Preparation of Novel Nonlinear Optical Polyester with Enhanced Thermal Stability of Dipole Alignment

Ju-Yeon Lee,[*] **Jin-Hyang Kim, Dong-Seon Won, and Han-Na Jang**

Institute of Functional Materials, Department of Chemistry, Inje University, Gimhae 621-749, Korea
[*]*E-mail: chemljy@inje.ac.kr*

Nonlinear optical (NLO) polymers have been extensively studied over the past decade because of their potential applications in the field of electro-optic devices.[1-3] A potential NLO polymer have to be mechanically very strong and thermally stable with high glass-transition temperatures (T_g). In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is important considerations. Two approaches to minimize the randomization of dipole alignment have been proposed. One is to use crosslinking method[4-6] and the other is to utilize high T_g polymers such as polyimides.[7] Polyesters with the NLO-chromophores in the main chain[8] or in side chain[9-11] were prepared and investigated. Main-chain NLO polymers 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. Side-chain NLO polymer systems 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. Recently we have prepared polyesters containing dioxynitrostilbenyl group as a NLO chromophore.[12,13] The resulting polymers exhibited thermal stability of second harmonic generation (SHG) up to T_g. This high thermal stability of optical nonlinearity stemmed from the stabili-

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

zation of dipole alignment of the NLO chromophore, which was a part of the polymer backbone. In this work we prepared novel polyester containing 2,3-dioxybenzylidene-malononitrile groups as NLO-chromophores. We selected 2,3-dioxybenzylidenemalononitrile groups as NLO-chromophores because they have a large dipole moment and are rather easy to synthesize. Furthermore, 2,3-dioxybenzyl-idenemalononitrile group constitutes novel Y-type NLO polyester (Fig. 1c), and this Y-type NLO polyester has not been reported in the literature. 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, 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'-vinyloxyethoxy)benzaldehyde (1) was prepared by the reaction of 2-chloroethyl vinyl ether with 2,3-dihydroxybenaldehyde. 2,3-Di-(2'-vinyloxyethoxy)benzyl-idenemalononitrile (2) was prepared by the condensation reaction of 1 with malononitrile. Compound 2 was hydrolyzed to yield acetaldehyde and diol 3. Diol 3 was condensed with terephthaloyl chloride in a dry DMF solvent to yield polyester 4 containing the NLO-chromophore 2,3-dioxy-benzylidenemalononitrile group The synthetic route for polyeater 4 is presented in Scheme 1. The polymerization yield was 88-92%. 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. ^{1}H NMR spectra of the polymers showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structures. The IR spectra of the same polymer samples show 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 2229 cm^{-1} and 1572 cm^{-1} due to the nitrile and olefin groups, respectively. These results are consistent with the proposed structures, indicating that the NLO-chromophore remained intact during the polymeri-
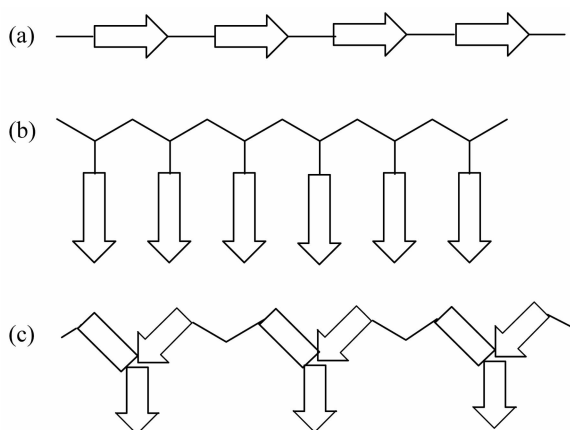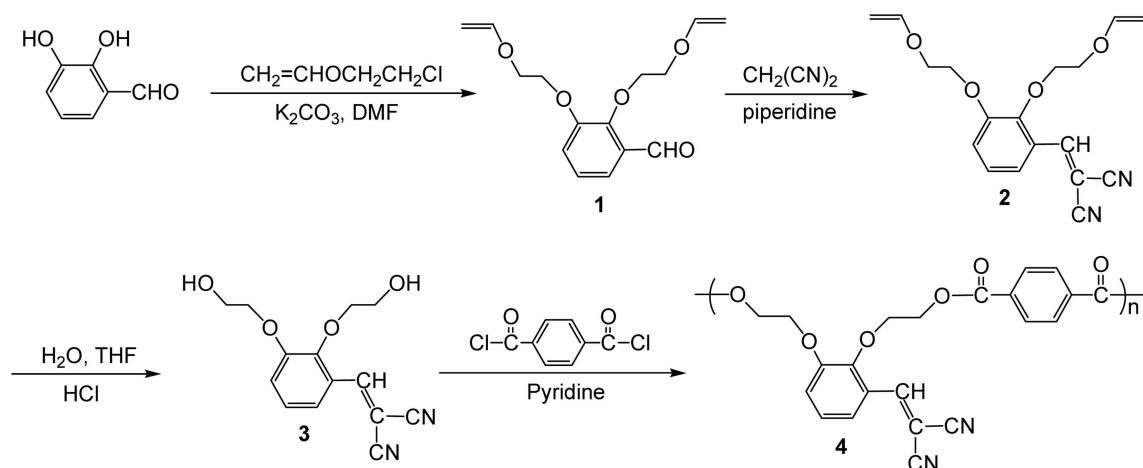
Scheme 1. Synthetic scheme and structure of polymer 4.

