

# Synthesis and Properties of Novel Y-type Nonlinear Optical Polyester Containing Dioxynitroazobenzene Group with Enhanced Thermal Stability of Dipole Alignment

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New Y-type polyester (**3**) containing nitrophenylazoresorcinoy groups as NLO chromophores, which are components of the polymer backbone, was prepared and characterized. Polyester **3** is soluble in common organic solvents such as *N,N*-dimethylformamide and acetone. It shows a thermal stability up to 240 °C in thermogravimetric analysis with glass-transition temperature ( $T_g$ ) obtained from differential scanning calorimetry near 116 °C. The second harmonic generation (SHG) coefficient ( $d_{33}$ ) of poled polymer film at the 1064 nm fundamental wavelength is around  $4.63 \times 10^{-9}$  esu. The dipole alignment exhibits a thermal stability even at 4 °C higher than  $T_g$ , and there is no SHG decay below 120 °C due to the partial main-chain character of polymer structure, which is acceptable for NLO device applications.

**Key Words** : Nonlinear optics, Polyester, Atomic force microscopy (AFM), Thermal stability, Second harmonic generation

## Introduction

Nonlinear optical (NLO) polymers received a great attention in recent years because of their potential applications in the field of electro-optic devices including ultrafast optical switches, high-speed optical modulators, and high-density optical data storage media.<sup>1-4</sup> NLO polymers have many advantages superior to conventional inorganic ones such as light weight, low cost, ultrafast response, wide response wave band, high optical damage threshold, and good processability to form optical devices. A potential NLO polymer must contain highly polarizable conjugated electronic systems and has to be mechanically very strong and thermally stable with a high glass transition temperature ( $T_g$ ). 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<sup>5-8</sup> and the utilization of polymers with high glass transition temperature ( $T_g$ ) such as polyimides.<sup>9-14</sup> Various polyesters with NLO chromophores in the main chain<sup>15,16</sup> or side chain<sup>17,18</sup> have been prepared and their NLO properties studied. Polyesters with amino-sulfone azobenzene chromophores in the main chain generate strong and stable reversible birefringence.<sup>15</sup> NLO polyesters containing azobenzene mesogens in the main chain exhibit high thermal and temporal stabilities.<sup>16</sup> Polyesters containing cyanophenylazoaniline moiety in the side chain show good temporal stability of second-order nonlinearity.<sup>17</sup> Main-chain NLO polymers usually have good thermal stability of dipole alignments, but they often do not dissolve in organic solvents, and their intractability make them unusable to fabricate stable films. Side-chain NLO polymers have the advantages

such as good solubility, homogeneity and high loading level of NLO chromophores, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we prepared novel polyesters containing dioxynitrostilbene,<sup>19</sup> dioxybenzylidenemalononitrile,<sup>20,21</sup> dioxybenzylidenecyanoacetate,<sup>22,23</sup> and tricyanovinylthienyl groups<sup>24,25</sup> as NLO chromophores. The resulting polymers exhibit enhanced thermal stability of second harmonic generation (SHG), which stems from the stabilization of dipole alignment of the NLO chromophores.

In this work reported here, we prepared new Y-type polyester containing nitrophenylazoresorcinoy groups as NLO chromophores. We selected the latter as NLO chromophores because they were expected to have high optical nonlinearities and we like to compare its properties with those of the polyester containing 3,4-dioxynitrostilbene. Furthermore, these nitrophenylazoresorcinoy groups constitute novel Y-type NLO polyesters,<sup>21</sup> and these Y-type NLO polyesters have not yet been reported in the literature. Thus, we synthesized a new type of NLO polyester, in which the pendant NLO chromophores are parts 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 such as solubility,  $T_g$ , thermal stability, surface morphology of polymer films, second harmonic generation activity and relaxation of dipole alignment.

## 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 pre-

pared by acid-catalyzed hydrolysis of **2** in DMF. Polyester **3** was synthesized through the reaction of monomer **2** containing NLO chromophore with stoichiometric amount of terephthaloyl chloride in pyridine. 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 90%.

