

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

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Extensive investigations have been directed to nonlinear optical (NLO) polymers over the past decade because of their potential applications in the field of telecommunications, optical signal processing and optical switching.¹ One of the current challenges is to design novel NLO polymers with optimized properties. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is an important consideration. Two approaches have been proposed to minimize the randomization. One is to use crosslinking method^{2,3} and the other is to use high T_g polymers such as polyimides.^{4,5} There are tremendous challenges in designing and synthesis of polymers of large NLO effects. Polyesters containing the chromophoric main chain⁶⁻⁸ or side chain⁹⁻¹¹ were prepared and characterized. Main chain polymers have good thermal stability of dipole alignments, but have a poor solubility in organic solvents, and this intractability makes it impossible to fabricate a stable noncentrosymmetric films. Side-chain polymer systems have the advantages such as homogeneity and high level of NLO chromophore density relative to the host-guest systems, but they often suffer from poor stability of dipole alignments at higher temperature. In

this work we prepared a novel polyester containing dioxy-nitrostilbenyl group as a NLO-chromophore. We selected 3,4-dioxy-nitrostilbenyl group as NLO-chromophore because it will have a large dipole moment and is rather easy to synthesize. Furthermore, 3,4-dioxy-nitrostilbenyl group constitutes a novel Y-type NLO polyester (Figure 1c), in which the pendant NLO chromophores are parts of the polymer backbone, and these Y-type NLO polyesters are not present in the literature. Thus, we synthesized a new type of NLO polyester. These mid-type NLO polymers are expected to have both of the merits of main chain- and side chain-NLO polymers; stabilization of dipole alignment and good solubility. After confirming the structure of the resulting polymers we investigated the properties such as solubility, thermal stability, and second harmonic generation (SHG) activity. We now report the results of the initial phase of the work.

Results and Discussion

3,4-Dihydroxyethoxy-4'-nitrostilbene (**1**) was prepared by the condensation of 4-nitrophenylacetic acid with 3,4-dihydroxybenzaldehyde according to a literature procedure.¹² Compound **1** was reacted with 2-chloroethyl vinyl ether to yield 3,4-di-(2-vinyloxyethoxy)-4'-nitrostilbene (**2**), which was hydrolyzed to yield acetaldehyde and 3,4-di-(2'-hydroxyethoxy)-4'-nitrostilbene (**3**). Monomer **3** was condensed with terephthaloyl chloride in a dry DMF solvent to yield polyester **4** containing the NLO-chromophore 3,4-dioxy-nitrostilbenyl group. The synthetic route for polyester **4** is presented in Scheme 1. The polymerization yield was 85-92%. The resulting polymer was purified by Soxhlet extraction for 2 days with diethyl ether as a solvent. The structural feature of this polymer is that it has pendant NLO chromophores that are parts of the polymer main chains. Thus, we obtained a new type of NLO polyester with side chain and main chain characteristics simultaneously. These mid-type NLO polymers are expected to have both of the merits of main chain and side chain NLO polymers. The chemical structure of the resulting polymer was confirmed by ¹H NMR, IR spectra and elemental analysis. ¹H 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 2.06-2.37

