

Synthesis and Nonlinear Optical Properties of Novel Y-Type Polyesters with Enhanced Thermal Stability of Second Harmonic Generation

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Abstract: 2,3-Di-(2'-hydroxyethoxy)-4'-nitrostilbene (**3**) was prepared and condensed with terephthaloyl chloride, adipoyl chloride, and sebacoyl chloride to yield novel Y-type polyesters (**4-6**) containing the NLO-chromophores 2,3-dioxynitrostilbenyl groups, which constituted parts of the polymer backbones. Polymers **4-6** were soluble in common organic solvents such as acetone and *N,N*-dimethylformamide. Polymers **4-5** showed thermal stability up to 300 °C in thermogravimetric analysis with glass transition temperatures (T_g), obtained from differential scanning calorimetry, in the range 81-95 °C. The second harmonic generation (SHG) coefficients (d_{33}) of the poled polymer films at the 1064 nm fundamental wavelength were around 3.68×10^{-9} esu. The dipole alignment exhibited high thermal stability up to T_g , and there was no SHG decay below T_g due to the partial main-chain character of the polymer structure.

Keywords: nonlinear optical, polyester, SHG, thermal stability, dipole alignment.

Introduction

It is well known that materials with highly dipolar electronic systems exhibit large nonlinear optical (NLO) properties. 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 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 electro-optic devices.¹⁻⁴ 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-linking system⁵⁻⁹ and the other is to utilize high T_g polymers such as polyimides.¹⁰⁻¹⁴ 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 impossible 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 relative to the main-chain systems, but

they often suffer from poor stability of dipole alignments at high temperatures. Recently we have prepared polyesters containing 3,4-dioxynitrostilbenyl group as a NLO chromophore.¹⁵ They exhibited second harmonic generation (SHG) stability up to 10 °C higher than T_g and no SHG decay was observed below 120 °C. This high thermal stability of optical nonlinearity stemmed from the stabilization of dipole alignment of the NLO chromophore, which was a part of the polymer backbone.

In this work we prepared another Y-type polyesters containing 2,3-dioxynitrostilbenyl groups as NLO-chromophores. We selected 2,3-dioxynitrostilbenyl groups as NLO-chromophores to compare their properties with those of 3,4-dioxynitrostilbene derivative and are rather easy to synthesize. Furthermore, as in the case of 3,4-dioxynitrostilbene derivative, 2,3-dioxynitrostilbenyl groups constitute novel Y-type NLO polyesters (Figure 1(c)) and they 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 morphology of poly-

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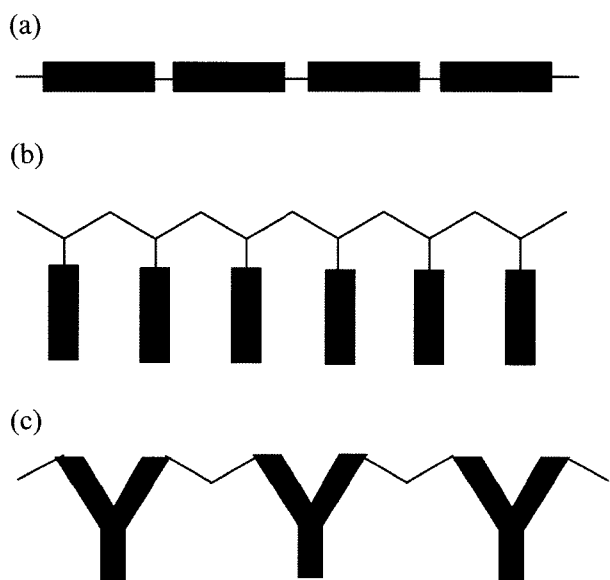


Figure 1. (a) Main-chain NLO polymers, (b) side-chain NLO polymers, and (c) Y-type NLO polymers.

mer films, SHG activity and relaxation of dipole alignment.