zation. 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 polymers was determined to be 16800 (M_w/M_n = 1.86) for polymer 4. Polydispersities were in the range of 1.84-1.95. The structural feature of these polymers is that they have 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. 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 in the range of of 0.28-0.30 dL/g. Polymer 4 showed strong absorption near 340 nm by the NLO-chromophore dioxybenzylidene-malononitrile group. We now have well defined polyester (4) and investigate the properties.

The thermal behavior of the polymers was 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 290 °C according to their TGA thermograms. The initial weight loss in the polymers begins at 278 °C. The T_g value of the polymer 4 measured by DSC were around 90 °C.

The NLO properties of polymers were studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. The UV-Vis absorption spectra of the polymer sample 4 before and after the poling are recorded. After the 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 was found to have a value of 0.23 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). 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 2. 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
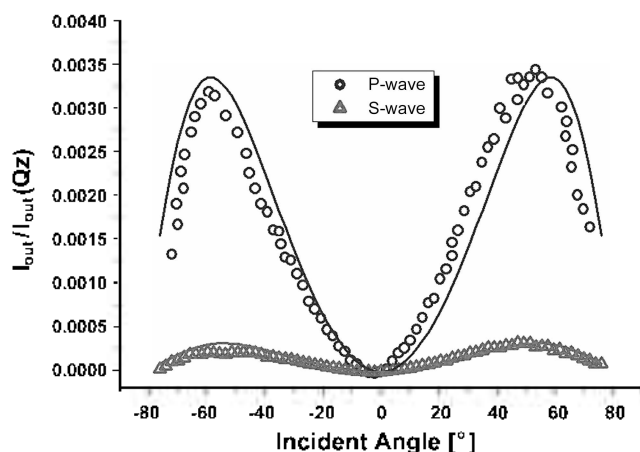
Table 1. Thermal Properties of Polymer 4

Polymer	$T_g{}^a$, °C	Degradation temp. °C[b]			Residue[b] at 800 °C. %
		5%-loss	20%-loss	40%-loss	
4	90	306	392	468	42.2

[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.

Table 2. 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	340	$(3.52 \pm 0.10) \times 10^{-9}$	0.23	$(1.43 \pm 0.04) \times 10^{-9}$	0.54	$n_1 = 1.60$
						$n_2 = 1.68$

[a]Polymer film. [b]SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.[15] [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.[14]

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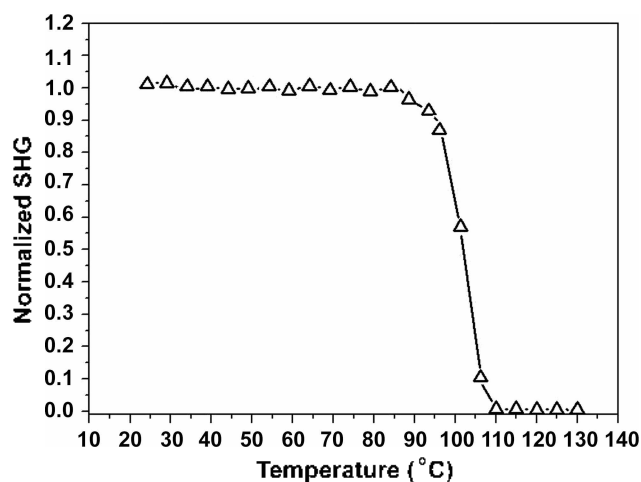

