

Preparation and Nonlinear Optical Properties of Novel Polyesters with Enhanced Thermal Stability of Second Harmonic Generation

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2,5-Di-(2'-hydroxyethoxy)-4'-nitrostilbene (**3**) was prepared and polycondensed with terephthaloyl chloride, adipoyl chloride, and sebacoyl chloride to yield novel T-type polyesters (**4-6**) containing the NLO-chromophores dioxynitrostilbenyl groups, which constituted parts of the polymer backbones. Polymers **4-6** are soluble in common organic solvents such as acetone and N,N-dimethylformamide. They showed thermal stability up to 260 °C in thermogravimetric analysis with glass-transition temperatures obtained from differential scanning calorimetry in the range 90-95 °C. The second harmonic generation (SHG) coefficients (d_{33}) of poled polymer films at the 1064 nm fundamental wavelength were around 1.42×10^{-9} esu. The dipole alignment exhibited high thermal stability up to 5 °C higher than glass-transition temperature (T_g), and there was no SHG decay below 100 °C due to the partial main-chain character of polymer structure, which is acceptable for NLO device applications.

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

Introduction

A lot of efforts have been directed to the synthesis of nonlinear optical (NLO) materials over the past decade because of their potential applications in the field of electro-optic device applications. The organic materials seem to be superior because of their higher nonlinear optical activity and faster response time than the inorganic ones. Among the organic materials the NLO polymers are receiving great attention, mainly because they offer many advantages such as mechanical endurance, light weight, chemical resistance, and good processability to form optical devices.¹⁻³ A potential NLO polymer must contain highly polarizable conjugated dipolar electronic systems and they have to be mechanically very strong and thermally stable with high glass-transition temperature (T_g). In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is an important consideration. Two approaches to minimize the randomization have been proposed. One is to use cross-linked system⁴⁻⁷ and the other is to utilize high T_g polymers such as polyimides.⁸ Various polyesters with the NLO-chromophores in the main chain⁹ or in side chain¹⁰⁻¹² were prepared and investigated. Main-chain NLO polymers 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 noncentrosymmetric films. Side-chain NLO polymer systems have the advantages such as good solubility, homogeneity and high loading level of NLO chromophore, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we have prepared novel NLO polyesters¹³⁻¹⁵ with enhanced thermal stability of dipole alignment by modification of

polymer structure.

In this work we prepared novel polyesters containing 2,5-dioxynitrostilbenyl groups as NLO-chromophores. We selected the latter because they have a large dipole moment and are rather easy to synthesize. Furthermore, 2,5-dioxynitrostilbenyl groups constitute novel T-type NLO polyesters (Fig. 1c), and these T-type NLO polyesters have not 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 backbones. These mid-type NLO polymers are expected to have the advantages of both main-chain and side-chain NLO polymers: stabilization of dipole alignment and good solubility. After confirming the structure of the resulting polymers we investigated their properties such as solubility, T_g , thermal stability, surface morpho-

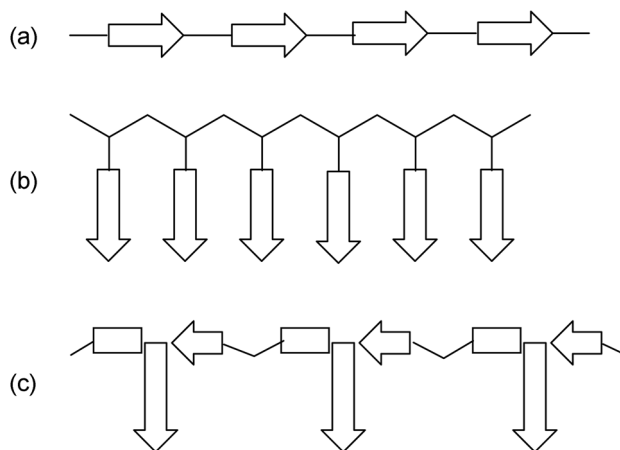
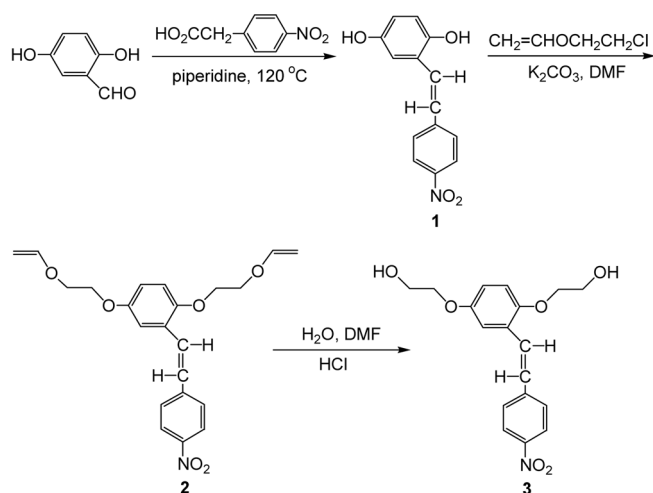


