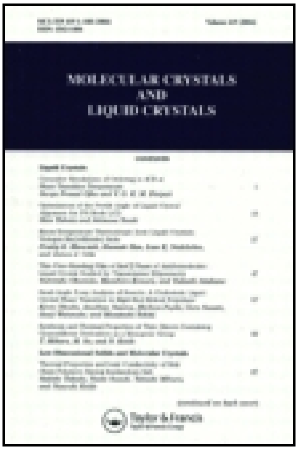

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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

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To cite this article: Han-Na Jang , Ga-Young Lee & Ju-Yeon Lee (2008): Synthesis and Properties of Novel Y-Type Nonlinear Optical Polyester with Enhanced Thermal Stability of Dipole Alignment, Molecular Crystals and Liquid Crystals, 492:1, 312/[676]-321/[685]

To link to this article: http://dx.doi.org/10.1080/15421400802330788

Mol. Cryst. Liq. Cryst., Vol. 492, pp. 312/[676]–321/[685], 2008
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802330788

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

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*3,4-Di-(2′-hydroxyethoxy)benzylidenemalononitrile (**3**) was prepared and condensed with terephthaloyl chloride to yield novel Y-type polyester (**4**) containing the NLO-chromophores dioxybenzylidenemalononitrile group, which constituted parts of the polymer backbone. Polyester **4** is soluble in common organic solvents such as acetone and dimethylsulfoxide. Polymer **4** showed thermal stability up to 300°C in thermogravimetric analysis with glass-transition temperature (T_g) measured from differential scanning calorimetry around 91°C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer films at the 1064 nm fundamental wavelength was around 4.39×10^{-9} esu. The dipole alignment exhibited high thermal stability up to T_g due to the partial main-chain character of polymer structure, which is acceptable for NLO device applications.*

Keywords: differential scanning calorimetry (DSC); NLO; polyester; 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 great attention, mainly because they offer many advantages such light

This work was supported by the Inje FIRST project of Inje University and partially by the BK21 project of the Ministry of Education and the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2007-313-C00498).

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weight and good processability to form electro-optic devices [1–2]. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is important considerations. Cross-linking method [3–5] and utilizing polymers with high glass-transition temperature (T_g) such as polyimides [6–8] have been proposed to minimize the randomization. Polymers with the NLO chromophores in the main chain [9] 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 polymers [10–11] have the advantages such as good solubility, homogeneity and high level of NLO chromophore, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we reported novel NLO polyesters with enhanced thermal stability of dipole alignments containing dioxynitrostilbenyl group [12]. In this work we prepared novel polyester containing 3,4-dioxybenyzylidenemalononitrile group as a NLO-chromophore. We selected the latter as a NLO-chromophore because it has a large dipole moment and are rather easy to synthesize. Furthermore, 3,4-dioxybenyzylidenemalononitrile group constitutes novel Y-type NLO polyester, in which the pendant NLO chromophores are parts of the polymer backbones (Fig. 1(c)). These

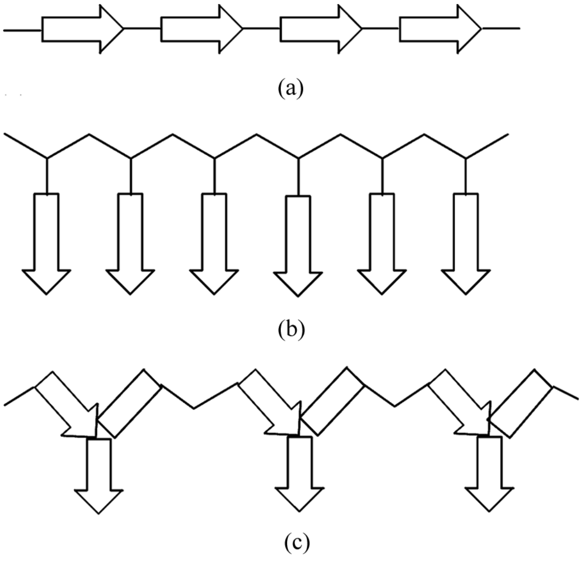


FIGURE 1 (a) Main-chain NLO polymers, (b) side chain NLO polymers, and (c) Y-type NLO polymers.