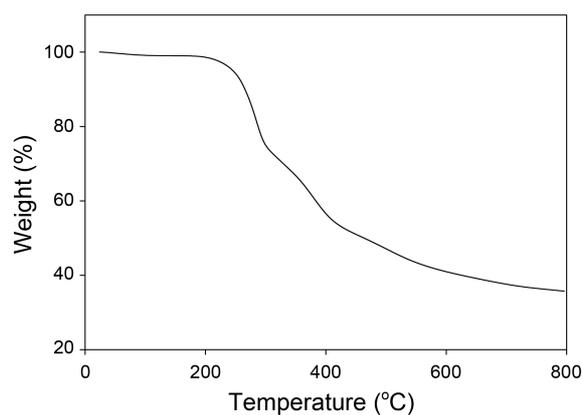
The chemical structure of the resulting polymer was confirmed by  $^1\text{H}$  NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structure.  $^1\text{H}$  NMR spectrum of the polymer showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The  $^{13}\text{C}$  NMR spectrum of the polymer **3** shows a signal near 165 ppm assigned to the carbonyl carbon indicates the presence of ester group. The IR spectrum of polymer **3** shows strong carbonyl peaks near  $1721\text{ cm}^{-1}$  indicating the presence of ester bond. The spectrum also shows strong absorption peak near  $1600\text{ cm}^{-1}$  due to azo group and absorptions at  $1521$  and  $1342\text{ cm}^{-1}$  due to nitro group indicating the presence of nitroazobenzene unit. These results are consistent with the proposed polymer structure, indicating that the NLO chromophore remained intact during the polymerization. The molecular weights shown in Table 1 were determined by GPC using polystyrene as the standard and THF as an eluent. The number average molecular weight ( $M_n$ ) of the polymer **3**, determined by GPC, was  $18,800\text{ g mol}^{-1}$  ( $M_w/M_n=1.97$ ). 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 in the range  $0.30\text{--}0.31\text{ dL g}^{-1}$ . Polymer **3** shows strong absorption near  $398\text{ nm}$  due to the NLO chromophore dioxynitroazobenzene group.

The striking feature of this polymerization system is that it gives unprecedented Y-type NLO polymer, in which the pendant NLO chromophores are parts of the polymer backbone. This Y-type NLO polymer is expected to have the advantages of both main-chain and side-chain NLO polymers. Thus, we obtained a new type of NLO polyester with side-

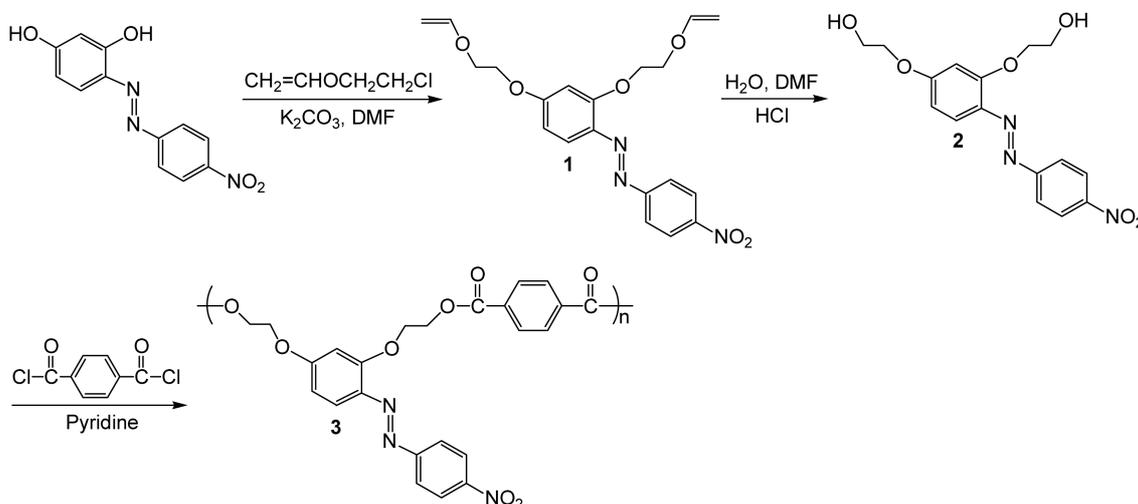
chain and main-chain characteristics. Having obtained the well defined Y-type polyester **3**, we investigated its properties.

