Preparation of Novel T-type Polyurethanes with High Thermal Stability of Second Harmonic Generation and Their Nonlinear Optical Properties

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2,5-Di-(2'-hydroxyethoxy)benzylidenemalononitrile (**3**) was prepared and polymerized with 2,4-toluenediisocyanate and 3,3'-dimethoxy-4,4'-biphenylenediisocyanate to yield novel T-type polyurethanes **4** and **5** containing 2,5-dioxybenzylidenemalononitrile, nonlinear optical (NLO)-chromophores as part of the polymer backbones. Polyurethanes **4** and **5** were soluble in common organic solvents such as acetone and N,N-dimethylformamide and showed a thermal stability up to 250 °C with glass-transition temperatures (T_g) in the range 119-146 °C. The second harmonic generation (SHG) coefficients (d_{33}) of poled polymer films at 1064 nm fundamental wavelength were around 5.82×10^{-9} esu. The dipole alignment exhibited high thermal stability up to T_g, and there was no SHG decay below 140 °C due to the partial main-chain character of the polymer structure, which was acceptable for nonlinear optical device applications.

Key Words : Nonlinear optics, Polyurethanes, Thermal stability, Second harmonic generation, Relaxation of dipole alignment

Introduction

Recently there has been an extensive research in the synthesis of nonlinear optical (NLO) polymers because of their potential applications in the field of electro-optic devices.[1,2] Inorganic materials such as lithium niobate have many disadvantages such as slow response time and degradative photorefractive effects, which limit their applications. NLO polymers, on the other hand, 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. One of the current challenges is to design novel NLO polymers having optimized properties. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is an important consideration; in this context two approaches to minimize the randomization have been proposed namely the use of cross-linking[3-6] and the utilization of high T_g polymers such as polyimides.[7,8] The polyurethane matrix forms extensive hydrogen bonding between urethane linkage and increases rigidity preventing the relaxation of induced dipoles.[9,10] Polyurethanes with a NLO chromophore, whose dipole moment is aligned transverse to the main chain backbone, showed a large second-order nonlinearity with good thermal stability.[11-12] Recently we reported novel Y-type NLO polyurethanes with enhanced thermal stability of second harmonic generation.[13-17] In this work we have prepared novel T-type polyurethanes containing 2,5-dioxybenzylidenemalononitrile group as a NLO-chromophore. We selected the latter because it has larger dipole moment than 2,5-dioxybenzylidenecyanoacetate group and is rather easy to synthesize. Furthermore, the 2,5-dioxybenzylidenemalononitrile groups constitute novel T-type NLO polyurthanes (see
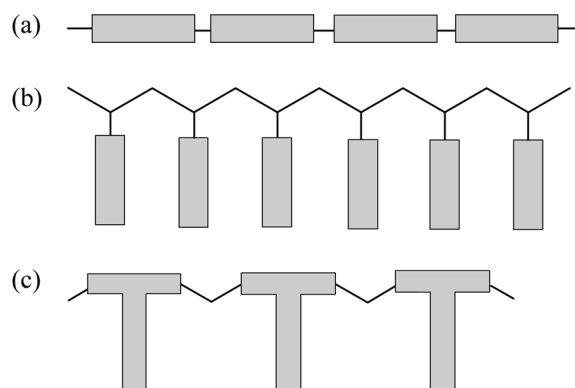

Figure 1. (a) Main-chain NLO polymers, (b) Side-chain NLO polymers, and (c) T-type NLO polymers.

Fig. 1c), and these T-type NLO polyurethanes have not been reported in the literature. Thus, we synthesized a new type of NLO polyurethane, in which the pendant NLO-chromophores are components of the polymer backbone. These mid-type NLO polymers are expected to have the advantages of both main-chain and side-chain NLO polymers namely stable dipole alignment and good solubility. After confirming the structure of the resulting polymers, we investigated their properties such as T_g, thermal stability, surface morphology, and second harmonic generation (SHG) activity (d_{33}).