Experimental

Materials. The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 4-Nitrophenylacetic acid, 2,3-dihydroxybenzaldehyde, 2-chloroethyl vinyl ether, and sebacoyl 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 2400CHN 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, oper-

ated 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 Measurements. 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 1,000-1,200 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 at 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.¹⁶ Second harmonic generation (SHG) measurement was carried out one day after poling. A continuum PY61 mode-locked Nd : YAG laser ($\lambda = 1,064 \text{ nm}$) 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 beam splitter and a photodiode were used to compensate for the intensity fluctuations of the fundamental beam (1,064 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 $d_{11} = 0.3 \text{ pm/V}$) 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° intervals using a rotation stage. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.¹⁷⁻¹⁹

Preparation of 2,3-Dihydroxy-4'-nitrostilbene (1). Compound **1** was prepared by a known method²⁰ from 2,3-dihydroxybenzaldehyde and 4-nitrophenylacetic acid, and recrystallized from 85% aqueous ethanol compound. **1**: mp = 216-218°C. ¹H-NMR (acetone-*d*₆): δ 2.82 (s, 2H, -OH), 7.17-7.31 (m, 3H, aromatic), 8.05-8.13 (m, 2H, aromatic), 8.29-8.37 (m, 4H, aromatic). IR (KBr): 3384 (s, O-H), 3030

(w, =C-H), 2868 (w, C-H), 1705, 1595 (vs, C=C), 1506, 1344 (vs, N=O) cm^{-1} .

Preparation of 2,3-Di-(2'-vinylxyethoxy)-4'-nitrostilbene (2). 2,3-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 10.73 g (90% yield) of **2**. mp = 172–174 °C. $^1\text{H-NMR}$ (DMSO- d_6) δ 4.03–4.16 (m, 6H, $\text{CH}_2=$, -O- CH_2 - CH_2 -O-), 4.25–4.43 (t, 6H, $\text{CH}_2=$, -O- CH_2 - CH_2 -O-), 6.56–6.66 (q, 2H, 2 =CH-O-), 7.29–7.43 (s, 4H, aromatic), 7.99–8.08 (d, 2H, aromatic), 8.27–8.38 (d, 2H, aromatic), 8.46 (s, 1H, aromatic). IR (KBr) 3047 (w, =C-H), 2941 (m, C-H), 1601 (s, C=C), 1526, 1350 (vs, N=O) cm^{-1} . Anal. Calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_6$: C, 66.49; H, 5.83; N, 3.52. Found: C, 66.58; H, 5.88; N, 3.45.

Preparation of 2,3-Di-(2'-hydroxyethoxy)-4'-nitrostilbene (3). Aqueous hydrochloric acid (1.5 M, 150 mL) was slowly added to a solution of 2,3-di-(2'-vinylxyethoxy)-4-nitrostilbene (**2**) (3.97 g, 0.01 mol) in 40 mL of DMF with stirring under nitrogen at 0 °C. The mixture was stirred at 0 °C for 20 h under nitrogen. The resulting solution was filtered and washed with 40 mL of water. The obtained pale yellow product was recrystallized from methanol to give 4.72 g (82% yield) of **3**. mp = 123–125 °C. $^1\text{H-NMR}$ (DMSO- d_6) δ 3.79 (s, 4H, -O- CH_2 - CH_2 -O-), 4.14 (s, 4H, -O- CH_2 - CH_2 -O-), 4.97 (br, 2H, -OH), 7.34 (s, 3H, aromatic), 7.94–8.08 (d, 2H, aromatic), 8.23–8.36 (d, 3H, aromatic), 8.44 (s, 1H, aromatic). IR (KBr) 3501 (s, O-H), 2930, 2883 (m, C-H), 1716, 1601 (s, C=C), 1512, 1344 (vs, N=O) cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_6$: C, 62.60; H, 5.54; N, 4.06. Found: C, 62.72; H, 5.58; N, 4.13.

