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Notes

Preparation of Novel T-Type Nonlinear Optical Polyimide with High Thermal Stability of Second Harmonic Generation

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Introduction

Nonlinear optical (NLO) materials have been extensively studied over the past decade because of their potential applications in the field of electro-optic devices.[1-6] Among them, NLO polymers are considered as candidate materials, mainly because they have many advantages such as mechanical endurance, low mass, and good processability. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically-induced dipole alignment is an important criteria; in this context, one approach to minimize the randomization of dipole alignment is to use of high glass-transition temperature (T_g) polymers such as polyimides.[7-13] Polyimides for NLO applications have attracted attentions because of their high T_g, 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. Main-chain NLO polymers 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. Side-chain polymer systems have advantages such as good solubility, homogeneity and a high loading level of NLO chromophores, but they often suffer from poor stability of dipole alignment at high temperatures. Recently we reported novel NLO polyimides containing dinitrostolbenyl group as NLO chromophores.[14,15] The resulting polyimides exhibited highly enhanced thermal stability of second harmonic generation.

In this work we prepared novel polyimide containing 2,5-dioxybenzylidenemalononitrile groups as a NLO-chromophore. We selected the latter because they have large dipole moments and are rather easy to synthesize. Furthermore 2,5-dioxybenzylidenemalononitrile group constitutes novel T-type NLO polyimide (Figure 1), and this T-type NLO polyimide has not yet been presented in the literature. Thus, we synthesized a new type of NLO polyimide, in which the pendant NLO chromophores are components of the polymer backbone. This mid-type NLO polymer is expected to have both the merits of main chain-chain and side chain-NLO polymers namely stable of dipole alignment and good solubility. After confirming the structure of the resulting polymer, we investigated its 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

Film Preparation and SHG Measurements. The alignment of the NLO-chromophore of the polymers was carried out by corona poling method. The refractive index of the sample was measured by the optical transmission technique.[16] Second harmonic generation (SHG) measurement was carried out one day after poling. The Maker Fringe pattern was obtained by 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.[17]

Preparation of 2,5-Di-(2-vinyloxyethoxy)benzaldehyde (1). 2,5-Dihydroxybenzaldehyde (13.8 g, 0.10 mol), anhydrous potassium carbonate (82.9 g, 0.60 mol), and 2-chloroethyl vinyl ether (26.6 g, 0.25 mol) were dissolved in 400 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80 °C for 15 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**. ^{1}H NMR ($CDCl_3$) δ 3.98-4.34 (m, 12H, 2 CH_2=, 2 -O-CH_2-CH_2-O-), 6.45-6.58 (m, 2H, 2 =CH-O-), 6.92-6.99 (m, 1H, aromatic), 7.15-7.21 (m, 1H, aromatic), 7.33-7.36 (d, 1H, aromatic), 10.46 (s, 1H, -CHO). IR (KBr) 3096, 3075 (w, =C-H), 2941, 2882 (s, C-H), 1676 (vs, C=O), 1624 (vs, C=C) cm^{-1}.

Preparation of 2,5-Di-(2-vinyloxyethoxy)benzylidenemalononitrile (2). Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,5-di-(2'-vinyloxyethoxy)benzaldehyde **1**

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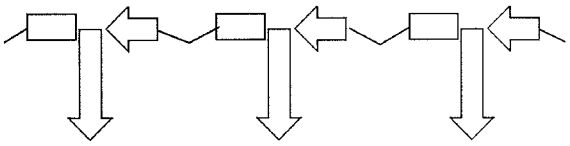


Figure 1. T-type NLO polymers.

(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 8.61 g (88% yield) of **2**. Mp=72-74 °C. ^{1}H NMR ($CDCl_3$) δ 4.02-4.40 (m, 12H, 2 CH_2=, 2 -O-CH_2-CH_2-O-), 6.46-6.58 (m, 2H, 2 =CH-O-) 6.94-6.98 (d, 1H, aromatic), 7.18-7.23 (q, 1H, aromatic), 7.75-7.78 (d, 1H, aromatic), 8.31 (s, 1H, Ph-CH=). IR (KBr) 3057 (w, =C-H), 2941, 2885 (m, C-H), 2222 (s, CN), 1624, 1578 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{18}H_{18}N_2O_4$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.36; H, 5.64; N, 8.50.