Figure 1. (a) Main-chain NLO polymers, (b) side-chain NLO polymers, and (c) T-type NLO polymers.



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

logy of polymer films, second harmonic generation (SHG) activity and relaxation of dipole alignment.

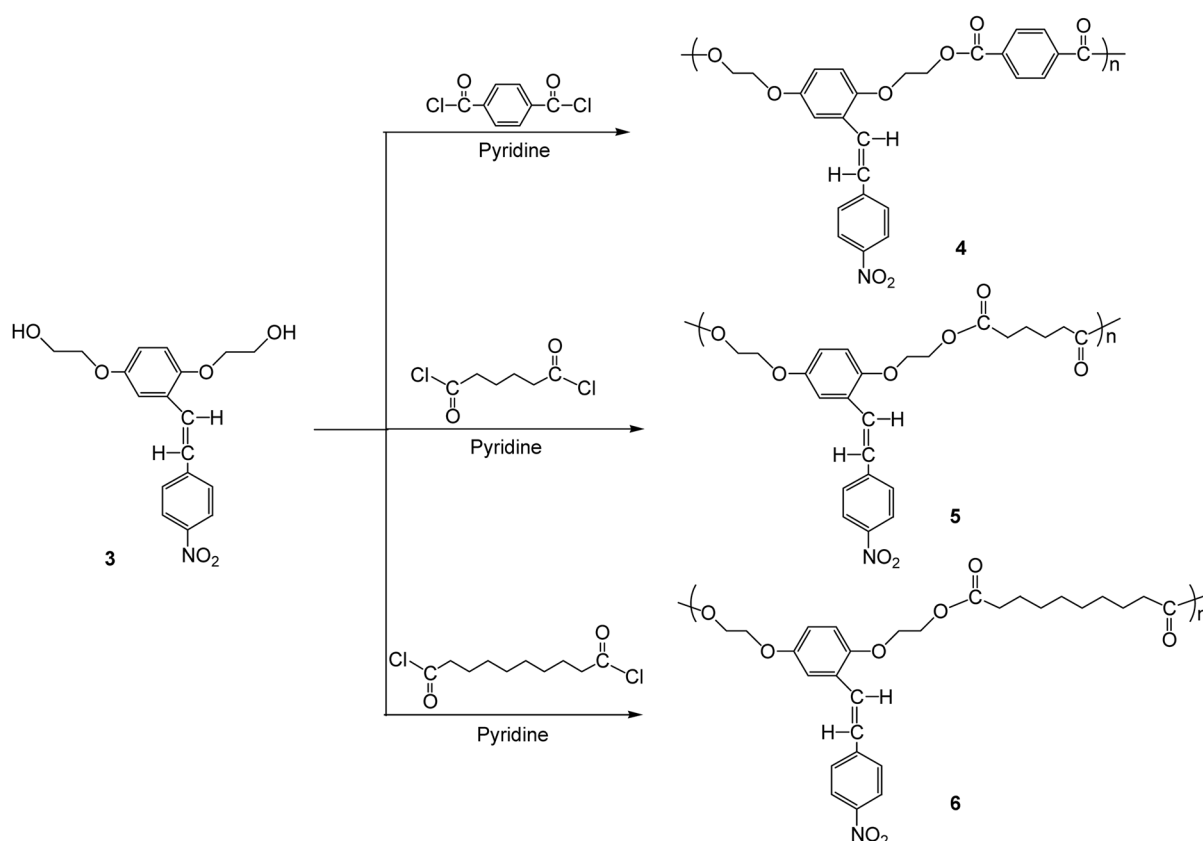
Results and Discussion

Synthesis and Characterization of Polymers 4-6. 2,5-Dihydroxyethoxy-4'-nitrostilbene (**1**) was prepared by the condensation of 4-nitrophenylacetic acid with 2,5-dihydroxybenzaldehyde according to a literature procedure¹⁶ Compound **1** was reacted with 2-chloroethyl vinyl ether to yield 2,5-di-(2-vinyloxyethoxy)-4'-nitrostilbene (**2**). Compound **2** was hydrolyzed to yield acetaldehyde and 2,5-di-(2'-hydroxyethoxy)-4'-nitrostilbene (**3**). The synthetic route for compound **3** is presented in Scheme 1. The chemical structure of the compounds was identified by ¹H NMR (Fig. 2), IR spectra, and elemental analysis. All the analytical data confirmed the expected chemical structure. Diol **3** was condensed with terephthaloyl chloride, adipoyl chloride, and sebacoyl chloride in a dry DMF solvent to yield T-type polyesters **4-6** containing the NLO-chromophore 3,4-dioxy-nitrostilbenyl group (Scheme 2). Polymerization results are summarized in Table 1. The polymerization yield was 90-95%. The chemical structures of the resulting polymers were confirmed by ¹H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structures. ¹H NMR spectra of the polymers showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structures, as shown in Figure 2. The signal at 2.05-2.36 ppm assigned to the α -proton indicates the formation of ester linkage. The IR spectra of the same polymer samples also show a strong carbonyl peak near 1722-1728 cm^{-1} indicating the presence of ester bond. For polymers **5** and **6**, the carbonyl absorptions appear at 1728 cm^{-1} , while the carbonyl absorption in polymer **4** appears at 1722 cm^{-1} due to conjugation with aromatic ring. The strong absorptions at 1572, 1520 and 1350 cm^{-1} due to trans double bond and nitro group indicates the presence of stilbene unit. These results are consistent with the proposed structures, indicating that the NLO-chromophore remained