Results and Discussion

Synthesis and Characterization of Polymers 4 and **5.** 2,5-Di-(2'-vinyloxyethoxy)benzaldehyde (**1**) was prepared by the reaction of 2-chloroethyl vinyl ether with 2,5-dihydroxybenaldehyde. 2,5-Di-(2'-vinyloxyethoxy)benzyl-
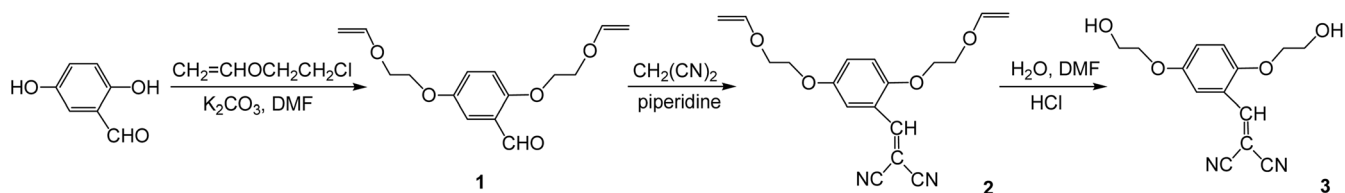
Scheme 1. Synthesis of diol **3**.
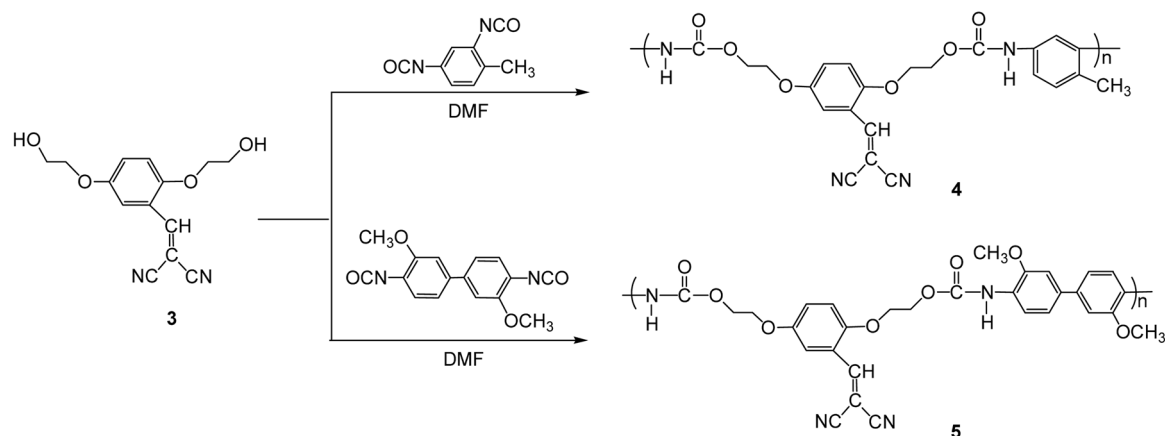
Scheme 2. Synthesis of polymers **4** and **5**.

idenemalononitrile (**2**) was prepared by the condensation reaction of compound **1** with malononitrile. Compound **2** was hydrolyzed to yield acetaldehyde and diol **3**. The synthetic route for compound **3** is presented in Scheme 1. Polymers **4** and **5** were prepared by the polyaddition reaction between a diol **3** and 2,4-toluenediisocyanate (TDI) and 3,3'-dimethoxy-4,4'-biphenylenediisocyanate (DMBPI) in a dry DMF solvent (see Scheme 2). Polymerization results are summarized in Table 1. All polymerizations were carried out under stoichiometric conditions. We obtained polyurethanes with similar molecular weights and compositions. The polymerization yield was in the range 82-90%. The structural feature of these polymers is that they have pendant NLO chromophores, which are parts of the polymer main chains. In this way the mid-type NLO polymers can have the advantages of both main-chain and side-chain NLO polymers simultaneously. The chemical structures of the compounds were identified by ^{1}H NMR and IR spectra, and elemental analysis. All the analytical data confirmed the expected chemical structure. Elemental analysis results fit the polymer structures. ^{1}H NMR spectra of the polymers showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structures. The signal at 8.59-9.72 ppm assigned to the amine proton indicates the formation of urethane linkage. The IR spectrum of the same polymer sample also show a strong carbonyl peak near 1722 cm^{-1} indicating the presence of urethane bond. The number-average molecular weights (M_n) of the polymer **4** was 16200 (M_w/M_n = 2.10). Polydispersities were in the range 1.90-2.12. Polymers **4** and **5** are soluble in common solvents such as acetone, DMF, and DMSO, but are not soluble in methanol and diethyl ether. The inherent

