

Synthesis of Novel Y-type Nonlinear Optical Polyester with Enhanced Thermal Stability of Second Harmonic Generation for Electro-Optic Applications

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Methyl 3,4-di-(2'-hydroxyethoxy)benzylidenecyanoacetate (**3**) was prepared and condensed with terephthaloyl chloride to yield novel Y-type polyester (**4**) containing 3,4-dioxybenzylidenecyanoacetate groups as NLO-chromophores, which constituted parts of the polymer main chains. The resulting polymer **4** is soluble in common organic solvents such as acetone and *N,N*-dimethylformamide. Polymer **4** shows thermal stability up to 280 °C in thermogravimetric analysis with glass-transition temperature obtained from differential scanning calorimetry near 105 °C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer films at the 1064 nm fundamental wavelength is around 2.42 pm/V. The dipole alignment exhibits high thermal stability up to near T_g , and there is 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, AFM, Second harmonic generation, Dipole alignment

Introduction

Recently nonlinear optical (NLO) polymers have been received a great attention because of their potential applications in the field of electro-optic devices such as optical switching, signal transmission, data storage *etc.*¹⁻⁶ 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 method⁷⁻¹¹ and the utilization of high T_g polymers such as polyimides.¹²⁻¹⁷ Various polyesters with NLO-chromophores in the main chain¹⁸ or in side chain¹⁹⁻²⁰ 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 dioxynitrostilbene²¹⁻²² or dioxybenzylidenemalononitrile²³ 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 reported here, we prepared novel polyester containing 3,4-dioxybenzylidenecyanoacetate groups as NLO chromophores. We selected the latter because they have a large dipole moment and are rather easy to synthesize. Furthermore, 3,4-dioxybenzylidenecyanoacetate groups constitute novel Y-type NLO polyesters (Fig. 1c), 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 components of the polymer backbones. This mid-type NLO polymer is 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 polymer we investigated its properties such as solubility, T_g , thermal stability, surface morphology of polymer films, second harmonic generation (SHG) activity and relaxation of dipole alignment.

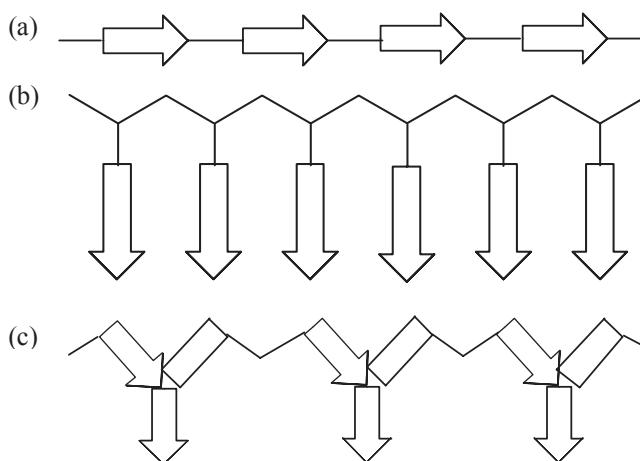
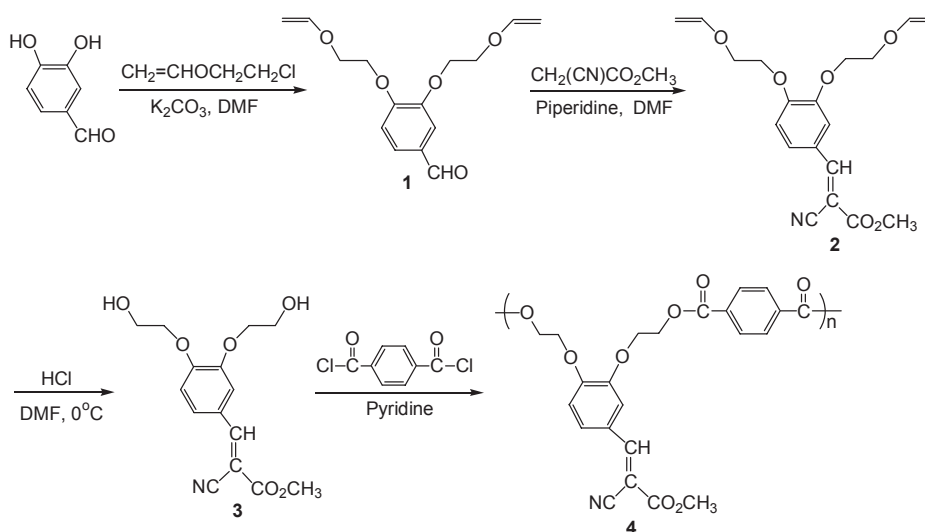


