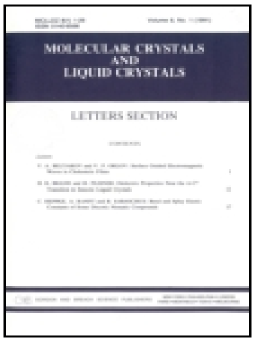

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Synthesis and Nonlinear Optical Properties of Novel Polyester Containing Nitrophenylazonitroresorcinoxy Group

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*A new X-type polyester (**4**) containing nitrophenylazonitroresorcinoxy groups as NLO chromophores, which are components of the polymer backbone was prepared. Polyester **4** is soluble in common organic solvents such as* N,N-*dimethylformamide 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 120°C. The second harmonic generation (SHG) coefficient* (d_{33}) *of poled polymer films at the 1064 nm fundamental wavelength is around* 5.08×10^{-9} *esu. The dipole alignment exhibits a thermal stability even at 5°C higher than* T_g, *and no SHG decay was observed below 125°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

Recently nonlinear optical (NLO) materials are extensively studied because of their potential applications in the field of electro-optic devices, including high speed optical modulators and ultrafast optical switches [1–4]. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of important criteria; 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 such as polyimides [6]. A potential NLO polymer must contain highly polarizable conjugated electronic systems and has to be mechanically very strong and thermally stable with high T_g. NLO polyesters containing azobenzene mesogens in the main chain exhibit high thermal and temporal stabilities [7-8]. Polyesters containing cyanophenylazoaniline moiety in the side chain show good temporal stability of second-order nonlinearity [9]. Recently we reported novel NLO polyesters containing nitrophenylazoresorcinol [10] and nitrophenylazocatechol [11], which showed enhanced thermal stability of dipole alignments. In this work reported here, we prepared new polyester

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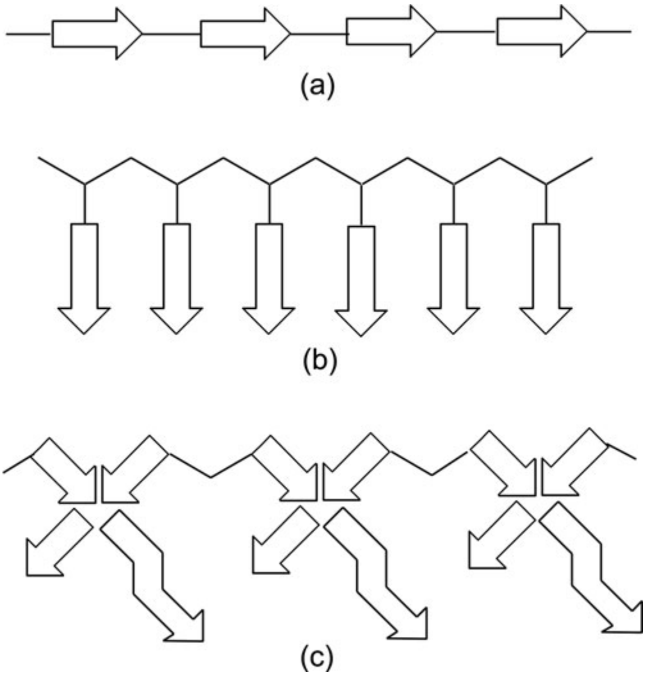


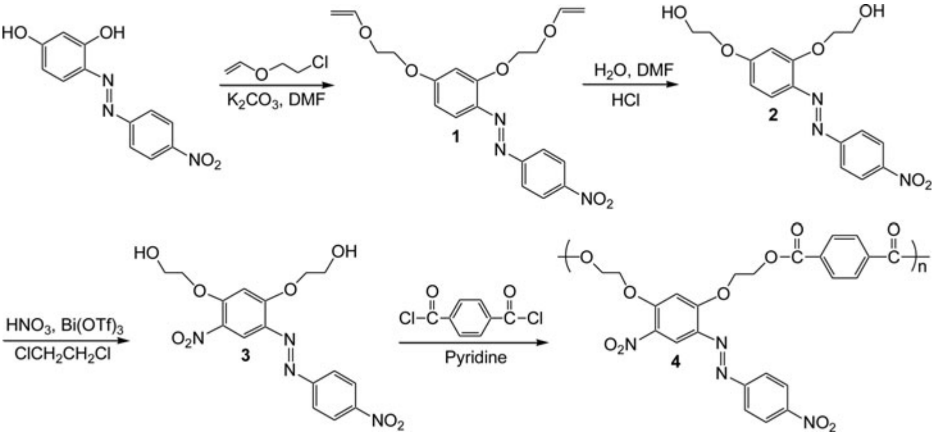
Figure 1. Main chain NLO polymers (a), Side chain NLO polymers (b), and X-type NLO polymers (c).