viscosity values were 0.28-0.30 dL g^{-1}. We now have well defined T-type polyurethanes, and investigated their properties in the following section.

Thermal Properties of the Polymers. The thermal behavior of the polymers was investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and T_g. The results are summarized in Table 2. In Figure 2 and Figure 3, TGA and DSC thermograms of the polymers **4** and **5** are presented, respectively. Polymers **4** and **5** showed a thermal stability up to 250 °C according to their TGA thermograms. The initial weight loss in the polymers begins at 260-294 °C. Polymer **5** showed a higher initial degradation temperature than **4**. The T_g values of the polymers **4** and **5** measured by DSC were 119 and 146 °C, respectively. Polymer **5** exhibited a higher T_g value and can probably be attributed to the rigidity of the polymer backbone containing biphenyl group.

Film Morphology of the Polymers. To induce non-

Table 1. Polymerization^a of **3**^{b} with TDI^c and DMBPI^d in DMF

Monomer	Monomer/ Sovent (mol^{-1})	Time (h)	Yield (%)	η_{inh}^e (dL g^{-1})	M_n^f	M_w^f
3, TDI	0.40	8	90	0.28	14800	28600
3, TDI	0.80	10	92	0.30	16200	30800
3, DMBPI	0.40	8	86	0.28	13500	28600
3, DMBPI	0.80	10	88	0.29	14600	28200

^{a}All polymerizations were carried out under stoichiometric conditions. ^{b}**3** = 2,5-Di-(2'-hydroxyethoxy)benzylidenemalononitrile. ^{c}TDI = 2,4-Toluendiisocyanate. ^{d}DMBPI = 3,3'-Dimethoxy-4,4'-biphenylenediiso-cyanate. ^{e}Inherent viscosity of polymer: Concentration of 0.5 g dL^{-1} in DMSO at 25 °C. ^{f}Measured by GPC in THF using polystyrene standard.
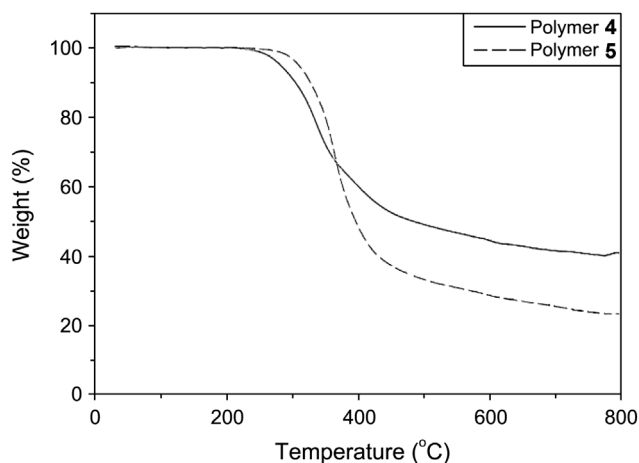
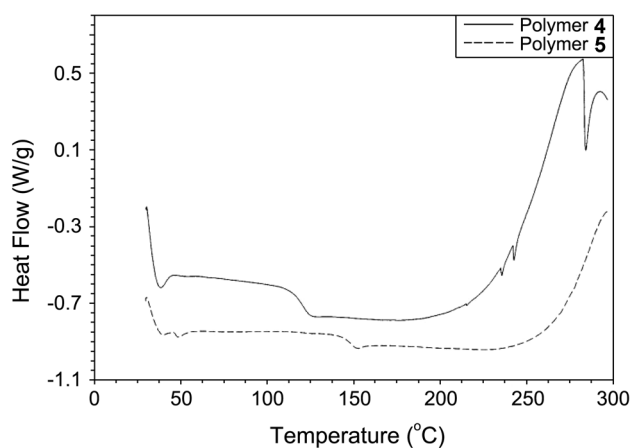**Figure 2**. TGA thermograms of polymers **4** and **5** at a heating rate of 10 ^{o}C/min under nitrogen.