Figure 1. (a) Main-chain NLO polymers, (b) side-chain NLO polymers, and (c) Y-type NLO polymers.

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Results and Discussion

Synthesis and characterization of polymer 4. 3,4-Di-(2'-vinyl-oxoethoxy)benzaldehyde (**1**) was prepared by the reaction of 2-chloroethyl vinyl ether with 3,4-dihydroxybenzaldehyde. Methyl 3,4-di-(2'-vinyl-oxoethoxy)benzylidenecyanoacetate (**2**) was prepared by the condensation reaction of **1** with methyl cyanoacetate. Compound **2** was hydrolyzed to diol **3**, and it was condensed with terephthaloyl chloride in a dry DMF solvent to



Scheme 1. Synthetic scheme and structure of polymers 4

Table 1. Polymerization of **3**^a with TPC^b in Pyridine

Monomer	Monomer/ Solvent (mol/L)	Diol 3 to R(COCl) ₂ (mol/mol)	Time (h)	Yield (%)	η_{inh}^c (dL/g)	M_n^d	M_w^d	PD ^e
3 , TPC	0.67	1.0	10	90	0.29	17400	31300	1.80
3 , TPC	0.80	1.0	12	91	0.30	17800	32700	1.84

^a**3** = Methyl 3,4-di-(2'-hydroxyethoxy)benzylidenecyanoacetate. ^bTPC = Terephthaloyl chloride. ^cInherent viscosity of polymer: Concentration of 0.5 g/dL in DMSO at 25 °C. ^dMeasured by GPC in THF using polystyrene standard. ^ePD = Polydispersity.

yield Y-type polyester **4** containing the NLO chromophore 3,4-dioxybenzylidenecyanoacetate group. Synthetic method of polymer **4** is summarized in Scheme 1 and polymerization results are summarized in Table 1. The polymerization yield was 90–91%. The chemical structure of the resulting polymer was confirmed by ¹H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structures. 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 polymer **4** shows a strong carbonyl peak near 1722 cm⁻¹ indicating the presence of ester bond. The spectrum also shows a strong nitrile peak near 2221 cm⁻¹. 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 eluent. The number average molecular weight (M_n) of the polymer was determined to be 17400 ($M_w/M_n = 1.80$) for polymer **4**. The structural feature of this polymer is that it gives unprecedented Y-type NLO polymers, in which the pendant NLO chromophores are part of the polymer backbone. Thus the resulting polymer (**4**) is a mid type of side chain- and main chain NLO polymers, 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 is around 0.30 dL/g. Polymer **4** shows strong absorption near 356 nm due to the NLO chromophore 3,4-dioxybenzylidenecyanoacetate group. Having obtained the well defined

Table 2. Optical and electrochemical properties of the synthesized polymers.

Polymer	T_g^a (°C)	Degradation temp (°C) ^b			Residue at 800 °C (wt %) ^b
		5 wt %-loss	20 wt %-loss	40 wt %-loss	
4	105	296	368	405	6.8

^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 TA Q50 thermogravimetric analyzer with a heating rate of 10 °C/min under nitrogen atmosphere.

polyester **4**, we investigate its properties.