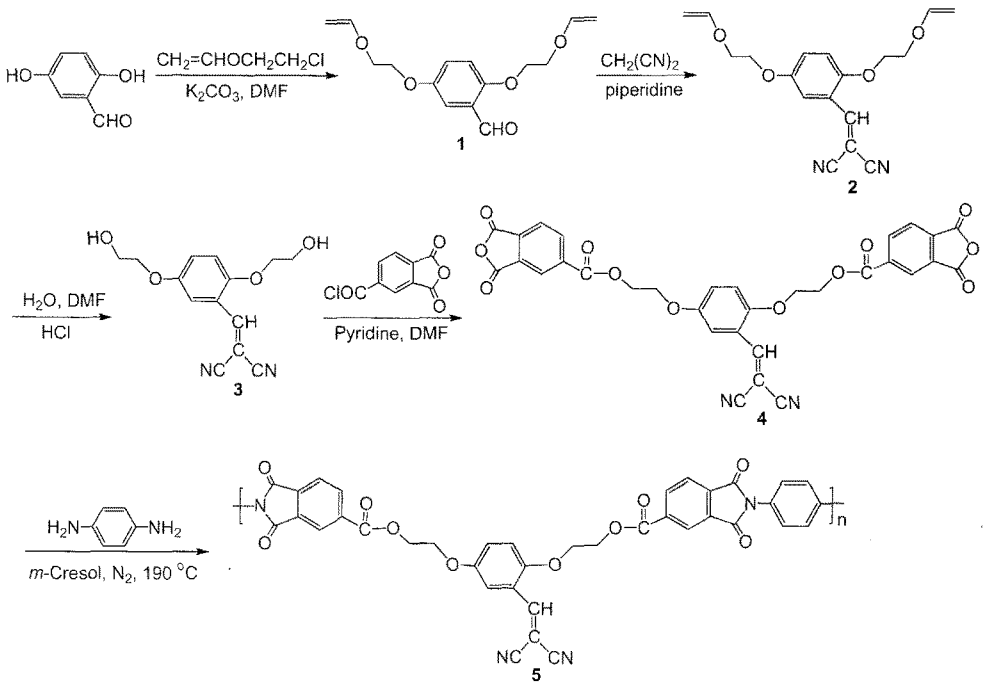
Preparation of 2,5-Di-(2-hydroxyethoxy)benzylidenemalononitrile (3). Aqueous hydrochloric acid (1.5 mol L^{-1}, 30 mL) was slowly added to a solution of 2,5-di-(2'-vinyloxyethoxy)benzylidenemalononitrile (**2**) (8.48 g, 0.026 mol) in 60 mL of dry THF with stirring under nitrogen at 0 °C. The mixture 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 6.06 g (85% yield) of **3**. Mp=138-140 °C. ^{1}H NMR (acetone-d_6) δ 3.74-3.94 (m, 4H, 2 -CH_2-OH), 3.94-4.12 (m, 2H, -OH), 4.12-4.22 (m, 4H, 2 -O-CH_2-), 7.15-7.32 (m, 2H, aromatic), 7.75 (s, 1H, aromatic), 8.58 (s, 1H, -Ph-CH=). IR (KBr) 3516, 3233 (s, O-H), 3045 (m, =C-H), 2941 (m, C-H), 2233 (m, CN), 1576 (s, C=C) cm^{-1}. Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.41; H, 5.22; N, 10.28.

