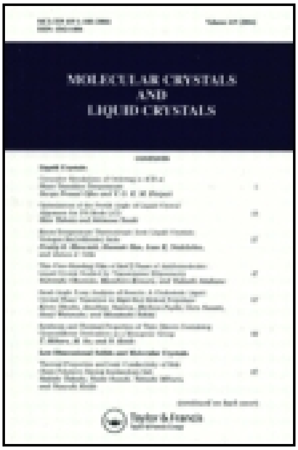

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Synthesis and Nonlinear Optical Properties of Novel Y-Type Polyesters with Enhanced Thermal Stability of Dipole Alignment

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Synthesis and Nonlinear Optical Properties of Novel Y-Type Polyesters with Enhanced Thermal Stability of Dipole Alignment

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*2,3-Di-(2′-hydroxyethoxy)-4′-nitrostilbene (***3***) was prepared and condensed with terephthaloyl chloride and adipoyl chloride to yield novel Y-type polyesters (***4–5***) containing the NLO-chromophores dioxynitrostilbenyl groups, which constituted parts of the polymer backbones. Polymers* **4–5** *were soluble in common organic solvents such as acetone and dimethylsulfoxide. They showed thermal stability up to 300°C in thermogravimetric analysis with glass-transition temperatures obtained from differential scanning calorimetry in the range of 83–95°C. The second harmonic generation (SHG) coefficients (d_{33}) of poled polymer films at the 1064 cm^{-1} fundamental wavelength were around 3.68×10^{-9} esu. The dipole alignment exhibited high thermal stability up to the glass-transition temperature due to the partial main-chain character of polymer structure, which was acceptable for NLO device applications.*

Keywords: atomic force microscopy (AFM); differential scanning calorimetry (DSC); NLO; polyesters; relaxation of dipole alignment; SHG coefficient; thermogravimetric analysis (TGA)

INTRODUCTION

Organic materials with nonlinear optical (NLO) effects have been extensively studied over the past decade because of their potential applications in the field of telecommunications, optical switching, etc. Among the organic materials the NLO polymers are receiving

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Address correspondence to Ju-Yeon Lee, Institute of Functional Materials, Department of Chemistry, Inje University, 607 Obang-dong, Gimhae 621-749, Korea. E-mail: chemljy@inje.ac.kr great attention, mainly because they offer many advantages such light weight and good processability to form electro-optic devices [1]. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is important considerations. Crosslinking method [2] and utilizing high T_g polymers such as polyimides [3,4] have been proposed to minimize the randomization. Polymers with the NLO chromophores in the main chain [5,6] have good thermal stability of dipole alignments, but they often do not dissolve in organic solvents, and the intractability of them make them impossible to fabricate stable noncentrosymmetric films. Polymers with the NLO chromophores in the side chain [7,8] have the advantages such as good solubility, homogeneity and high level of NLO chromophore relative to the main-chain systems, but they often suffer from poor stability of dipole alignments at high temperatures. In this work we prepared novel Y-type polyesters containing 2,3-dioxynitrostilbenyl groups as NLO-chromophores. We selected 2,3-dioxynitrostilbenyl groups as NLO-chromophores because they have a large dipole moment and are rather easy to synthesize. Furthermore, 2,3-dioxynitrostilbenyl groups constitute novel Y-type NLO polyesters, in which the pendant NLO chromophores are parts of the polymer backbones (Fig. 1c). 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 the properties such as solubility, T_g, thermal stability, surface morphology of polymer film, second harmonic generation (SHG) activity and relaxation of dipole alignment. We now report the results of the initial phase of the work.

EXPERIMENTAL

Materials

Synthetic methods of diol **3** and polymers **4–5** are summarized in Schemes 1 and 2. Compound **3**: Yield: 4.72 g (82%). Melting point: 123–125°C. ^{1}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 $C_{18}H_{19}NO_6$: C, 62.60; H, 5.54; N, 4.06. Found: C, 62.72; H, 5.58; N, 4.13. Polymer **4**: Inherent viscosity (η_{inh}) $= 0.28\,dL\,g^{-1}$ ($c = 0.5\,g\,dL^{-1}$ in m-cresol at 25°C). $M_n = 22{,}900$, $M_w = 39{,}500$ (styragel HR5E4E;