Figure 3. DSC thermograms of polymers **4** and **5** at a heating rate of 10 ^{o}C/min under nitrogen.

Table 2. Thermal Properties of Polymers **4** and **5**

Polymer	$T_g{}^a$ (^{o}C)	Degradation temperature (^{o}C)^b				Residue at 800 ^{o}C (%)^b
		Initial-loss	5%-loss	20%-loss	40%-loss	
4	119	260	281	306	402	40.2
5	146	294	305	348	375	23.7

^{a}Determined from DSC curves measured on a TA 2920 differential scanning calorimeter with a heating rate of 10 ^{o}C/min under nitrogen atmosphere. ^{b}Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10 ^{o}C/min under nitrogen atmosphere.
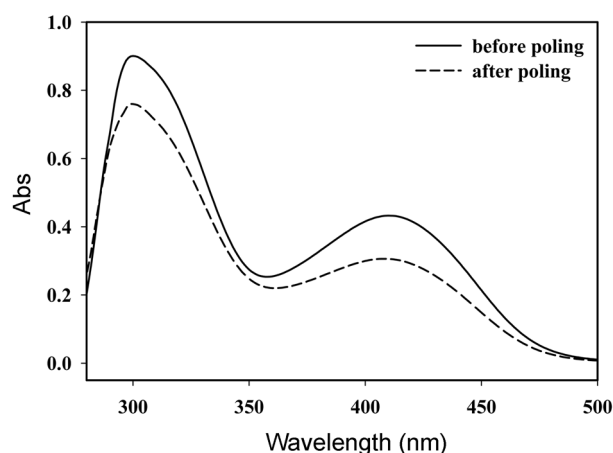

Figure 4. UV-Vis absorption spectra of a film of polymer **4** before and after poling.
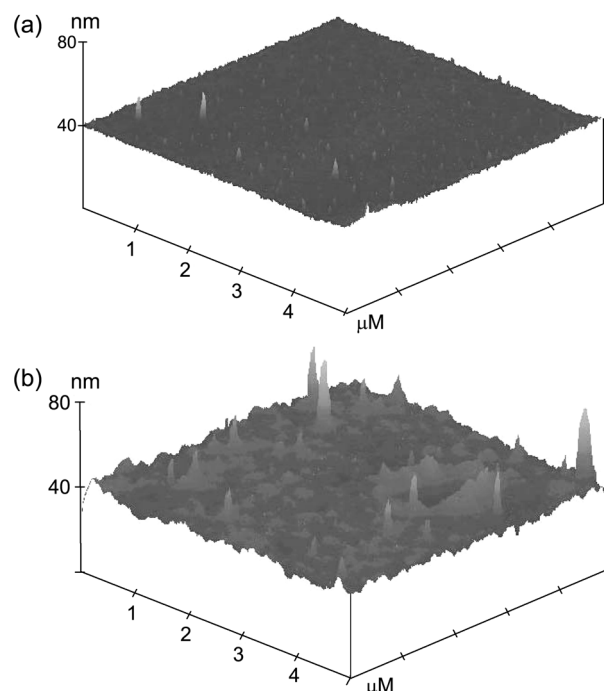
Figure 5. AFM images of spin-coated film of polymer **4**: (a) before corona-poling; (b) after corona-poling.