Thermal properties of the polymer 4. The thermal behavior of the polymer was investigated using 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. TGA and DSC thermograms of polymer **4** are shown in Fig. 2 and Fig. 3, respectively. Polymer **4** has a thermal stability up to 280 °C according to its TGA thermogram. The T_g value of the polymer **4** measured using DSC is near 105 °C. The TGA and DSC studies show that the decomposition temperature of the polyester **4** is higher than that of poling temperature. This indicates that corona poling at 110 °C for a short term is feasible without damaging the NLO chromophore.

Nonlinear optical properties of the polymer. The NLO properties of polymer were studied using the SHG method. To in-

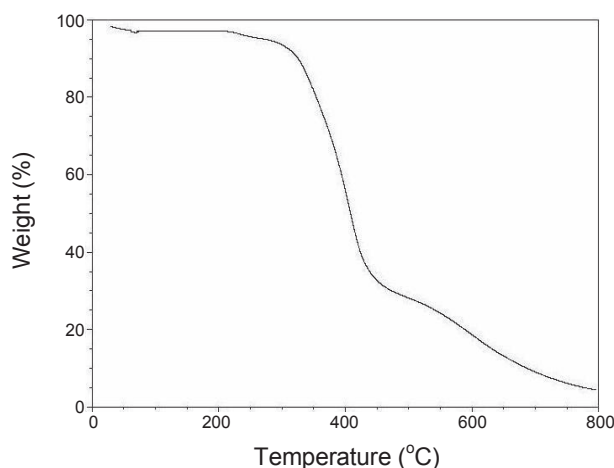


Figure 2. TGA thermogram of polymer **4** obtained at a heating rate of 10 °C/min under nitrogen.

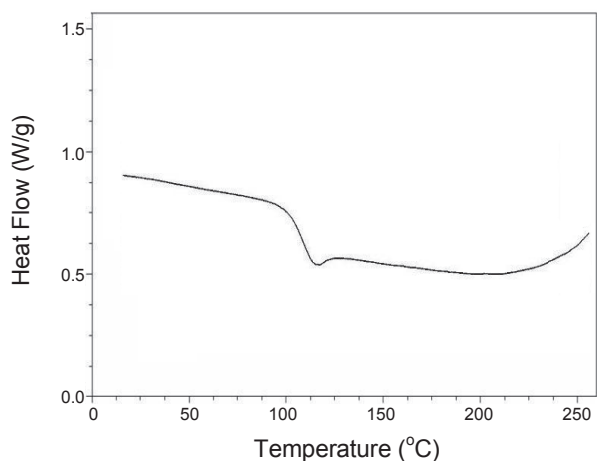


Figure 3. DSC thermogram of polymer **4** obtained at a heating rate of 10 °C/min under nitrogen.

duce noncentrosymmetric polar order, the spin-coated polymer films were corona-polled. As the temperature was raised gradually to 110 °C, 6.5 kV of corona voltage was applied and kept at that temperature for 30 min. The poling was confirmed from UV-visible spectra. Fig. 4 shows the UV-visible absorption spectra of the polymer **4** before and after poling. After electric poling, the dipole moments of the NLO chromophores were aligned and the UV-visible spectrum of polymer **4** exhibits 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 is equal to 0.21 for polymer **4** ($\Phi = 1 - A_1/A_0$, where $A_0 = 0.501$ and $A_1 = 0.398$ are the absorbances of the polymer film before and after poling, respectively).