intact during the polymerization. The molecular weights were determined by GPC using polystyrene as the standard and THF as an eluent. The number average molecular weight (M_n) of the polymers was determined to be 16600 ($M_w/M_n = 1.98$) for polymer **5**. Polydispersities were in the range of 1.79-2.12. The structural feature of these polymers is that they have pendant NLO chromophores, which are parts of the polymer main chains. Thus the resulting polymers (**4-6**) are mid type of side chain- and main chain NLO polymers, and are expected to have both of their merits. The polymers **4-6** were soluble in common solvents such as acetone, DMF, and DMSO, but were not soluble in methanol and diethyl ether. Polymers **4-6** isolated from methanol were yellow colored amorphous materials. The inherent viscosities were in the range of 0.30-0.35 dL/g. Polymers **4-6** showed strong absorption near 375 nm by the NLO-chromophore dioxynitrostilbenyl group. We now have well defined polyesters (**4-6**) and investigate their properties.

Thermal Properties of the Polymers. The thermal behavior of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g). The results are summarized in Table 2. In Figure 2, TGA thermograms of the polymers **4-6** are presented. Polymer **4** showed a thermal stability up to 300 °C from the TGA thermogram, but polymers **5-6** exhibited lower thermal stability than polymer **4**, as shown in Figure 2. Glass transition temperature (T_g) values of the polymers **4-6** measured by DSC were in the range 90-95 °C. These T_g values are higher than those of the polyesters containing 2,3-dioxynitrostilbenyl group.¹⁵ The TGA and DSC studies showed that the decomposition temperature of the polyesters **4-6** was higher than the corresponding T_g . This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

Nonlinear Optical Properties of the Polymers. The NLO properties of polymers were studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. As the temperature was raised to 5-10 °C higher than T_g , 6.5 kV of corona voltage was applied and kept at that temperature for 30 min. The UV-Vis absorption spectra of the polymer **5** before and after poling are presented in Figure 3. After electric poling, the dipole moments of the NLO-chromophores were aligned and the UV-Vis spectrum of polymer **5** 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 Φ was equal to 0.18 for polymer **5** ($\Phi = 1 - A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after poling). For the purpose of investigating surface morphology of polymer films, domain structures of NLO-chromophores for the thin-film were obtained using atomic force microscopy (AFM). Figure 4 shows AFM scans of the spin-coated film before and after poling for polymer **5**. AFM images show that the surface of the film



Scheme 2. Synthetic scheme and structures of polymers 4-6.