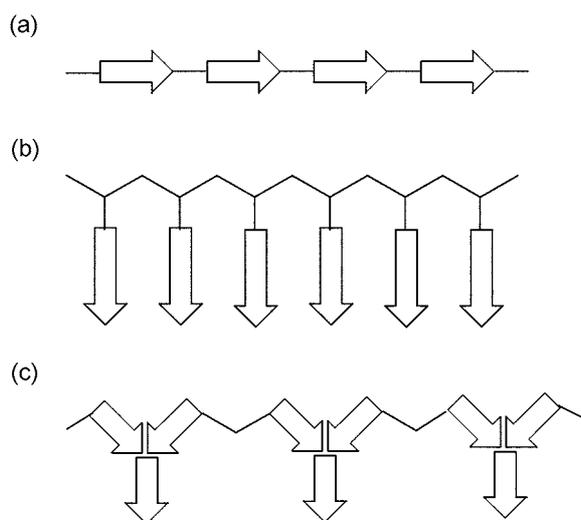
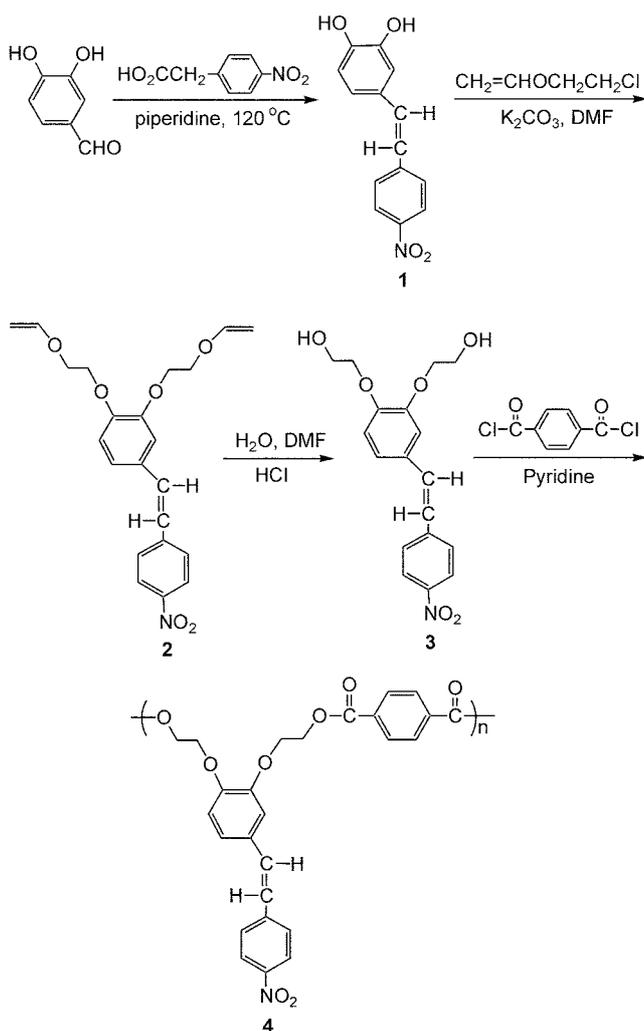


Figure 1. (a) Main Chain NLO polymers, (b) side chain NLO polymers, and (c) Y-type NLO polymers.

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Scheme 1. Synthetic route to polymer **4**.

ppm assigned to the α -proton indicates the formation of ester linkage. The signal at 8.07–8.27 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 cm^{-1} indicating the presence of ester bond. The strong absorptions at 1520 and 1344 cm^{-1} due to nitro group indicate 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 weight was determined by GPC using polystyrene as the standard and THF as a eluent. The number average molecular weight (M_n) determined by GPC was 14500 ($M_w/M_n=1.97$) for polymer **4**. This polymer was well soluble in common solvents such

as acetone, DMF, and DMSO, but were not soluble in methanol and diethyl ether. The inherent viscosities were in the range of 0.30 dL/g . Polymer **4** showed strong absorption near 390 nm by the NLO-chromophore dioxynitrostilbenyl group. We now have well defined Y-type polyester (**4**) and investigate its properties.

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). Polymer **4** showed a thermal stability up to $300\text{ }^\circ\text{C}$ from their TGA thermograms. The initial weight loss in the polymer **4** begins around $298\text{ }^\circ\text{C}$. Glass transition temperature (T_g) of the polymer **4** measured by DSC was around $110\text{ }^\circ\text{C}$. This is relatively a high value compared 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 temperature of the polyester **4** was higher than the corresponding T_g . This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