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). Fig. 5 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 and clean before poling (see Fig. 5a). However,

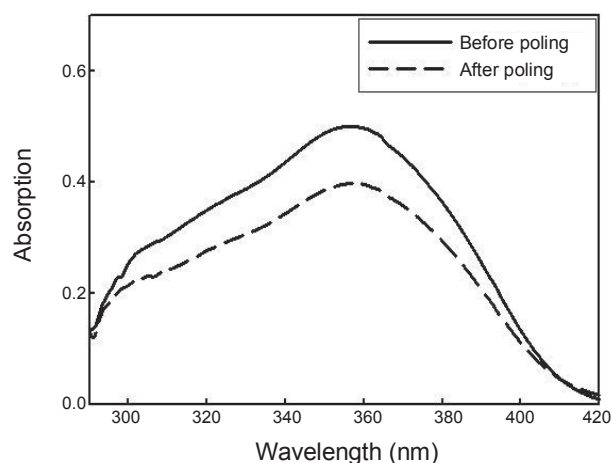


Figure 4. UV-visible absorption spectra of a film of polymer **4** before and after poling.

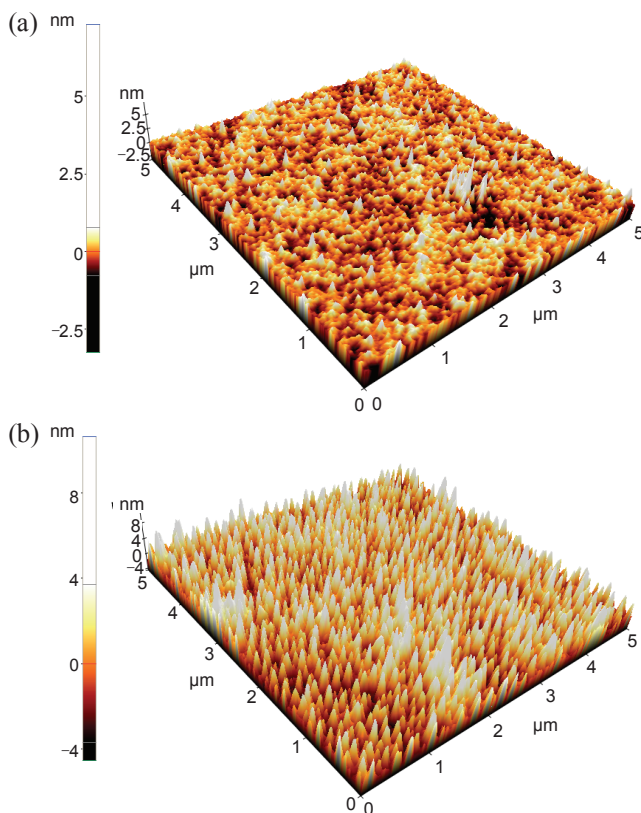


Figure 5. AFM images of spin-coated film of polymer **4**: (a) before corona-poling; (b) after corona-poling.

this good quality film was dramatically changed after poling, resulting in numerous sharp hills and valleys in the surface structure, which means that the NLO chromophores are aligned the poling direction as shown in Fig. 5b. The rms roughness for this image is *ca.* 4.6 nm.²⁴

The refractive index of the sample was measured by the optical transmission technique.²⁵ The transmittance of thin film includes information on the thickness, refractive index and its extinction coefficient. Thus, we can determine those parameters

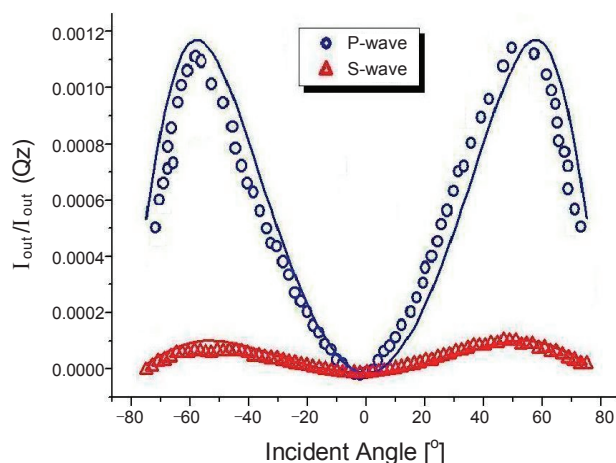


Figure 6. Angular dependence of SHG signal in a poled film of polymer **4**.

