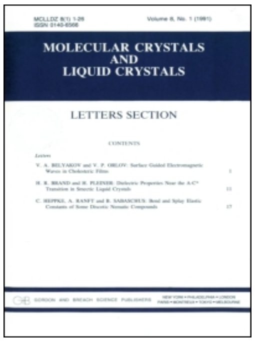

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Synthesis and nonlinear optical properties of novel polyester containing nitrothiazolylazoresorcinoxy group

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ABSTRACT

Novel Y-type polyester **4** containing 4-(5-nitro-2-thiazolylazo)resorcinoxy group as nonlinear optical (NLO) chromophore, which constitutes parts of the polymer backbone, was prepared and characterized. Polyester **4** is soluble in common organic solvents such as *N,N*-dimethylformamide and acetone. Polyester **4** shows a thermal stability up to 240°C from thermogravimetric analysis with glass-transition temperature obtained from differential scanning calorimetry of near 106°C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer film at the 1064 nm fundamental wavelength is 8.43×10^{-9} esu. The poled polymer film exhibits an enhanced thermal stability of dipole alignment and there was no negligible decay of the SHG signal over hundreds of hours at 70°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

In the past decade, the researches have focused on the design and syntheses of nonlinear optical (NLO) polymers because of their potential applications in the field of electro-optic devices including ultrafast optical switches and high-density optical data storage media [1–7]. Compared with traditional inorganic materials, NLO polymers have many advantages such as larger nonlinear optical coefficients, light weight, low cost, ultrafast response, wide response wave band, high optical damage threshold, and good processability to form optical devices. In the developments of NLO polymers, stabilization of electrically induced dipole alignment is one of important considerations. Several approaches have been proposed to minimize the randomization, namely the use cross-linking method [8–11] and utilization of high glass-transition temperature (T_g) polyimides [12–14]. In general, 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 films. Side-chain NLO polymers have good solubility, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we prepared novel NLO polyesters containing dioxybenzylidenecyanoacetate [15], nitrophenylazoresorcinol [16], nitrophenylazocatechol [17], and dioxynitrobenzylidenemalononitrile [18], which showed enhanced thermal stability. In this work reported here, we prepared a new polyester containing 4-(5-nitro-2-

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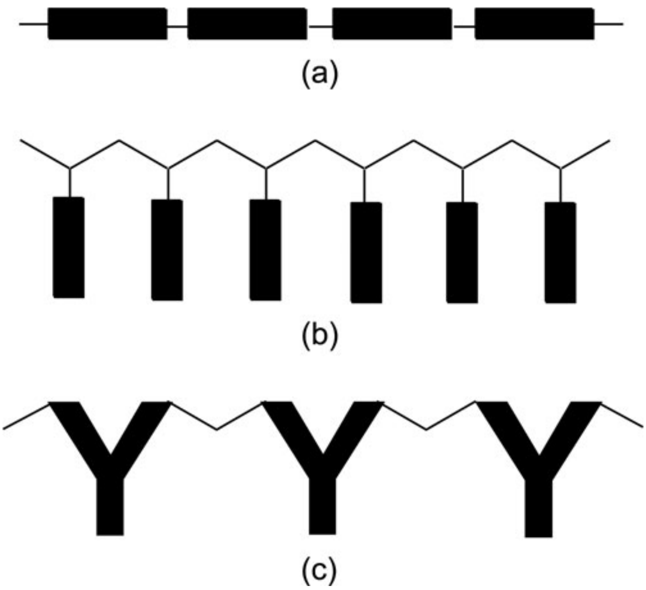