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 $120\text{ }^\circ\text{C}$, 6.5 kV of corona voltage was applied and kept $120\text{ }^\circ\text{C}$ for 30 min . The UV-Vis absorption spectra of the polymer sample **4** before and after the poling were recorded. After the electric poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectrum 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 Φ was found to have a value of 0.14 ($\Phi = 1 - A_1/A_0$, A_0 and A_1 are the absorbances of the polymer film before and after poling, respectively). The decrease in absorbance after poling is an indicator of the dipole alignment. The refractive index of the sample was measured by the optical transmission technique.¹³ SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser.^{14,15} In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. 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. Nonlinear optical properties of polymer **4** are summarized in Table 1. The values of d_{31} and d_{33} for polymer **4** were 1.42×10^{-8} and 3.51×10^{-8} esu,

Table 1. Nonlinear Optical Properties of Polymer **4**

Polymer	λ_{max}^a (nm)	d_{33}^b (esu)	Φ^c	d_{31}^b (esu)	film thickness ^d (μm)	n
4	382	3.51×10^{-8}	0.14	1.42×10^{-8}	0.30	$n_1 = 1.73, n_2 = 1.76$

^aPolymer film. ^bSHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.¹⁴ ^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.¹³

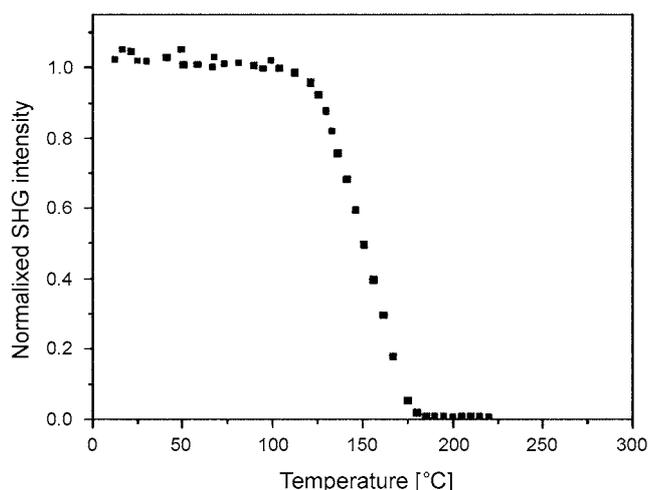


Figure 2. Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 10 °C/min.

respectively. Since the second harmonic wavelength was at 532 nm, which is not in the absorptive region of the resulting polyester, 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. In Figure 2, we present the dynamic thermal stability study of the NLO activity of the film **4**. 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 °C/min from 30 °C to 300 °C. The polymer film exhibited a thermal stability even at 10 °C higher than T_g and no significant SHG decay was observed below 120 °C. In general, side chain NLO polymers lose thermal stability of dipole alignment around T_g . Stabilization of dipole alignment is a characteristic of main chain NLO polymers. The exceptionally high thermal stability of second harmonic generation of polymer **4** 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. 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. The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 4-Nitrophenylacetic acid, 3,4-dihydroxybenzaldehyde, and 2-chloroethyl vinyl ether were used as received. Terephthaloyl chloride (TPC) was purified by sublimation under vacuum. 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.

Instrumentation. 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 (DSC) in a nitrogen atmosphere. DuPont 951 thermogravimetric analyzer (TGA) with a heating rate of 10 °C/min up to 800 °C was used for the thermal degradation study of polymer under nitrogen. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymer 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 Measurements. The polymer film was prepared from a 10% by weight DMF solution 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 60 °C at a range from 1200 to 1600 rpm. The films were dried for 48 hr under vacuum at 60 °C. The alignment of the NLO-chromophore of the polymer 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 1.0 cm. As the temperature was raised gradually to 120 °C, 6.5 kV of corona voltage was applied and kept at 120 °C 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.¹³ The transmittance of thin film includes on the information of the thickness, refractive index and extinction coefficient of that. Thus, we can determine these parameters by analyzing the transmittance. Second harmonic generation (SHG) measurement was carried out one day after poling. A Q-switched Nd:YAG laser ($\lambda = 1064$ nm) with pulse width of 10 ns and repetition rate of 10 Hz was used as the fundamental light source and Y-cut quartz was used as reference. IR laser passes through the attenuator and half wave plate, and polarizer was incident to the side of the film surface on the ITO glass. The second harmonic light from a sample was passed through a band-pass filter to remove a fundamental wave. The SHG signals from the *p*-polarized were accumulated using a photomultiplier tube and averaged. The Maker Fringe pattern was obtained from 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.^{14,15}

