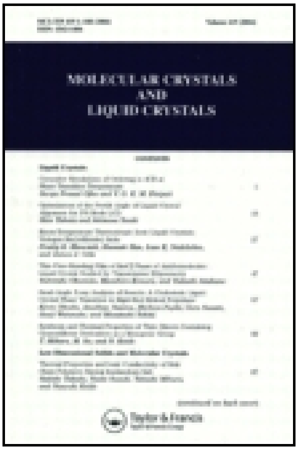

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Synthesis and Nonlinear Optical Properties of Novel Y-type Polyimides with Highly Enhanced Thermal Stability of Second Harmonic Generation

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Synthesis and Nonlinear Optical Properties of Novel Y-type Polyimides with Highly Enhanced Thermal Stability of Second Harmonic Generation

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*2,3-Bis-(3,4-dicarboxyphenylcarboxyethoxy)-4′-nitrostilbene dianhydride (**4**) was prepared and reacted with 4,4′-oxydianiline and 4,4′-diaminobenzanilide to yield unprecedented novel polyimides **5–6** containing 2,3-dioxynitrostilbenyl groups as NLO-chromophores, which constituted parts of the polymer backbones. The resulting polyimides **5–6** were soluble in polar solvents such as DMSO and DMF. Polymers **5–6** showed a thermal stability up to 300°C in TGA thermograms with* T_g *values from DSC thermograms in the range of 135–141°C. The SHG coefficients* (d_{33}) *of poled polymer films were around* 6.14×10^{-9} *esu. The dipole alignment of poled polymer films exhibited exceptionally high thermal stability even at 30°C higher than* T_g *and there was no SHG decay below 170–190°C 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; polyimides; relaxation of dipole alignment; SHG coefficient; thermogravimetric analysis (TGA)

INTRODUCTION

In the developments of nonlinear optical (NLO) polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is important considerations. Two approaches to minimize

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Address correspondence to Ju-Yeon Lee, Institute of Basic Sciences, Department of Chemistry, Inje University, 607 Obang-dong, Kimhae 621-749, Korea. E-mail: chemljy@inje.ac.kr the randomization have been proposed. One is to use crosslinking method [1] and the other is to utilize high glass-transition temperature (T_g) polymers such as polyimides [2–7]. Polyimide materials have attracted attentions because of their high T_g, which can be utilized to stabilize the dipole alignment of the NLO chromophore at high temperatures. Another advantage of polyimide is their high thermal stability that enables them to endure at an elevated temperature in electro-optic devices. There are two types of NLO polyimides, which have been used either as polymer hosts for composite materials or as polymer backbones for side-chain NLO chromophores. In general, side-chain polymer systems have the advantages such as good solubility, homogeneity and high level of NLO chromophores, but they tend to lose nonlinear optical activity below T_g by randomization of NLO chromophores [5]. Stabilization of dipole alignment is a characteristic of main-chain NLO polymers. Recently we reported novel T-type NLO polyimides with high thermal stability of second harmonic generation [8]. In this work we prepared novel polyimides containing 2,3-dioxynitrostilbenyl groups as NLO-chromophores. We selected 2,3-dioxynitrostilbenyl groups as NLO-chromophores because they have large dipole moments and are rather easy to synthesize. Furthermore 2,3-dioxynitrostilbenyl groups constitute novel Y-type NLO polyimides (Fig. 1b), and these Y-type NLO polyimides are not presented in the literature. Thus, we designed and synthesized new type of NLO polyimides, in which the pendant NLO chromophores are parts of the polymer backbones. These mid-type NLO polymers are expected to have

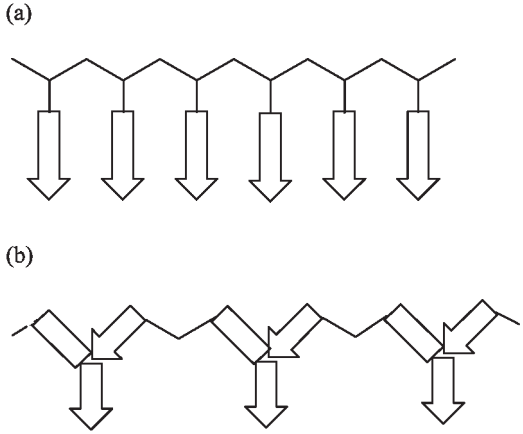


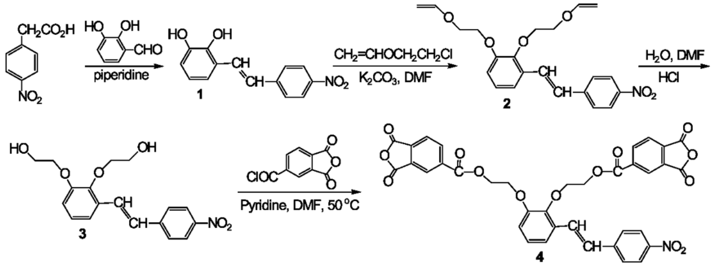
FIGURE 1 (a) Side chain NLO polymers and (b) Y-type NLO polymers.