centrosymmetric polar order, the spin-coated polymer films were corona-poled. As the temperature was raised gradually to 5-10 ^{o}C higher than T_g, 6.5 kV of corona voltage was applied and kept that temperature for 30 min. The poling was confirmed by UV-vis spectrum. Polymers **4** and **5** showed strong absorption near 408 nm by the NLO-chromophore 2,5-dioxybenzylidenemalononitrile group. The UV-vis absorption spectra of the polymer sample **4** before and after poling are presented in Figure 4. After electric poling, the dipole moments of the NLO-chromophores were aligned and UV-vis spectra of polymer **4** exhibited a slight blue shift and a decrease in absorption due to birefringence. From the absorbance change, the order parameter of the poled film could be estimated, which is related to the poling efficiency. The estimated order parameter value F was equal to 0.29 for polymer **4** ($\Phi = 1-A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after poling, respectively). The decrease in absorbance after poling was an indicator of the dipole alignment. For the purpose of investigating surface morphology of polymer films, domain structures of NLO-chromophores for the thin-film samples were obtained with atomic force microscopy (AFM). Figure 5 shows AFM scans of the spin-coated film before and after

poling for polymer **4**. AFM images show that the surface of the film sample is extremely flat and smooth. However, this good quality film was dramatically changed after poling,

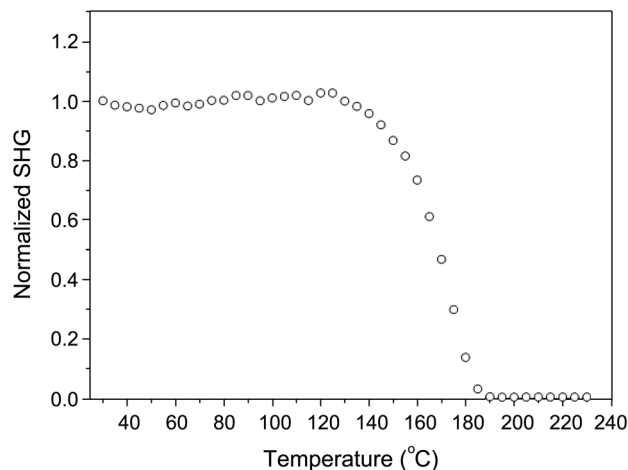**Table 3**. Nonlinear Optical Properties of Polymers **4** and **5**

Polymer	$\lambda_{max}{}^a$ (nm)	$d_{33}{}^b$ (esu)	Φ^c	film thickness^d (μm)	$d_{31}{}^b$ (esu)	n
4	408	$(5.82 \pm 0.36) \times 10^{-9}$	0.29	0.53	$(2.36 \pm 0.16) \times 10^{-9}$	$n_1 = 1.57$ $n_2 = 1.65$
5	407	$(5.59 \pm 0.28) \times 10^{-9}$	0.14	0.51	$(2.28 \pm 0.16) \times 10^{-9}$	$n_1 = 1.58$ $n_2 = 1.64$

^{a}Polymer film after corona poling. ^{b}SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.[19] ^{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 by the optical transmission technique.[18]
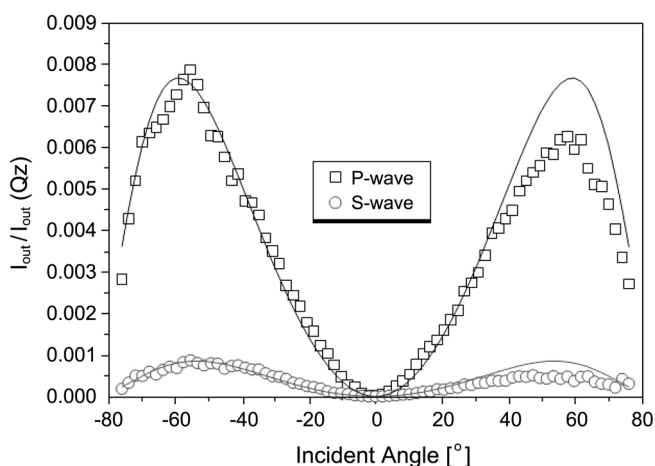
Figure 6. Angular dependence of SHG signal in a poled film of polymer **5**.

