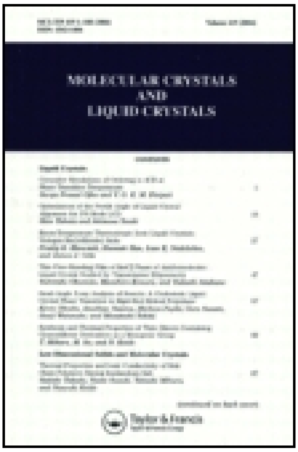

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Synthesis and Properties of Novel Y-type Nonlinear Optical Polyester Containing Tricyanovinylthiazole

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A novel Y-type polyester **4** *containing 5-methyl-4-{5-(1,2,2-tricyanovinyl)-2-thiazolylazo}resorcinoxy groups as nonlinear optical (NLO) chromophores was prepared and characterized. Polyester* **4** *is soluble in common organic solvents such as acetone and N,N-dimethylformamide. It shows a thermal stability up to 250°C from thermogravimetric analysis thermogram with a glass-transition temperature* (T_g) *obtained from differential scanning calorimetry thermogram of around 94°C. The second harmonic generation (SHG) coefficient* (d_{33}) *of poled polymer film at 1064 nm fundamental wavelength is* 8.12×10^{-9} *esu. The dipole alignment exhibits a thermal stability even at 6°C higher than* T_g *and there is no significant SHG decay below 100°C due to the partial main-chain character of the polymer structure, which is acceptable for nonlinear optical device applications.*

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

Introduction

Organic nonlinear optical (NLO) materials have been extensively studied over the past decade because of their potential applications in the field of electro-optic devices [1–4]. Among the organic materials the NLO polymers are considered candidate materials, mainly because they offer many advantages such as light weight, chemical resistance, and good processability to form optical devices. One of the current tasks is to design novel NLO polymers having optimized properties. In the developments of NLO polymers, stabilization of electrically induced dipole alignment is one of important considerations. Two approaches have been proposed to minimize the randomization, that is to use cross-linking method [5,6] and to utilize high T_g polymers such as polyimides [7]. 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 reported novel NLO polyesters

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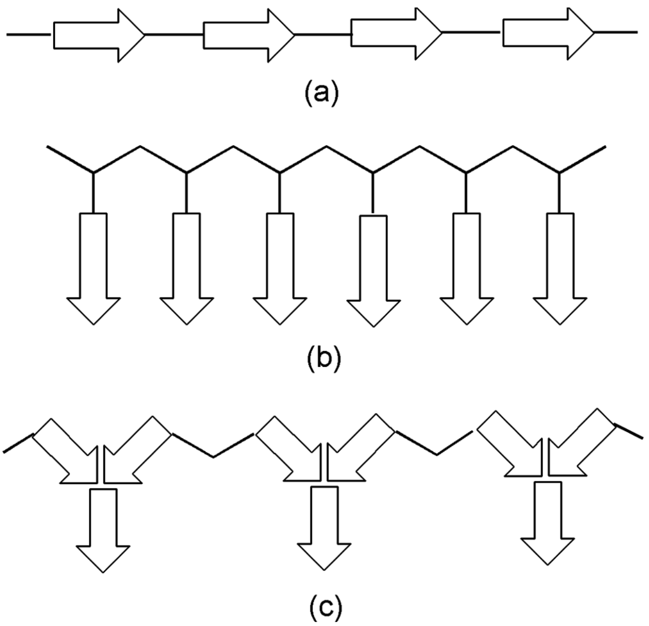


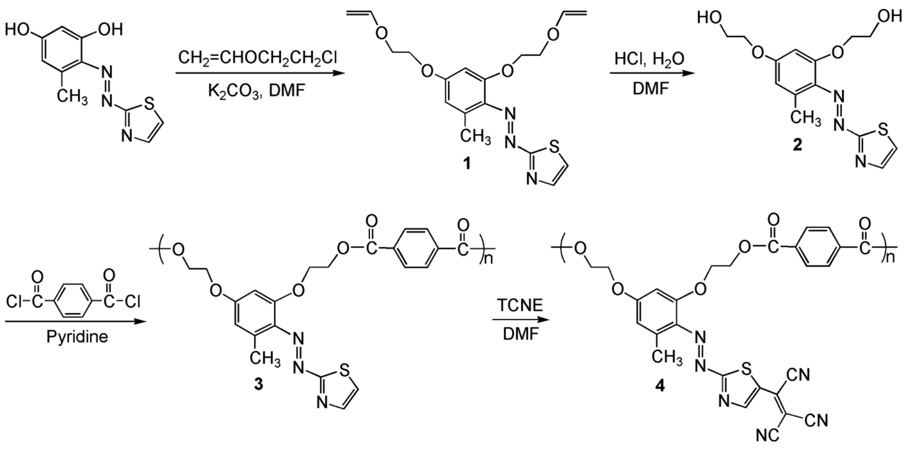
Figure 1. Main chain NLO polymers (a), Side chain NLO polymers (b), and Y-type NLO polymers (c).