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 nitro-

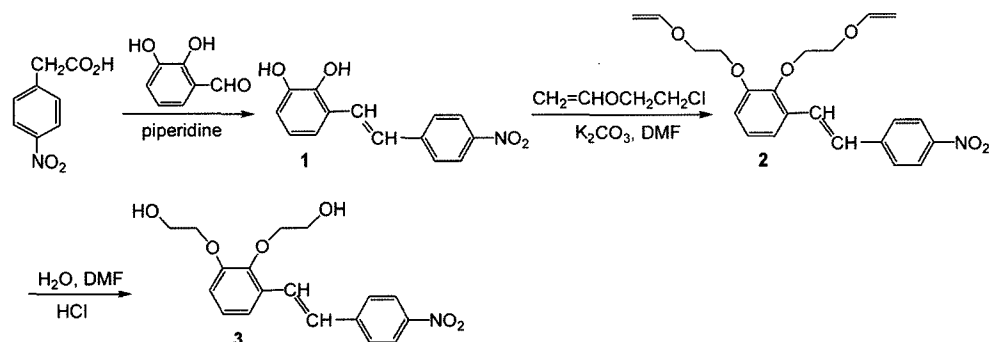
gen. The resulting solution was refluxed in an oil bath kept at 80 °C under a nitrogen atmosphere. After heating 10 h with stirring the resulting polymerization solution was poured into 400 mL of methanol. The precipitated polymer was collected and reprecipitated from DMSO into methanol. The polymer was further purified by extraction in a Soxhlet extractor with diethyl ether and dried under vacuum, yielding 4.28 g (90% yield) of polymer **4**: $\eta_{inh} = 0.28$ dL/g (c, 0.5 g/dL in DMSO at 25 °C). $^1\text{H-NMR}$ (DMSO- d_6) δ 4.57 (s, 4H, -O- CH_2 - CH_2 -O-), 4.72 (s, 4H, -O- CH_2 - CH_2 -O-), 7.33–7.53 (m, 4H, aromatic), 7.95–8.08 (m, 5H, aromatic), 8.25–8.35 (m, 3H, aromatic), 8.42–8.46 (d, 1H, aromatic). IR (KBr) 3105 (w, =C-H), 2953 (s, C-H), 1722 (vs, C=O), 1647, 1601 (s, C=C), 1520, 1350 (vs, N=O) cm^{-1} . Anal. Calcd for $(\text{C}_{26}\text{H}_{21}\text{NO}_8)_n$: C, 65.68; H, 4.45; N, 2.95. Found: C, 65.79; H, 4.53; N, 3.05.

Polymer **5**: $\eta_{inh} = 0.26$ dL/g (c, 0.5 g/dL in DMSO at 25 °C). $^1\text{H-NMR}$ (DMSO- d_6) δ 1.55 (s, 4H, - CH_2 - CH_2 -), 2.35 (s, 4H, 2- CH_2 -CO-), 4.36 (s, 4H, 2 -O- CH_2 - CH_2 -O-), 4.39 (s, 4H, 2 -O- CH_2 - CH_2 -O-), 7.27–7.43 (m, 3H, aromatic), 7.98–8.07 (d, 2H, aromatic), 8.27–8.36 (d, 3H, aromatic), 8.44 (s, 1H, aromatic). IR (KBr) 3105 (w, =C-H), 2941 (m, C-H), 1734 (vs, C=O), 1699, 1601 (s, C=C), 1520, 1350 (vs, N=O) cm^{-1} . Anal. Calcd for $(\text{C}_{24}\text{H}_{25}\text{NO}_8)_n$: C, 63.29; H, 5.53; N, 3.08. Found: C, 63.37; H, 5.64; N, 3.17.

