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Synthesis and Electro-Optic Properties of Novel Polyester Containing Dioxybenzylidenecyanoacetate as a NLO-Chromophore

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*A novel polyester (***4***) containing dioxybenzylidenecyanoacetate group as a NLO-chromophore was prepared and characterized. Polyester* **4** *was soluble in common organic solvents such as acetone and DMSO. Polymer* **4** *showed thermal stability up to 280°C in TGA thermogram with T_g value measured from DSC thermogram near 108°C. The SHG coefficient* (d_{33}) *of poled polymer film at the 1064 nm fundamental wavelength was around 3.54×10^{-9} esu. The dipole alignment exhibited a thermal stability up to near T_g and no significant SHG decay was observed below 95°C due to the partial main-chain character of polymer structure, which was acceptable for NLO device applications.*

Keywords: differential scanning calorimetry (DSC); NLO; polyester; relaxation of dipole alignment; SHG coefficient; thermogravimetric analysis (TGA)

INTRODUCTION

Recently nonlinear optical (NLO) polymers are studied extensively because of their potential applications in the field of electro-optic devices [1–4]. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of important considerations [5]. Cross-linking method [6–7] and utilizing polymers with high glass-transition temperature (T_g) such as polyimides [8–10] have been proposed to minimize the randomization. In general, polymers with the NLO chromophores in

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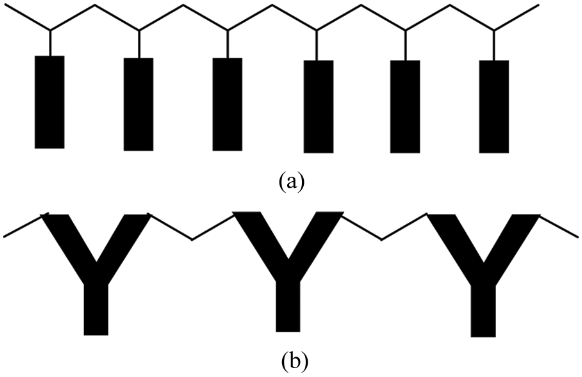


FIGURE 1 (a) Side chain NLO polymers and (b) Mid-type NLO polymers.

the main chain 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 noncentrosymmetric films. On the other hand, side chain NLO polymers 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 [11] and dioxybenzylidenemalononitrile [12]. In this work we prepared novel polyester containing 2,4-dioxybenyzylidenecyanoacetate group as a NLO-chromophore. We selected the latter as a NLO-chromophore because it has a large dipole moment and is rather easy to synthesize. Furthermore, 2,4-dioxybenyzylidenecyanoacetate group constitutes a novel NLO polyester, in which the pendant NLO chromophores are parts of the polymer backbones (Fig. 1b). This mid-type NLO polymer is expected to have the advantages of both main-chain and side-chain NLO polymers namely stabilization of dipole alignment and good solubility. After confirming the structure of the resulting polymer we investigated its properties such as 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

Synthetic method of diol **3** and polymer **4** are summarized in Scheme 1. 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 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 20 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 methanol and dried under vacuum, yielding 3.49 g (91% yield) of polymer **4**: $\eta_{inh} = 0.30$ dL/g (c, 0.5 g/dL in DMSO at 25°C). ^{1}H NMR (DMSO-d_6) δ3.65–3.73 (s, 3H, -COOCH$_3$), 4.55 (s, 4H, 2 -Ph-O-CH$_2$-), 4.68 (s, 4H, 2 COO-CH$_2$-), 6.75–6.95 (m, 2H, aromatic), 8.05 (s, 4H, aromatic), 8.18 (d, 1H, aromatic), 8.54 (s, 1H, aromatic). IR (KBr) 2955 (m, C-H), 2220 (s, CN), 1722 (vs, C = O), 1586 (s, C = C) cm^{-1}. Anal. Calcd for $(C_{23}H_{19}NO_8)_n$: C, 63.16; H, 4.37; N, 3.20. Found: C, 63.24; H, 4.43; N, 3.17.

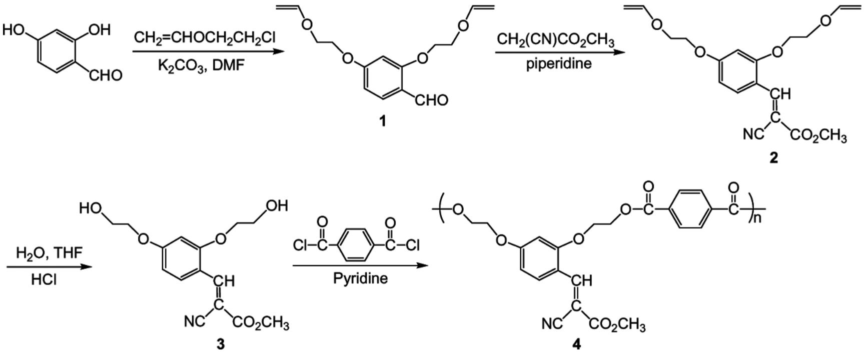
Measurements

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-3100S spectrophotometer, respectively. T_g value was measured on a TA 2920 differential scanning calorimeter (DSC) in a nitrogen atmosphere. TA Q50 thermogravimetric analyzer (TGA) with a heating rate of 10°C/min up to 800°C was used for the thermal degradation 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). The alignment of the NLO-chromophore of the polymer 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

