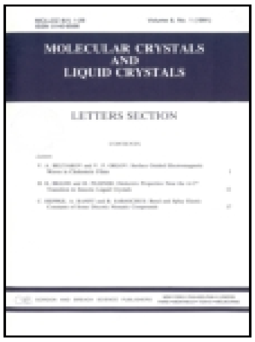

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Synthesis and Properties of Novel Nonlinear Optical Polyester Containing Cyanovinylnitroresorcinoxy Group

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*Novel X-type polyester **5** containing 4-(2'-carbomethoxy-2'-cyano)vinyl-6-nitroresorcinoxy group as nonlinear optical (NLO) chromophore, which constitutes parts of the polymer backbone, was prepared and characterized. Polyester **5** is soluble in common organic solvents such as* N,N*-dimethylformamide and acetone. Polyester **5** shows a thermal stability up to 280°C from thermogravimetric analysis with glass-transition temperature obtained from differential scanning calorimetry of near 116°C. The second harmonic generation (SHG) coefficient* (d_{33}) *of poled polymer film at the 1064 nm fundamental wavelength is* 4.25×10^{-9} *esu. The dipole alignment exhibits a thermal stability even at 4°C higher than glass-transition temperature* (T_g)*, and no significant SHG decay is observed below 120°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

The design and synthesis of organic nonlinear optical (NLO) polymers are important because of their potential applications in the field of electro-optic devices including ultrafast optical switches and high-density optical data storage media [1–4]. 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 [5-6] and utilization of high glass-transition temperature (T_g) polymers such as polyimides [7-8]. 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 [9], nitrophenylazocatechol [10], and dioxynitrobenzylidenemalononitrile [11]. In this work reported here, we prepared a new polyester containing

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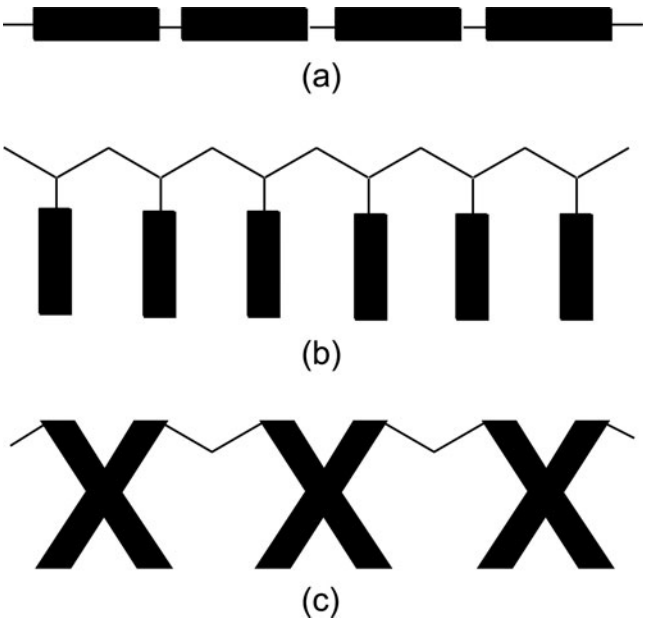


Figure 1. Main chain NLO polymers (a), Side chain NLO polymers (b), and X-type NLO polymers (c).

4-(2’-carbomethoxy-2’-cyano)vinyl-6-nitroresorcinoxy group as NLO chromophore. We selected the latter as NLO chromophore because it is expected to have high optical nonlinearities and high thermal stability. Furthermore these groups can be incorporated into novel X-type NLO polyesters (see Fig. 1c). The structure of NLO chromophore and this X-type NLO polyester has not yet been described in the literature. This X-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, and exhibit higher NLO activity and thermal stability due to a quadruple conjugation and nitro group than Y-type NLO polymer of double conjugation [9]. 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

Polymer **4** was prepared according to a procedure similar to that reported already [9]. Synthetic method of polymer **5** was as follows. Polymer **4** (4.37 g, 0.10 mol) was dissolved in 25 mL of DMF at room temperature and stirred for 30 min under a nitrogen atmosphere. A mixture of nitric acid (8 mL) and acetic acid (16 mL) were added drop-wise to the solution and stirred for 48 hr at 40°C under a nitrogen atmosphere. The reaction mixture was poured to 500 mL of ice water and the precipitated polymer was separated with suction. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum, yielding 4.24 g (88% yield) of polymer **5**. The degree of nitration estimated by ^{1}H NMR spectrum was about 86%. 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 3.95-3.99 (s, 3H, $-COOCH_3$), 4.42-4.56 (s, 4H, 2-PhOCH$_2$-), 4.58-4.76 (d, 4H, 2COOCH$_2$-), 6.85-6.98 (m, 1H, aromatic), 7.95-8.17 (s, 5H, aromatic), 8.36 (s, 1H, aromatic). IR (KBr) 3040 (w, = C$-$H), 2959 (m, C$-$H), 2224 (s, CN), 1722 (vs, C = O), 1609 (s, C = C), 1576, 1254 (s, N = O) cm^{-1}. Anal. Calcd for $(C_{23}H_{18}N_2O_{10})_n$: C, 57.26; H, 3.76; N, 5.81. Found: C, 57.35; H, 3.88; N, 5.72.