**Thermal Properties of Polymer.** The thermal behavior of the polymer was investigated by TGA and DSC to determine the thermal degradation pattern and glass transition temperature. The results are summarized in Table 1. The TGA thermogram of the polymer **3** is shown in Figure 1. Polymer **3** has a thermal stability up to  $240\text{ }^\circ\text{C}$  according to its TGA thermogram. This thermal stability is lower than that of the polyester containing 3,4-dioxynitrostilbene.<sup>19</sup> The  $T_g$  value of the polymer **3** measured using DSC is near  $116\text{ }^\circ\text{C}$ . This is higher value compared to that of polyester containing 3,4-dioxynitrostilbene group, which has near  $110\text{ }^\circ\text{C}$ .<sup>19</sup> The TGA and DSC studies show that the decomposition temperature of the polymer **3** is higher than the corresponding  $T_g$  value. This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

**Film Morphology of Polymer.** To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. As the temperature was raised to  $5\text{--}10\text{ }^\circ\text{C}$  higher than  $T_g$ , a corona voltage of  $6.5\text{ kV}$  was applied and



**Figure 1.** TGA thermogram of polymer **3** obtained at a heating rate of  $10\text{ }^\circ\text{C/min}$  under nitrogen.



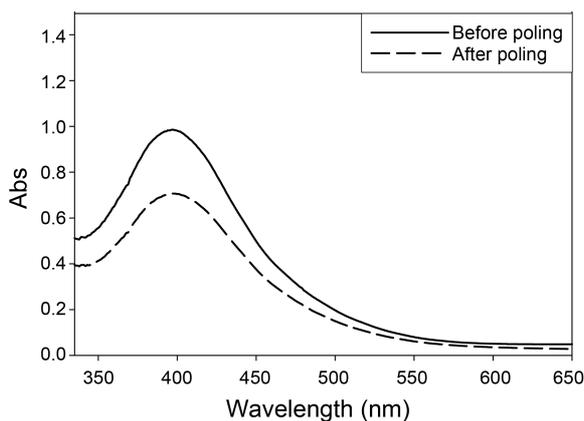
**Scheme 1.** Synthetic scheme and structure of polymer **3**.

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

Polymer	$T_g^a$ , °C	Degradation temp, °C <sup>b</sup>			$M_n^c$	$M_w^c$
		5 wt %- Loss	20 wt %- Loss	40 wt %- Loss		
<b>3</b>	116	241	284	388	18,800	37,100
<b>4<sup>d</sup></b>	110	335	383	462	15,300	30,800

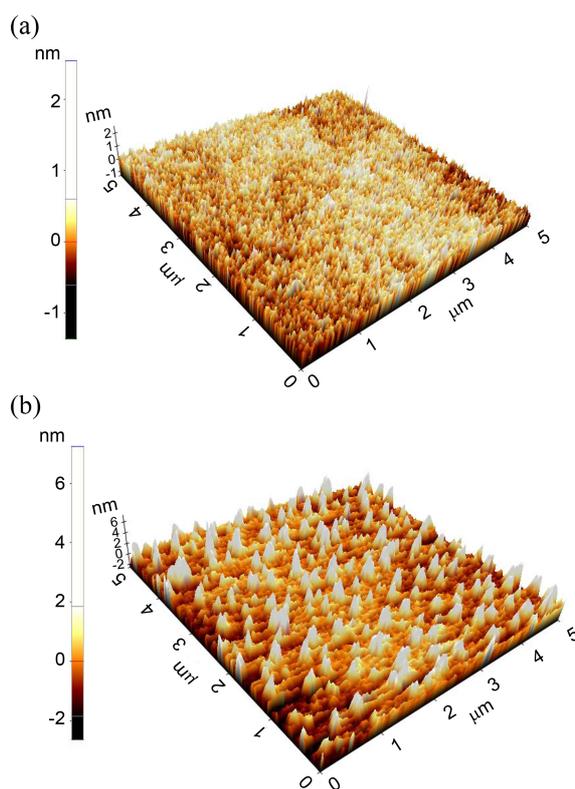
<sup>a</sup>Determined from DSC curves measured with a TA 2920 differential scanning calorimeter with a heating rate of 10 °C/min under nitrogen atmosphere. <sup>b</sup>Determined from TGA curves measured with a TA Q50 thermogravimetric analyzer with a heating rate of 10 °C/min under nitrogen atmosphere. <sup>c</sup>Measured by gel permeation chromatography (GPC) in THF using polystyrene standard. <sup>d</sup>Polyester containing 3,4-dioxynitrostilbene.<sup>19</sup>

