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Novel Y-Type Polyimide with Highly Enhanced Thermal Stability of Second Harmonic Generation

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Abstract: 3,4-Bis-(3,4-dicarboxyphenylcarboxyethoxy)-4'-nitrostilbene dianhydride was prepared and reacted with 4,4'-(hexafluoroisopropylidene)dianiline to yield a novel Y-type polyimide containing the 3,4-dioxynitrostilbenyl group as an NLO-chromophore, which constituted part of the polymer backbone. The resulting polyimide was soluble in polar solvents such as acetone and *N,N*-dimethylformamide. The polymer exhibited good thermal stability up to 370 °C in the thermogravimetric analysis. The glass-transition temperature (T_g) obtained from the differential scanning calorimetry thermogram was near to 153 °C. The second harmonic generation (SHG) coefficient (d_{33}) of the poled polymer film at the fundamental wavelength of 1064 cm^{-1} was around 2.15×10^{-8} esu (9.01 pm/V). The dipole alignment exhibited exceptionally high thermal stability even at a temperature 30 °C above the T_g, and there was no SHG decay below 180 °C because of the partial main chain character of the polymer structure.

Keywords: nonlinear optical, polyimides, differential scanning calorimetry (DSC), SHG coefficient, relaxation of dipole alignment.

Introduction

A lot of efforts have been focused on the synthesis of nonlinear optical (NLO) materials over the past decade because of their potential applications in the field of electro-optic devices.[1] Among organic materials, NLO polymers are considered candidate materials, mainly because they have many advantages such as mechanical endurance, light weight, and good processability.[2] In the developments of NLO polymers for electro-optic device applications, stabilization of electrically-induced dipole alignment is an important criteria. One approach to minimize the randomization of dipole alignment is to use polymers with high glass-transition temperatures (T_g's) such as polyimides.[3] Polyimides for NLO applications have attracted attentions because of their high T_gs, which can be used to stabilize the dipole orientation of the NLO chromophore at high temperatures. Another advantage of polyimides is their high thermal stability, which enables them to endure at elevated temperature in electro-optic devices. There are two types of NLO polyimides, which have been used as polymer hosts for composite materials and as polymer backbones for side-chain NLO chromophores. Side-chain polymer systems have advantages such as homogeneity and a high level of NLO chromophores with respect to the host-guest systems, which suffer from poor homogeneity of chromophores and diffusion of the chromophores at high temperatures. Recently we reported a novel Y-type NLO polyesters with enhanced thermal stability of second harmonic generation.[4] They exhibited thermal stability up to their T_gs.

In this work we prepared novel Y-type polyimide containing 3,4-dioxynitrostilbenyl groups as a NLO-chromophore. We selected 3,4-dioxynitrostilbenyl group as a NLO-chromophore because it has a large dipole moment and are rather easy to synthesize. Furthermore 3,4-dioxynitrostilbenyl group constitutes a novel Y-type NLO polyimide [(Figure 1(c)], and this Y-type NLO polyimide has not presented in the literature. Thus, we designed and synthesized a new type of NLO polyimide, in which the pendant NLO chromophores are parts of the polymer backbones. These mid-type NLO polymers are expected to have 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 properties such as thermal stability, second harmonic generation (SHG) activity, and relaxation of dipole alignment. We

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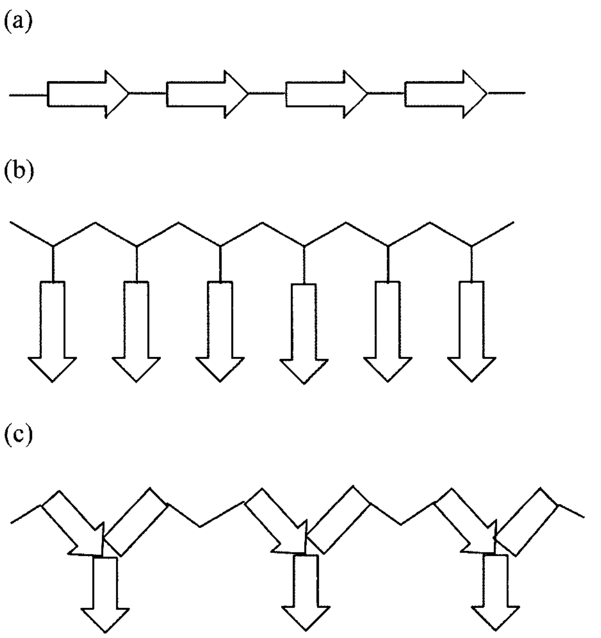