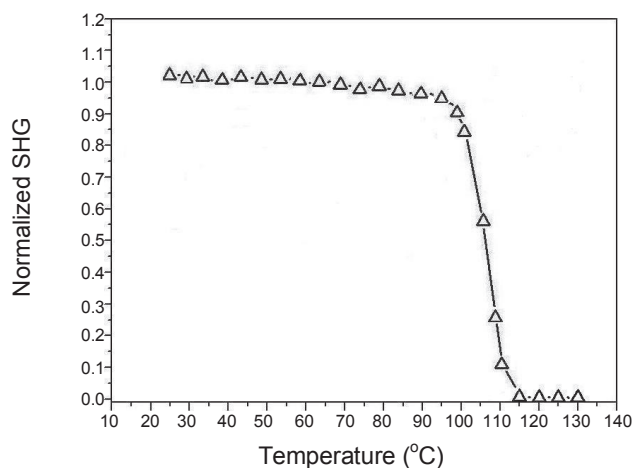


Figure 7. Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 3.5 °C/min.

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 polymers, the angular SHG dependence was recorded. Fig. 6 shows the angular dependence of SHG signal for 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. Nonlinear optical properties of polymer **4** are summarized in Table 3. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure.²⁶ The values of d_{31} and d_{33} for polymer **4** are 0.87 and 2.42 pm/V, respectively. Since the second harmonic wavelength is at 532 nm, which is not in the absorptive region of the resulting polyurethane, there is 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 2.77 is in good agreement with the predicted value.

To evaluate the high-temperature stability of the polymers,

Table 3. Nonlinear Optical Properties of Polymer **4**

Polymer	λ_{\max}^a (nm)	d_{33}^b (pm/V)	Φ^c	d_{31}^b (pm/V)	film thickness ^d (μm)	n
4	356	2.42	0.21	0.87	0.51	$n_1 = 1.61$ $n_2 = 1.68$

^aPolymer film after corona poling. ^bSHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes. ²⁶ SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. ^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.²⁵

we studied the temporal stability of the SHG signal. Fig. 7 shows the dynamic thermal stability study of the NLO activity of a film of polymer **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 3.5 °C/min from 30 to 150 °C. The polymer film exhibits a thermal stability up to near T_g and no significant SHG decay was observed below 100 °C. 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 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. The polymers also shows good long-term thermal stability of d_{33} except for the small activity loss within a few days after poling, which are acceptable for NLO device applications. Thus, we obtained a new type of NLO polyester having the advantages of both main-chain and side-chain NLO polymers: stabilization of dipole alignment and good solubility.

Conclusions

We synthesized novel Y-type polyester **4** with pendant NLO chromophores, which are part of the polymer main chain. This mid-type NLO polyester is soluble in common organic solvents. The resulting polymer **4** shows a thermal stability up to 280 °C from TGA thermogram with T_g value near 105 °C. The SHG coefficient (d_{33}) of corona-poled polymer film is around 2.42 pm/V. The structural feature of this polymer is that they exhibit SHG stability up to near T_g and no SHG decay is observed below 100 °C. This high thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophore, which constitute a part of the polymer backbone.

Experimental Section

Materials. Reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 3,4-Dihydroxybenzaldehyde and 2-chloroethyl vinyl ether 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. 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-visible absorption spectra were measured using 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 in a nitrogen atmosphere. TA Q50 thermogravimetric analyzer with a heating rate of $10^\circ\text{C}/\text{min}$ up to 800°C was used for the thermal degradation pattern of polymer 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. Melting points were measured with a Büchi 530 melting point apparatus and are corrected. 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 $0.45\ \mu\text{m}$ Teflon[®] membrane filter. The polymer films were 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 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°C higher than T_g , a corona voltage of 6.5 kV of 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 by the optical transmission technique.²⁵ 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 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 $d_{11} = 0.3\ \text{pm/V}$) was used as a reference for determining the relative intensities of the second harmonic 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.²⁶

