Synthesis and Electro-Optic Properties of Novel T-Type Polyester with High Thermal Stability of Dipole Alignment

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Functional polymers of nonlinear optical (NLO) activities have been extensively studied over the past decade because of their potential applications in the field of telecommunications, optical switching, etc.[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 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] Polymers 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 Y-type polyesters containing 3,4-dioxynitrostilbenyl group as a NLO chromophore.[12] They exhibited second harmonic generation (SHG) stability up to 10 °C higher than T_g and no SHG decay was observed below 120 °C. This high thermal stability of optical nonlinearity stemmed from the stabilization of dipole alignment of the NLO chromophore, which was a part of the polymer backbone. In this work we prepared novel T-type polyesters containing 2,5-dioxynitrostilbenyl groups as NLO-chromophores. We selected 2,5-dioxynitrostilbenyl groups as NLO-chromophores because they have a large dipole moment and are rather easy to synthesize. Furthermore, 2,5-dioxynitrostilbenyl groups constitute novel T-type NLO polyesters (Fig. 1c), and these T-type NLO polyesters have not been reported in the literature. Thus, we synthesized a new type of NLO polyester, in which the pendant NLO chromophores are parts of the polymer backbones. 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
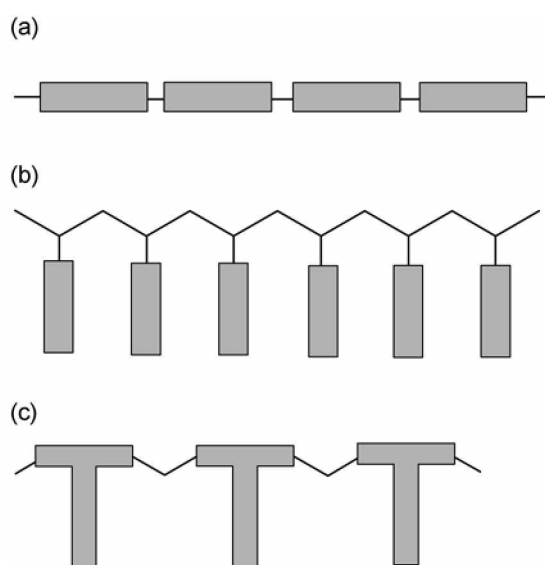
(a)

(b)

(c)

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

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.

Results and Discussion

Synthesis and Characterization of Polymer 4. 2,5-Dihydroxyethoxy-4'-nitrostilbene (1) was prepared by the condensation of 4-nitrophenylacetic acid with 2,5-dihydroxybenzaldehyde according to a literature procedure.[13] Compound 1 was reacted with 2-chloroethyl vinyl ether to yield 2,5-di-(2-vinyloxyethoxy)-4'-nitrostilbene (2). Compound 2 was hydrolyzed to yield acetaldehyde and 2,5-di-(2'-hydroxyethoxy)-4'-nitrostilbene (3). Diol 3 was condensed with terephthaloyl chloride chloride in a dry DMF solvent to yield T-type polyester 4 containing the NLO-chromophore 2,5-dioxynitrostilbenyl group. The synthetic route for polymer 4 is presented in Scheme 1. The polymerization yield was 90-95%. 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.
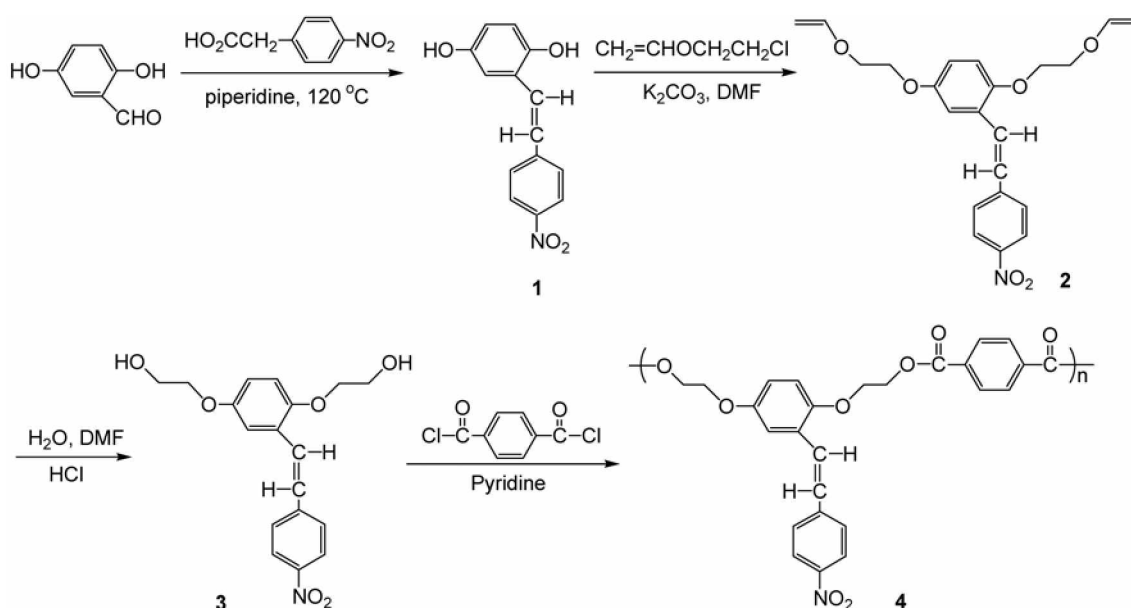
Scheme 1. Synthetic scheme and structure of polymer 4.