Monomer **3** was condensed with terephthaloyl chloride in a dry DMF solvent to yield polyester **4** containing 2,4-dioxybenzylidenecyanoacetate group as a NLO-chromophore. The synthetic route for polymer **4** is presented in Scheme 1. The chemical structure of the resulting polymer was confirmed by ^{1}H NMR, IR spectra, and elemental analysis. ^{1}H 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 polymer showed a strong



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

carbonyl peak near 1722 cm^{-1} indicating the presence of ester bond. The same polymer sample also shows strong absorption peaks near 2220 cm^{-1} and 1586 cm^{-1} due to the nitrile and olefin group, respectively. These results are consistent with the proposed structure, indicating that the NLO-chromophore remained intact during the polymerization. The number average molecular weight (M_n) of the polymer **4** determined by GPC was 18200 ($M_w/M_n = 1.91$). 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, and is expected to have both of their merits. Polymer **4** was soluble in common solvents such as acetone, DMF, and DMSO, but was not soluble in methanol and diethyl ether. The inherent viscosity was near 0.30 dL/g. Polymer **4** showed strong absorption near 364 nm by the NLO-chromophore 2,4-dioxybenzylidenecyanoacetate group. Having well defined polyester (**4**) and we investigate its properties.

Thermal Properties of Polymer

The thermal behavior of the polymer was investigated by TGA and DSC to determine the thermal degradation pattern and T_g. Polymer **4** showed a thermal stability up to 280°C according to its TGA thermogram. The T_g value of the polymer **4** measured by DSC was around 108°C. This T_g value is lower than those of polyurethane derivatives [15]. The TGA and DSC studies showed that the decomposition temperature of the polyester **4** was higher than the corresponding T_g value. This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

Nonlinear Optical Properties of Polymer

The NLO properties of polymer were studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. As the temperature was raised gradually to 115°C, 6.5 kV of corona voltage was applied and this temperature was maintained for 30 min. The poling was confirmed by UV-Vis spectrum. After 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 of polymer **4** was equal to 0.13. 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. 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. Figure 2 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 samples and recorded. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with Pascal fitting program according to the literature procedure [14]. The values of d_{33} and d_{31} for polymer **4** were $(3.54 \pm 0.09) \times 10^{-9}$ and $(1.26 \pm 0.06) \times 10^{-9}$ esu, respectively. These values are somewhat larger than those of T-type polyurethane derivatives [15]. 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.

TABLE 1 Nonlinear Optical Properties of Polymer **4**

Polymer	$\lambda_{max}{}^{a}$ (nm)	$D_{33}{}^{b}$ (esu)	Φ ^{c}	$d_{31}{}^{b}$(esu)	Film thickness^{d} (μm)	n
4	364	$(3.54 \pm 0.09) \times 10^{-9}$	0.13	$(1.26 \pm 0.06) \times 10^{-9}$	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].

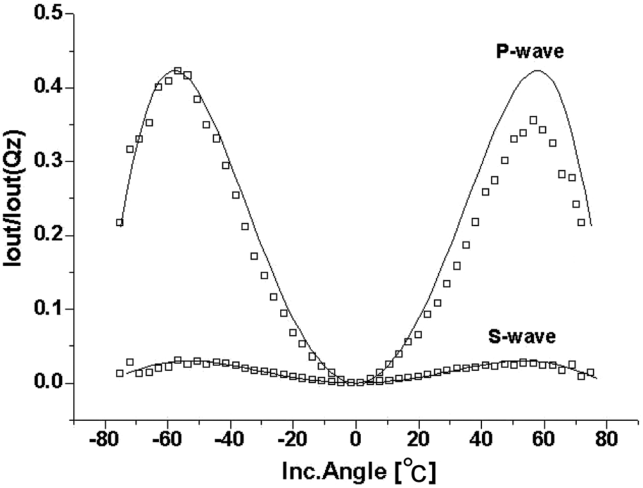


FIGURE 2 Angular dependence of SHG signal in a poled film of polymer **4**.

To evaluate the high-temperature stability of the polymer, we studied the temporal stability of the SHG signal. In Figure 3, 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

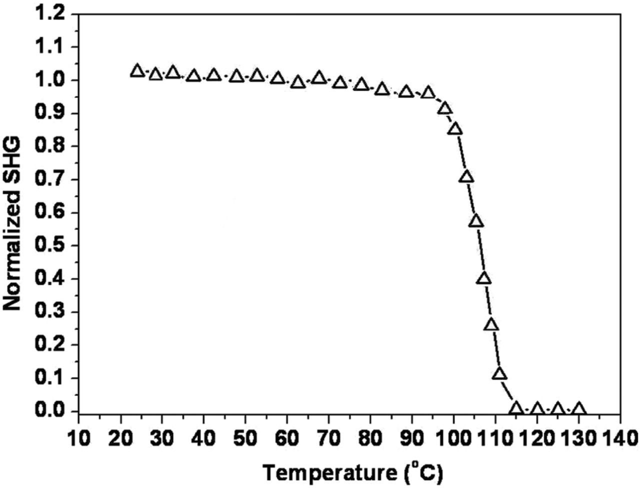


FIGURE 3 Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 3.5°C/min.

of the poled polymer film as a function of temperature, *in situ* SHG measurements were performed at a heating rate of 3.5°C/min from 25°C to 140°C. The polymer film exhibited a thermal stability up to near T_g and no significant SHG decay was observed below 95°C, as shown in Figure 3. 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 NLO polyester having both of the merits of main chain- and side-chain NLO polymers namely stable dipole alignment and good solubility.

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