both of the merits of 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, second harmonic generation (SHG) activity, and relaxation of dipole alignment. We now report the results of the initial phase of the work.

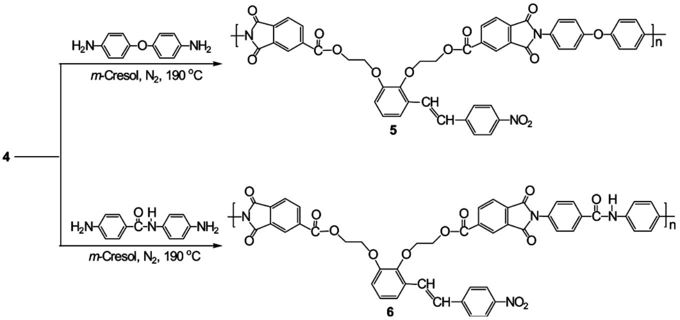
EXPERIMENTAL

Materials

Synthetic methods of dianhydride **4** and polymers **5–6** are summarized in Schemes 1 and 2. Compound **4**: Yield: 5.06 g (73%). Melting point: 180–182°C. IR (KBr): 3121 (w, =C−H), 2953 (w, C−H), 1850, 1780 (s, C=O, dianhydride), 1728 (vs, C=O, ester), 1601 (s, C=C), 1520, 1344 (vs, N=O) $\mathrm{cm^{-1}}$. ^{1}H NMR (DMSO-d_6): $\delta = 4.54$–4.62 (m, 4H, 2 $-\mathrm{CH_2}-\mathrm{O}-$), 4.69–4.79 (m, 4H, 2 $\mathrm{Ph}-\mathrm{O}-\mathrm{CH_2}-$), 7.31–7.51 (m, 4H, aromatic), 7.97–8.49 (m, 11H, aromatic). Anal. Calcd for $\mathrm{C_{36}H_{23}NO_{14}}$: C 63.34; H 3.34, N 2.02. Found C 63.42, H 3.41, N 2.08. Polymer **5**: Inherent viscosity (η_{inh}) $= 0.28\,\mathrm{dL\,g^{-1}}$ ($c = 0.5\,\mathrm{g\,dL^{-1}}$ in *m*-cresol at 25°C). $M_n = 22{,}900$, $M_w = 39{,}500$ (styragel HR5E4E; solvent THF). IR (KBr): 1780 (m, C=O), 1722 (vs, C=O), 1601 (m, C=C), 1501 (s, N=O), 1379 (m, CN), 1350 (s, N=O), 731 (s, imide ring) $\mathrm{cm^{-1}}$. ^{1}H NMR (DMSO-d_6): $\delta = 4.55$–4.64 (s, 4H, 2 $-\mathrm{CH_2}-\mathrm{O}-$), 4.72–4.80 (s, 4H, 2 $\mathrm{Ph}-\mathrm{O}-\mathrm{CH_2}-$), 7.02–7.52 (m, 13H, aromatic), 7.95–8.02 (d, 2H, aromatic), 8.05–8.11 (d, 2H, $\mathrm{Ph}-\mathrm{CH}{=}\mathrm{CH}-\mathrm{Ph}$), 8.25–8.32 (t, 3H, aromatic), 8.38–8.45 (d, 3H, aromatic). Anal. Calcd for $(\mathrm{C_{48}H_{31}N_3O_{13}})_n$: C 67.21; H 3.64; N 4.90. Found C 67.31, H 3.58, N 4.99. Polymer **6**: Inherent viscosity (η_{inh}) $= 0.27\,\mathrm{dL\,g^{-1}}$ ($c = 0.5\,\mathrm{g\,dL^{-1}}$ in *m*-cresol at 25°C). $M_n = 20{,}200$, $M_w = 37{,}600$ (styragel HR5E4E; solvent THF). IR (KBr): 1774 (m, C=O), 1720 (vs, C=O), 1653, 1605 (s, C=C), 1512



SCHEME 1 Synthetic method of compound **4**.



