 (d, 1H, aromatic), 6.84 (s, 1H, aromatic), 7.70–7.73 (d, 1H, aromatic), 7.96–7.99 (d, 2H, aromatic), 8.39–8.42 (d, 2H, aromatic). IR (KBr) 3325 (m, 0-H), 2948 (m, C-H), 1600 (vs, N=N), 1519, 1337 (vs, N=0) cm⁻¹. Anal. Calcd for C₁₆H₁₇N₃O₆: C, 55.33; H, 4.93; N, 12.10. Found: C, 55.25; H, 4.98; N, 12.15.

Preparation of 2,4-Di-(2'-hydroxyethoxy)-5-nitro-4'-nitroazobenzene (3)

Compound 2 (2.0 g, 5.76 mmol) was dissolved in 40 mL of dry 1,2-dichloroethane under nitrogen. To the resulted solution was added bismuth (III) trifluoromethanesulfonate (0.30 g, 0.46 mmol) and 60-wt % nitric acid (60%, 0.91 g, 8.64 mmol). The mixture was refluxed in an oil bath kept at 75 °C for 8 h under nitrogen. The resulting solution was cooled to room temperature, neutralized with 5 g of anhydrous sodium bicarbonate, diluted with 100 mL of water with stirring, extracted with 50 mL of diethyl ether three times, and separated. Rotary evaporation of solvent gave product, which was dissolved in 50 mL of dichloromethane, washed with water (100 mL) and saturated aqueous sodium bicarbonate (50 mL), dried with anhydrous sodium carbonate, filtered, and concentrated by rotary evaporator. The combined product was purified by column chromatography (ethyl acetate/

methanol = 1/2 by volume) gave 1.69 g (75% yield) of pure product **3**.

¹H NMR (DMSO- d_6) δ 3.78–3.82 (t, 2H, $-0-CH_2-$), 3.84– 3.88 (t, 2H, $-0-CH_2-$), 4.37–4.40 (t, 2H, Ph- $0-CH_2-$), 4.43–4.46 (t, 2H, Ph- $0-CH_2-$), 5.02–5.04 (t, 1H, -0H), 5.05–5.07 (t, 1H, -0H), 7.17 (s, 1H, aromatic), 8.05–8.08 (d, 2H, aromatic), 8.28 (s, 1H, aromatic), 8.42–8.45 (d, 2H, aromatic). IR (KBr) 3320 (m, 0-H), 2943 (m, C-H), 1610 (vs, N=N), 1519, 1344 (vs, N=0) cm⁻¹. Anal. Calcd for C₁₆H₁₆N₄O₈: C, 48.98; H, 4.11; N, 14.28. Found: C, 48.92; H, 4.06; N, 14.22.

Synthesis of Polyurethane 4

A representative polyaddition reaction procedure was as follows. Dimethoxy-4,4'-biphenylenediisocyanate (2.96 g, 0.01 mol) was added slowly to a solution of 3.92 g of diol **3** (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 15 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. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum to give 6.19 g (90% yield) of polymer **4**.

Inherent viscosity (η_{inh}): 0.30 dL g⁻¹ (c, 0.5 g dL⁻¹ in DMSO at 25 °C). ¹H NMR (DMSO- d_6) δ 3.75–4.05 (m, 8H, 2 –OCH₃, –O–CH₂–), 4.36–4.72 (m, 6H, –O–CH₂–, 2 Ph-O–CH₂–), 6.65–6.74 (m, 1H, aromatic), 6.86–7.34 (m, 6H, aromatic), 7.65–7.74 (s, 1H, aromatic), 7.91–8.05 (m, 1H, aromatic), 8.16–8.31 (m, 2H, aromatic), 8.52–8.66 (d, 1H, aromatic), 8.91–9.05 (d, 2H, N–H). IR (KBr) 3432 (s, N–H), 2952 (m, C–H), 1730 (s, C=O), 1609 (s, N=N), 1520, 1343 (vs, N=O) cm⁻¹. Anal. Calcd for (C₃₂H₂₈N₆O₁₂)_n: C, 55.82; H, 4.10; N, 12.20. Found: C, 55.91; H, 4.16; N, 12.28.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymer