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 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.

EXPERIMENTAL

Materials

3,4-(2′-Vinyloxyethoxy)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°C. ^{1}H NMR ($CDCl_3$) δ 4.04–4.36 (m, 12H, 2 CH_2=, 2–O–CH_2–CH_2–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) 3099, 3080 (w, =C–H), 2952, 2872 (m, C–H), 1672 (vs, C=O), 1612 (vs, C=C), 1575 (s, C=C) cm^{-1}.

3,4-Di-(2′-vinyloxyethoxy)benzylidenemalononitrile (2). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 3,4-di-(2′-vinyloxyethoxy)benzaldehyde **1** (8.35 g, 30 mmol) and malononitrile (2.18 g, 33 mmol) in 170 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 (80 mL), water (30 mL), and cold 1-butanol (20 mL). The obtained pale yellow product was recrystallized from 1-butanol to give 8.42 g (86% yield) of **2**. Mp = 66–68°C. ^{1}H NMR ($CDCl_3$) δ 4.02–4.39 (m, 12H, 2 CH_2=, 2–O–CH_2–CH_2–O–), 6.47–6.58 (m, 2H, 2 =CH–O–), 6.96–7.03 (d, 1H, aromatic), 7.37–7.45 (d, 1H, aromatic), 7.58–7.69 (d, 2H, aromatic, –Ph–CH=). IR (KBr) 3036 (w, =C–H), 2941, 2890 (m, C–H), 2222 (s, CN), 1636, 1618, 1583 (s, C=C) cm^{-1}. Anal. Calcd for $C_{18}H_{18}N_2O_4$:C, 66.25; H, 5.56; N, 8.58. Found: C, 66.36; H, 5.66; N, 8.48.

3,4-Di-(2′-hydroxyethoxy)benzylidenemalononitrile (3). Aqueous hydrochloric acid (1.5 M, 150 mL) was slowly added to a solution of 3,4-di-(2′-vinyloxyethoxy)benzylidenemalononitrile (**2**) (6.89 g, 0.021 mol) in 50 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 50 mL of water. The obtained pale yellow product was recrystallized from ethyl acetate to give 4.72 g (82% yield) of **3**. Mp: 108–110°C. ^{1}H NMR (acetone-d_6) δ 2.78–2.87 (d, 2H, −OH), 3.87–3.98 (m, 4H, 2 $-CH_2$-OH), 4.09–4.28 (m, 4H, 2 $-O-CH_2-$), 7.21–7.27 (d, 1H, aromatic), 7.63–7.65 (d, 1H, aromatic), 7.76 (s, 1H, aromatic), 8.14 (s, 1H, −Ph−CH=). IR (KBr) 3337 (s, O−H), 3045 (w, =C−H), 2930 (m, C−H), 2222 (s, CN), 1607, 1583 (s, C=C) cm^{-1}. Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.40; H, 5.25; N, 10.28.

Synthesis of polyester 4. A representative polycondensation procedure was as follows: Terephthaloyl chloride (2.03 g, 0.01 mol) and diol **3** (2.74 g, 0.01 mol) were disolved 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 3.56 g (88% yield) of polymer **4**. $\eta_{inh} = 0.26$ dL/g (c, 0.5 g/dL in DMSO at 25°C). ^{1}H NMR (DMSO-d_6) δ 4.17–4.68 (m, 8H, $2-O-CH_2-CH_2-O-$), 7.12–7.38 (m, 1H, aromatic), 7.25–7.97 (m, 6H, aromatic), 8.15–8.37 (m, 1H, aromatic). IR (KBr) 2959 (m, C−H), 2227 (s, CN), 1722 (vs, C=O), 1584 (s, C=C) cm^{-1}. Anal. Calcd for $(C_{22}H_{16}N_2O_6)_n$:C, 65.34; H, 3.99; N, 6.93. Found: C, 65.42; H, 4.08; N, 6.98.