containing nitrophenylazonitroresorcinoxy group as NLO chromophore. We selected the latter as NLO chromophore because it was expected to have high optical nonlinearities and thermal stability. Furthermore, this nitrophenylazonitroresorcinoxy group constitutes novel X-type NLO polyesters (Fig. 1c), and this X-type NLO polyester has not yet been reported in the literature. The X-type NLO polymer is expected to exhibit higher NLO activity and thermal stability due to a quadruple conjugation and nitro group than Y-type NLO polymer of double conjugation [10]. Thus, we synthesized a new type of NLO polyester, in which the pendant NLO chromophores are parts of the polymer backbone. This X-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 thermal stability, 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** is summarized in Scheme 1. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum, yielding 4.70 g (90% yield) of polymer **4**. 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 4.52-4.80 (m, 8H, 2 $-O-CH_2-CH_2-O-$),



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

6.76-7.12 (d, 1H, aromatic), 7.78-8.45 (m, 9H, aromatic). IR (KBr) 3084 (w, = C−H), 2935 (m, C−H), 1723 (vs, C=O), 1520 (s, N=O), 1341 (vs, N=O), 1420 (m, N = N), 1182 (vs, N = N) cm^{-1}. Anal. Calcd for $(C_{24}H_{18}N_4O_{10})_n$: C, 55.18; H, 3.47; N, 10.73. Found: C, 55.28; H, 3.56; N, 10.68.

Measurements

Infrared (IR) spectra were obtained with a Varian FT IR-1000 IR spectrophotometer. ^{1}H NMR spectra were obtained with a Varian VNMRS 500MHz 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 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 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 4

Monomer **3** was prepared by the reaction of compound **2** with nitric acid and bismuth (III) trifluoromethanesulfonate in anhydrous 1,2-dichloroethane according to a literature procedure [14]. Polyester **4** was synthesized through the reaction of monomer **3** containing NLO chromophore with stoichiometric amount of terephthaloyl chloride in pyridine. The synthetic route for polymer **4** is presented in Scheme 1. The chemical structure of the resulting polymer was confirmed by ^{1}H NMR, IR spectra, and elemental analysis. 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 peak near 1723 cm^{-1} indicating the presence of ester bond. The spectrum also shows strong absorption peaks near absorptions at 1520 and 1341 cm^{-1} due to nitro group and absorptions at 1420 and 1182 cm^{-1} due to azo group indicating the presence of nitroazobenzene unit. These results are consistent with the proposed polymer structure, indicating that the NLO chromophore remained intact during the polymerization. The molecular weights were determined by GPC using polystyrene as the standard and THF as an eluent. The number average molecular weight (M_n) of the polymer **4,** determined by GPC, was 16,300 g mol^{-1} ($M_w/M_n = 1.94$). 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 0.30-0.32 dL g^{-1}. Polymer **4** shows strong absorption near 399 nm due to the NLO chromophore nitrophenylazonitroresorcinoxy group. The striking feature of this polymerization system is that it gives unprecedented X-type NLO polymer, in which the pendant NLO chromophores are parts of the polymer backbone. This X-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 X-type polyester **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 glass transition temperature. Polymer **4** shows a thermal stability up to 280°C from its TGA thermogram. This thermal stability is much higher than that of the Y-type polyester containing nitrophenylazoresorcinol, which is near 240°C [10]. T_g value of the polymer **4** measured by DSC is around 120°C. This T_g value is higher than that of the Y-type polyester containing nitrophenylazoresorcinoxy group [10], which is probably due to a nitro group and a quadruple conjugation.