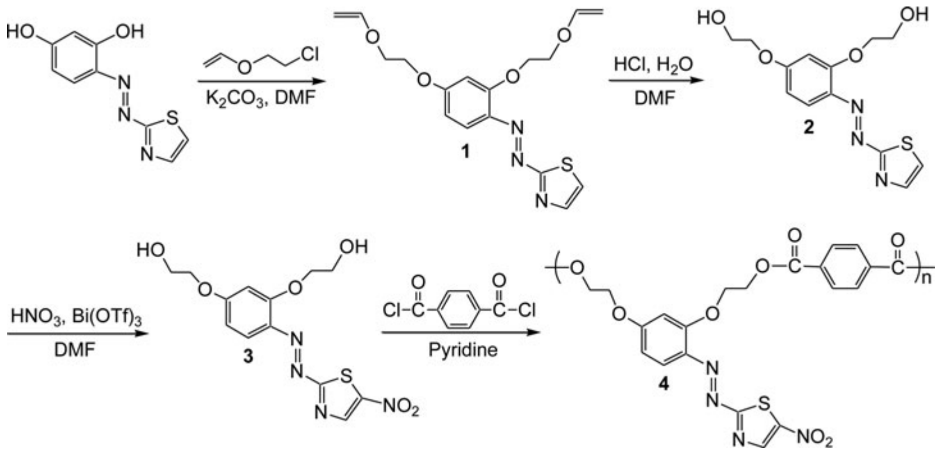
Figure 1. Main chain NLO polymers (a), Side chain NLO polymers (b), and Y-type NLO polymers (c).

thiazolylazo)resorcinoxy groups as NLO chromophores. We selected the latter as NLO chromophores because they were expected to have high optical nonlinearities due to a double conjugation and nitro group. Furthermore, these 4-(5-nitro-2-thiazolylazo)resorcinoxy 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 backbone. This Y-type NLO polymer is expected to have the merits of both main-chain (Fig. 1a) and side-chain (Fig. 1b) NLO polymers, namely stable dipole alignment and good solubility. After confirming the structure of the resulting polymer, we investigated its properties such as second harmonic generation activity and relaxation of dipole alignment. We now report the results of the initial phase of the work.

Experimental

Materials

Synthetic method of polymer **4** was as follows. Terephthaloyl chloride (2.03 g, 10 mmol) and diol **3** (3.54 g, 10 mmol) were dissolved in 25 mL of anhydrous pyridine under nitrogen. The resulting solution was refluxed in an oil bath kept at 90°C under a nitrogen atmosphere. After heating 20 h with stirring the resulting polymerization solution was poured into 400 mL of methanol. The precipitated polymer was collected and re-precipitated from DMSO into methanol. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum, yielding 4.36 g (90% yield) of polymer **4**. Inherent viscosity (η_{inh})=0.30 dL g^{-1} (c, 0.5 g dL^{-1} in DMSO at 25°C). ^{1}H NMR (DMSO-d_6) δ 4.23–4.76 (m, 8H, 2 $-CH_2-O-$, 2 Ph$-O-CH_2-$), 6.68–6.79 (m, 1H, aromatic), 6.82–6.97 (m, 1H, aromatic), 7.67–7.78 (m, 1H, aromatic), 7.86–8.18 (m, 5H, aromatic). IR (KBr) 3084 (w,$=$C$-$H), 2930 (m, C$-$H), 1721 (vs, C$=$O), 1597 (s, N$=$N), 1520, 1345 (s, N$=$O), 1190 (m, N$=$N) cm^{-1}.



Scheme 1. Synthetic scheme and structure of polyester **4**.

Anal. Calcd for $(C_{21}H_{16}N_4O_8S)_n$: C, 52.07; H, 3.33; N, 11.56; S, 6.62. Found: C, 52.15; H, 3.39; N, 11.65; S, 6.56.

Measurements

IR, ^{1}H NMR, and UV-visible spectra were obtained with a Varian FT IR-1000 IR spectrophotometer, Varian VNMRS 500MHz NMR spectrometer, and SECOMAM Model UVIKON XS 99-90289 spectrophotometer, respectively. T_g values were measured on a TA 2920 differential scanning calorimeter (DSC) in a nitrogen atmosphere. TA Q50 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 alignment of the NLO chromophore of the polymer was carried out by corona poling method. The refractive index of the polymer sample was measured by the optical transmission technique [19]. The transmittance of thin film gives information on the thickness, refractive index and extinction coefficient of the film. Thus, we can determine these parameters by analyzing the transmittance. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [20].