Figure 1. (a) Main-chain NLO polymers, (b) side chain NLO polymers, and (c) Y-type NLO polymers.

now report the results of the initial phase of the work.

Experimental

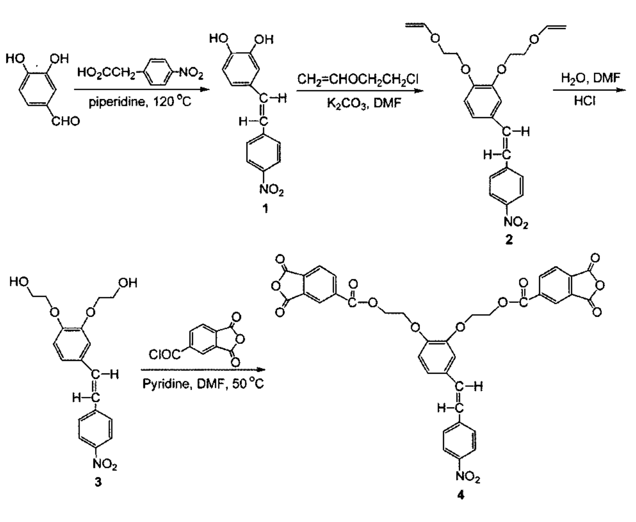
Materials and Measurements. The reagent-grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 3,4-Dihydroxy-4'-nitrostilbene (**1**), 3,4-di-(2'-vinyloxyethoxy)-4'-nitrostilbene (**2**) and 3,4-di-(2'-hydroxyethoxy)-4'-nitrostilbene (**3**) were prepared by a known method.[4] Film preparation and SHG measurements were performed according to the procedures reported already.[4] The refractive index of the sample was measured by the optical transmission technique.[5] 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.[6]

Preparation of 3,4-Bis-(3,4-dicarboxyphenylcarboxyethoxy)-4'-nitrostilbene dianhydride (4). Compound **3** (3.45 g, 0.01 mol) was dissolved in dry DMF (20 mL) and pyridine (20 mL) at 50 °C under nitrogen. Trimellitic anhydride chloride (8.42 g, 0.04 mol) was added to the mixture with stirring under at 50 °C. The resulting solution was stirred for 12 h at room temperature. The resulting solution was diluted with 250 mL of water and stirred for 1 h to dissolve pyridine hydrochloride. The product was filtered, and washed successively with water and methanol. Thus obtained deep brown product was dried at 50 °C under vacuum to give pure **4**. Yield: 5.20 g (75%). mp: 148-150 °C. ^{1}H-NMR (DMSO-d_6) δ 4.35-4.46 (s, 4H, 2 -CH_2-O-), 4.52-4.65 (s, 4H, 2 Ph-O-CH_2-), 7.08-7.45 (m, 5H, aromatic), 7.66-7.79 (m, 4H, aromatic), 8.04-8.09 (d, 2H, Ph-CH=CH-Ph), 8.17-8.23 (d, 4H, aromatic). IR (KBr) 3082 (w, =C-H), 2953 (w, C-H), 1850, 1780 (m, C=O, dianhydride), 1722 (vs, C=O, ester), 1583 (s, C=C), 1512, 1344 (vs, N=O) cm^{-1}. Anal. Calcd for $C_{36}H_{23}NO_{14}$: C, 63.34; H, 3.34; N, 2.02. Found: C, 63.45 H, 3.41; N, 2.10.