¹H NMR spectra of the polymers showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structures. The signal at 2.05-2.36 ppm assigned to the α-proton indicates the formation of ester linkage. The IR spectra of the same polymer samples also show a strong carbonyl peak near 1722-1728 cm^{-1} indicating the presence of ester bond. The carbonyl absorption for polymer 4 appears at 1722 cm^{-1} due to conjugation with aromatic ring. 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 15800 (M_w/M_n = 1.94) for polymer 4. Polydispersities were in the range of 1.67-2.11. 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 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. The inherent viscosities were around 0.30 dL/g. Polymer 4 showed strong absorption near 376 nm by the NLO-chromophore dioxynitrostilbenyl group. We now have well defined polyester (4) and 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 its TGA thermogram. The initial weight loss in the polymers

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	95	305	401	568	46.1

^{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.
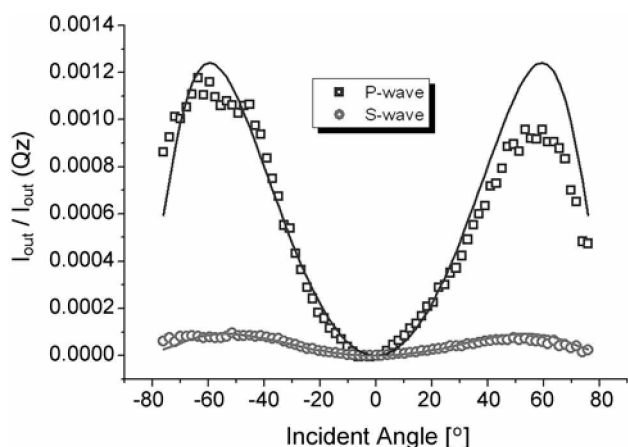
begins around 346 °C. Glass transition temperature (T_g) value of polymer 4 measured by DSC was around 95 °C. This is relatively high values compared to those of common polyesters and probably attributed to the rigid stilbene unit in the polymer pendant group. The TGA and DSC studies showed that the decomposition temperature of the polyester 4 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 Polymer. 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 F was found to have a value of 0.19 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
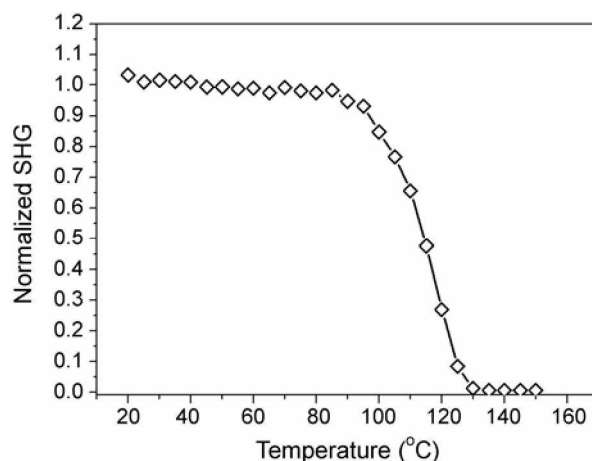
Table 2. Nonlinear Optical Properties of Polymer **4**