3,4-Dihydroxy-4-nitrostilbene (1). Compound **1** was

prepared by a known method¹² from 3,4-dihydroxybenzaldehyde and 4-nitrophenylacetic acid and was recrystallized from 80% aqueous ethanol. **1**: Mp=178-180 °C. ¹H NMR (DMDO-*d*₆) δ 6.73-6.77 (d, 1H, Ph-CH=), 6.92-6.97 (q, 1H, aromatic), 7.03-7.10 (m, 2H, aromatic), 7.31-7.38 (d, 1H, Ph-CH=), 7.75-7.80 (d, 2H, aromatic), 8.15-8.19 (d, 2H, aromatic), 9.05 (s, 1H, -OH), 9.34 (s, 1H, -OH). IR (KBr) 3443 (s, O-H), 3031 (w, =C-H), 2875 (w, C-H), 1589 (s, C=C), 1520, 1344 (vs, N=O) cm⁻¹.

3,4-Di-(2'-vinylxyethoxy)-4'-nitrostilbene (2). 3,4-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=76-78 °C. ¹H NMR (DMSO-*d*₆) δ 3.95-4.06 (s, 6H, CH₂=, -O-CH₂-CH₂-O-), 4.17-4.31 (d, 6H, CH₂=, -O-CH₂-CH₂-O-), 6.51-6.62 (q, 2H, 2 =CH-O-), 6.69-7.51 (m, 5H, aromatic), 7.76-7.85 (d, 2H, aromatic), 8.16-8.25 (d, 2H, aromatic). IR (KBr) 3058 (w, =C-H), 2941, 2883 (m, C-H), 1624, 1589 (s, C=C), 1520, 1344 (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.

3,4-Di-(2'-hydroxyethoxy)-4'-nitrostilbene (3). Aqueous hydrochloric acid (1.5 M, 30 mL) was slowly added to a solution of 3,4-di-(2'-vinylxyethoxy)-4'-nitrostilbene (**2**) (9.93 g, 0.025 mol) in 60 mL of dry DM 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=158-160 °C. ¹H NMR (DMSO-*d*₆) δ 3.69-3.77 (m, 4H, 2 -O-CH₂-), 3.98-4.08 (m, 4H, 2 Ph-O-CH₂-), 4.82-4.88 (q, 2H, 2 -OH), 6.98-7.02 (d, 1H, Ph-CH=), 7.14-7.18 (d, 1H, aromatic), 7.25-7.33 (t, 2H, aromatic), 7.41-7.48 (d, 1H, Ph-CH=), 7.78-7.82 (d, 2H, aromatic), 8.18-8.22 (d, 2H, aromatic). IR (KBr) 3337 (s, O-H), 2930 (m, C-H), 1589 (s, C=C), 1512, 1339 (vs, N=O) cm⁻¹. Anal. Calcd for C₁₈H₁₉NO₆: C, 62.60; H, 5.54; N, 4.06. Found: C, 62.52; H, 5.48; N, 4.11.

Synthesis of Polyester 4. A representative polycondensation procedure 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 25 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**: Inherent viscosity (η_{inh}): 0.28 dL g⁻¹ (c = 0.5 g dL⁻¹ in DMSO at 25 °C). *M_n*: 14,500. *M_w*: 28,600 (styragel HR5E4E; solvent THF). IR (KBr) 3107 (w, =C-H), 2936, 2875 (m, C-H), 1722 (vs, C=O), 1589 (s, C=C), 1520, 1344 cm⁻¹ (vs, N=O). ¹H NMR (DMSO-*d*₆, δ): 4.17-4.61 (d, 8H, 2 -O-CH₂-CH₂-O-), 6.88-8.27 (m, 13H, aromatic). Anal. Calcd for (C₂₆H₂₁NO₈)_n: C, 65.68; H, 4.45; N, 2.95. Found: C, 65.81; H, 4.54; N, 3.07.

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