Table 1. Polymerization of 3 with TPC, APC and SCC in Pyridine

Monomer ^{a-d}	Monomer/ Solvent (mol/L)	Diol 3 to R(COCl) ₂ (mol/mol)	Time (h)	Yield (%)	η_{inh}^e (dL/g)	M_n^f	M_w^f
3, TPC	0.67	1.0	10	92	0.30	15800	30600
3, TPC	0.80	1.0	12	93	0.32	16300	32500
3, APC	0.67	1.0	10	90	0.30	16600	32800
3, APC	0.80	1.0	12	92	0.31	16500	29600
3, SCC	0.67	1.0	10	92	0.32	15200	31100
3, SCC	0.80	1.0	12	95	0.35	17400	36900

^a3 = 2,5-Di-(2'-hydroxyethoxy)-4-nitrostilbene. ^bTPC = Terephthaloyl chloride. ^cAPC = Adipoyl chloride. ^dSCC = Sebacoyl chloride. ^eInherent viscosity of polymer (0.5 g/dL in DMSO at 25 °C). ^fMeasured by GPC in THF using polystyrene standard.

sample is extremely flat and smooth. 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 are aligned the poling direction (see Fig. 4). The refractive index of the sample was measured by the optical transmission technique.¹⁷ The transmittance of thin film includes information on the thickness, refractive index and extinction coefficient of that. So we could determine those parameters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG depend-

Table 2. Thermal Properties of Polymers 4-6

Polymer	T_g , °C	Degradation temp, °C			Residue at 800 °C, wt%
		5 wt%- loss	20 wt%- loss	40 wt%- loss	
4	95	305	401	568	46
5	94	257	398	497	47
6	90	278	410	465	38

ence was recorded. Figure 5 shows the angular dependence of SHG signal in a poled polymer 5. 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 to the samples and recorded. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure.¹⁸ Nonlinear optical properties of polymers 4-6 are summarized in Table 3. The values of d_{33} and d_{31} for polymer 5 were $(1.38 \pm 0.10) \times 10^{-9}$ and $(0.51 \pm 0.04) \times 10^{-9}$ esu, which were similar with those of polymer 4.¹⁹ According to our experimental experience, the d_{33} and d_{31} values of polymers 4-6 are somewhat smaller than those of the polyesters containing 2,3-dioxynitrostilbenyl group.¹⁵ Since the second harmonic wavelength is at 532 nm, which is not in the absorptive region of the resulting polyesters, 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 2.7 is in good

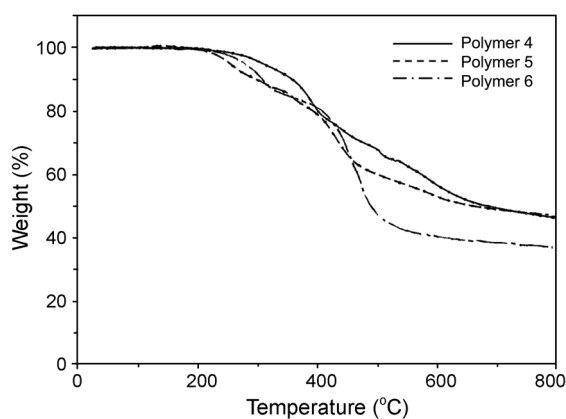


Figure 2. TGA thermograms of polymers **4-6** at a heating rate of 10 °C/min under nitrogen.