this temperature was maintained for 30 min. The poling was confirmed from UV-visible spectra. The UV-visible absorption spectra of the polymer **3** before and after poling are presented in Figure 2. After electric poling, the dipole moments of the NLO chromophores were aligned and the UV-visible spectrum of polymer **3** exhibits 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  $\Phi$  is equal to 0.28 for polymer **3** ( $\Phi=1-A_1/A_0$ , where  $A_0=0.9857$  and  $A_1=0.7056$  are the absorbances of the polymer film before and after poling, respectively). For the purpose of investigating the surface morphology of polymer film, domain structures of NLO chromophores for the thin-film samples were obtained using atomic force microscopy (AFM). Figure 3 shows AFM scans of a spin-coated film of polymer **3** before and after poling. AFM images show that the surface of the film

**Figure 2.** UV-visible absorption spectra of a film of polymer **3** before and after poling.**Table 2.** Nonlinear Optical Properties of Polymer 3

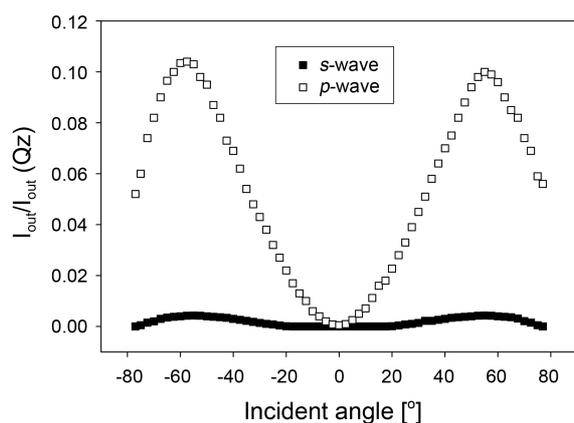
Polymer	$\lambda_{max}^a$ (nm)	$d_{33}^b$ (esu)	$\Phi^c$	$d_{31}^b$ (esu)	Film thickness <sup>d</sup> ( $\mu\text{m}$ )	$n$
<b>3</b>	398	$4.63 \times 10^{-9}$	0.28	$1.58 \times 10^{-9}$	0.48	$n_1 = 1.728$
<b>4<sup>e</sup></b>	382	$3.51 \times 10^{-8}$	0.14	$1.41 \times 10^{-8}$	0.30	$n_1 = 1.730$

<sup>a</sup>Polymer film after corona poling. <sup>b</sup>SHG coefficients ( $d_{33}$ ) were derived from the analysis of measured Maker-fringes.<sup>27</sup> <sup>c</sup>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. <sup>d</sup>Film thickness was determined using the optical transmission technique.<sup>26</sup> <sup>e</sup>Polyester containing 3,4-dioxynitrostilbene.<sup>19</sup>

**Figure 3.** AFM images of spin-coated film of polymer **3**: (a) before corona-poling; (b) after corona-poling.

sample is extremely flat and smooth before poling (Fig. 3(a)). However, this good-quality film was dramatically changed after poling, resulting in numerous hills and valleys in the surface structure, which means that the NLO chromophores were aligned in the poling direction (Fig. 3(b)).

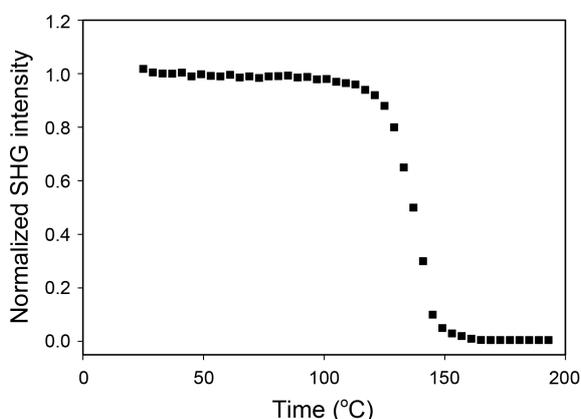
**Nonlinear Optical Properties of Polymer.** The NLO properties of polymer were studied using the SHG method. The refractive index of the sample was measured using the optical transmission technique.<sup>26</sup> The transmittance of thin film gives information on the thickness, refractive index and extinction coefficient. So we could determine these parameters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. Nonlinear optical properties of polymer **3** are summarized in Table 2. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Figure 4 shows the angular dependence of SHG signal for a poled polymer **3**. The SHG values were compared with those obtained from a Y-cut quartz plate. To calculate the  $d_{31}$