Compound 1 was prepared by the reaction of 2-chloroethyl vinyl ether with 4-(4-nitrophenylazo)resorcinol. Compound 2 was prepared by acid-catalyzed hydrolysis of 2 in DMF. Compound 2 was reacted with nitric acid and bismuth(III) trifluoromethanesulfonate in anhydrous 1,2-dichloroethane according to a literature procedure³⁵ to yield compound **3**. Diol 3 was condensed with 3,3'-dimethoxy-4,4'-biphenylenediisocyanate in a dry DMF solvent to yield novel polyurethane 4 containing 4-(4-nitrophenylazo)-6-nitroresorcinoxy group as NLO chromophore. The synthetic route for polymer 4 is presented in Scheme 1. The resulting polymer was purified by Soxhlet extraction with methanol as a solvent. The polymerization yield was 90%. The chemical structure of the polymer was identified using ¹H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structures. ¹H NMR spectrum of the polymer **4** has a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The



SCHEME 1 Synthetic route to and structure of polymer 4.

signal at 8.91-9.05 ppm of ¹N NMR spectrum of polymer 4 assigned to the amine proton indicates the formation of urethane linkage. The IR spectrum of polymer 4 shows strong carbonyl peaks near 1730 cm⁻¹ indicating the presence of urethane bond. The spectrum also shows strong absorption peak near 1609 cm^{-1} due to azo group and absorptions at 1520 and 1343 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. $M_{\rm p}$ of the polymer 4, determined using GPC, is 16,500 g mol⁻¹ ($M_{\rm w}/$ $M_{\rm n} = 1.86$). The polymer **4** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity is 0.30 dL g^{-1} . Polymer 4 shows strong absorption near 382 nm due to the 4-(4-nitrophenylazo)-6-nitroresorcinoxy group NLO chromophore. The striking feature of this polymerization system is that it gives unprecedented X-type NLO polymers, in which the pendant NLO chromophores are part of the polymer backbone. These X-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 X-type polyurethane **4**, we investigated its properties.

Thermal Properties of Polymer

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 4 are shown in Figures 2 and 3, respectively. Polymer 4 has a thermal stability up to 270 °C according to its TGA thermogram. The initial weight loss in the polymer begins at about 270 °C in TGA thermogram, which is also shown in DSC thermogram. The $T_{\rm g}$ value of the polymer 4 measured using DSC is near 134 °C. This $T_{\rm g}$ value is higher than that of the Y-type polyurethane containing nitrophenylazoresorcinol, which is near 102 °C.³⁰ The TGA and DSC studies show that the decomposition temperature of the polymer 4 is much higher than the corresponding $T_{\rm g}$ value. This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

Nonlinear Optical Properties of Polymer

The NLO properties of polymers were studied using the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. As the

TABLE 1 Thermal P	roperties	of Poly	ymer 4
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Degradation Temperature (°C) ^b							
Polymer	T _g ^a (°C)	5 wt % Loss	20 wt % Loss	40 Wt % Loss	Residue at 800 °C (%) ^b		
4	134	278	306	391	39.6		
PU °	102	276	296	332	43.3		

 a Determined from DSC curves measured with a TA 2920 differential scanning calorimeter with a heating rate of 10 $^\circ \rm C~min^{-1}$ under nitrogen atmosphere.

 $^{\rm b}$ Determined from TGA curves measured with a TA Q50 thermogravimetric analyzer with a heating rate of 10 $^{\circ}{\rm C}$ min $^{-1}$ under nitrogen atmosphere.

^c Y-type polyurethane containing nitrophenylazoresorcinol.³⁰





FIGURE 2 TGA thermogram of polymer **4** obtained at a heating rate of 10 $^{\circ}$ C min⁻¹ under nitrogen.

temperature was raised gradually to 5–10 $^{\circ}$ C higher than T_{g} , a corona voltage of 6.5 kV was applied and this 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 poling was confirmed from UV-visible spectra. Figure 4 shows the UV-visible absorption spectra of the polymer 4 before and after poling. After electric poling, the dipole moments of the NLO chromophores were aligned and UV-visible absorption of polymer 4 exhibits a decrease in absorption due to birefringence. From the absorbance change, the order parameter of the poled films can be estimated, which is related to the poling efficiency. The estimated order parameter value Φ is equal to 0.32 for polymer **4** ($\Phi = 1 - A_1/A_0$, where $A_0 = 0.9933$ and $A_1 = 0.6716$ are the absorbances of the polymer film before and after poling, respectively).

The poling was also confirmed by atomic force microscopy (AFM). Figure 5 shows AFM scans of the spin-coated film of polymer **4** before and after poling. AFM images show that the surface of the film sample is quite flat and broad before poling [Fig. 5(a)]. However, this film was dramatically



FIGURE 4 UV-visible absorption spectra of a film of polymer **4** before and after poling.