containing dioxynitrostilbene [8] or dioxybenzylidenemalononitrile [9], which showed enhanced thermal stability of dipole alignments. In this work reported here, we have prepared a novel polyester containing 5-methyl-4-{5-(1,2,2-tricyanovinyl)-2-thiazolylazo}resorcinoxy groups as NLO chromophores. We selected the latter because they are expected to have a large NLO activity. Furthermore, these groups can be incorporated into novel Y-type NLO polyesters (see Fig. 1c). The structure of NLO chromophores and these Y-type NLO polyesters have not yet been described in the literature. Thus we formulated a new type of NLO polyester, in which the pendant NLO chromophores are components 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 thermal and nonlinear optical properties. We now report the results of the initial phase of the work.

Experimental

Materials

Polymer **4** was prepared according to the Scheme 1. The polymer was re-precipitated from DMSO into methanol and further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum, yielding 4.94 g (88% yield) of polymer **4**. Inherent viscosity (η_{inh}) = 0.30 dL/g (c, 0.5 g/dL in DMSO at 25°C). ^{1}H NMR (DMSO-d_6) δ (ppm): 2.52 (s, 3H, -CH_3), 3.93–4.08 (m, 4H, 2 -CH_2-O-), 4.33–4.76 (m, 4H, 2 Ph-O-CH_2-), 7.15–7.43 (s, 4H, aromatic), 7.62–7.85 (m, 1H, aromatic),



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

8.16–8.28 (m, 1H, aromatic), 8.93–9.12 (d, 1H, aromatic). IR (KBr disc) (cm^{-1}): 3085 (w, =C-H), 2956 (m, C-H), 2220 (s, CN), 1719 (vs, C=O), 1590 (s, C=C). Anal. Calcd for $(C_{27}H_{26}N_6O_6S)_n$: C, 57.64; H, 4.66; N, 14.94; S, 5.70. Found: C, 57.73; H, 4.73; N, 14.86; S, 5.78.

Measurements

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-3100S spectrophotometer, respectively. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. T_g values were measured using a TA 2920 differential scanning calorimeter DSC in a nitrogen atmosphere. A TA Q50 thermogravimetric analyzer with a heating rate of 10°C min^{-1} 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; tetrahydrofuran (THF) solvent). The alignment of the NLO chromophore of the polymers was carried out using a corona poling method. The refractive index of the sample was measured using the optical transmission technique [10]. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [11].

Results and Discussion

Synthesis and Characterization of Polymer 4

Polyester **3** was synthesized through the reaction of monomer **2** containing NLO chromophore with stoichiometric amounts of of terephthaloyl chloride in pyridine. Polymer **3** was reacted with tetracyanoethylene in anhydrous DMF to yield polyester **4** containing 5-methyl-4-{5-(1,2,2-tricyanovinyl)-2-thiazolylazo}resorcinoxy groups as NLO chromophores. The synthetic route for polymer **4** is presented in Scheme 1. The chemical structure of the polymer was identified by ^{1}H NMR, IR spectra, and elemental analysis. ^{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 signal at 2.52 ppm is assigned to the methyl proton of dioxybenzene ring. The signal at 3.93–4.76 ppm is due to the ethylene protons attached to oxygen. The aromatic protons are shown in the range 7.15–9.12 ppm. The IR spectrum of the polymer **4** shows a strong carbonyl peaks near 1719 cm^{-1} indicating the presence of ester bond. The spectrum also shows strong absorption peak near 2220 cm^{-1} indicating the presence of nitrile group. These results are consistent with the proposed structure, indicating that the tricyanovinyl groups are attached well to the thiazole rings. The molecular weights were determined using GPC with polystyrene as the standard and THF as the eluent. The number-average molecular weight (M_n) of the polymer **4** is 17200 ($M_w/M_n = 1.94$). The inherent viscosity value is 0.30 dL/g. Polymer **4** shows strong absorption near 399 nm due to the 5-methyl-4-{5-(1,2,2-tricyanovinyl)-2-thiazolylazo}resorcinoxy group NLO chromophore. The structural feature of this polymer is that it has pendant NLO chromophores, which are parts of the polymer main chain. Thus the resulting polymer **4** is mid type of side-chain and main-chain NLO polymers, and is expected to have both of their merits. The polymer **4** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. Having obtained the well defined polymer **4**, we investigated its properties.