Preparation of 2,5-Bis(3,4-dicarboxyphenylcarboxyethoxy)-1-(2,2-dicyanovinyl)benzene dianhydride (4). Compound 3 (2.74 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 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. The obtained deep brown product was dried at 50 °C under vacuum to give pure **4**. Yield: 4.67 g (75%). ^{1}H NMR (DMSO-d_6) δ 4.36-4.74 (t, 8H, 2 -O-CH_2CH_2-O-), 7.24-7.35 (t, 1H, benzylic), 7.45-7.72 (m, 3H, aromatic), 7.96-8.258 (m, 3H, aromatic), 8.54 (s, 1H, aromatic), 8.72 (d, 2H, aromatic). IR (KBr) 3072 (w, =C-H), 2960 (w, C-H), 2224 (s, CN), 1780 (m, C=O, dianhydride), 1722 (vs, C=O, ester), 1606 (s, C=C) cm^{-1}. Anal. Calcd for $C_{32}H_{18}N_2O_{12}$: C, 61.74; H, 2.91; N, 4.50. Found: C, 61.81 H, 2.96; N, 4.58.

Synthesis of Polyimide 5. A representative synthetic procedure of polyimide 5 was as follows. Anhydride 4 (6.22 g, 0.01 mol) was added slowly to a solution of 1,4-phenylenediamine (1.08 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 6.24 g (90% yield) of polymer 5. Inherent viscosity (η_{inh}): 0.28 dL g^{-1} (c = 0.5 g dL^{-1} in *m*-cresol at 25 °C). ^{1}H NMR (DMSO-d_6) δ 4.08-4.85 (m, 8H, 2 -O-CH_2-CH_2-O-), 6.26-6.72 (m, 3H, benzylic, aromatic), 6.77-7.23 (m, 2H, aromatic), 7.38-7.74 (m, 3H, aromatic), 7.82-8.53 (m, 4H, aromatic), 8.91-9.12 (m, 2H, aromatic). IR (KBr) 3072 (w, =C-H), 2958 (w, C-H), 2221 (w, CN), 1780 (m, C=O), 1723 (vs, C=O), 1616 (s, C=C), 1378 (s, C-N), 726 (s, imide ring) cm^{-1}. Anal. Calcd for $(C_{38}H_{22}N_4O_{10})_n$: C, 65.71; H, 3.19; N, 8.07. Found: C, 65.63; H, 3.26; N, 8.15.

Results and Discussion

The synthetic methods for intermediates and final polymer is summarized in Scheme I. Compound **1** was prepared through the condensation of 2-chloroethyl vinyl ether with 2,5-dihydroxybenzaldehyde. Compound **2** was prepared by the condensation reaction of **1** with malononitrile, and was hydrolyzed to yield compound **3**. Chromophore-containing monomer **4** was prepared by the reaction of diol **3** with trimellitic anhydride acid chloride in dry DMF in the presence of pyridine. Polyimide **5** was synthesized through the reaction of aromatic dianhydride monomer **4** containing NLO-chromophore with stoichiometric amount of 1,4-phenylenediamine in *m*-cresol. The polymerization yield was 90%. The resulting polymer was purified by Soxhlet extraction with diethyl ether as a solvent. The structural feature of this polymer is that it has pendant NLO chromophores that are parts of the polymer main chain. Thus, we obtained a new type of NLO polyimide with side-chain and main-chain characteristics. This mid-type NLO polymer was expected to have the advantages of both main-chain and side-chain NLO polymers. The chemical structure of the resulting polymer was confirmed with ^{1}H NMR, IR spectra and elemental analysis. The elemental analysis results fit the polymer structures. ^{1}H NMR spectrum of the polymer showed a



Scheme I. Synthetic scheme and structure of polymer **5**.

signal broadening due to polymerization, but the chemical shifts were consistent with the proposed polymer structures. The IR spectrum supported the formation of polyimide. The IR spectra of the polymer sample showed peaks near 1780 and 726 cm^{-1} that were characteristic bands of imide asymmetric carbonyl stretching and imide ring deformation, respectively. IR spectrum of the same polymer sample also show strong absorption peaks near 2224, 1723, and 1378 cm^{-1} due to nitrile stretching, 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. The molecular weight was determined by GPC with polystyrene as the standard and THF as the eluent. The number average molecular weight (M_n) of polymer **5**, determined by GPC, was near 20,400 (M_w/M_n= 1.89). Polyimide **5** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity (η_{inh}) was around 0.28 dL g^{-1}. Polymer **5** showed strong absorption near 408 nm by the NLO-chromophore 2,5-dioxybenzylidenemalononitrile group.