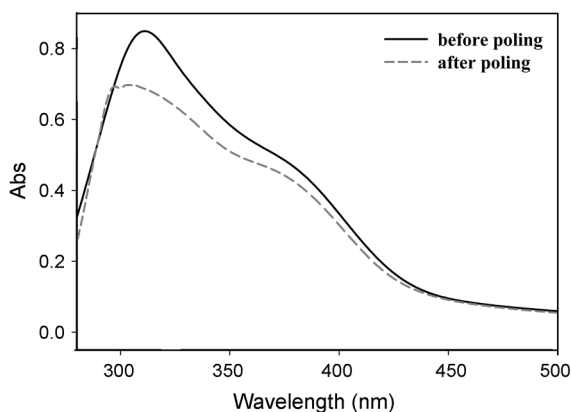


Figure 3. UV-Vis absorption spectra of a film of polymer **5** before and after poling.

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 6, 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 3 °C/min from 30 °C to 150 °C. The polymer film exhibited a thermal stability up to 5 °C higher than T_g and no significant SHG decay was observed below 100 °C for polymer **5**. In general, side chain NLO polymers lose thermal stability of dipole alignment below

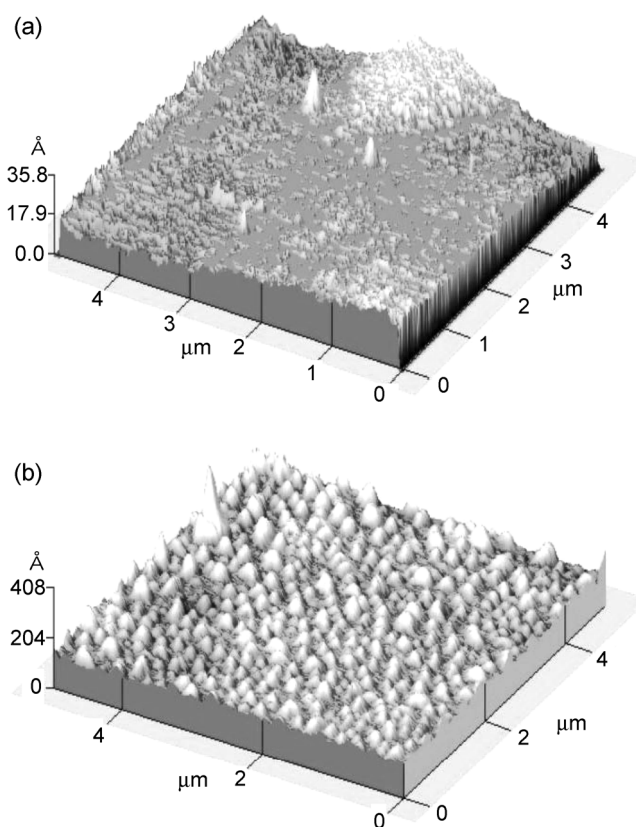


Figure 4. AFM images of spin-coated film of polymer **5**: (a) before corona-poling; (b) after corona-poling.

T_g . Stabilization of dipole alignment is a characteristic of main chain NLO polymers. The high thermal stability of second harmonic generation of polymers 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 a new type of NLO polyester having both of the merits of main chain- and side-chain NLO polymers: stabilization of dipole alignment and good solubility.

Conclusions

Novel T-type NLO polyesters (**4-6**) with pendant NLO chromophores, which are parts of the polymer backbones, were prepared and characterized. Polymers **4-6** are soluble in common organic solvents. The resulting polymers **4-6**

Table 3. Nonlinear Optical Properties of Polymers **4-6**

Polymer	λ_{\max}^a (nm)	d_{33}^b (esu)	Φ^c	d_{31}^b (esu)	film thickness ^d (μm)	n
4	376	$(1.42 \pm 0.09) \times 10^{-9}$	0.19	$(0.52 \pm 0.03) \times 10^{-9}$	0.47	$n_1 = 1.58$ $n_2 = 1.66$
5	375	$(1.38 \pm 0.10) \times 10^{-9}$	0.18	$(0.51 \pm 0.04) \times 10^{-9}$	0.51	$n_1 = 1.63$ $n_2 = 1.73$
6	376	$(1.16 \pm 0.08) \times 10^{-8}$	0.51	$(0.43 \pm 0.03) \times 10^{-9}$	0.48	$n_1 = 1.61$ $n_2 = 1.69$