Polymer	$\lambda_{max}{}^a$ (nm)	$d_{33}{}^b$ (esu)	Φ^c	$d_{31}{}^b$ (esu)	film thickness^d (μm)	n
4	376	$(1.42 \pm 0.09) \times 10^{-9}$	0.19	$(0.52 \pm 0.03) \times 10^{-9}$	0.47	$n_1 = 1.58$ $n_2 = 1.66$

^{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.

performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. Nonlinear optical properties of polymer **4** is 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 fitting program according to the literature procedure.[15] The values of d_{33} and d_{31} for polymer **4** were ($1.42 \pm 0.09) \times 10^{-9}$ and ($0.52 \pm 0.03) \times 10^{-9}$ 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. In the isotropic model, the ratio of d_{33}/d_{31} is predicted to be about 3. Our d_{33}/d_{31} value of 2.73 is in good agreement with the predicted 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. 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 exceptional high thermal stability of second harmonic gener-

ation of polymers **4-6** 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. 4-Nitrophenylacetic acid, 2,5-dihydroxybenzaldehyde, and 2-chloroethyl vinyl ether. Terephthaloyl chloride (TPC) was purified by sublimation under vacuum. 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 can determine 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 2,5-Dihydroxy-4'-nitrostilbene (1). Compound **1** was prepared by a known method[13] from 2,5-

dihydroxybenzaldehyde and 4-nitrophenylacetic acid, and recrystallized from 80% aqueous ethanol. ^{1}H NMR (acetone-d_6) δ 2.79 (s, 2H, -OH). 7.12-7.35 (m, 4H, aromatic), 8.06-8.15 (d, 2H, aromatic). 8.23-8.37 (t, 3H, aromatic). IR (KBr) 3408 (s, O-H). 3032 (w, =C-H). 2876 (w, C-H). 1574 (vs, C=C), 1510, 1348 (vs, N=O) cm^{-1}.

Preparation of 2,5-Di-(2'-vinyloxyethoxy)-4'-nitrostilbene (2). Compound 2 was prepared according to a literature procedure[12] from 2,5-dihydroxy-4'-nitrostilbene and 2-chloroethyl vinyl ether in dry DMF, and recrystallized from ethanol. Mp = 146-148 °C. ^{1}H NMR (DMSO-d_6) δ 3.96-4.07 (d, 6H, CH$_2$=, -O-CH$_2$-CH$_2$-O-), 4.18-4.30 (d, 6H, CH$_2$=, -O-CH$_2$-CH$_2$-O-), 6.52-6.63 (q, 2H, 2 =CH-O-). 7.26-7.47 (m, 4H, aromatic), 7.95-8.05 (d, 2H, aromatic), 8.26-8.42 (t, 3H, aromatic). IR (KBr) 3059 (w, =C-H), 2953 (m, C-H), 1572 (s, C=C), 1512, 1350 (vs, N=O) cm^{-1}. Anal. Calcd for C$_{22}$H$_{23}$NO$_6$: C, 66.49; H, 5.83; N, 3.52. Found: C, 66.60; H, 5.89; N, 3.46.