Thermal Properties of Polymer

The thermal behavior of the polymer was investigated by TGA and DSC to determine the thermal degradation pattern and T_g. Polymer **4** showed a thermal stability up to 250°C according to its TGA thermogram. The degradation temperature (T_d) of polymer **4** is near 297°C. The T_g value of the polymer **4** measured by DSC was around 94°C. This T_g value is similar with those of the Y-type polyesters containing dioxynitrostilbene, which are in the range 90–95°C [8], but is higher than those with dioxybenzylidenemalononitrile, which are near 83°C [9].

Nonlinear Optical Properties of Polymer

Spin-coated polymer films were corona-poled to induce noncentrosymmetric polar order. As the temperature was raised gradually to 100°C, a corona voltage of 6.5 kV was applied and this temperature was maintained for 30 min. 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 polymer **4** exhibits 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. NLO properties of polymer **4** are summarized in Table 1. Figure 2 shows the angular dependence of SHG signal in a poled polymer **4**. 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 Pascal fitting program according to the literature procedure [11]. The measured values of d_{33} and d_{31} for polymer **4** were 8.12×10^{-9} and 2.56×10^{-9} esu, respectively. These values are higher than those of the polyesters containing dioxynitrostilbene [8] or dioxybenzylidenemalononitrile [9].

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

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	d_{31}[b] (esu)	Film thickness[c] (μm)	*n*
4	399	8.12×10^{-9}	2.56×10^{-9}	0.51	1.532

[a] Polymer film after poling.

[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [11].

[c] Film thickness was determined by the optical transmission technique [10].

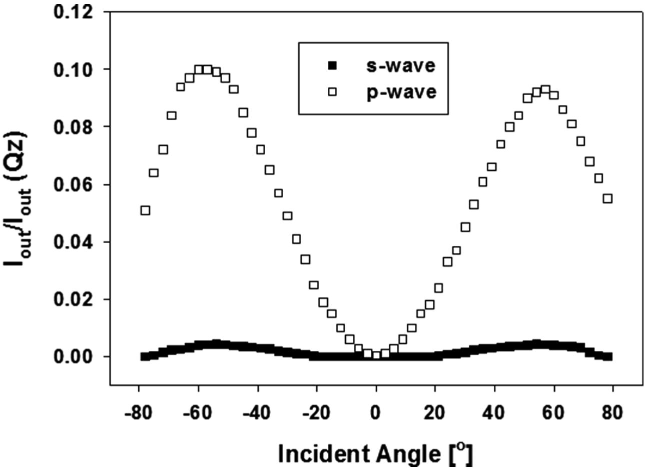


Figure 2. Angular dependence of SHG signal for a poled film of polymer **4**.

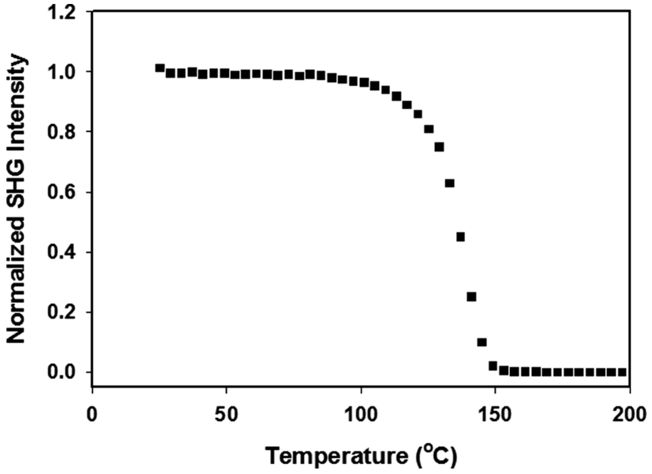


Figure 3. Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 3.5°C/min.

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 **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 measurements were performed at a heating rate of 3.5°C/min from 25°C to 200°C. The polymer film exhibits a greater thermal stability even at 6°C higher than T_g, and no significant SHG decay is observed below 100°C. The enhanced SHG thermal stability of polymer **4** is due to the stabilization of dipole alignment of NLO chromophore, which stems from the partial main-chain character of the polymer structure.

Conclusions

We synthesized novel Y-type polyester **4** with pendant NLO chromophores, which are parts of the polymer backbone. This Y-type NLO polyurethane is soluble in common organic solvents and shows a thermal stability up to 250°C from TGA thermogram with T_g value near 94°C. The SHG coefficient (d_{33}) of corona-poled polymer film is 8.12×10^{-9} esu. The dipole alignment exhibits a thermal stability even at 6°C higher than T_g, and no SHG decay is observed below 100°C. This high thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophores, which constitute parts of the polymer backbone.

Acknowledgment

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