The thermal behavior of the polymer was investigated by thermogravimetric analysis and differential scanning calorimetry to determine the thermal degradation pattern and glass transition temperature (T_g). Polymer **5** showed a thermal stability up to 340 °C according to its TGA thermogram. T_g value of polymer **5** measured by DSC was near 190 °C. This is rather low T_g value compared to those of common rigid polyimides, which can probably be 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 value. This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

The NLO property of polymer was studied by the SHG method. To induce noncentrosymmetric polar order, we corona-poled the spin-coated polymer film. As the temperature was raised gradually to 200 °C, 6.5 KV of corona voltage was applied and this temperature was maintained for 30 min. After electric poling, the dipoles 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, being related to the poling efficiency. The estimated order parameter value (Φ) of polymer **5** was equal to 0.21 (Φ= 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.[16] The transmittance of thin film includes information on 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 1,064 nm with a mode-locked Nd-YAG laser. To determine the microscopic second-order susceptibility of the polymer, we recorded the angular SHG dependence.

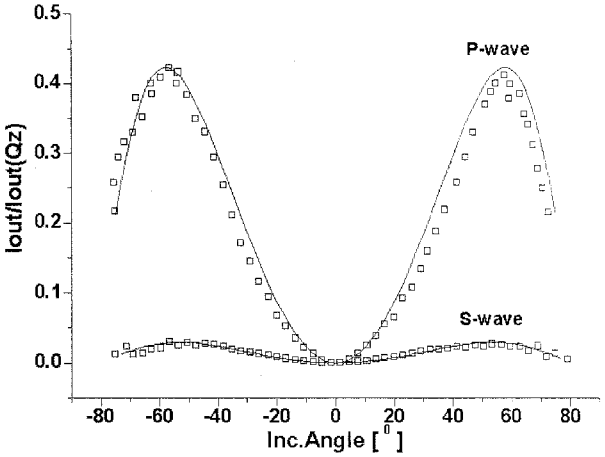


Figure 2. Angular dependence of SHG signal in a poled film of polymer **5**.

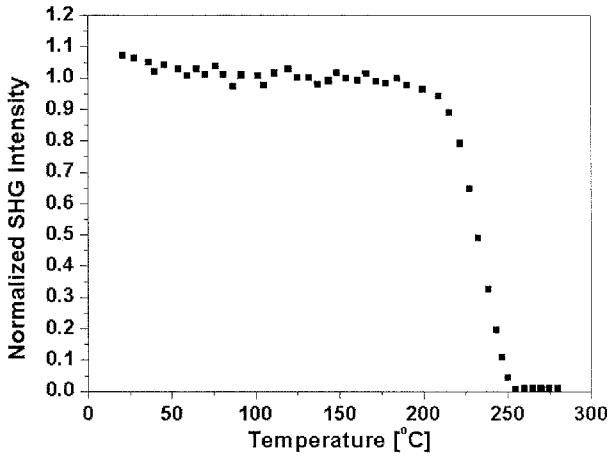


Figure 3. Normalized SHG signal of polymer **5** as a function of temperature at a heating rate of 10 °C/min.

Figure 2 shows the angular dependence of SHG signal in a poled polymer **5**. The SHG value was compared with that 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 the Pascal fitting program according to the literature procedure.[17] The values of d_{31} and d_{33} for polymer **5** were 1.42×10^{-9} and 4.13×10^{-9} esu, respectively. Because of the second harmonic wavelength was at 532 nm, which is 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 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 **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 greater thermal stability even at 20 °C higher than T_g and no significant SHG decay was observed below 210 °C. In general, side-chain NLO polymers lose the thermal stability of dipole alignment around T_g. The stabilization of dipole alignment is a characteristic of main-chain NLO polymers. The 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 merits of both main-chain and side-chain NLO polymers: stabilization of dipole alignment and good solubility. We are now in the process of extending the polymerization system to the synthesis of other type of NLO polymers and the results will be reported elsewhere.

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