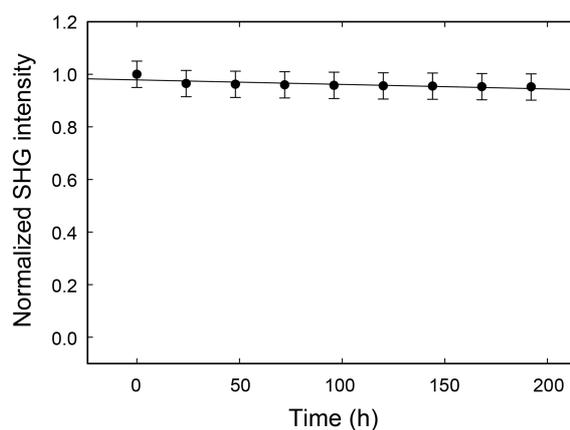
**Figure 4.** Angular dependence of SHG signal for a poled film of polymer **3**.

and  $d_{33}$  values, both *s*-polarized and *p*-polarized IR laser were directed at the samples. SHG coefficients ( $d_{33}$ ) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure.<sup>27</sup> The values of  $d_{33}$  and  $d_{31}$  for polymer **3** are  $4.63 \times 10^{-9}$  and  $1.58 \times 10^{-9}$  esu, respectively. This  $d_{33}$  value is lower compared to that of polyester containing 3,4-dioxynitrostilbene group, which has near  $3.51 \times 10^{-8}$  esu.<sup>19</sup> Since the second harmonic wavelength is at 532 nm, which is not in the absorptive region of the resulting polyester, there is no 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 2.93 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 5 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 measurements were performed at a heating rate of 3.5 °C/min from 30 to 200 °C. The dipole alignment exhibits a thermal stability even at 4 °C higher than  $T_g$ , and there is no SHG decay below 120 °C due to the partial main-chain character of the polymer



**Figure 5.** Normalized SHG signal of polymer **3** as a function of temperature at a heating rate of 4.5 °C/min.



**Figure 6.** Normalized SHG signal of polymer **3** as a function of baking time at 80 °C in air.

structure. This SHG thermal stability is similar with that of polyester containing 3,4-dioxynitrostilbene group.<sup>19</sup> In Figure 6, we present the temporal stability of the polymer film in which there was no negligible decay of the SHG signal over hundreds of hours. 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 high thermal stability of second harmonic generation of polymer **3** is due to the stabilization of dipole alignment of NLO chromophore, which stems from the partial main chain character of the polymer structure. Thus, we obtained another new NLO polyester having the merits of both main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility.

## Conclusions

New Y-type polyester **3** with pendant NLO chromophores as parts of the polymer main chain was synthesized. This Y-type NLO polyester **3** is soluble in common organic solvents and displayed a thermal stability up to 240 °C with a  $T_g$  of 116 °C. The SHG coefficient ( $d_{33}$ ) of corona-poled polymer film is  $4.63 \times 10^{-9}$  esu. Polymer **3** exhibits SHG stability even at 4 °C higher than glass transition temperature ( $T_g$ ), and no SHG decay is observed below 120 °C. This high thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophores, which are parts of the polymer backbone. 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.

