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Synthesis and Properties of Novel Nonlinear Optical Polyester Containing Nitrophenylazocatecholic Group

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*A new Y-type polyester (**3**) containing nitrophenylazocatecholic groups as NLO chromophores, which are parts of the polymer backbone was prepared. Polyester **3** is soluble in common organic solvents such as acetone and dimethylsulfoxide. It shows a thermal stability up to 280°C from thermogravimetric analysis with glass-transition temperature* (T_g) *obtained from differential scanning calorimetry near 86°C. The second harmonic generation (SHG) coefficient* (d_{33}) *of poled polymer film at the 1064 nm fundamental wavelength is around* 4.42×10^{-9} *esu. The dipole alignment exhibits a thermal stability even at 4°C higher than* T_g*, and no SHG decay was observed below 90°C due to the partial main-chain character of polymer structure, which is acceptable for NLO device applications.*

Keywords Differential scanning calorimetry (DSC); dipole alignment; NLO; polyester; SHG coefficient; thermogravimetric analysis (TGA)

Introduction

Nonlinear optical (NLO) polymers have been extensively studied over the past decade because of their potential applications in electro-optic and photonic devices such as modulators and switches, due to their larger optical nonlinearity, lower dielectric constants, ultrafast response time and easier processability [1–3]. One of the current tasks is to design novel NLO polymers having optimized properties. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of important criteria [4]; in this context, two approaches to minimize the randomization have been proposed, namely the use of cross-linking method [5] and the utilizing high glass-transition temperature (T_g) polymers [6]. Polyesters containing amino-sulfone azobenzene chromophores in the main chain exhibit strong and stable reversible birefringence [7]. NLO polyesters with azobenzene mesogens in the main chain show high thermal and temporal stabilities [8]. Polyesters having cyanophenylazoaniline moiety in the side chain display good temporal stability of second-order nonlinearity [9]. In general, polymers with the NLO chromophores in the main chain have good thermal stability of dipole

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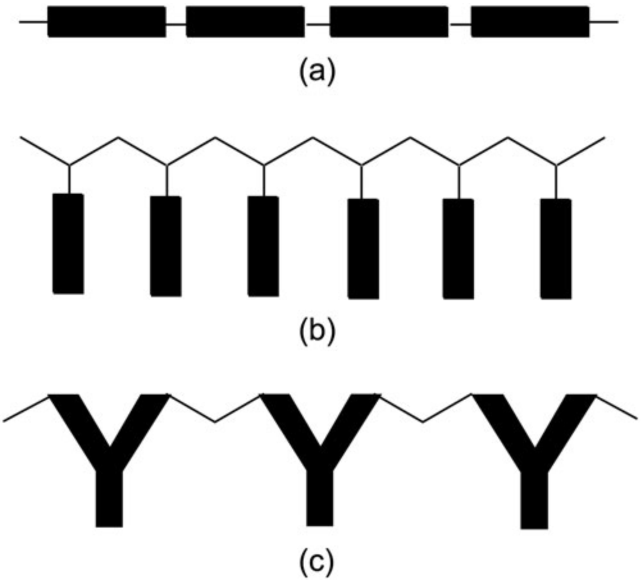


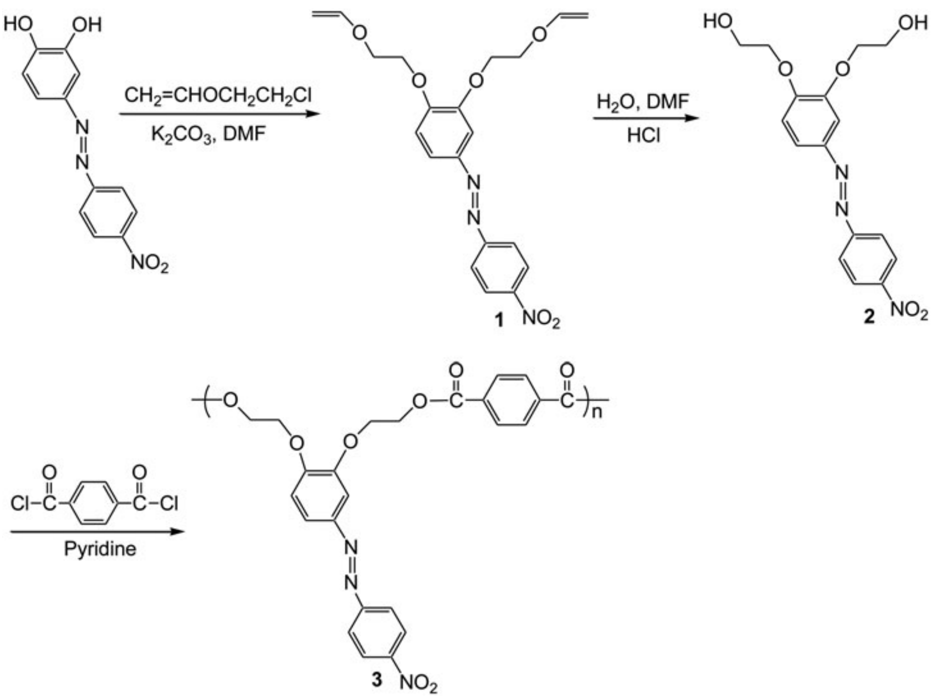
Figure 1. Main chain NLO polymers (a), side chain NLO polymers (b), and Y-type NLO polymers (c).