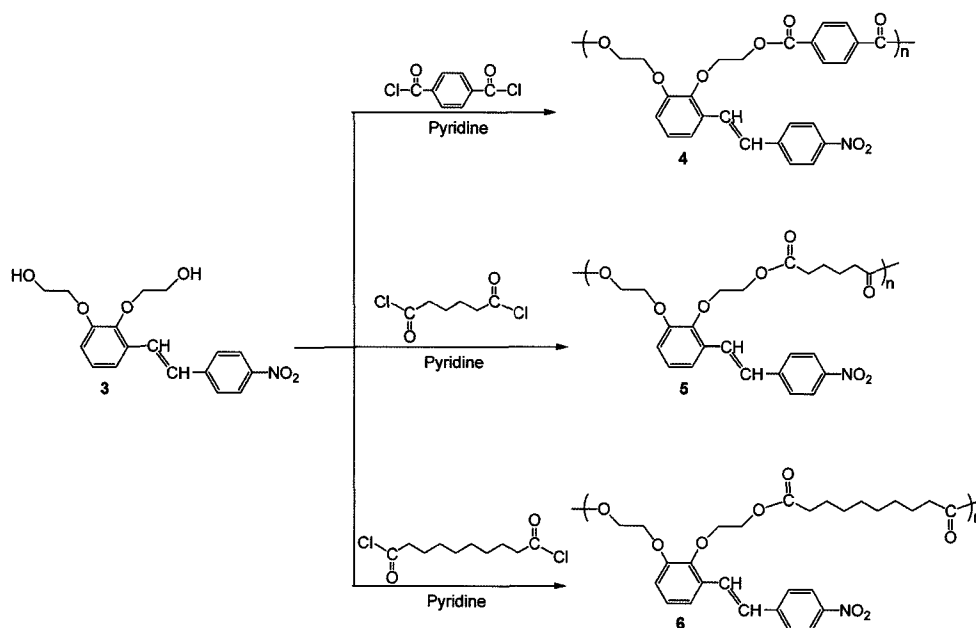
Polymer **6**: $\eta_{inh} = 0.27$ dL/g (c, 0.5 g/dL in DMSO at 25 °C). $^1\text{H-NMR}$ (DMSO- d_6) δ 0.98–1.26 (d, 8H, -(CH_2) $_4$ -), 1.36–1.54 (s, 4H, -(CH_2) $_2$ -), 2.24–2.33 (m, 4H, 2 - CH_2 -CO-), 4.33–4.46 (m, 8H, 2 -O- CH_2 - CH_2 -O-), 7.27–7.43 (m, 3H, aromatic), 7.97–8.07 (d, 2H, aromatic), 8.27–8.36 (d, 3H, aromatic), 8.46 (s, 1H, aromatic). IR (KBr) 3105 (w, =C-H), 2930, 2852 (s, C-H), 1734 (s, C=O), 1595 (s, C=C), 1520, 1350 (vs, N=O) cm^{-1} . Anal. Calcd for $(\text{C}_{26}\text{H}_{29}\text{NO}_8)_n$: C, 64.58; H, 6.05; N, 2.90. Found: C, 64.68; H, 6.14; N, 2.98.

Results and Discussion

Synthesis and Characterization of Polymers 4-6. 2,3-Dihydroxyethoxy-4'-nitrostilbene (**1**) was prepared by the condensation of 4-nitrophenylacetic acid with 2,3-dihydroxybenzaldehyde according to a literature procedure.²⁰ Com-



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



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

compound **1** was reacted with 2-chloroethyl vinyl ether to yield 2,3-di-(2-vinyloxyethoxy)-4'-nitrostilbene (**2**), which was hydrolyzed to yield acetaldehyde and 2,3-di-(2'-hydroxyethoxy)-4'-nitrostilbene (**3**). The synthetic route for compound **3** is presented in Scheme I. Diol **3** was condensed with terephthaloyl chloride, adipoyl chloride, and sebacoyl chloride in a dry DMF solvent to yield Y-type polyesters **4-6** containing the NLO-chromophore 2,3-dioxynitrostilbenyl group (Scheme II). Polymerization results are summarized in Table I. The polymerization yield was 85-92%. The chemical structures of the resulting polymers were confirmed by $^1\text{H-NMR}$, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structures. $^1\text{H-NMR}$ 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 2.24-2.35 ppm assigned to the α -proton indicates the formation of ester linkage. The

signal at 7.97-8.07 ppm assigned to the vinyl proton indicates the presence of stilbene unit. The IR spectra of the same polymer samples also show a strong carbonyl peak near $1722\text{-}1734\text{ cm}^{-1}$ indicating the presence of ester bond. For polymers **5** and **6**, the carbonyl absorptions appear at 1734 cm^{-1} , while the carbonyl absorption in polymer **4** appears at 1722 cm^{-1} due to conjugation with aromatic ring. The strong absorptions at 1520 and 1350 cm^{-1} due to 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 eluent. The number average molecular weight (M_n) of the polymers was determined to be 14,800 ($M_w/M_n = 2.05$) for polymer **4**. Polydispersities were in the range 1.82-2.15. The structural feature of these polymers is that they have pendant NLO chromophores,