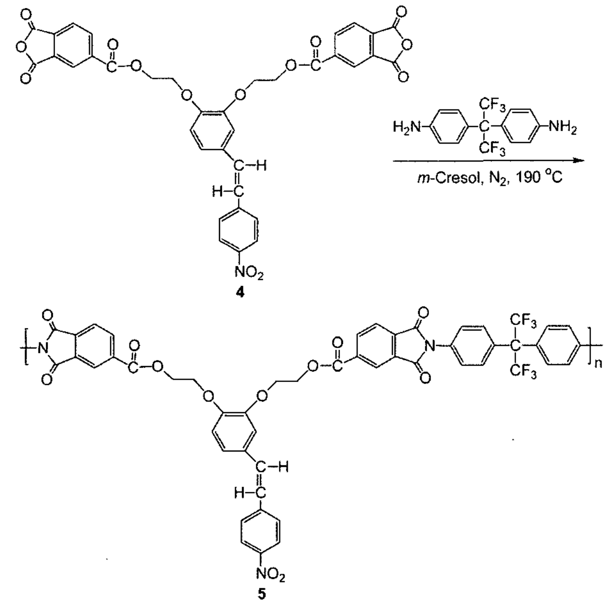
Synthesis of Polyimide 5. The polymerization was carried out in a drybox at room temperature. A representative synthetic procedure of polyimide **5** was as follows. Anhydride **4** (6.93 g, 0.01 mol) was added slowly to a solution of 4,4'-(hexafluoroisopropylidene)dianiline (3.34 g, 0.01 mol) in 60 mL of dry *m*-cresol over 1 h. The polymerization was allowed to continue at 50 °C for 12 h. The mixture was gradually elevated to 190 °C and then stirred for 12 h. The polymer solution was poured into 400 mL of methanol. The precipitated polymer was collected and further purified by extraction in a Soxhlet extractor with diethyl ether for two days. The final product was dried under vacuum to give 9.26 g (92% yield) of polymer **5**. Inherent viscosity (η_{inh}): 0.26 dL g^{-1} (c = 0.5 g dL^{-1} in *m*-cresol at 25 °C). ^{1}H-NMR (DMSO-d_6) δ 4.37-4.50 (s, 4H, 2 -CH_2-O-), 4.54-4.68 (s, 4H, 2 Ph-O-CH_2-), 7.07-7.78 (m, 13H, aromatic), 7.93-8.32 (s, 10H, Ph-CH=CH-Ph, aromatic). IR (KBr) 3375 (m, N-H), 3076 (w, =C-H), 2964 (w, C-H), 1780 (m, C=O), 1722 (vs, C=O), 1595 (s, C=C), 1520 (vs, N=O), 1379 (m, CN), 1344 (s, N=O), 725 (s, imide ring) cm^{-1}. Anal. Calcd for $(C_{51}H_{31}N_3O_{13}F_6)_n$: C, 60.78; H, 3.10; N, 4.17. Found: C, 60.89; H, 3.19; N, 4.27.

Results and Discussion

3,4-Di-(2'-hydroxythoxy)-4'-nitrostilbene (**3**) was prepared by hydrolysis of 3,4-di-(2-vinyloxyethoxy)-4'-nitrostilbene (**2**). Chromophore-containing dianhydride **4** was prepared through the reaction of diol **3** with trimellitic anhydride acid



Scheme I. Synthesis of compound **4**.



Scheme II. Synthesis of polymer **5**.

chloride in dry DMF in the presence of pyridine. The synthetic method of monomer **4** is summarized in Scheme I. The chemical structures of the compounds were identified by ^{1}H-NMR, IR spectra and elemental analysis. All the analytical data confirmed the expected chemical structure. In the IR spectrum of **4**, a peak characteristic of a carbonyl group of dianhydride appeared at 1850 and 1780 cm^{-1}. IR spectra of the same sample also showed a strong carbonyl peak near 1722 cm^{-1} indicating the presence of aromatic ester bond. The strong absorptions at 1512 and 1344 cm^{-1} due to nitro group indicated the presence of stilbene unit.

