

Synthesis and Nonlinear Optical Properties of Novel Polyester with 2,3-Dioxybenzylidenecyanoacetate

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Nonlinear optical (NLO) polymers received a great attention in recent years because of their potential applications in the field of electro-optic devices.^{1,3} A potential NLO polymer 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 criteria; in this context, two approaches have been proposed to minimize the randomization of dipole alignment namely the use cross-linking method^{4,7} and the utilization of high T_g polymers such as polyimides.⁸ Various polyesters with NLO-chromophores in the main chain⁹ or in side chain¹⁰ have been prepared and their properties studied. In general, 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 films. Side-chain NLO polymer systems have the advantages such as good solubility, homogeneity and high loading level of NLO chromophores relative to the main-chain systems, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we have prepared novel polyesters containing dioxynitrostilbene¹¹⁻¹² or 2,3-dioxybenzylidenemalononitrile¹³ as NLO chromophores. The resulting polymers exhibited enhanced thermal stability of second harmonic generation (SHG), which stemmed from the stabilization of dipole alignment of the NLO chromophore. In this work we prepared another novel polyester containing 2,3-dioxybenzylidenecyanoacetate groups as NLO-chromophores. We selected the latter because they have a large dipole moment and are rather easy to synthesize. Furthermore, 2,3-dioxyben-

zylidenecyanoacetate group constitutes novel Y-type NLO polyester (Fig. 1b), and this Y-type NLO polyester has not yet been reported in the literature. Thus, we synthesized a new type of NLO polyester, in which the pendant NLO chromophores are components of the polymer backbone. This mid-type NLO polymer is expected to have the advantages of both main-chain and side-chain NLO polymers namely stable dipole alignment and good solubility. After confirming the structure of the resulting polymer we investigated its properties such as solubility, T_g , thermal stability, second harmonic generation (SHG) activity and relaxation of dipole alignment. We now report the results of the initial phase of the work.

Results and Discussion

2,3-Di-(2'-vinylloxyethoxy)benzaldehyde (**1**) was prepared by the reaction of 2-chloroethyl vinyl ether with 2,3-dihydroxybenzaldehyde. Methyl 2,3-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**2**) was prepared by the condensation reaction of compound **1** with methyl cyanoacetate. Compound **2** was hydrolyzed to yield acetaldehyde and diol **3**. Monomer **3** was condensed with terephthaloyl chloride in a dry DMF solvent to yield polyester **4** containing the NLO-chromophore 2,3-dioxybenzylidenecyanoacetate group. The synthetic route for polyester **4** is presented in Scheme 1. The polymerization yield was 90%. The chemical structure of the resulting polymer was confirmed by ¹H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structure. ¹H NMR spectrum of the polymer showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The IR spectrum of the same polymer shows a strong carbonyl peak near 1722 cm⁻¹ indicating the presence of ester bond. The same polymer sample also shows a strong absorption peak near 2224 cm⁻¹ and 1605 cm⁻¹ due to the nitrile and olefin groups, respectively. These results are consistent with the proposed structure, 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 polymer **4** was determined to be 16,200 ($M_w/M_n = 1.94$). The structural feature of this polymer is that it has pendant NLO chromophores, which are parts of the polymer main chains. Thus the resulting polymer **4** is a mid type of side-chain and main-chain NLO polymer,

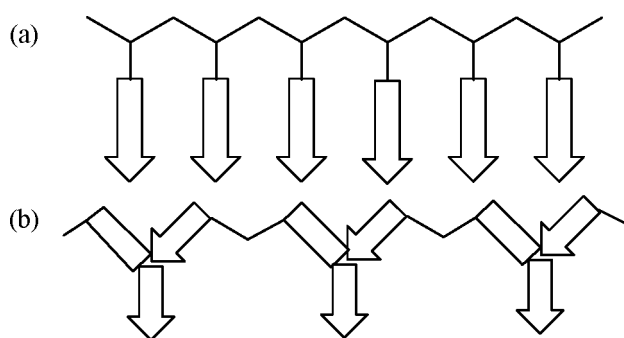
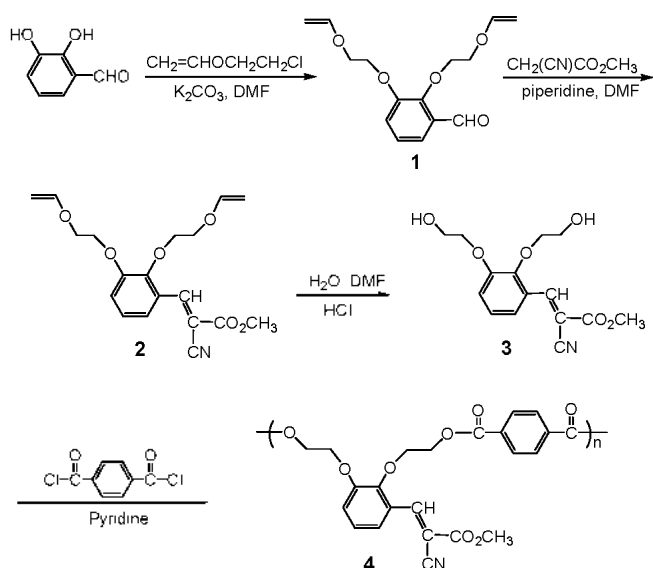


Figure 1. (a) Side-chain NLO polymers and (b) Y-type NLO polymers.