^aPolymer film. ^bSHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.¹⁸ ^cOrder 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. ^dFilm thickness was determined by the optical transmission technique.¹⁷

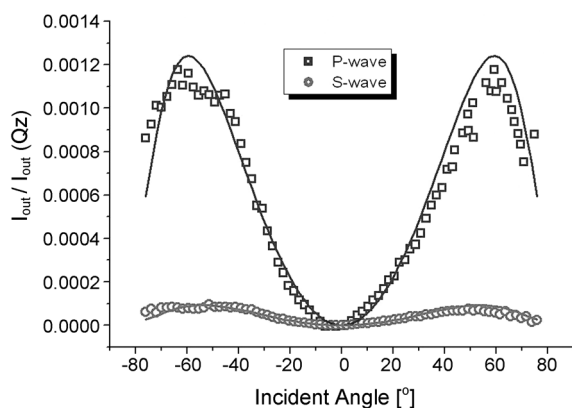


Figure 5. Angular dependence of SHG signal in a poled film of polymer 5.

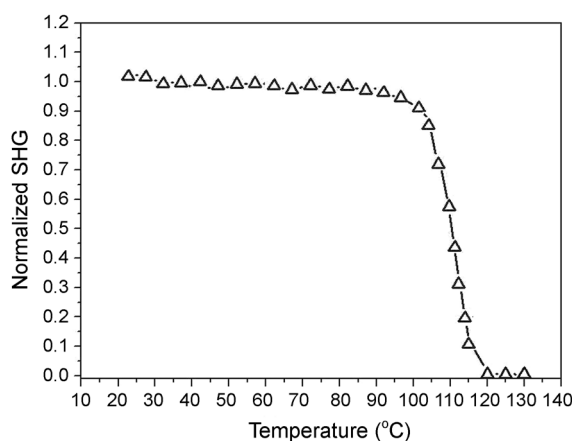


Figure 6. Normalized SHG signal of polymer 5 as a function of temperature at a heating rate of 3 °C/min.

showed a thermal stability up to 260 °C with T_g values in the range 90–95 °C. The SHG coefficients (d_{33}) of poled polymer films were around 1.42×10^{-9} esu. Poled polymer films exhibited a thermal stability of SHG up to 5 °C higher than T_g due to the partial main-chain character of the polymer structure, which is acceptable for NLO device applications.

Experimental Section

Materials. The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 4-Nitrophenylacetic acid, 2,5-dihydroxybenzaldehyde, 2-chloroethyl vinyl ether, and sebacyl chloride (SCC) were used as received. Terephthaloyl chloride (TPC) was purified by sublimation under vacuum. Adipoyl chloride (APC) was purified by distillation under reduced pressure. Piperidine was treated with potassium hydroxide and then distilled over barium oxide to remove trace amounts of water. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure.

Measurements. IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ^1H NMR spectra were obtained on a Varian 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 °C/min up to 800 °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 with a 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® 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 °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 °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.¹⁷ Second harmonic generation measurement was carried out one 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 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.¹⁸

Preparation of 2,5-Dihydroxy-4'-nitrostilbene 1. Compound **1** was prepared by a known method from 2,5-dihydroxybenzaldehyde and 4-nitrophenylacetic acid, and recrystallized from 80% aqueous ethanol. ¹H NMR (acetone- d_6) δ 2.79 (s, 2H, -OH), 7.12-7.35 (m, 4H, aromatic), 8.06-8.15 (d, 2H, aromatic), 8.23-8.37 (t, 3H, aromatic). IR (KBr) 3408 (s, O-H), 3032 (w, =C-H), 2876 (w, C-H), 1574 (vs, C=C), 1510, 1348 (vs, N=O) cm^{-1} .