Figure 7. Normalized SHG signal of polymer **5** as a function of temperature at a heating rate of 10 ℃/min.

resulting in numerous hills and valleys in the surface structure, which means that the NLO-chromophores were aligned in the poling direction, as shown in Figure 5(b).

Nonlinear Optical Properties of the Polymers. The NLO properties were studied by the SHG method. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. The refractive index of the sample was measured by the optical transmission technique.[18] The transmittance of thin film includes information on the thickness, refractive index and its extinction coefficient. Thus, we could determine these parameters by analyzing the transmittance. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded and compared with the values obtained from Y-cut quartz plate. Figure 6 shows the angular dependence of SHG signal in a poled polymer **5**. The measurements were taken after the poled film was stand at room temperature for 2 days to remove the residue charge by the poling electric field. For the calculation of the d_{31} and d_{33} values, both *s*-polarized and *p*-polarized IR laser were directed to the samples and recorded. The SHG coefficient d_{33} was calculated through the method developed by Herman and Hyden.[19] Nonlinear optical properties of polymers **4** and **5** are summarized in Table 3. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure.[20] The values of d_{31} and d_{33} for polymer **4** were 2.36×10^{-9} and 5.82×10^{-9} esu, respectively. As expected, these d_{31} and d_{33} values are larger than those of the polyurethanes with 2,5-dioxybenz-

ylidenecyanoacetate as a NLO chromophore.[17] Because the second harmonic wavelength was at 532 nm, which was not in the absorptive region of the resulting polyurethane, there was not 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 around 2.5 is in good agreement with the predicted value.

To evaluate the high-temperature stability of the polymers, we studied the temporal stability of the SHG signal. In Figure 7 we present the dynamic thermal stability study of the NLO activity of the film **5**. To investigate the real-time NLO decay of the SHG signal of the poled polymer films as a function of temperature, *in situ* SHG measurements were performed at a heating rate of 10 ℃/min from 30 ℃ to 250 ℃. The polymer films **4** and **5** exhibited greater thermal stability and no significant SHG decay was observed below 140 ℃. In general, side chain NLO polymers loose thermal stability below T_g. The stabilization of the dipole alignment is a characteristic of main-chain NLO polymers. The high thermal stability of second harmonic generation of polymers **4** and **5** was due to the stabilization of dipole alignment of NLO chromophore, which stemmed from the partial main chain character of the polymer structure. Thus, we obtained a new type of NLO polyurethane having the advantages of both main-chain and side-chain NLO polymers: stabilization of dipole alignment and good solubility.

Conclusions

Novel T-type polyurethanes **4** and **5** with pendant NLO

chromophores as part of the polymer main chains were synthesized. These mid-type NLO polyurethanes are soluble in common organic solvents and polymers **4** and **5** displayed a thermal stability up to 250 $^{\circ}$C and T_g values in the range 119-146 $^{\circ}$C. The SHG coefficient (d_{33}) of corona-poled polymer film was 5.82×10^{-9} esu. The striking feature of these polymers is that they exhibit SHG stability up to T_g and no significant SHG decay was observed below 140 $^{\circ}$C. The high thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO-chromophore.

Experimental Section

Materials. The reagent-grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2-Chloroethyl vinyl ether and 2,5-dihydroxybenzaldehyde were used as received. 2,4-Toluenediisocyanate (TDI) was purified by distillation under reduced pressure. 3,3'-Dimethoxy-4,4'-biphenylenediisocyanate (DMBPI) was recrystallized from ethyl acetate. Piperidine was dried with calcium hydride and fractionally distilled. *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. ^{1}H NMR spectra were obtained on a Varian 300 MHz NMR spectrometer. UV-Vis absorption spectra were measured on a Shimadzu UV-3100S spectrophotometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The glass transition temperatures (T_g) were measured on a TA 2920 differential scanning calorimeter in a nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of 10 $^{\circ}$C/min up to 800 $^{\circ}$C was used for the thermal degradation study of polymers under nitrogen. The number average molecular weight (M_n) and weight average molecular weight (M_w) of the polymers were estimated by gel permeation chromatography (GPC) (columns styragel HR5E4E; solvent THF). Atomic force microscopy (AFM) images were recorded with a Park Science Instrument Autoprobe CP, operated in a contact mode, which measures topography. Melting points were measured in Buchi 530 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