Scheme 1. Synthetic scheme and structure of polymer **4**.

and is expected to have both of their merits. The polymer **4** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity was 0.28 dL/g. Polymer **4** showed strong absorption near 313 nm by the NLO-chromophore 2,3-dioxybenzylidenecyanoacetate group. We now have well defined polyester (**4**) and investigate its properties.

The thermal behavior of the polymer was investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g). DSC thermogram of polymer **4** is presented in Fig. 2. Polymer **4** showed a thermal stability up to 260 °C according to its TGA thermogram. The T_g value of the polymer **4** measured by DSC were around 100 °C. This T_g value is somewhat higher than that of the polyester containing 2,3-dioxybenzylidenemalononitrile.¹³ 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 polymer **4** were studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer film was corona-poled. The poling was confirmed by UV-Vis spectra. After electric poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectrum of polymer **4** exhibited 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 of polymer **4** was equal to 0.18 for polymer **4** ($\Phi = 1 - A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after poling). For the purpose of investigating surface morphology of polymer films, domain structures of NLO-chromophores for the thin-film samples were obtained using atomic force microscopy (AFM). Fig. 3 shows AFM scans of the spin-coated film before and after poling polymer **4**. AFM images show that the surface of the film sample is flat

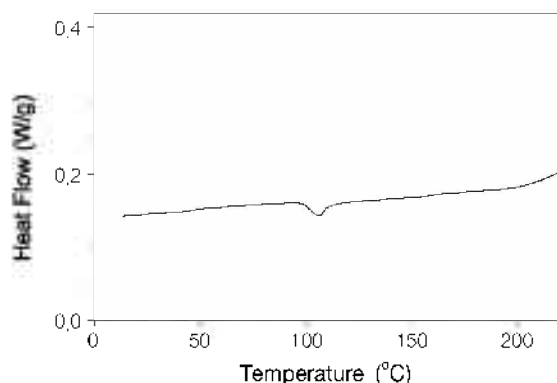


Figure 2. DSC thermogram of polymer **4** at a heating rate of 10 °C/min under nitrogen.

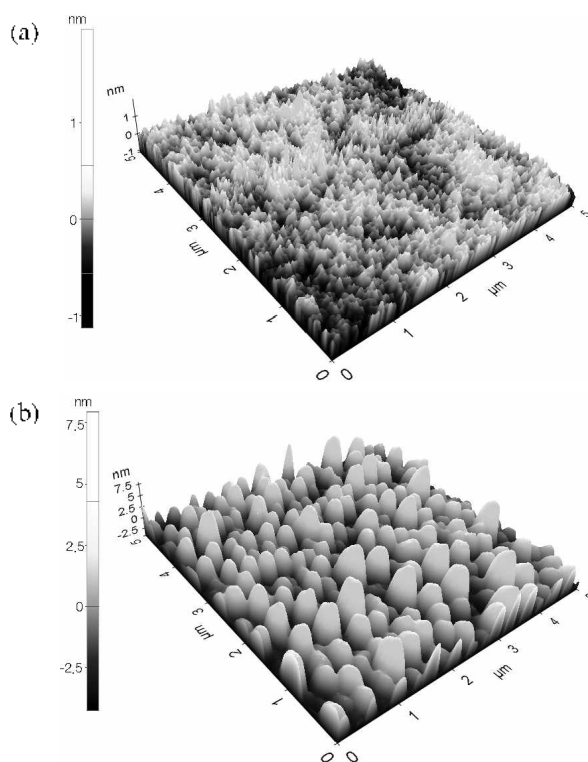


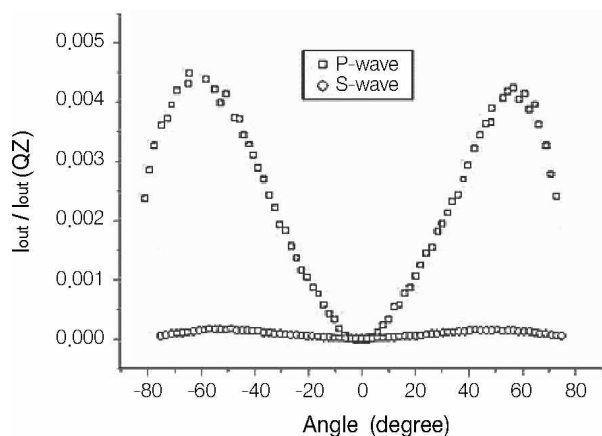
Figure 3. AFM images of spin-coated film of polymer **4**: (a) before corona-poling; (b) after corona-poling.