Preparation of 2,5-Di-(2'-vinyloxyethoxy)-4'-nitrostilbene 2. 2,5-Dihydroxy-4'-nitrostilbene (7.71 g, 0.03 mol), anhydrous potassium carbonate (24.9 g, 0.18 mol), and 2-chloroethyl vinyl ether (8.52 g, 0.08 mol) were dissolved in 100 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80 °C for 15 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 200 mL of water, stirred, filtered, and the obtained product was washed with 100 mL of water. Thus obtained product was recrystallized from ethanol to give 10.25 g (86% yield) of **2**. Mp = 146-148 °C. ¹H NMR (DMSO- d_6) δ 3.96-4.07 (d, 6H, CH₂=, -O-CH₂-CH₂-O-), 4.18-4.30 (d, 6H, CH₂=, -O-CH₂-CH₂-O-), 6.52-6.63 (q, 2H, 2 =CH-O-), 7.26-7.47 (m, 4H, aromatic), 7.95-8.05 (d, 2H, aromatic), 8.26-8.42 (t, 3H, aromatic). IR (KBr) 3059 (w, =C-H), 2953 (m, C-H), 1572 (s, C=C), 1512, 1350 (vs, N=O) cm^{-1} . Anal. Calcd for C₂₂H₂₃NO₆: C, 66.49; H, 5.83; N, 3.52. Found: C, 66.60; H, 5.89; N, 3.46.

Preparation of 2,5-Di-(2'-hydroxyethoxy)-4'-nitrostilbene 3. Aqueous hydrochloric acid (1.5 M, 30 mL) was slowly added to a solution of 2,5-di-(2'-vinyloxyethoxy)-4'-nitrostilbene (**2**) (9.93 g, 0.025 mol) in 60 mL of dry DMF 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 7.41 g (yield 86%) of **3** (Scheme 1). Mp = 168-170 °C. ¹H NMR (DMSO- d_6) δ 3.62-3.78 (m, 4H, -O-CH₂-CH₂-O-), 3.92-4.08 (t, 4H, -O-CH₂-CH₂-O-), 7.20-7.46 (m, 4H, aromatic), 7.91-8.02 (d, 2H, aromatic), 8.20-8.43 (t, 3H, aromatic). IR (KBr) 3420 (s, O-H), 2936, 2870 (m, C-H), 1585 (s, C=C), 1518, 1344 (vs, N=O) cm^{-1} . Anal. Calcd for C₁₈H₁₉NO₆: C, 62.60; H, 5.54; N, 4.06. Found: C, 62.68; H, 5.63; N, 4.12.

Synthesis of Polyesters 4-6. A representative polycondensation procedure (the case of **4**) was as follows: Terephthaloyl chloride (2.03 g, 0.01 mol) and diol **3** (3.45 g, 0.01 mol) were dissolved in 30 mL of anhydrous pyridine under nitrogen. The resulting solution was refluxed in an oil bath kept at 80 °C under a nitrogen atmosphere. After heating 10 h with stirring the resulting polymerization solution was poured into 400 mL of methanol. 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, yielding 4.37 g (92% yield) of polymer **4**. Inherent viscosity (η_{inh}) = 0.30 dL/g (c = 0.5 g/dL in DMSO at 25 °C). ¹H NMR (DMSO- d_6) δ 4.36-4.45 (s, 4H, 2 -CH₂-O-), 4.63-4.69 (s, 4H, 2 Ph-O-CH₂-), 7.27-7.45 (m, 3H, aromatic), 7.95-8.13 (m, 6H, aromatic), 8.27-8.39 (m, 4H, aromatic). IR (KBr) 2941, 2883 (C-H, w), 1722 (vs, C=O), 1572 (s, C=C), 1520, 1350 (s, N=O) cm^{-1} . Anal. Calcd for (C₂₆H₂₁NO₈)_n: C, 65.68; H, 4.45; N, 2.95. Found: C, 65.78; H, 4.53; N, 3.04. Polymer **5**: η_{inh} = 0.30 dL/g (c = 0.5 g/dL in DMSO at 25 °C). ¹H NMR (DMSO- d_6) δ 1.41-1.57 (s, 4H, -CH₂-CH₂-), 2.15-2.36 (d, 4H, 2 -CH₂-CO-), 4.15-4.43 (d, 8H, 2 -O-CH₂-CH₂-O-), 7.20-7.44 (m, 4H, aromatic), 7.92-8.03 (t, 2H, aromatic), 8.25-8.39 (m, 3H, aromatic). IR (KBr) 2953, 2885 (C-H, m), 1722 (vs, C=O), 1572 (s, C=C), 1520, 1350 (vs, N=O) cm^{-1} . Anal. Calcd for (C₂₄H₂₅NO₈)_n: C, 63.29; H, 5.53; N, 3.08. Found: C, 63.36; H, 5.62; N, 3.15. Polymer **6**: η_{inh} = 0.32 dL/g (c = 0.5 g/dL in DMSO at 25 °C). ¹H NMR (DMSO- d_6) δ 1.03-1.27 (s, 8H, -(CH₂)₄-), 1.33-1.52 (s, 4H, 2 -(CH₂)₂-), 2.09-2.32 (m, 4H, 2 -CH₂-CO-), 4.18-4.39 (d, 8H, 2 -O-CH₂-CH₂-O-), 7.23-7.44 (m, 4H, aromatic), 7.93-8.03 (t, 2H, aromatic), 8.27-8.38 (m, 3H, aromatic). IR (KBr) 2930, 2860 (C-H, s), 1728 (vs, C=O), 1572 (s, C=C), 1520, 1350 (vs, N=O) cm^{-1} . Anal. Calcd for (C₂₆H₂₉NO₈)_n: C, 64.58; H, 6.05; N, 2.90. Found: C, 64.66; H, 6.14; N, 2.98.