Film Preparation and SHG Measurement. The polymer film was prepared from a 10 wt% by weight polymer solution in DMF deposited on an indium-tin oxide (ITO) covered glass. Prior to film casting, the polymer solution was filtered through 0.45 μm Teflon$^{\circledR}$ membrane filter. The film was spin cast at room temperature in the range 1000-1200 rpm. The films were dried for 12 h under vacuum at 60 $^{\circ}$C. The alignment of the NLO-chromophore of the polymers was carried out by 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 $^{\circ}$C higher than

T_g, 6.5 kV of corona voltage was applied and kept that temperature 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 by the optical transmission technique.[18] Second harmonic generation measurement was carried out one day after poling. 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. A beam splitter and a photodiode were used to compensate for the intensity fluctuations of the fundamental beam (1064 nm). The polarity of the fundamental laser beam was adjusted using a half-wave plate before it hit the sample. The electric field vector of the incident beam was either parallel (*p*-polarization) or perpendicular (*s*-polarization) to the plane of incidence. Only the *p*-polarized SH beam was made to enter a photomultiplier tube (PMT) by using a prism and a SH pass filter. An analyzer was used to confirm the polarization direction of the SH signal. A poled polymer film was mounted on the rotator coupled to a step motor. The output signals from the photodiode and 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) 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.[19]

2,5-Di-(2'-vinyloxyethoxy)benzaldehyde (1). 2,5-Di-hydroxybenzaldehyde (13.8 g, 0.10 mol), anhydrous potassium carbonate (82.9 g, 0.60 mol), and 2-chloroethyl vinyl ether (16.0 g, 0.25 mol) were dissolved in 400 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80 $^{\circ}$C for 15 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 recrystallized from 1-butanol yielded 24.5 g (88% yield) of pure product **1**. ^{1}H NMR (CDCl$_3$) δ 3.98-4.34 (m, 12H, 2 CH$_2$=, 2 -O-CH$_2$-CH$_2$-O-), 6.45-6.58 (m, 2H, 2 =CH-O-), 6.92-6.99 (m, 1H, aromatic), 7.15-7.21 (m, 1H, aromatic), 7.33-7.36 (d, 1H, aromatic), 10.46 (s, 1H, -CHO). IR (KBr) 3096, 3075 (w, =C-H), 2941, 2882 (s, C-H), 1676 (vs, C=O), 1624 (vs, C=C) cm^{-1}.

2,5-Di-(2'-vinyloxyethoxy)benzylidenemalononitrile (2). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,5-di-(2'-vinyloxyethoxy)benzaldehyde **1** (8.35 g, 30 mmol) and malononitrile (2.18 g, 33 mmol) in 170 mL of 1-butanol with stirring at 0 $^{\circ}$C under nitrogen. After stirring for 4 h at 0 $^{\circ}$C, the reaction mixture was cooled to −10 $^{\circ}$C for crystallization. The product was filtered and washed successively with cold 1-butanol (80 mL), water (30 mL), and cold 1-

butanol (20 mL). The obtained pale yellow product was recrystallized from 1-butanol to give 8.61g (88% yield) of **2**. Mp = 72-74 °C. ^{1}H NMR (CDCl$_3$) δ 4.02-4.40 (m, 12H, 2 CH$_2$=, 2 -O-CH$_2$-CH$_2$-O-), 6.46-6.58 (m, 2H, 2 =CH-O-) 6.94-6.98 (d, 1H, aromatic), 7.18-7.23 (q, 1H, aromatic), 7.75-7.78 (d, 1H, aromatic), 8.31 (s, 1H, Ph-CH=). IR (KBr) 3057 (w, =C-H), 2941, 2885 (m, C-H), 2222 (s, CN), 1624, 1578 (vs, C=C) cm^{-1}. Anal. Calcd for C$_{18}$H$_{18}$N$_2$O$_4$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.36; H, 5.64; N, 8.50.