Results and discussion

Synthesis and characterization of polymer

The synthetic route for polyester **4** is presented in Scheme 1. Monomer **3** was condensed with terephthaloyl chloride in a dry DMF solvent to yield Y-type polyester **4** containing nitrothiazolylazoresorcinoxy groups as NLO chromophores. The synthetic route for polymer **4** is presented in Scheme 1. The resulting polymer was purified by Soxhlet extraction for two days with methanol as a solvent. The polymerization yield was 90%. The chemical structure of the resulting polymer was confirmed by ^{1}H NMR, IR spectra, and elemental analysis. The ^{1}H NMR and IR spectra of the polymer **4** are shown in Fig. 2 and Fig. 3, respectively. Elemental analysis results fit the polymer structure. ^{1}H NMR spectrum of the polymer showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The IR spectrum of polymer **4** shows strong carbonyl peaks near 1721 cm^{-1} indicating the presence of ester bond. The spectrum also shows strong absorption peak

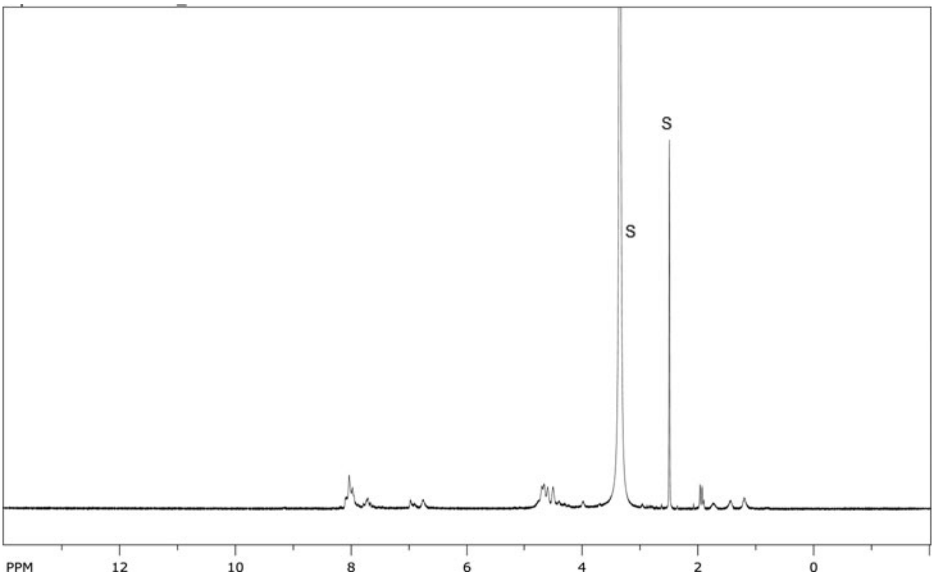


Figure 2. ^{1}H NMR spectrum of polymer **4** taken in DMSO-d_6 at room temperature.

near 1597 cm^{-1} due to azo group and absorptions at 1520 and 1345 cm^{-1} due to nitro group indicating the presence of nitrothiazole unit. These results are consistent with the proposed polymer structure, indicating that the NLO chromophore remained intact during the polymerization. The polymer **4** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity is in the range 0.30–0.31 dL g^{-1}. The striking feature of this polymerization system is that it gives unprecedented Y-type NLO polymer, in which the pendant NLO chromophores are parts of the polymer backbone. This Y-type NLO polymer is expected to have the advantages of both main-chain and side-chain NLO polymers. Thus, we obtained a new type of NLO polyester with side-chain and main-chain characteristics. Having obtained the well-defined Y-type polyester **4**, we investigated its properties.

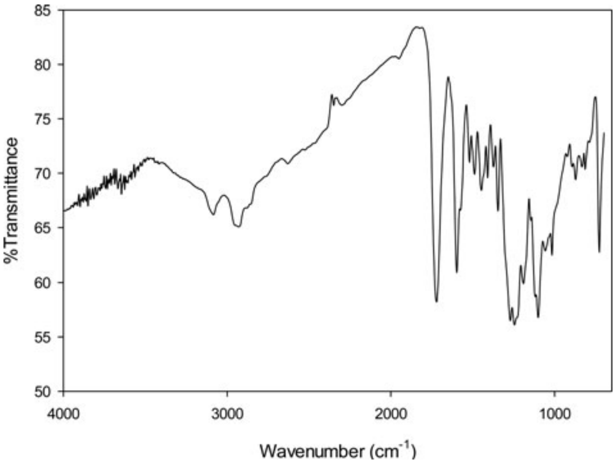


Figure 3. FT IR spectrum of polymer **4** taken at room temperature.

Table 1. Nonlinear optical properties of polyester **4**.