Figure 3. Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 3 °C/min.

fitting program according to the literature procedure.[15] The values of d_{33} and d_{31} for polymer **4** were $(3.52 \pm 0.10) \times 10^{-9}$ and $(1.43 = 0.04) \times 10^{-9}$ esu, respectively. 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 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 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 150 °C. The polymer film exhibited a thermal stability up to 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 around 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.

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. Malononitrile was recrystallized from water and 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.

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. ^{1}H NMR (CDCl$_3$) δ 3.95-4.47 (m, 12H, 2 CH$_2$=, 2 -O-CH$_2$-CH$_2$-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 2,3-Di-(2'-vinyloxyethoxy)benzylidene-malononitrile (2). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,3-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 8.11 g (83% yield) of **2**. Mp = 60-62 °C. ^{1}H NMR (CDCl$_3$) δ 3.90-4.42 (m. 12H, 2 CH$_2$=, 2 -O-CH$_2$-CH$_2$-O-), 6.45-6.57 (m. 2H, 2 =CH-O-). 7.13-7.20 (d. 2H. aromatic), 7.80-7.87 (t. 1H, aromatic). 8.47 (s, 1H. Ph-CH=). IR (KBr) 3116, 3059 (w, =C-H), 2941, 2885 (m, C-H), 2233 (s, CN), 1618, 1572 (vs, C=C) cm^{-1}. Anal. Calcd for C$_{18}$H$_{18}$N$_2$O$_4$: C, 66.25; H. 5.56; N, 8.58. Found: C. 66.16; H. 5.4; N. 8.65.

Preparation of 2,3-Di-(2'-hydroxyethoxy)benzylidene-malononitrile (3). Aqueous hydrochloric acid (1.5 M, 30 mL) was slowly added to a solution of 2,3-di-(2'-vinyloxy-ethoxy)benzylidenemalononitrile (**2**) (8.48 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 5.85 g (82% yield) of **3**. Mp = 116-118 °C. ^{1}H NMR (acetone-d_6) δ 3.75-3.96 (m, 4H. 2 -CH$_2$-OH). 4.12-4.25 (m, 4H, 2 -O-CH$_2$-), 4.26-4.34 (t. 2H, -OH). 7.21-7.29 (t, 1H, aromatic), 7.37-7.44 (d. 1H. aromatic). 7.72-7.78 (d. 1H, aromatic), 8.75 (s. 1H, -Ph-CH=). IR (KBr) 3360, 3256 (s. O-H). 3044 (w, =C-H). 2941 (m. C-H), 2222 (m, CN). 1572 (vs, C=C) cm^{-1}. Anal. Calcd for C$_{14}$H$_{14}$N$_2$O$_4$: C, 61.31; H, 5.14; N. 10.21. Found: C. 61.23; H. 5.22; N, 10.13.

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 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 diethyl ether and dried under vacuum. yielding 3.68 g (91% yield) of polymer **4**: η_{inh} = 0.29 dL/g (c, 0.5 g/dL in DMSO at 25 °C). ^{1}H NMR (DMSO-d_6) δ 4.38-4.52 (s, 4H. 2 -CH$_2$-O-), 4.57-4.72 (s. 4H, 2 Ph-O-CH$_2$-), 7.20-7.35 (s. 1H. aromatic). 7.37-7.53 (s, 1H. aromatic), 7.54-7.66 (s. 1H. aromatic), 7.81-8.03 (d, 4H. aromatic), 8.42-8.52 (s, 1H, aromatic). IR (KBr) 3049 (w, =C-H), 2958 (m, C-H), 2229 (s. CN). 1722 (vs. C=O). 1572 (s, C=C) cm^{-1}. Anal. Calcd for (C$_{22}$H$_{16}$N$_2$O$_6$)$_n$: C, 65.34; H. 3.99; N. 6.93. Found: C. 65.43; H. 3.92; N. 6.98.

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