2,5-Di-(2'-hydroxyethoxy)benzylidenemalononitrile (3). Aqueous hydrochloric acid (1.5 M, 30 mL) was slowly added to a solution of 2,5-di-(2'-vinyloxyethoxy)benzyl-idenemalononitrile (**2**) (8.48 g, 0.026 mol) in 60 mL of dry THF with stirring under nitrogen at 0 °C. The mixture was stirred at 80 °C for 8 h under nitrogen. The resulting solution was extracted with diethyl ether (80 mL) three times. The organic layer was washed successively with saturated sodium chloride, sodium hydrogen carbonate, and water, followed by drying with anhydrous magnesium sulfate. Rotary evaporation of diethyl ether gave crude product. The obtained pale yellow product was recrystallized from ethyl acetate to give 6.06 g (85% yield) of **3**. Mp = 138-140 °C. ^{1}H NMR (acetone-d_6) δ 3.74-3.94 (m, 4H, 2 -CH$_2$-OH), 3.94-4.12 (m, 2H, -OH), 4.12-4.22 (m, 4H, 2 -O-CH$_2$-), 7.15-7.32 (m, 2H, aromatic), 7.75 (s, 1H, aromatic), 8.58 (s, 1H, -Ph-CH=). IR (KBr) 3516, 3233 (s, O-H), 3045 (m, =C-H), 2941 (m, C-H), 2233 (m, CN), 1576 (s, C=C) cm^{-1}. Anal. Calcd for C$_{14}$H$_{14}$N$_2$O$_4$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.41; H, 5.22; N, 10.28.

Synthesis of polyurethanes 4 and 5. A representative polyaddition reaction procedure (the case of **4**) was as follows: 2,4-Toluenediisocyanate (1.74 g, 0.01 mol) was added slowly to a solution of 2.74 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 10 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 diethyl ether and dried under vacuum to give 4.13 g (92% yield) of polymer **4**: η_{inh}=0.30 dL g^{-1} (c, 0.5 g dL^{-1} in DMSO at 25 °C). ^{1}H NMR (DMSO-d_6) δ 2.07 (s, 3H, -CH$_3$), 4.14-4.47 (t, 8H, 2 -O-CH$_2$-CH$_2$-O-), 6.92-7.59 (m, 6H, aromatic), 8.40-8.45 (d, 1H, Ph-CH=), 8.92-8.98 (d, 1H, N-H), 9.63-9.72 (d, 1H, N-H). IR (KBr) 3337 (s, N-H), 2953 (m, C-H), 2222 (m, CN),

1722 (vs, C=O), 1595 (s, C=C) cm^{-1}. Anal. Calcd for (C$_{23}$H$_{20}$N$_4$O$_6$)$_n$: C, 61.60; H, 4.50; N, 12.49. Found: C, 61.68; H, 4.59; N, 12.58. Polymer **5**: η_{inh}=0.29 dL g^{-1} (c, 0.5 g dL^{-1} in DMSO at 25 °C). ^{1}H NMR (DMSO-d_6) δ 3.88 (s, 6H, 2 -OCH$_3$), 4.17-4.53 (q, 8H, 2 -O-CH$_2$-CH$_2$-O-), 7.16-7.39 (d, 6H, aromatic), 7.57-7.76 (d, 2H, aromatic), 8.20 (d, 1H, aromatic), 8.47 (s, 1H, aromatic), 8.59-8.66 (d, 1H, N-H), 9.02 (s, 1H, N-H). IR (KBr) 3420 (m, N-H), 2941 (m, C-H), 2233 (m, CN), 1728 (s, C=O), 1583 (s, C=C) cm^{-1}. Anal. Calcd for (C$_{30}$H$_{26}$N$_4$O$_8$)$_n$: C, 63.15; H, 4.59; N, 9.82. Found: C, 63.25; H, 4.64; N, 9.88.

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