Nonlinear Optical Properties of Polymer

The NLO properties of polymer were studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer film was corona-poled. As the temperature was raised to 120°C, 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 by UV-visible spectrum. After electric poling, the dipole moments of the NLO chromophores were aligned and the UV-visible absorption of polymer **4** exhibits a slight blue shift and a decrease in absorption due to birefringence. The estimated order parameter value Φ is equal to 0.32 for polymer **4** ($\Phi = 1\text{-}A_1/A_0$, where $A_0 = 1.0184$ and $A_1 = 0.6922$ are the absorbances of the polymer film before and after poling, respectively). SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. Nonlinear optical properties of polymer **4** are summarized in Table 1. 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 **4**. The SHG values were compared with those obtained from a Y-cut quartz plate (d_{11} for quartz was 0.79×10^{-9} esu). 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]. The measured values of d_{33} and d_{31} for polymer **4** are 5.08×10^{-9} esu and 1.72×10^{-9}

Table 1. Nonlinear Optical Properties of Polymer **4**

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	Φ[c]	d_{31}[b] (esu)	film thickness[d] (μm)	n
4	397	5.08×10^{-9}	0.32	1.72×10^{-9}	0.50	1.725

[a] Polymer film after poling.

[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [13].

[c] Order parameter $\Phi = 1\text{-}A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after corona poling, respectively.

[d] Film thickness was determined by the optical transmission technique [12].

esu, respectively. This d_{33} value is higher than that of the Y-type polyester, which is near 4.63×10^{-9} esu [10].

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 4°C/min from 25 to 200°C. The polymer film exhibits a greater thermal stability even at 5°C higher than T_g and no significant SHG decay is observed below 125°C. This SHG thermal stability is higher than that of the Y-type polyester, which is probably due to a nitro group and a quadruple conjugation. 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 polymer systems have good solubility and high loading level of NLO chromophores, but they often suffer from poor stability of dipole alignments at high temperatures. The high 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. Thus, we obtained new NLO polyester having the merits of

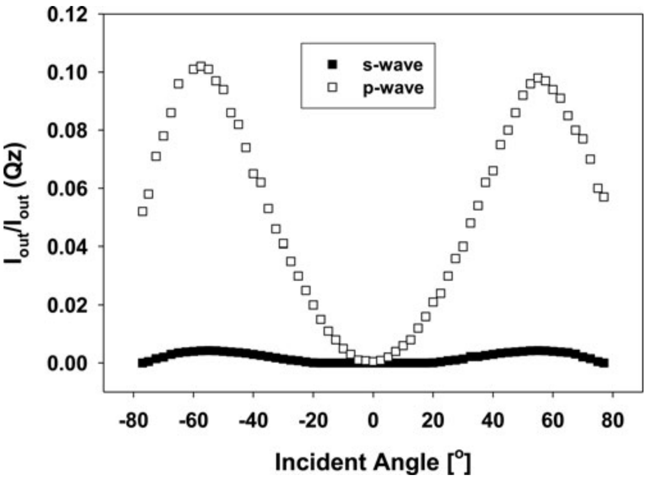


Figure 2. Angular dependence of SHG signal for a poled film of polymer **4**.

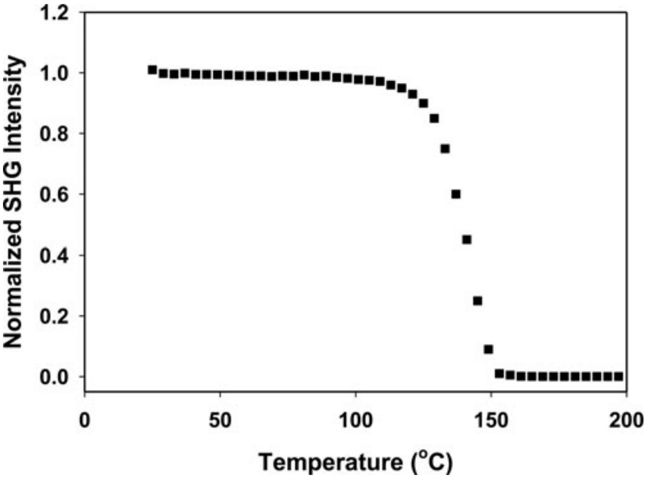


Figure 3. Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 4°C/min.

both main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility.

Conclusions

A novel X-type NLO polyester **4** with pendant NLO chromophores as parts of the polymer backbone was prepared and characterized. This X-type polymer **4** is soluble in common organic solvents and shows a thermal stability up to 280°C with T_g value around 120°C. The SHG coefficient (d_{33}) of corona-poled polymer film was 5.08×10^{-9} esu. This polymer exhibits SHG stability even at 5°C higher than T_g and no significant SHG decay is observed below 125°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 main chain.

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