Preparation of 3,4-(2'-vinylxyethoxy)benzaldehyde (1). 3,4-Dihydroxybenzaldehyde (13.8 g, 0.10 mol), anhydrous potassium carbonate (82.9 g, 0.60 mol), and 2-chloroethyl vinyl ether (16.0 g, 0.25 mol) were dissolved in 400 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 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 24.4 g (88% yield) of pure product **1**. mp $56 - 57^\circ\text{C}$. ^1H NMR (CDCl_3) δ 4.04-4.36 (m, 12H, 2 $\text{CH}_2 = 2\text{-O-CH}_2\text{-CH}_2\text{-O-}$), 6.50-6.62 (m, 2H, 2 = CH-O-), 7.01-7.06 (d, 1H, aromatic), 7.45-7.42 (d, 2H, aromatic), 9.86 (s, 1H, -CHO). IR (KBr disc) 3099, 3080 (w, = C-H), 2952, 2872 (m, C-H), 1672 (vs, C=O), 1612 (vs, C=C), 1575 (s, C=C) cm^{-1} .

Preparation of methyl 3,4-di-(2'-vinylxyethoxy)benzylidenecyanoacetate (2). Piperidine (0.085 g, 1.0 mmol) was added to a solution of 3,4-di-(2'-vinylxyethoxy)benzaldehyde **1** (5.57 g, 20 mmol) and methyl cyanoacetate (2.18 g, 22 mmol) in 140 mL of 1-butanol with stirring at 0°C under nitrogen. After stirring for 4 h at 0°C , the reaction mixture was cooled to -10°C for crystallization. The product was filtered and washed successively with cold 1-butanol (60 mL), water (20 mL), and cold 1-butanol (15 mL). The obtained pale yellow product was recrystallized from 1-butanol to give 6.49g (86% yield) of **2**. mp $86 - 87^\circ\text{C}$. ^1H NMR (CDCl_3) δ 3.92 (s, 3H, $-\text{CO}_2\text{CH}_3$), 4.02-4.38 (m, 12H, 2 $\text{CH}_2 = 2\text{-O-CH}_2\text{-CH}_2\text{-O-}$), 6.48-6.60 (m, 2H, 2 = CH-O-) 6.95-7.02 (d, 1H, aromatic), 7.47-7.54 (m, 1H, aromatic), 7.75-7.79 (m, 1H, aromatic), 8.11 - 8.16 (m, 1H, aromatic). IR (KBr disc) 3113 (w, =C-H), 2954, 2934, 2876 (m, C-H), 2222 (s, CN), 1720 (vs, C=O), 1638, 1591 (vs, C=C) cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.61; H, 5.83; N, 3.82.

Preparation of methyl 3,4-di-(2'-hydroxyethoxy)benzylidenecyanoacetate (3). Aqueous hydrochloric acid (1.5 M, 30 mL) was slowly added to a solution of methyl 3,4-di-(2'-vinylxyethoxy)benzylidenecyanoacetate (**2**) (9.34 g, 0.026 mol) in 60 mL of dry THF 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 6.79 g (85% yield) of **3**. mp $120 - 122^\circ\text{C}$. ^1H NMR (CDCl_3) δ 2.80-2.88 (m, 2H, -OH), 3.86-3.88 (s, 3H, CO_2CH_3), 3.89-3.97 (m, 4H, 2 $-\text{CH}_2\text{-O-}$), 4.14-4.27 (m, 4H, 2 Ph-O- $\text{CH}_2\text{-}$), 7.18-7.22 (m, 1H, aromatic), 7.68-7.73 (m, 1H, aromatic), 7.84-7.86 (m, 1H, aromatic), 8.22 (s, 1H, -Ph-CH=). IR (KBr disc): 3580, 3377 (s, O-H), 3103 (w, =C-H), 2934, 2876 (m, C-H), 2220 (m, CN), 1724 (vs, C=O), 1589 (vs, C=C) cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_6$: C,

58.63; H, 5.57; N, 4.56. Found: C, 58.74 H, 5.65; N, 4.68.