Preparation of 2,5-Di-(2'-hydroxyethoxy)-4'-nitrostilbene (3). Compound 3 was prepared by hydrolysis of 2,5-di-(2'-vinyloxyethoxy)-4'-nitrostilbenee (2) according to a literature procedure,[12] and recrystallized from ethyl acetate. Melting point: 168-170 °C. IR (KBr): 3420 (s, O-H), 2936, 2870 (m, C-H), 1585 (s, C=C), 1518, 1344 (vs, N=O) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ =3.62-3.78 (m, 4H, -O-CH$_2$-CH$_2$-O-), 3.92-4.08 (t, 4H, -O-CH$_2$-CH$_2$-O-), 7.20-7.46 (m, 4H, aromatic), 7.91-8.02 (d, 2H, aromatic), 8.20-8.43 (t, 3H, aromatic). Anal. Calcd for C$_{18}$H$_{19}$NO$_6$: C, 62.60; H, 5.54; N, 4.06. Found: C, 62.68; H, 5.63; N, 4.12.

Synthesis of Polyester 4. Terephthaloyl chloride (2.03 g, 0.01 mol) and diol 3 (3.45 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 25 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 4.37 g (92% yield) of polymer 4: η_{inh} = 0.30 dL/g (c. 0.5 g/dL in DMSO at 25 °C). ^{1}H NMR (DMSO-d_6) δ 4.36-4.45 (s, 4H, 2 -CH$_2$-O-), 4.63-4.69 (s, 4H, 2 Ph-O-CH$_2$-). 7.27-7.45 (m, 3H, aromatic), 7.95-8.13 (m, 6H, aromatic), 8.27-8.39 (m, 4H, aromatic). IR (KBr) 2941, 2883 (C-H, w), 1722 (vs, C=O), 1572 (s, C=C), 1520, 1350 (s, 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, 65.78; H, 4.53; N, 3.04.

References

1. *Molecular Nonlinear Optics Materials Physics and Devices*; Zyss, J., Ed.; Academic Press: Orlando, 1994.
2. Park, G.; Jung, W. S.; Ra, C. S. *Bull. Korean Chem. Soc.* **2004**, *25*, 1427.
3. Cho, M. J.; Kim, J. Y.; Kim, J. H.; Lee, S. H.; Dalton, L. R.; Choi, D. H. *Bull. Korean Chem. Soc.* **2005**, *26*, 77.
4. Han, K. S.; Park, S. K.; Shim, S. Y.; Jahng, W. S.; Kim, N. J. *Bull. Korean Chem. Soc.* **1998**, *19*, 1165.
5. Han, K. S.; Park, S. K.; Shim, S. Y.; Lee, Y. S.; Jahng, W. S.; Kim, N. J. *Bull. Korean Chem. Soc.* **1998**, *19*, 1168.
6. Cho, B. R.; Kim, Y. H.; Son, K. W.; Khalil, C.; Kim, Y. H.; Jeon, S.-J. *Bull. Korean Chem. Soc.* **2002**, *23*, 1253.
7. Kim, M. H.; Jin, J.-I.; Lee, C. J.; Kim, N. J.; Park, C. H. *Bull. Korean Chem. Soc.* **2002**, *23*, 964.
8. Lee, J.-H.; Lee, K.-S. *Bull. Korean Chem. Soc.* **2000**, *21*, 847.
9. Lee, S.-H.; Lim, K.-C.; Jeon, J.-T.; Song, S.-J. *Bull. Korean Chem. Soc.* **1996**, *17*, 11.
10. Lee, S.-H.; Song, W.-S.; Jung, M.-J.; Jeon, I.-C.; Ahn, B.-G.; Song, S.-J. *Bull. Korean Chem. Soc.* **1997**, *18*, 8.
11. Lee, S.-H.; Kim, Y.-K.; Won, Y.-H. *Macromolecules* **1999**, *32*, 342.
12. Lee, J.-Y.; Jung, W.-T.; Lee, W.-J. *Polym. Int.* **2006**, *55*, 248.
13. Cullinane, N. M. *J. Chem. Soc.* **1923**, *123*, 2053.
14. Cisneros, J. I. *Appl. Opt.* **1998**, *37*, 5262.
15. Herman, W. N.; Hayden, L. M. *J. Opt. Soc. Am. B.* **1995**, *12*, 416.