Measurements

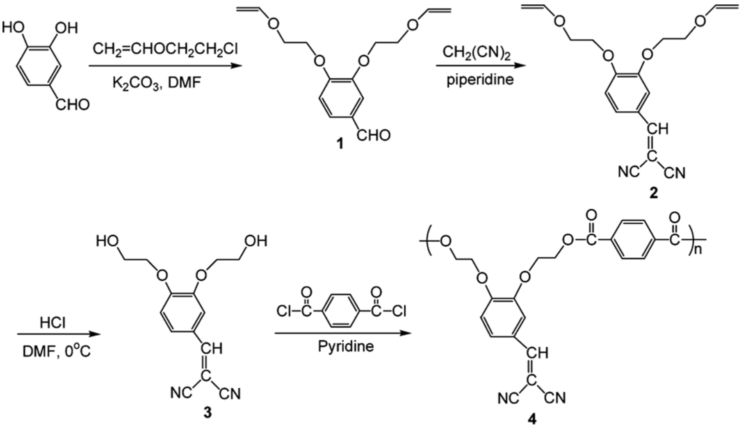
IR, ^{1}H NMR, and UV-Vis spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer, Varian 300 MHz NMR spectrometer, and Shimadzu UV-3100S spectrophotometer, respectively. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. T_g values were measured on a 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. The refractive index of the polymer sample was measured by the optical transmission technique [13]. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [14].

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymer 4

3,4-Di-(2′-vinyloxyethoxy)benzaldehyde (**1**) was prepared by the reaction of 2-chloroethyl vinyl ether with 3,4-dihydroxybenaldehyde. 3,4-Di-(2′-vinyloxyethoxy)benzylidenemalononitrile (**2**) was prepared by the condensation reaction of **1** with malononitrile, and was hydrolyzed to yield acetaldehyde and diol **3**. The synthetic route for compound **3** is presented in Scheme 1. Diol **3** was condensed with terephthaloyl chloride in a dry DMF solvent to yield Y-type polyester **4** containing the NLO-chromophore 3,4-dioxybenzylidenemalononitrile group (Scheme 1). The polymerization yield was 90%. The chemical structures of the resulting polymer were confirmed by ^{1}H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structure. ^{1}H NMR spectra 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



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

polymer sample showed a strong carbonyl peak near 1722 cm^{-1} indicating the presence of ester bond. The same polymer sample also showed a strong nitrile peak near 2227 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 polymers was determined to be 16800 ($M_w/M_n = 1.90$) for polymer **4**. 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 mid type of side chain- and main chain NLO polymer, and is expected to have both of their merits. The polymer **4** was soluble in common solvents such as acetone, DMF, and DMSO, but was not soluble in methanol and diethyl ether. Polymer **4** isolated from methanol were yellow colored amorphous materials. The inherent viscosities were around 0.26 dL/g. Polymer **4** showed strong absorption near 364 nm by the NLO-chromophore dioxybenzylidenemalononitrile group. Having well defined polyester (**4**) and we investigate its properties.

Thermal Properties of Polymer

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 1. Polymer **4** showed a thermal stability up to 300°C from TGA thermogram. T_g value of the polymer **4** measured by DSC was around 91°C. The TGA and DSC studies showed that the decomposition temperature of the polyester **4** was higher than the corresponding T_g. This indicates

TABLE 1 Thermal Properties of Polymer **4**

		Degradation temp, °C[b]				
Polymer	T_g^a °C	5 wt%-loss	10 wt%-loss	20 wt%-loss	40 wt%-loss	Residue[b] at 800°C, wt%
4	91	318	335	376	448	31.6

[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 theromogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

Nonlinear Optical Properties of Polymer

The NLO property of polymer was studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. As the temperature was raised to 105°C, 6.5 kV of corona voltage was applied and this temperature was maintained for 30 min. The poling was confirmed by UV-Vis spectra. Figure 2 shows the UV-Vis absorption spectra of the polymer **4** before and after poling. After electric poling, the dipole moment of the NLO-chromophore was aligned and the UV-Vis spectrum of polymer 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 0.30 for polymer **4** ($\Phi = 1 - A_1/A_0$, where $A_0 = 0.982$ and $A_1 = 0.684$ are the absorbances of the polymer film before and after poling, respectively). The refractive index of the sample was measured by the optical transmission technique [13]. The NLO properties were studied 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 polymer **4** are summarized in Table 2. In order to determine the macroscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Figure 3 shows the angular dependence of