SCHEME 2 Synthetic method of polymers **5–6**.

(vs, N=O), 1373 (m, CN), 1344 (s, N=O), 729 (s, imide ring) cm^{-1}. ^{1}H NMR (DMSO-d_6): $\delta = 4.55$–4.64 (s, 4H, 2 $-CH_2-O-$), 4.72–4.79 (s, 4H, 2 $Ph-O-CH_2-$), 7.72–7.53 (m, 9H, aromatic), 7.85–8.13 (m, 9H, aromatic, Ph−CH=CH−Ph), 8.25–8.33 (d, 3H, aromatic), 8.35–8.46 (d, 3H, aromatic), 10.23 (d, 1H, amide N−H). Anal. Calcd for $(C_{49}H_{32}N_4O_{13})_n$: C, 66.52; H, 3.64; N, 6.33. Found C 66.43, H 3.68, N 6.25.

Instrumentation

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 (6.5 kV, 150°C, 30 min). 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 5–6

Synthetic method of monomer **4** is summarized in Scheme 1. The polymers **5–6** were synthesized by reacting aromatic dianhydride monomer **4** containing NLO-chromophore with stoichiometric amounts of the corresponding aromatic diamine in *m*-cresol (Scheme 2). The polymerization yield was 86–92%. The resulting polymers were purified by Soxhlet extraction for 2 days with diethyl ether as a solvent. The chemical structures of the resulting polymers were confirmed by ^{1}H NMR, IR spectra, and elemental analysis. ^{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 polymer samples show peaks near 1780 and 731 cm^{-1} that are characteristic bands of imide asymmetric carbonyl stretching and imide ring deformation, respectively. IR spectra of the same polymer samples also show strong absorption peaks near 1722 cm^{-1} and 1379 cm^{-1} due to a symmetric carbonyl stretching and C$-$N stretching of imide ring, respectively. These results are consistent with the proposed structures, indicating that the NLO-chromophore remained intact during the imidization process. The M_n was determined by GPC to be 22900 ($M_w/M_n = 1.71$) for polymer **5**. Polydispersities were in the range of 1.63–1.97. The polyimides **5–6** were soluble in common solvents such as 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 **5–6** showed strong absorption near 340 nm by the NLO-chromophore dioxynitrostilbenyl group. The striking feature of these polymers was that they had pendant NLO chromophores that were parts of the polymer main chains. Thus, we obtained a new type of NLO polyimide with side chain and main chain characteristics. These mid-type NLO polymers were expected to have the advantage of both main-chain and side-chain NLO polymers. We now have well defined polymers **5–6** and investigate their properties.

Thermal Properties of Polymers

The thermal behavior of the polymers was investigated by TGA and DSC to determine the thermal degradation pattern and T_g. The results are summarized in Table 1. Polymers **5–6** showed thermal stability up to 300°C from their TGA thermograms as shown in Table 1. T_g values of the polymers **5–6** measured by DSC were around

TABLE 1 Thermal Properties of Polymers **5–6**

Polymer	$T_g{}^a$ (°C)	Degradation temp (°C)^b 5% loss	 20% loss	 40% loss	Residue^b at 800°C (%)
5	135	324	405	519	37.2
6	141	302	397	551	44.5

^{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.

135–141°C. These are rather low values compared to those of common rigid polyimides and probably attributed to the flexibility in the polymer backbone containing ether linkages. The TGA and DSC studies showed that the decomposition temperature of the polyimides **5–6** 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. The spin-coated polymer films were corona-poled to induce noncentrosymmetric polar order. UV-Vis absorption spectra of the polymer samples before and after the poling were recorded. After the electric poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectra of polymers exhibited a slight blue shift and a decrease in absorption due to birefringence. The estimated order parameter value Φ was found to have a value of 0.26 for polymer **5** ($\Phi = 1 - A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after poling). The decrease in absorbance after poling is an indicator of the dipole alignment. Domain structures of NLO-chromophores for the poled thin-film samples were obtained using atomic force microscopy (AFM). AFM images showed that the good quality film was dramatically changed after poling, resulting in numerous hills and valleys in the surface structure, which were aligned the poling direction. The refractive index of the sample was measured by the optical transmission technique [9]. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. In order to determine the microscopic