Table I. 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	90	0.28	14,200	28,500
3 , TPC	0.67	1.0	10	90	0.28	14,200	28,500
3 , TPC	0.80	1.0	12	91	0.30	14,800	30,400
3 , APC	0.67	1.0	10	86	0.26	13,500	24,600
3 , APC	0.80	1.0	12	87	0.26	14,200	29,500
3 , SCC	0.67	1.0	10	86	0.27	12,700	27,200
3 , SCC	0.80	1.0	12	88	0.28	12,400	26,600

^a**3** = 2,3-Di-(2'-hydroxyethoxy)-4-nitrostilbene. ^bTPC = Terephthaloyl chloride. ^cAPC = Adipoyl chloride. ^dSCC = Sebacoyl chloride. ^eInherent viscosity of polymer: Concentration of 0.5 g/dL in DMSO at 25 °C. ^fMeasured by GPC in THF using polystyrene standards.

Table II. Thermal Properties of Polymers 4-6

Polymer	T_g^a (°C)	Degradation temp. (°C) ^b				Residue ^b at 800 °C (wt%)
		5 wt%-loss	10 wt%-loss	20 wt%-loss	40 wt%-loss	
4	95	368	389	403	470	32.2
5	83	329	356	386	508	14.5
6	81	268	302	338	424	19.2

^aDetermined from DSC curves measured on a TA 2920 differential scanning calorimeter with a heating rate of 10 °C/min under nitrogen atmosphere.

^bDetermined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10 °C/min under nitrogen atmosphere.

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 0.25-0.30 dL/g. Polymers 4-6 showed strong absorption near 340 nm by the NLO-chromophore 2,3-dioxynitrostilbenyl group. We now have well defined polyesters (4-6) and investigate their properties.

Thermal Properties of the Polymers 4-6. 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 II. In Figure 2, TGA thermograms of the polymers 4-6 are presented. Polymers 4-5 showed a thermal stability up to 300 °C from their TGA thermograms. The initial weight loss in the polymers begins around 346 °C for polymer 4. Glass transition temperature (T_g) values of the polymers 4-6 measured by DSC were around 81-95 °C, which are quite lower than those of the polyesters derived from 3,4-dioxynitrostilbenyl group.¹⁵ However, these are relatively high values com-

pared to those of common polyesters and probably attributed to the rigid stilbene unit in the polymer pendant group. The TGA and DSC studies showed that the decomposition temperatures of the polyesters 4-6 were higher than the corresponding T_g values. This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

Nonlinear Optical Properties of the Polymers 4-6. 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 that temperature for 30 min. The UV-Vis absorption spectra of the polymer sample 6 before and after poling are presented in Figure 3. After electric poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectrum of polymer 6 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 found to have a value of 0.17 for polymer 6 ($\Phi = 1 - A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after poling, respectively). For the purpose of investigating surface morphology of polymer films domain

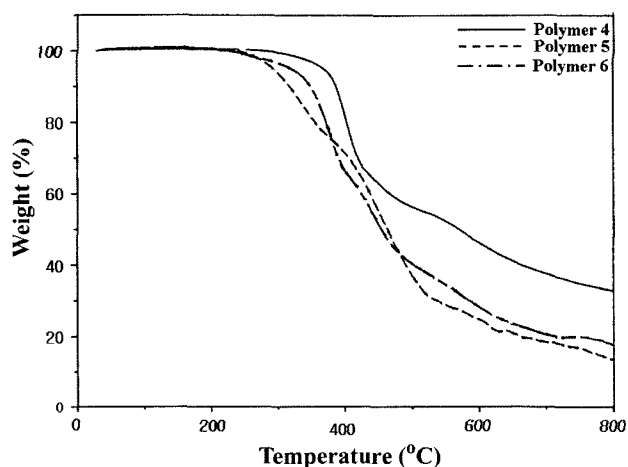


Figure 2. TGA thermograms of polymers 4-6 at a heating rate of 10 °C/min under nitrogen.