Polymer	d_{33}[a] (esu)	d_{31}[a] (esu)	film thickness[b] (μm)	*n*	d_{33}/d_{31}
4	8.43×10^{-9}	2.74×10^{-9}	0.51	1.554	3.08

[a] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [20].
[b] Film thickness was determined by the optical transmission technique [19].

Thermal properties of polymer

The thermal behavior of the polymer was investigated using TGA and DSC to determine the thermal degradation pattern and glass transition temperature. Polymer **4** has a thermal stability up to 240°C according to its TGA thermogram. The T_g value of the polymer **4** measured using DSC is near 106°C. This T_g value is lower than that of the polyester containing nitrophenylazoresorcinoxy group, which is near 116°C [16].

Nonlinear optical properties of polymer

The NLO properties of polymers were studied using the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer films were 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 films were cooled to room temperature in the presence of the electric field. Finally, the electric field was removed. The poling was confirmed from UV-visible spectra. After electric poling, the dipole moments of the NLO chromophores were aligned and UV-visible absorption of polyester **4** exhibits a decrease in absorption due to birefringence. SHG measurements were performed at a fundamental wavelength of 1064 nm with a mode locked Nd-YAG laser. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. The SHG values were compared with those obtained from a Y-cut quartz plate (d_{11} for quartz was 0.79×10^{-9} esu). To calculate the d_{31} and d_{33} values, both *s*-polarized and *p*-polarized IR laser were directed at the samples. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure [20]. The NLO properties of polyester **4** are summarized in Table 1. The values of d_{31} and d_{33} for polyester **4** are 2.74×10^{-9} and 8.43×10^{-9} esu, respectively. This d_{33} value is higher than that of the polyester containing nitrophenylazoresorcinoxy groups, which is near 4.63×10^{-9} esu [16].

To evaluate the high-temperature stability of the polymer, we studied the temporal stability of the SHG signal. Figure 4 shows the dynamic thermal stability study of the NLO activity of a film of polymer **4**. 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 200°C. The polymer film exhibits a thermal stability even at 4°C higher than T_g, and no significant SHG decay is observed below 110°C for polyester **4**. The polymer film also shows a temporal stability as a function of baking time at 70°C, in which there was no negligible decay of the SHG signal over hundreds of hours. In general, side-chain NLO polymers lose the thermal stability of dipole alignment below T_g. Stabilization of dipole alignment is a characteristic of main-chain NLO polymers. The enhanced thermal stability of second harmonic generation of polyester **4** is due to the stabilization of dipole alignment of NLO chromophores, which stems from the partial main-chain character of the

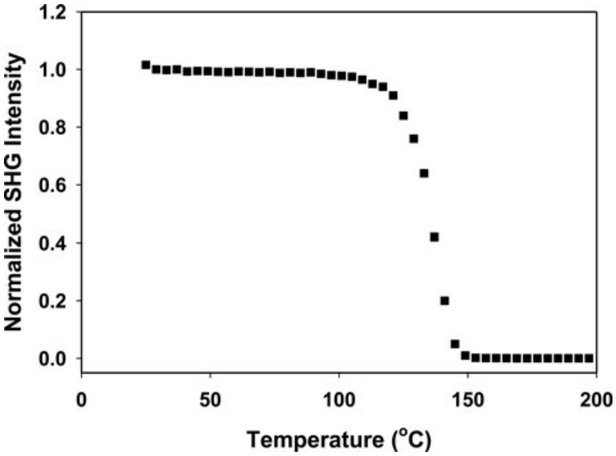


Figure 4. Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 4°C/min.

polymer structure. Thus, we obtained a new Y-type NLO polyester having the advantages of both main-chain and side-chain NLO polymers, namely stable of dipole alignment and good solubility.

Conclusions

New Y-type polyester **4** with pendant NLO chromophores as parts of the polymer main chain was synthesized. This Y-type NLO polyester **4** is soluble in common organic solvents and displays a thermal stability up to 240°C with T_g values near 106°C. The SHG coefficient (d_{33}) of corona-poled polymer film is 8.43 $\times$ 10^{-9} esu. Polyester **4** exhibits SHG stability up to 110°C and there was no negligible decay of the SHG signal over hundreds of hours at 70°C. This enhanced thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophores, which are parts of the polymer backbone.

Acknowledgments

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