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 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 3.93 g (90% yield) of polymer **4**. Inherent viscosity (η_{inh}) = 0.29 dL/g ($c = 0.5$ g/dL in DMSO at 25 °C). $M_n = 17400$, $M_w = 31300$ (styragel HR5E4E; solvent THF). 1H NMR ($CDCl_3$) δ 3.84 (s, 3H, -COOCH₃), 4.28-4.65 (t, 8H, 2 -O-CH₂-CH₂-O-), 7.16-7.37 (t, 2H, aromatic), 7.65-8.06 (m, 4H, aromatic), 8.13-8.32 (m, 2H, aromatic). IR (KBr disc) 2956 (m, C-H), 2221 (s, CN), 1722 (vs, C=O), 1590 (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, 3.19.

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References

- Marks, T. J.; Ratner, M. A. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 155.
- Lee, C.; Park, S.-K.; Yang, M.; Lee, N.-S.; Kim, N. J. *Bull. Korean Chem. Soc.* **2007**, *28*, 447.
- Lee, S. K.; Cho, M. J.; Jin, J.-I.; Choi, D. H. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 531.
- Yoon, Z. S.; Easwaramoorthi, S.; Kim, D. *Bull. Korean Chem. Soc.* **2008**, *29*, 197.
- Jin, F.-L.; Park, S.-J. *Bull. Korean Chem. Soc.* **2008**, *29*, 2521.
- Li, Z.; Dong, S.; Li, P.; Li, Z.; Ye, C.; Qin, J. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 2983.
- Han, K. S.; Park, S. K.; Shim, S. Y.; Jahng, W. S.; Kim, N. J. *Bull. Korean Chem. Soc.* **1998**, *19*, 1165.
- Cho, B. R.; Kim, Y. H.; Son, K. W.; Khalil, C.; Kim, Y. H.; Jeon, S.-J. *Bull. Korean Chem. Soc.* **2002**, *23*, 1253.
- Kim, T.-D.; Luo, J.; Tian, Y.; Ka, J.-W.; Tucker, N. M.; Haller, M.; Kang, J.-W.; Jen, A. K.-Y. *Macromolecules* **2001**, *39*, 1676.
- Liu, Y.-L.; Hsieh, C.-Y. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 905.
- Moon, J. R.; Kim, B. S.; Kim, J.-H. *Bull. Korean Chem. Soc.* **2006**, *27*, 981.
- Chen, T.; Jen, A. K. Y.; Cai, Y. *Macromolecules* **1996**, *29*, 535.
- Saadeh, H.; Gharavi, A.; Yu, D.; Yu, L. *Macromolecules* **1997**, *30*, 5403.
- Tsutsumi, N.; Morishima, M.; Sakai, W. *Macromolecules* **1998**, *31*, 7764.
- Liu, J.-G.; Nakamura, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 5606.
- Hoang, M. A.; Kim, M. H.; Cho, M. J.; Kim, K. H.; Kim, K. N.; Jin, J.-I.; Choi, D. H. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 5064.
- Ryu, S.; Kim, J. H.; Lee, S. H.; Lee, M.-H. *Bull. Korean Chem. Soc.* **2008**, *29*, 1689.
- 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.
- Ambrosanio, 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.; Jung, W.-T. *Bull. Korean Chem. Soc.* **2007**, *28*, 329.
- Lee, J.-Y.; Kim, J.-H.; Won, D.-S.; Jang, H.-N. *Bull. Korean Chem. Soc.* **2007**, *28*, 1433.
- Walther, F.; Heckl, W. M.; Stark, R. W. *Appl. Sur. Sci.* **2008**, *254*, 7290.
- Cisneros, J. I. *Appl. Opt.* **1998**, *37*, 5262.
- Herman, W. N.; Hayden, L. M. *J. Opt. Soc. Am. B* **1995**, *12*, 416.