alignments, but they often do not dissolve in organic solvents, and their intractability make them unusable to fabricate stable noncentrosymmetric films. Side chain NLO polymers have the advantages such as good solubility and homogeneity, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we reported novel NLO polyesters containing dioxynitrostilbene [10] or tricyanovinylthiazole [11], which showed enhanced thermal stability of dipole alignments. In this work reported here, we prepared new Y-type polyester containing nitrophenylazocatecholic groups as NLO chromophores. We selected the latter as NLO chromophores because they are expected to have high optical nonlinearities. Furthermore, these nitrophenylazocatecholic groups constitute novel Y-type NLO polyesters (Fig. 1c), and these Y-type NLO polyesters have not yet 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. This Y-type NLO polymer is expected to have the advantages of both main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility. After confirming the structure of the resulting polymer, we investigated its thermal and nonlinear optical properties. We now report the results of the initial phase of the work.

Experimental

Materials

Synthetic method of polymer **3** is summarized in Scheme 1. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum, yielding 4.20 g (88% yield) of polymer **3**. Inherent viscosity (η_{inh}) = 0.31 dL/g (c, 0.5 g/dL in DMSO at 25°C). ^{1}H NMR (DMSO-d_6) δ 4.35–4.67 (m, 8H, 2 -O-CH$_2$-CH$_2$-O-), 7.32–7.37 (s, 1H, aromatic), 7.58–7.61 (s, 1H, aromatic), 7.67–8.08 (d, 7H, aromatic), 8.31–8.43 (m, 2H,



Scheme 1. Synthetic scheme and structure of polymer **3**.

aromatic). IR (KBr) 2928 (m, C-H), 1722 (vs, C=O), 1592 (s, N=N), 1520, 1344 (s, N=O) cm^{-1}. Anal. Calcd for $(C_{24}H_{19}N_3O_8)_n$: C, 60.38; H, 4.01; N, 8.80. Found: C, 60.46; H, 4.08; N, 8.72.

Measurements

Infrared (IR) spectra were obtained with a Varian FT IR-1000 IR spectrophotometer. ^{1}H NMR spectra were obtained with a Varian VNMRS 500 MHz NMR spectrometer. UV-visible absorption spectra were obtained with a SECOMAM Model UVIKON XS 99-90289 spectrophotometer. T_g values were measured using a TA 2920 differential scanning calorimeter (DSC) in a nitrogen atmosphere. A TA Q50 thermogravimetric analyzer (TGA) with a heating rate of 10°C/min up to 800°C was used for the thermal degradation of polymers under nitrogen. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymers were estimated using gel permeation chromatography (GPC; styragel HR5E4E columns; THF solvent). The refractive index of the sample was measured using the optical transmission technique [12]. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [13]. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.

Results and Discussion

Synthesis and Characterization of Polymer 3

Polyester **3** was synthesized through the reaction of monomer **2** containing NLO chromophore with stoichiometric amounts of terephthaloyl chloride in pyridine. The synthetic route for polymer **3** is presented in Scheme 1. The chemical structure of the resulting polymer was confirmed by ^{1}H NMR, IR spectra, and elemental analysis. The chemical shifts in ^{1}H NMR spectrum of the polymer are consistent with the proposed polymer structure. The IR spectrum of polymer **3** shows strong carbonyl peak near 1722 cm^{-1} indicating the presence of ester bond. The spectrum also shows strong absorption peak near 1592 cm^{-1} due to azo group and absorptions at 1520 and 1344 cm^{-1} due to nitro group indicating the presence of nitroazobenzene unit. These results are consistent with the proposed structure, indicating that the NLO chromophores remained intact during the polymerization. The number average molecular weight (M_n) of the polymer **3,** determined by GPC, was 16,500 ($M_w/M_n = 1.92$). The structural feature of this polymer is that it has pendant NLO chromophores, which are parts of the polymer main chains. Thus the resulting polymer **3** is mid type of side-chain and main-chain NLO polymer, and is expected to have both of their merits. The polymer **3** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity value is 0.31 dL/g. Polymer **3** shows strong absorption near 385 nm due to the nitrophenylazocatecholic NLO chromophore.

Thermal Properties of Polymer

The thermal behavior of the polymer was investigated by TGA and DSC to determine the thermal degradation pattern and glass transition temperature. Polymer **3** shows a thermal stability up to 280°C from its TGA thermogram. The 5% weight loss degradation temperature of polymer **3** is near 285°C. T_g value of the polymer **3** measured by DSC is around 86°C. This T_g value is lower than that of the polyester containing dioxynitrostilbene, which is near 110°C [10]. The lower T_g value of polymer **3** is probably due to the easier *cis-trans* isomerization of diazo linkage than that of carbon-carbon double bond.