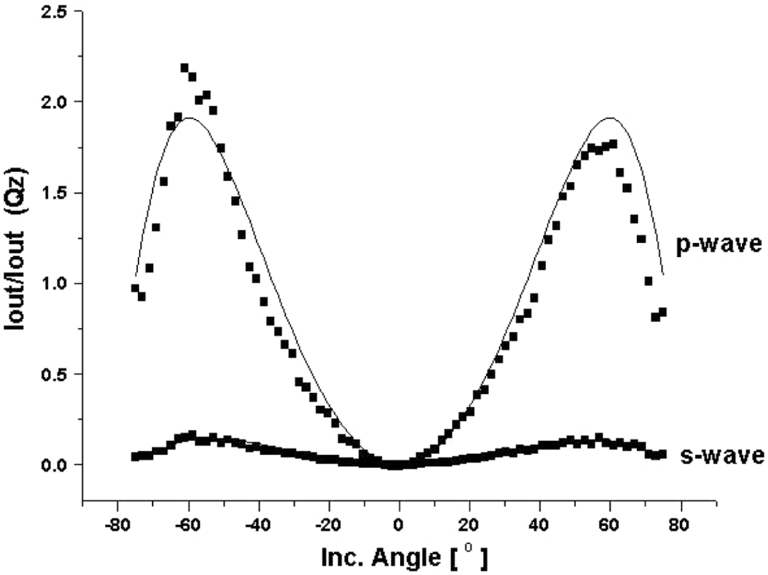


FIGURE 2 Angular dependence of SHG signal in a poled film of polymer **5**.

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 **5**. 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. The values of d_{31} and d_{33} for polymer **6** were 2.54×10^{-9} and 6.14×10^{-9} esu, respectively. Nonlinear optical properties of polymers **5–6** are summarized in Table 2. Since the second harmonic wavelength was at 532 nm, which is not in the

TABLE 2 Nonlinear Optical Properties of Polymers **5–6**

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	ϕ[c]	Film thickness[d]	d_{31}[b] (esu)	d_{33}/d_{31}
5	338	2.46×10^{-9}	0.15	0.26	1.04×10^{-9}	2.37
6	340	6.14×10^{-9}	0.10	0.29	2.54×10^{-9}	2.42

[a] Polymer film after corona poling.

[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].

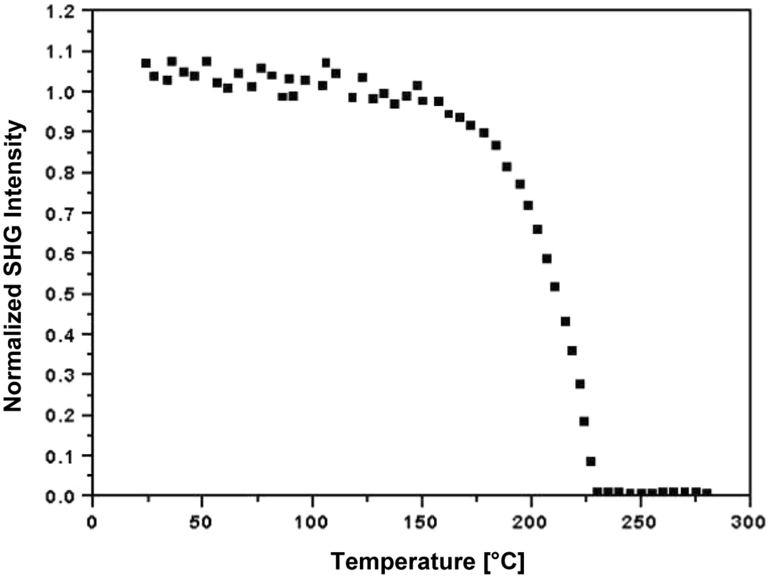


FIGURE 3 Normalized SHG signal of polymer **6** as a function of temperature at a heating rate of 10°C/min.

absorptive region of the resulting polymer, 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 **6**. 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 10°C/min from 30°C to 250°C. The poled film of polymers **5–6** exhibited a thermal stability even at 30°C higher than T_g and no significant SHG decay was observed below 170°C, which was acceptable for NLO device applications. Side-chain NLO polymers usually lose thermal stability of dipole alignment around T_g. Stabilization of dipole alignment is a characteristic of main-chain NLO polymers. The exceptionally high thermal stability of second harmonic generation of polymers **5–6** was probably 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 polyimide having the advantage of both main-chain and side-chain NLO polymers: the stabilization of dipole alignment and good solubility.

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