and clean before poling (see Fig. 3a). 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 as shown in Fig. 3b. The refractive index of the sample was measured by the optical transmission technique.¹⁴ SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. NLO properties of polymer **4** are summarized in Table 1. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Fig. 4 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

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

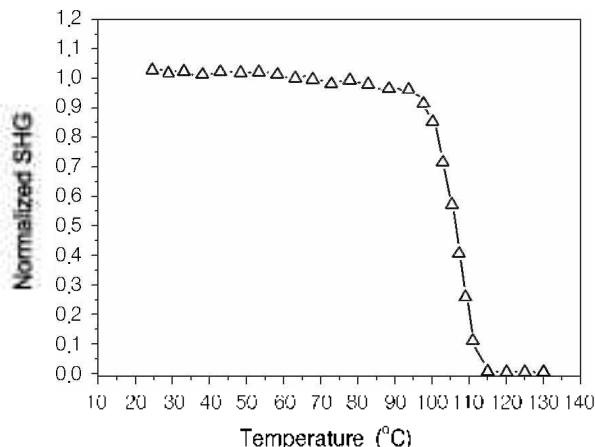
Polymer	λ_{max}^a (nm)	d_{33}^b (esu)	Φ^c	d_{31}^b (esu)	film thickness ^d (μm)	n
4	313	$(3.47 \pm 0.09) \times 10^{-9}$	0.18	$(1.35 \pm 0.04) \times 10^{-9}$	0.54	$n_1=1.63$ $n_2=1.71$

^aPolymer film. ^bSHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.¹⁵ ^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.¹¹

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

samples and recorded. SHG coefficients were derived from the analysis of measured Maker-fringes with Pascal fitting program according to the literature procedure.¹⁵ The values of d_{33} and d_{31} for polymer **4** were $(3.47 \pm 0.09) \times 10^{-9}$ and $(1.35 \pm 0.04) \times 10^{-9}$ esu, respectively. These values are similar with those for the polyester containing 2,3-dioxybenzylidene-malononitrile group.¹³ Since the second harmonic wavelength was at 532 nm, which is not in the absorptive region of the resulting polyesters, 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 Fig. 5, 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 3 °C/min from 30 °C to 140 °C. The polymer thin film exhibited a thermal stability up to T_g and no significant SHG decay was observed below 100 °C, as shown in Fig. 6. This SHG thermal stability is somewhat higher than that of the polyester containing 2,3-dioxybenzylidene-malononitrile group.¹³ In general, side chain NLO polymers lose thermal stability of dipole alignment below T_g . Stabilization of dipole alignment is a characteristic of main chain NLO polymers. The enhanced 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 another new NLO polyester having both the merits of main-chain and side-chain NLO polymers namely stable dipole alignment and good solubility.

**Figure 5.** Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 3 °C/min.

Experimental Section

Materials. The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2,3-Dihydroxybenzaldehyde, 2-chloroethyl vinyl ether, and tetrahydrofuran (THF) were used as received. Terephthaloyl chloride (TPC) was purified by sublimation under vacuum. Methyl cyanoacetate was distilled 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 300MHz NMR spectrometer. UV-Vis absorption spectra were measured on a Shimadzu UV-3100S spectrophotometer. Elemental analyses were performed using a Perkin-Elmer 2400 CIIN elemental analyzer. The glass transition temperatures (T_g) were measured on a TA 2920 differential scanning calorimeter in a nitrogen atmosphere. TA Q50 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. Viscosity values were obtained by using a Cannon-Fenske viscometer.

Film Preparation and SHG Measurements. The refractive index of the sample was measured by the optical transmission technique.¹⁴ The transmittance of thin film includes on the information of the thickness, refractive index and extinction coefficient of that. Thus, we determined these parameters by analyzing the transmittance. Second harmonic generation (SHG) measurement was carried out one day after poling. 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.¹⁵