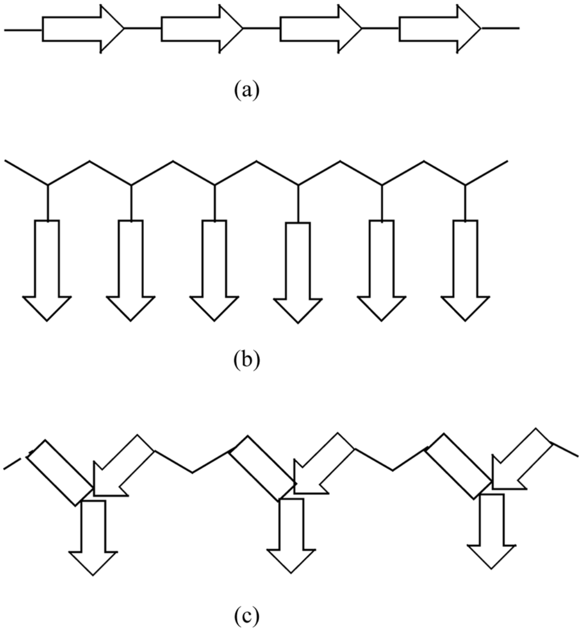
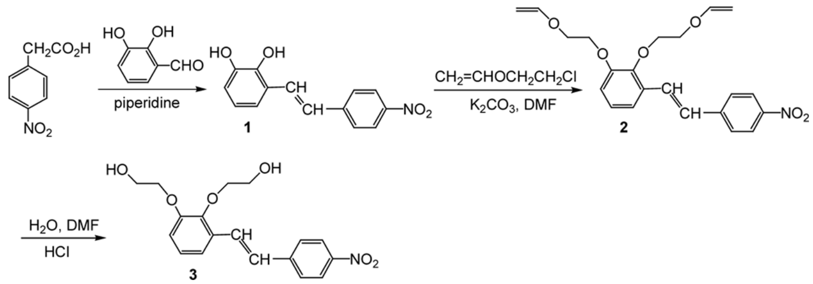
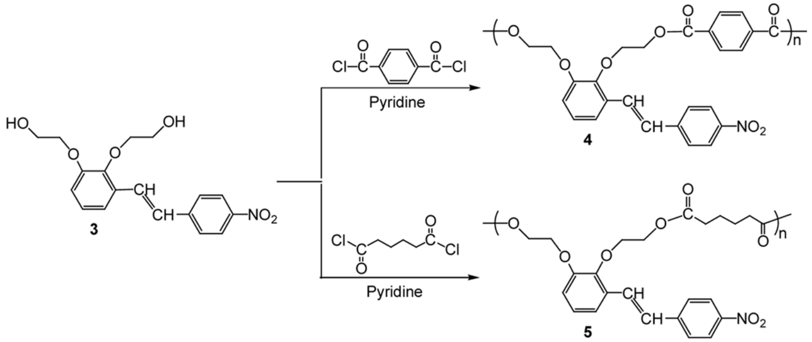


FIGURE 1 (a) Main-chain NLO polymers, (b) side chain NLO polymers, and (c) Y-type NLO polymers.

solvent THF). ^{1}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 $(C_{26}H_{21}NO_8)_n$: C, 65.68; H, 4.45; N, 2.95. Found: C, 65.79;



SCHEME 1 Synthetic method of compound **3**.



SCHEME 2 Synthetic method of polymers **4–5**.

H, 4.53; N, 3.05. Polymer **5**: Inherent viscosity (η_{inh}) = 0.25 dL g^{-1} (c = 0.5 g dL^{-1} in *m*-cresol at 25°C). M_n = 20,200, M_w = 37,600 (styragel HR5E4E; solvent THF). ^{1}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 $(C_{24}H_{25}NO_8)_n$: C, 63.29; H, 5.53; N, 3.08. Found: C, 63.37; H, 5.64; N, 3.17.

Measurements

IR, ^{1}H NMR, and UV-Vis spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer, Varian 300 MHz NMR spectrometer, and Shimadzu UV-3100 S spectrophotometer, respectively. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. T_gs 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 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). The alignment of the NLO-chromophore of the polymers was carried out by corona poling method. Atomic force microscopy (AFM) images were recorded with a Park Science Instrument Autoprobe CP, operated in a contact mode, which measures topography.