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References

- Marks, T. J.; Ratner, M. A. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 155.
- Cho, M. J.; Kim, J. Y.; Kim, J. H.; Lee, S. H.; Dalton, L. R.; Choi, D. H. *Bull. Korean Chem. Soc.* **2005**, *26*, 77.
- Lee, C.; Park, S.-K.; Yang, M.; Lee, N.-S.; Kim, N. J. *Bull. Korean Chem. Soc.* **2007**, *28*, 447.
- Han, K. S.; Park, S. K.; Shim, S. Y.; Jahng, W. S.; Kim, N. J. *Bull. Korean Chem. Soc.* **1998**, *19*, 1165.
- Han, K. S.; Park, S. K.; Shim, S. Y.; Lee, Y. S.; Jahng, W. S.; Kim, N. J. *Bull. Korean Chem. Soc.* **1998**, *19*, 1168.
- Cho, B. R.; Kim, Y. H.; Son, K. W.; Khalil, C.; Kim, Y. H.; Jeon, S.-J. *Bull. Korean Chem. Soc.* **2002**, *23*, 1253.
- Moon, J. R.; Kim, B. S.; Kim, J.-H. *Bull. Korean Chem. Soc.* **2006**, *27*, 981.
- Kim, M. H.; Jin, J.-I.; Lee, C. J.; Kim, N. J.; Park, C. H. *Bull. Korean Chem. Soc.* **2002**, *23*, 964.
- Lee, J.-H.; Lee, K.-S. *Bull. Korean Chem. Soc.* **2000**, *21*, 847.
- Lee, S.-H.; Kim, Y.-K.; Won, Y.-H. *Macromolecules* **1999**, *32*, 342.
- Renate, D.; Walter, M. F. F.; Dietmar, K.; Hans, J. *Dyes and Pigments* **1997**, *34*, 13.
- Ambrosiano, P.; Centore, R.; Concilio, S.; Panunzi, B.; Sirigu, A.; Tirelli, N. *Polymer* **1999**, *40*, 4923.
- Lee, J.-Y.; Jung, W.-T.; Lee, W.-J. *Polym. Int.* **2006**, *55*, 248.
- Lee, J.-Y.; Kim, J.-H.; Won, D.-S.; Jang, H.-N. *Bull. Korean Chem. Soc.* **2007**, *28*, 1433.
- Kim, J.-H.; Lee, J.-Y.; Won, D.-S.; Rhee, B. K. *Macromol. Res.* **2007**, *15*, 506.
- Cullinane, N. M. *J. Chem. Soc.* **1923**, *123*, 2053.
- Cisneros, J. I. *Appl. Opt.* **1998**, *37*, 5262.
- Herman, W. N.; Hayden, L. M. *J. Opt. Soc. Am. B* **1995**, *12*, 416.
- Lee, J.-Y.; Kim, J.-H.; Jung, W.-T. *Bull. Korean Chem. Soc.* **2007**, *28*, 329.