Preparation of 2,3-(2'-Vinyloxyethoxy)benzaldehyde (1). 2,3-Dihydroxybenzaldehyde (13.8 g, 0.10 mol), anhydrous potassium carbonate (36 g, 0.36 mol), and 2-chloroethyl vinyl ether (26.6 g, 0.25 mol) were dissolved in 200 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 100 °C for 40 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 300 mL of water, and extracted with 300 mL of diethyl ether three times. The organic layer was washed with saturated aqueous sodium chloride solution, and dried with anhydrous magnesium sulfate. Rotary evaporation of diethyl ether gave crude product, which was recrystallized from 1-butanol yielded 24.5 g (88% yield) of pure product **1**. Mp = 48-50 °C. ¹H NMR (CDCl₃) δ 3.95-4.47 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.44-6.57 (m, 2H, 2 =CH-O-), 7.09-7.19 (m, 2H, aromatic), 7.42-7.48 (m, 1H, aromatic), 10.48 (s, 1H, -CHO). IR (KBr) 3098, 3076 (w, =C-H), 2953, 2883 (s, C-H), 1682 (vs, C=O), 1618 (vs, C=C) cm⁻¹.

Preparation of Methyl 2,3-Di-(2'-vinyloxyethoxy)benzylidenecyanoacetate (2). Piperidine (0.043 g, 0.5 mmol) was added to a solution of **1** (2.78 g, 10 mmol) and methyl cyanoacetate (1.98 g, 20 mmol) in 30 mL of DMF with stirring at room temperature under nitrogen. After stirring for 10 h at room temperature, the reaction mixture was diluted with 50 mL of water, and extracted with 80 mL of diethyl ether three times. The organic layer was dried with anhydrous magnesium sulfate. Rotary evaporation of diethyl ether gave crude product, which was recrystallized from 1-butanol yielded 2.87 g (80% yield) of pure product **2**. Mp = 53-55 °C. ¹H NMR (CDCl₃) δ 3.92 (s, 3H, -CO₂CH₃), 3.98-4.43 (m, 12H, 2 CH₂=, 2 -O-CH₂-CH₂-O-), 6.46-6.59 (m, 2H, 2 =CH-O-), 7.08-7.19 (m, 2H, aromatic), 7.90-7.96 (d, 1H, aromatic), 8.86 (s, 1H, benzylic). IR (KBr) 3047 (w, =C-H), 2941, 2856 (m, C-H), 2222 (s, CN), 1728 (vs, C=O), 1618, 1591 (vs, C=C) cm⁻¹. Anal. Calcd for C₁₉H₂₁NO₆: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.59; H, 5.95; N, 3.84.

Preparation of Methyl 2,3-Di-(2'-hydroxyethoxy)benzylidenecyanoacetate (3). Aqueous hydrochloric acid (1.5 M, 30 mL) was slowly added to a solution of **2** (3.59 g, 0.01 mol) in 30 mL of dry DMF with stirring under nitrogen at 0 °C. The mixture was stirred at 0 °C for 12 h under nitrogen. The resulting solution was filtered and washed with to give 2.61 g

(85% yield) of **3**. Mp = 124-126 °C. ¹H NMR (DMSO-*d*₆) δ 3.58 (m, 2H, -CH₂-O-), 3.75 (m, 2H, -CH₂-O-), 3.83 (s, 3H, CO₂CH₃), 4.05 (t, 2H, Ph-O-CH₂-), 4.16 (t, 2H, 2 Ph-O-CH₂-), 4.81 (t, 1H, -OH), 4.89 (t, 1H, -OH), 7.21 (t, 1H, aromatic), 7.32 (d, 1H, aromatic), 7.72 (d, 1H, aromatic), 8.82 (s, 1H, -Ph-CH=). IR (KBr) 3318, 3219 (s, O-H), 2928, 2876 (m, C-H), 2225 (m, CN), 1724 (vs, C=O), 1612 (vs, C=C) cm⁻¹. Anal. Calcd for C₁₅H₁₇NO₆: C, 58.63; H, 5.57; N, 4.56. Found: C, 58.72; H, 5.65; N, 4.64.

Synthesis of Polyester 4. A representative polycondensation procedure was as follows: Terephthaloyl chloride (2.03 g, 0.01 mol) and diol **3** (3.07 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 12 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 3.93 g (90% yield) of polymer **4**: η_{inh} = 0.28 dL/g (c. 0.5 g/dL in DMSO at 25 °C). ¹H NMR (DMSO-*d*₆) δ 3.56-3.64 (s, 3H, CO₂CH₃), 4.33-4.71 (d, 8H, 2 Ph-O-CH₂-CH₂-O-), 7.24 (s, 1H, aromatic), 7.42 (s, 1H, aromatic), 7.62-8.03 (m, 5H, aromatic), 8.55 (s, 1H, -Ph-CH=). IR (KBr) 2955 (m, C-H), 2224 (m, CN), 1722 (vs, C=O), 1605 (s, C=C) cm⁻¹. Anal. Calcd for (C₂₃H₁₉NO₈)_n: C, 63.16; H, 4.37; N, 3.20. Found: C, 63.23; H, 4.42; N, 3.25.

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