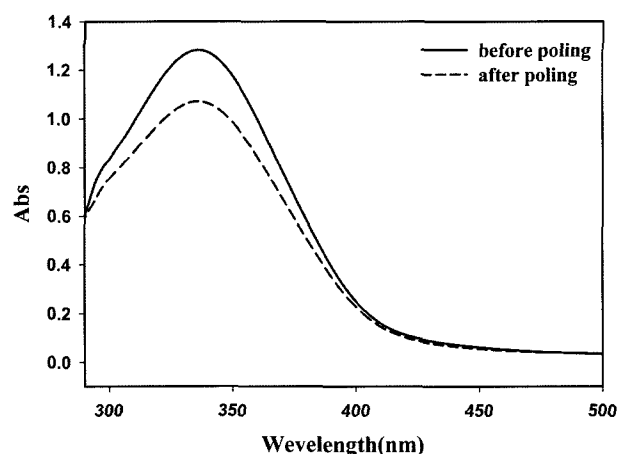


Figure 3. UV-Vis absorption spectra of a film of polymer 6 before and after poling.

structures of NLO-chromophores for the thin-film samples were obtained using atomic force microscopy (AFM). Figure 4 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, resulting in numerous hills and valleys in the surface structure, which probably means that the NLO-chromophores are aligned the poling direction (see Figure 4). The refractive index of the sample was measured by the optical transmission technique.¹⁶ The transmittance of thin film includes information on the thickness, refractive index and extinction coefficient of that. So we could determine

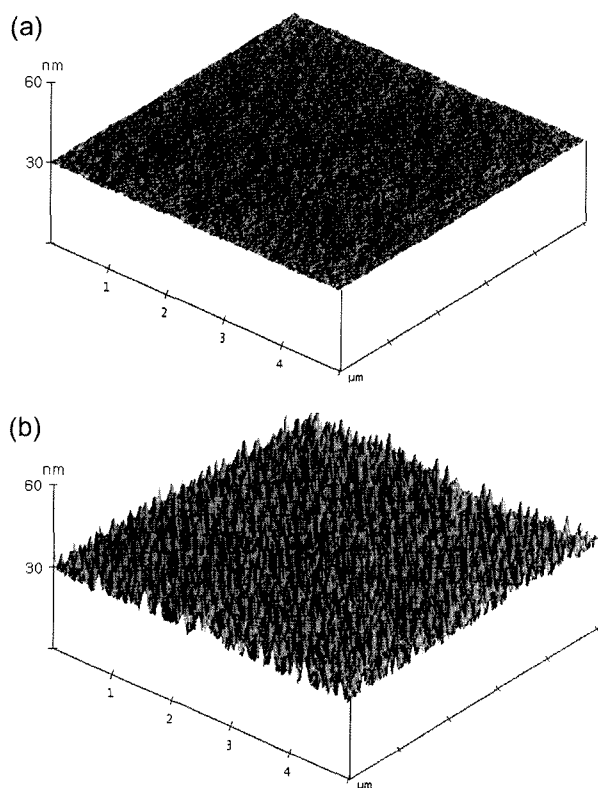


Figure 4. AFM images of spin-coated film of polymer 4: (a) before corona-poling and (b) after corona-poling.

those parameters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of 1,064 nm using a mode locked Nd-YAG laser.¹⁷⁻²⁰ Nonlinear optical properties of polymers 4-6 are summarized in Table III. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Figure 5 shows the angular dependence of SHG signal in a poled 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 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.¹⁹ The values of d_{31} and d_{33} for polymer 4 were $(1.61 \pm 0.08) \times 10^{-9}$ and $(3.68 \pm 0.18) \times 10^{-9}$ esu, respectively. These d_{31} and d_{33} values are somewhat lower than those of 3,4-dioxynitrostilbene derivatives,¹⁵ and can probably be attributed to the shorter effective conjugation length. Since the second harmonic wavelength was at 532 nm, which is not in the absorptive region of the resulting polyurethane, there was not resonant contribution to this d_{33} value.