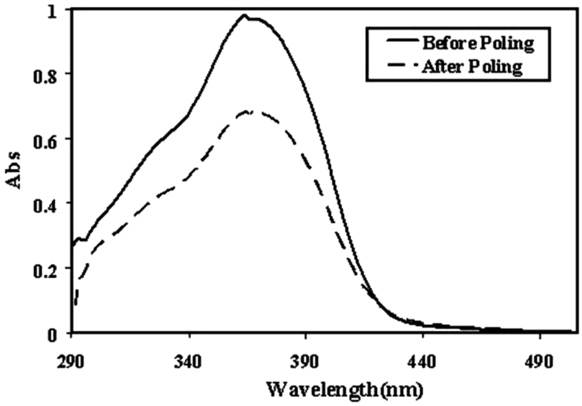


FIGURE 2 UV-Vis absorption spectra of a film of polymer **4** before and after poling.

TABLE 2 Linear and 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	364	$(4.39 \pm 0.13) \times 10^{-9}$	0.30	$(1.58 \pm 0.08) \times 10^{-9}$	0.52	1.60

[a] Polymer film.

[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [14].

[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 [13].

SHG signal in a poled polymer **4**. The SHG values were compared with those obtained from a Y-cut quartz plate. SHG coefficient (d_{33}) was derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure [14]. The values of d_{31} and d_{33} for polymer **4** were $(1.58 \pm 0.08) \times 10^{-9}$ and $(4.39 \pm 0.13) \times 10^{-9}$ esu, respectively. Because 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 polymer, we studied the temporal stability of the SHG signal.

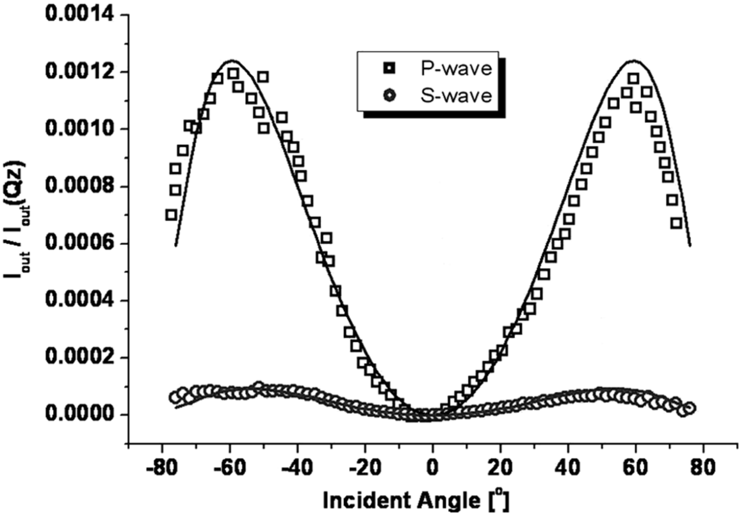


FIGURE 3 Angular dependence of SHG signal in a poled film of polymer **4**.

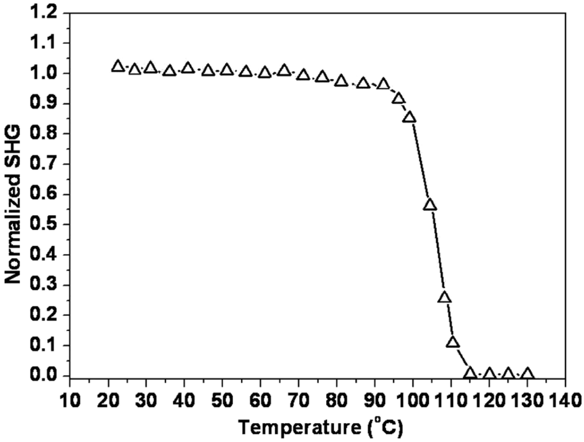


FIGURE 4 Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 3°C/min.

In Figure 4, 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 film 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 to 150°C. The polymer film exhibited a high 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 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. 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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