Polyimide **5** was synthesized through the reaction of aromatic dianhydride monomer **4** containing NLO-chromophore with stoichiometric amounts of the corresponding aromatic diamine in *m*-cresol (see Scheme II). The polymerization yield was 92%. The striking feature of these polymers is 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. The chemical structures of the resulting polymers were confirmed with ^{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 were consistent with the proposed polymer structures. The IR spectra supported the formation of polyimide. The IR spectra of the polymer samples showed peaks near 1780 and 725 cm^{-1} that were 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 and 1379 cm^{-1} due to symmetric carbonyl stretching and C-N stretching of imide ring, respectively. These results are consistent with the proposed structures, indicating that the NLO-chromophores remained intact during the polymerization. Polyimide **5** was soluble in common solvents such as acetone, DMF, and DMSO, but they were not soluble in methanol and diethyl ether. The η_{inh} value was 0.26 dL/g. Polymer **5** showed strong absorption near 380 nm by the NLO-chromophore dioxynitrostilbenyl group.

The thermal behaviors of the polymer was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g). Polymer **5** showed a thermal stability up to 370 °C according to their TGA thermograms. T_g value of **5** measured by DSC was around 153 °C. This is rather low T_g values compared to those of common rigid polyimides and can probably attributed to the flexibility of the polymer backbone containing ether linkages. The TGA and DSC studies showed that the decomposition temperature of the polyimide **5** was higher than the corresponding T_g. This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

The NLO properties of polymer were studied by the SHG method. We corona-poled the spin-coated polymer film to induce noncentrosymmetric polar order. As the temperature was raised gradually to 160 °C, 6.5 kV of corona voltage was applied and kept that temperature for 30 min. The 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 spectrum of polymer **5** 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 0.22 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, respectively). The decrease in absorbance after poling was an indicator of the dipole alignment. The refractive index of the sample was measured by the optical transmission technique.[5] The transmittance of thin film includes on the information of the thickness and refractive index and its extinction coefficient. Thus, we could determine these parameters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of 1064 nm with a mode-locked Nd-YAG laser. We recorded the angular SHG dependence to determine the microscopic second-order susceptibility of the polymer. 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. For the calculation of 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 proce-

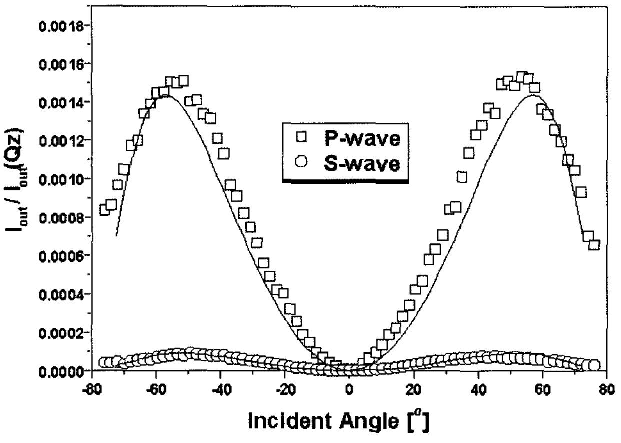


Figure 2. Angular dependence of a SHG signal in a poled film of polymer **5**.

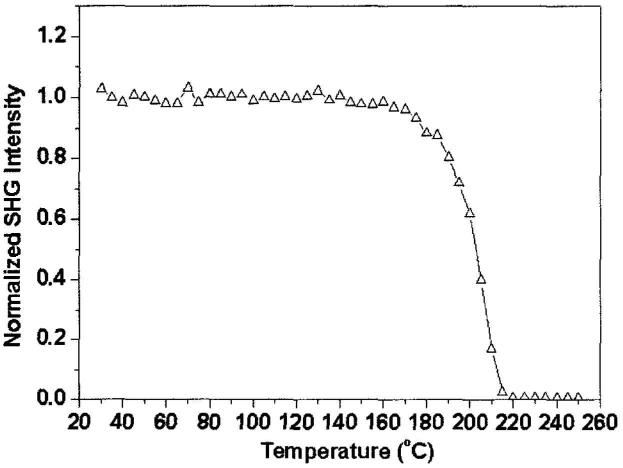


Figure 3. Normalized SHG signal of polymer **5** as a function of temperature at a heating rate of 10 °C/min.