Nonlinear Optical Properties of Polymer

The NLO properties of polymer **3** were studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer film was corona-poled. As the temperature was raised gradually to 5–10°C higher than T_g, a corona voltage of 6.5 kV was applied and this temperature was maintained for 30 min. The film was cooled to room temperature in the presence of the electric field. Finally, the electric field was removed. After electric poling, the NLO chromophores were aligned and the UV-visible absorption of polymer **3** exhibits a slight blue shift and a decrease in absorption due to birefringence. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. 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 **3**. The SHG values were compared with those obtained from a Y-cut quartz plate. SHG coefficients (d_{33}, d_{31}) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure [13]. Nonlinear optical properties of polymer **3** are summarized in Table 1. The values of d_{33} and d_{31} for polymer **3** are 4.42×10^{-9} esu and 1.49×10^{-9} esu, respectively. This d_{33} value is lower than that of polyester containing 3,4-dioxynitrostilbene group, which has near 3.59×10^{-8} esu [10]. The lower optical nonlinearity of the polymer **3** is probably due to the easier *cis-trans* isomerization of diazo linkage. Since the second

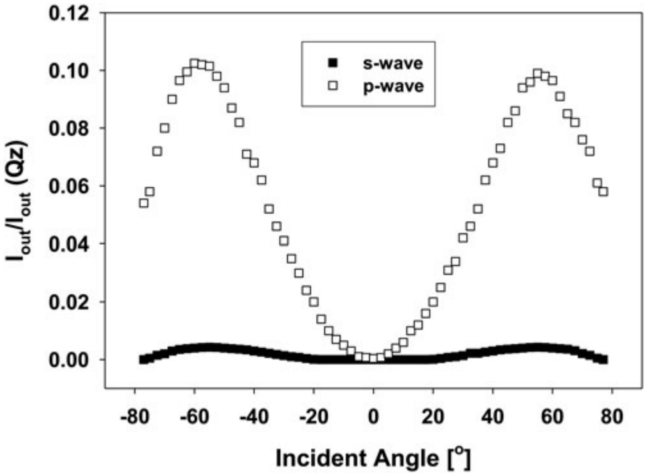


Figure 2. Angular dependence of SHG signal for a poled film of polymer **3**.

harmonic wavelength is at 532 nm, which is not in the absorptive region of the resulting polyester, there is 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. Figure 3 shows the dynamic thermal stability study of the NLO activity of a film of polymer **3**. To investigate the real time NLO decay of the SHG signal of the poled polymer film as a function of temperature, *in situ* SHG measurement was performed at a heating rate of 4°C/min from 30 to 180°C. The polymer film exhibits a thermal stability even at 4°C higher than T_g and no significant SHG decay is observed below 90°C. The SHG thermal stability of polymer **3** is lower than that of polyester containing 3,4-dioxynitrostilbene group, which may stem from the easier *cis-trans* isomerization of diazo linkage and/or lower T_g value. In general, main-chain NLO polymers have good thermal stability of dipole alignments, and side-chain NLO polymer systems have good solubility. The SHG thermal stability of polymer **3** up to 90°C 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 made new NLO polyester with stable dipole alignment and good solubility.

Table 1. Nonlinear optical properties of polymer **3**

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	d_{31}[b] (esu)	Film thickness[c] (μm)	n
3	385	4.42×10^{-9}	1.49×10^{-9}	0.50	1.724

[a] Polymer film after poling.
[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [13].
[c] Film thickness was determined by the optical transmission technique [12].

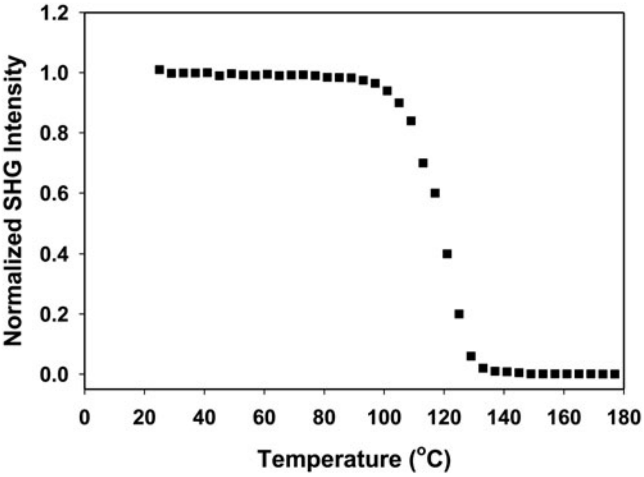


Figure 3. Normalized SHG signal of polymer **3** as a function of temperature at a heating rate of 4°C/min.

Conclusions

A novel Y-type NLO polyester **3** with pendant NLO chromophores as parts of the polymer backbones was prepared and characterized. This Y-type polymer **3** is soluble in common organic solvents and shows a thermal stability up to 280°C with T_g value around 86°C. The SHG coefficient (d_{33}) of corona-poled polymer film is 4.42×10^{-9} esu. Polymer **3** exhibits SHG stability even at 4°C higher than T_g and no significant SHG decay is observed below 90°C. This enhanced thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophores, which constitute parts of the polymer main chains.

Acknowledgment

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