## Experimental Section

**Materials.** Reagent-grade chemicals were purchased from Aldrich or AlfaAesar and purified by either distillation or recrystallization before use. 4-(4-Nitrophenylazo)resorcinol and 2-chloroethyl vinyl ether were used as received. Terephthaloyl chloride (TPC) was purified by sublimation under

vacuum. *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 Shimadzu FT IR-8201PC infrared spectrophotometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained with a Varian 300 MHz NMR spectrometer. UV-visible absorption spectra were obtained with a Shimadzu UV-3100S spectrophotometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer.  $T_g$  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  $10\text{ }^\circ\text{C min}^{-1}$  up to  $800\text{ }^\circ\text{C}$  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 Measurement.** Polymer films were prepared from a 10 wt % polymer solution in DMF deposited on an indium-tin oxide (ITO) covered glass. Prior to film casting, the polymer solution was filtered through  $0.45\text{ }\mu\text{m}$  Teflon<sup>®</sup> 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  $60\text{ }^\circ\text{C}$ . 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  $^\circ\text{C}$  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.<sup>26</sup> 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 one day after poling. A continuum PY61 mode-locked Nd:YAG laser ( $\lambda = 1064\text{ nm}$ ) 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 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  $d_{11}=0.3\text{ pm/V}$ ) 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  $0.5^\circ$  intervals using a rotation stage. SHG

coefficients ( $d_{33}$ ) were derived from the analysis of measured Maker-fringes.<sup>27</sup>

**Preparation of 2,4-Di-(2'-vinloxyethoxy)-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  $90\text{ }^\circ\text{C}$  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**.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.06-4.47 (m, 12H, 2  $\text{CH}_2=$ , 2 -O- $\text{CH}_2$ - $\text{CH}_2$ -O-), 6.52-6.71 (m, 4H, 2 =CH-O-, aromatic), 7.79-7.83 (d, 1H, aromatic), 7.94-7.99 (d, 2H, aromatic), 8.32-8.37 (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)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_6$ : 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 ( $1.5\text{ mol L}^{-1}$ , 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  $50\text{ }^\circ\text{C}$  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**.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ )  $\delta$  3.79-3.91 (m, 4H, 2 -O- $\text{CH}_2$ -), 4.17-4.23 (t, 2H, Ph-O- $\text{CH}_2$ -), 4.29-4.35 (t, 2H, Ph-O- $\text{CH}_2$ -), 4.98-5.04 (t, 2H, 2 -OH), 6.72-6.76 (d, 1H, aromatic), 6.89-6.91 (d, 1H, aromatic), 7.75-7.79 (d, 1H, aromatic), 8.02-8.06 (d, 2H, aromatic), 8.45-8.49 (d, 2H, aromatic). IR (KBr) 3283 (s, O-H), 2942 (m, C-H), 1600 (vs, N=N), 1515, 1335 (vs, N=O), 1180 (m, N=N)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_6$ : C, 55.33; H, 4.93; N, 12.10. Found: C, 55.25; H, 4.98; N, 12.15.

**Synthesis of Polymer 3.** A representative polycondensation reaction procedure was as follows. Terephthaloyl chloride (2.03 g, 10 mmol) and diol **2** (3.47 g, 10 mmol) were dissolved in 25 mL of anhydrous pyridine under nitrogen. The resulting solution was refluxed in an oil bath kept at  $90\text{ }^\circ\text{C}$  under a nitrogen atmosphere. After heating 20 h with stirring the resulting polymerization solution was poured into 400 mL of methanol. The precipitated polymer was collected and re-precipitated from DMSO into methanol. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum, yielding 4.29 g (90% yield) of polymer **3**. Inherent viscosity ( $\eta_{\text{inh}}$ ) =  $0.31\text{ dL g}^{-1}$  (c,  $0.5\text{ g dL}^{-1}$  in DMSO at  $25\text{ }^\circ\text{C}$ ).  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ )  $\delta$  4.45-4.87 (m, 8H, 2 -O- $\text{CH}_2$ - $\text{CH}_2$ -O-),

6.68-6.82 (s, 1H, aromatic), 6.85-7.10 (s, 1H, aromatic), 7.58-8.33 (s, 9H, aromatic).  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  67.04, 71.95, 102.99, 110.01, 119.36, 122.41, 124.46, 126.42, 128.89, 131.07, 133.35, 137.18, 148.03, 156.24, 159.35, 165.35. IR (KBr) 3085 (w, =C-H), 2926 (m, C-H), 1721 (vs, C=O), 1600 (s, N=N), 1521, 1342 (vs, N=O), 1180 (m, N=N)  $\text{cm}^{-1}$ . Anal. Calcd for  $(\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}_8)_n$ : C, 60.38; H, 4.01; N, 8.80. Found: C, 60.48; H, 4.09; N, 8.72.

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