dure.[6] The values of d_{31} and d_{33} for polymer **5** were 7.71 × 10^{-9} esu (3.23 pm/V) and 2.15 × 10^{-8} esu (9.01 pm/V), respectively. Because of the second harmonic wavelength was at 532 nm, which was not in the absorptive region of the resulting polymer, 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. In Figure 3, we present the dynamic thermal stability study of the NLO activity of the film **5**. To investigate the real-time NLO decay of the SHG signal of the poled polymer films as a function of temperature, we performed *in situ* SHG measurements at a heating rate of 10 °C/min from 30 to 300 °C. The polymer film exhibited a thermal stability even at 30 °C higher than T_g and no significant SHG decay was observed below 180 °C. In general, side-chain NLO polymers loose thermal stability of dipole alignment around T_g. The stabilization of dipole alignment is a characteristic of main-chain NLO polymers. The exceptionally high thermal stability of SHG of polymer **5** was due to the stabilization of dipole alignment of NLO chromophore, which stemmed from the partial main-chain character of the polymer structure. Thus, we obtained a new type of NLO polyimide having the advantages of both main-chain and side-chain NLO polymers: the stabilization of dipole alignment and good solubility.

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References

(1) K. R. Yoon, H. Lee, B. K. Rhee, and C. Jung, *Macromol. Res.*, **12**, 581 (2004).
(2) M. J. Cho, S. K. Lee, J.-I. Jin, and D. H. Choi, *Macromol. Res.*, **14**, 603 (2006).
(3) (a) D. Yu, A. Gharavi, and L. Yu, *J. Am. Chem. Soc.*, **117**, 11680 (1995). (b) D. Yu, A. Gharavi, and L. Yu, *Macromolecule*, **28**, 784 (1995). (c) R. D. Miller, D. M. Burand, M. Jurich, V. Y. Lee, C. R. Moylan, J. I. Thackara, R. J. Twieg, T. Verbiest, and W. Volksen, *Macromolecules*, **28**, 4970 (1995). (d) T. Chen, A. K. Y. Jen, and Y. J. Cai, *J. Am. Chem. Soc.*, **117**, 7295 (1995). (e) D. Yu, A. Gharavi, and L. Yu, *Macromolecules*, **29**, 6139 (1996). (f) H. Saadeh, A. Gharavi, D. Yu, and L. Yu, *Macromolecules*, **30**, 5403 (1997). (g) H. K. Kim, I. K. Moon, M. Y. Lin, and K.-Y. Choi, *Korea Polym. J.*, **5**, 57 (1997). (h) N. Tsutsumi, M. Morishima, and W. Sakai, *Macromolecules*, **31**, 7764 (1998). (i) M. H. Kim, J.-I. Jin, C. J. Lee, N. J. Kim, and C. H. Park, *Bull. Korean Chem. Soc.*, **23**, 964 (2002). (j) S. J. Shin, J. H. Chi, W. C. Zin, T. Chang, M. Ree, and J. C. Jung, *Polymer(Korea)*, **30**, 97 (2006). (k) M. Ree, *Macromol. Res.*, **14**, 1 (2006).
(4) J.-Y. Lee, W.-T. Jung, and W.-J. Lee, *Polym. Int.*, **55**, 248 (2006).
(5) J. I. Cisneros, *Appl. Opt.*, **37**, 5262 (1998).
(6) W. N. Herman and L. M. Hayden, *J. Opt. Soc. Am. B.*, **12**, 416 (1995).