The refractive index of the polymer sample was measured by the optical transmission technique [9]. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [10].

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymers 4–5

The synthetic route for compound **3** is presented in Scheme 1. Diol **3** was condensed with with terephthaloyl chloride and adipoyl chloride in a dry DMF solvent to yield Y-type polyesters **4–5** containing the NLO-chromophore 2,3-dioxynitrostilbenyl group (Scheme 2). The polymerization yield was 85–92%. The chemical structures of the resulting polymers were confirmed by ^{1}H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structures. The signal at 2.35 ppm assigned to the α-proton indicates the formation of ester linkage for polymer **5**. The signal at 7.95–8.08 ppm assigned to the vinyl proton for polymers **4–5** indicates the presence of stilbene unit. The IR spectra of the same polymer samples also show a strong carbonyl peak near 1722–1734 cm^{-1} indicating the presence of ester bond. 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 14800 ($M_\mathrm{w}/M_\mathrm{n} = 2.05$) for polymer **4**. Polydispersities were in the range of 1.82–2.15. 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 (**4–5**) are mid type of side chain- and main chain NLO polymers, and are expected to have both of their merits. The polymers **4–5** were 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 0.25–0.30 dL/g. Polymers **4–5** showed strong absorption near 340 nm by the NLO-chromophore dioxynitrostilbenyl group. Having well defined polyesters (**4–5**), we investigate their properties.

Thermal Properties of Polymers

The thermal behavior of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter

TABLE 1 Thermal Properties of Polymers **4–5**

Polymer	T_g^a, °C	Degradation temp, °C[b] 5%-loss	10%-loss	20%-loss	40%-loss	Residue[b] at 800°C, %
4	95	368	389	403	470	32.2
5	83	329	356	386	508	45.8

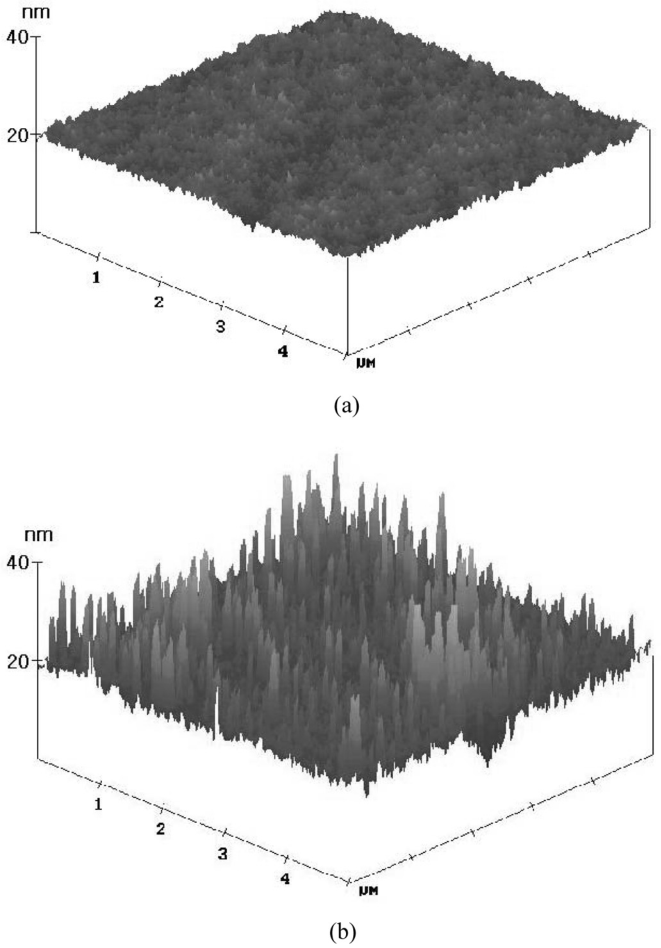
[a] Determined from DSC curves measured on a TA 2920 differential scanning calorimeter with a heating rate of 10°C/min under nitrogen atmosphere.

[b] Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

(DSC) to determine the thermal degradation pattern and glass transition temperature (T_g). The results are summarized in Table 1. Polymers **4–5** showed a thermal stability up to 300°C from their TGA thermograms. Glass transition temperature (T_g) values of the polymers **4–5** measured by DSC were around 83–95°C. These are relatively high values 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 polyesters **4–5** 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 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 that temperature for 30 min. After the electric poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectrum of polymers 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 0.38 for polymer **4** ($\Phi = 1 - A_1/A_0$, where $A_0 = 1.786$ and $A_1 = 1.107$ 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 samples were obtained using atomic force microscopy (AFM). Figure 2 shows AFM scans of the spin-coated film before and after poling for polymer **5**.