To evaluate the high-temperature stability of the polymers, we studied the temporal stability of the SHG signal.

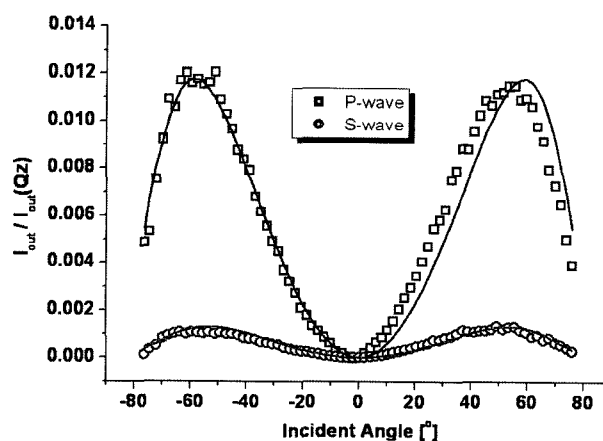


Figure 5. Angular dependence of SHG signal in a poled film of polymer 4.

Table III. 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	341	$(3.68 \pm 0.18) \times 10^{-9}$	0.38	$(1.61 \pm 0.08) \times 10^{-9}$	0.53	$n_1 = 1.61$ $n_2 = 1.69$
5	338	$(1.74 \pm 0.14) \times 10^{-9}$	0.26	$(0.83 \pm 0.07) \times 10^{-9}$	0.49	$n_1 = 1.55$ $n_2 = 1.63$
6	336	$(1.65 \pm 0.12) \times 10^{-8}$	0.17	$(0.76 \pm 0.06) \times 10^{-9}$	0.51	$n_1 = 1.57$ $n_2 = 1.65$

^aPolymer film after corona poling. ^bSHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.¹⁶ ^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.¹⁹

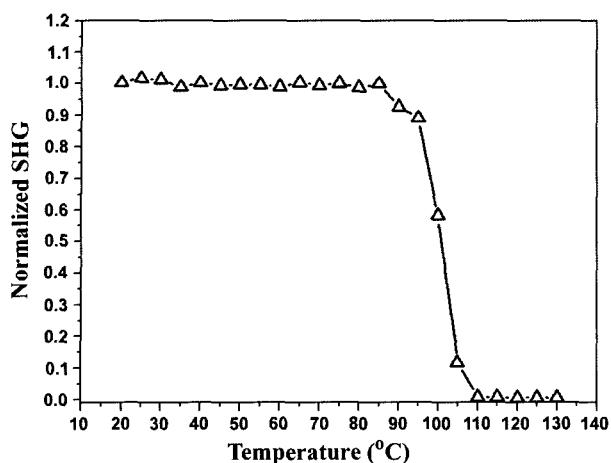


Figure 6. Normalized SHG signal of polymer 4 as a function of temperature at a heating rate of 3 °C/min.

In Figure 6, we present the dynamic thermal stability study of the NLO activity of the film 4. To investigate the real time 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 to 200 °C. The polymer film exhibited a greater thermal stability up to T_g and no significant SHG decay was observed below 95 °C for polymer 4. 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. This high thermal stability of second harmonic generation of polymers 4-6 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

We synthesized new Y-type polyesters 4-6 with pendant NLO chromophores, which are parts of the polymer main chains. These mid-type NLO polyesters are soluble in common organic solvents. The resulting polymers 4-5 showed thermal stability up to 300 °C from TGA thermograms with T_g values around 81-95 °C. The SHG coefficients (d_{33}) of corona poled polymer films were 3.68×10^{-9} esu. The resulting polymers exhibited SHG stability up to T_g and no SHG decay was observed below T_g . This high thermal stability of optical nonlinearity stemmed from the stabilization of dipole alignment of the NLO-chromophore, which was a

part 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.

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