FIGURE 3 DSC thermogram of polymer **4** obtained at a heating rate of 10 $^{\circ}$ C min⁻¹ under nitrogen.

changed after poling, resulting in numerous hills and valleys in the surface structure, which means that the NLO chromophores are aligned in the poling direction [Fig. 5(b)].

The refractive index of the sample was measured using the optical transmission technique.³³ The transmittance of thin film gives information on the thickness, refractive index, and extinction coefficient. Thus, we could determine these



FIGURE 5 AFM images of spin-coated film of polymer **4**: (a) before corona-poling; (b) after corona-poling.



FIGURE 6 Angular dependence of SHG signal for a poled film of polymer 4.

parameters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of 1064 nm with a mode-locked Nd-YAG laser and optical parametric oscillator. In order to determine the microscopic secondorder susceptibility of the polymer, the angular SHG dependence was recorded. Figure 6 shows the angular dependence of SHG signal for a poled sample of polymer 4. 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 4 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.³⁴ The values of d_{31} and d_{33} for polymer **4** are 1.76 \times 10⁻⁹ and 5.37 \times 10⁻⁹ esu, respectively. This d_{33} value is higher than that of the Ytype polyurethane 4 containing nitrophenylazoresorcinol, which is near 4.92 \times 10^{-9} esu. 30 As 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 3.05 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. Figure 7

1.2 Normalized SHG Intensity 1.0 0.8 0.6 0.4 0.2 0.0 0 50 100 150 200 Temperature (°C)

FIGURE 7 Normalized SHG signal of polymer 4 as a function of temperature at a heating rate of 4 °C min⁻¹.

shows the dynamic thermal stability study of the NLO activity of a film of polymer 4. 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 °C min⁻¹ from 30 to 200 °C. The polymer film exhibits a thermal stability up to T_{g} , and no significant SHG decay is observed below 135 °C. This SHG thermal stability is higher than that of the Y-type polyurethane containing nitrophenylazoresorcinol, which is near 100 °C.²⁶ In Figure 8, we present the temporal stability of the polymer film in which there was no negligible decay of the SHG signal over hundreds of hours. We measured normalized SHG signal of polymer 4 as a function of baking time at 80 °C, which is enough for electrooptic device applications. 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 polymer also shows good long-term thermal stability of d_{33} except for the small activity loss within a few days after poling. The enhanced thermal stability of SHG of polymer 4 at high temperature is due to the stabilization of dipole alignment of NLO chromophores, which stems from the partial main-chain character of the polymer structure and partly by hydrogen bonds between the neighboring urethane linkages. Thus, we obtained a new type of NLO polyurethane having the advantages of both main-chain and side-chain NLO

Polymer	λ_{\max}^{a} (nm)	d ₃₃ ^b (esu)	Φ^{c}	Film Thickness ^d (μm)	d ₃₁ ^b (esu)	n
4	382	$5.37 imes10^{-9}$	0.32	0.52	$1.76 imes10^{-9}$	<i>n</i> ₁ = 1.715
						<i>n</i> ₂ = 1.741
PU ^e	399	$4.91 imes10^{-9}$	0.13	0.52	$1.64 imes10^{-9}$	<i>n</i> ₁ = 1.716
						$n_2 = 1.743$

technique.33

TABLE 2 Nonlinear Optical Properties of Polymer 4

^a Polymer film after corona poling.

 $^{\rm b}$ SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.34

^c Order parameter $\Phi = 1 - A_1/A_0$, 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

^e Y-type polyurethane containing nitrophenylazoresorcinol.³⁰



FIGURE 8 Normalized SHG signal of polymer 4 as a function of baking time at 80 $^\circ$ C in air.

polymers, namely stabilization of dipole alignment and good solubility.

CONCLUSIONS

Novel X-type polyurethane **4** with pendant NLO chromophores, which are parts of the polymer backbone, was prepared and characterized. The resulting X-type NLO polyurethane **4** is soluble in common organic solvents. Polymer **4** shows a thermal stability up to 270 °C from TGA thermogram with T_g value near 134 °C. The SHG coefficient (d_{33}) of corona-poled polymer film is 5.37 x 10⁻⁹ esu. Polymer **4** exhibits SHG stability up to 135 °C. This enhanced thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophores, which are components of the polymer backbone and partly by hydrogen bonds between the neighboring urethane linkages. 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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