(a)

(b)

FIGURE 2 AFM images of spin-coated film of polymer **5**: (a) before corona-poling; (b) after corona-poling.

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 means that the NLO-chromophores are aligned the poling direction (see Fig. 2). The approximate lengths of aligned NLO-chromophores of the polymers estimated from AFM images were around 8 nm. The refractive index of the sample was measured by the optical transmission technique [9]. The NLO properties were studied

TABLE 2 Linear and Nonlinear Optical Properties of Polymers **4–5**

Polymer	$\lambda^{a}_{\max}$ (nm)	d^{b}_{33}(esu)	Φ^{c}	d^{b}_{31}(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	$n_1 = 1.55$ $n_2 = 1.63$

[a] Polymer film.

[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [10].

[c] Order 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.

[d] Film thickness was determined by the optical transmission technique [9].

by the SHG method. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. Linear and nonlinear optical properties of polymers **4–5** are summarized in Table 2. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Figure 3 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. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with Pascal fitting program

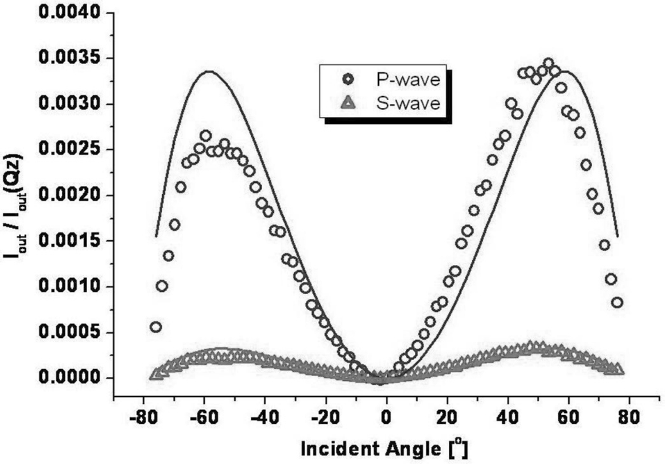


FIGURE 3 Angular dependence of SHG signal in a poled film of polymer **5**.

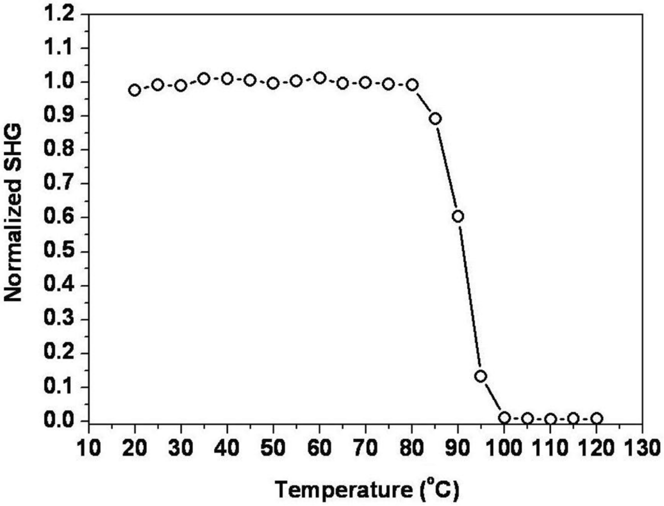


FIGURE 4 Normalized SHG signal of polymer **5** as a function of temperature at a heating rate of 3°C/min.

according to the literature procedure [10]. The values of d_{31} and d_{33} for polymer **4** were $(3.68 \pm 0.18) \times 10^{-9}$ and $(1.61 \pm 0.08) \times 10^{-9}$ esu, respectively. 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. In Figure 4, we present the dynamic thermal stability study of the NLO activity of the film **5**. 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 under a temperature raise at a heating rate of 3°C/min from 30°C to 150°C. The polymer film exhibited a thermal stability up to T_g and no significant SHG decay was observed below 85°C for polymer **5**. 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 high thermal stability of second harmonic generation of polymers **4–5** 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.

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