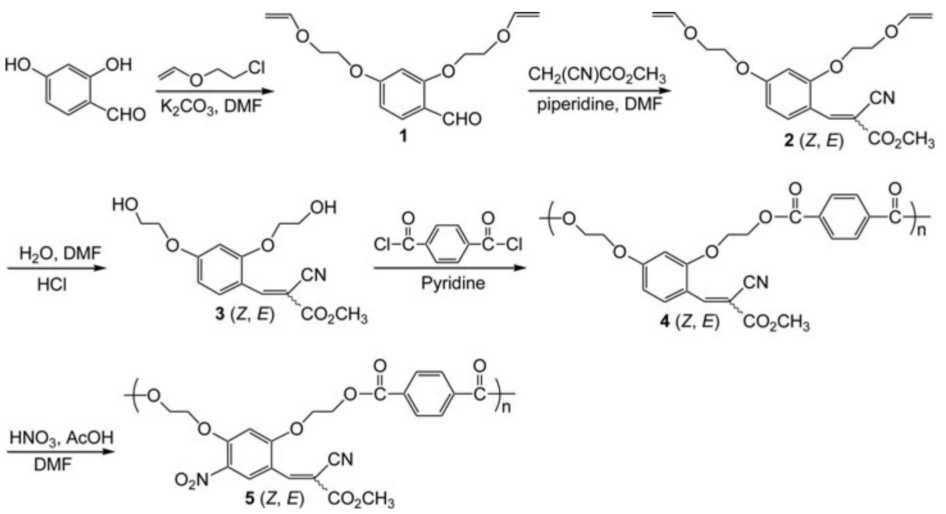
Measurements

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 number average molecular weight (M_n) and weight average molecular weight (M_w) of the polymer were estimated by gel permeation chromatography (GPC) (columns styragel HR5E4E; solvent THF). 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 [12]. 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 [13].

Results and Discussion

Synthesis and Characterization of Polymer

The synthetic route for polyester **5** is presented in Scheme 1. Diol **3** (*Z* and *E*) was condensed with terephthaloyl chloride (TPC) in a dry DMF solvent to yield polyester **4**. Polymer **4** was reacted with nitric acid and acetic acid in anhydrous DMF to yield X-type polyester **5** containing 4-(2'-carbomethoxy-2'-cyano)vinyl-6-nitroresorcinoxy groups as NLO chromophores. The degree of nitration was 86%. The chemical structure of the polymer was identified by ^{1}H NMR, IR spectra, and elemental analysis. ^{1}H NMR spectrum and elemental analysis results of the polymer are fit the polymer structure. The IR spectrum of polyester **5** shows strong carbonyl peaks near 1722 cm^{-1} indicating the presence of ester bond. The spectrum also shows strong absorption peak near 2224 cm^{-1} indicating the presence of nitrile group, and two strong absorption bands due to the nitro group in the NLO chromophore appeared near 1576 cm^{-1} and 1254 cm^{-1}. These results are consistent with the proposed structure. The molecular weights were determined by GPC with polystyrene as the standard and THF as the eluent. M_n of the polyester **5**, determined using GPC, is 15,600 (M_w/M_n = 1.92). The polyester **5** 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. Polyester **5** shows strong absorption near 367 nm due to the 4-(2'-carbomethoxy-2'-cyano)vinyl-6-nitroresorcinoxy group NLO chromophore. Thus, we obtained a new X-type NLO polyester with side-chain and main-chain characteristics. Having obtained the well defined polyester **5**, we investigated its properties.



Scheme 1. Synthetic scheme and structure of polyester **5**.

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 **5** shows a thermal stability up to 280°C from its TGA thermogram. T_g value of polymer **5** measured using DSC is near 116°C. This T_g value is higher than that of the Y-type polyester **4** [9], which is probably due to a nitro group and a quadruple conjugation.

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. Polyester **5** shows strong absorption near 367 nm before electric poling. After electric poling, the dipole moments of the NLO chromophores were aligned and UV-visible absorption of polyester **5** exhibits a slight blue shift showing absorption near 365 nm, and a decrease in absorption due to birefringence [14]. 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 [13]. The NLO properties of polyester **5** are summarized in Table 1. The values of d_{31} and d_{33} for polyester **5** are 1.51×10^{-9} and 4.25×10^{-9} esu, respectively. This d_{33} value is higher than that of the Y-type polyester **4**, which is 3.54×10^{-9} esu [9].

Table 1. Nonlinear Optical Properties of Polyester **5**

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	d_{31}[b] (esu)	film thickness[c] (μm)	n
5	365	4.25×10^{-9}	1.51×10^{-9}	0.52	1.58

[a] Polymer film after corona 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].

To evaluate the high-temperature stability of the polymer, we studied the temporal stability of the SHG signal. Figure 2 shows the dynamic thermal stability study of the NLO activity of a film of polyester **5**. 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 120°C for polyester **5**. This SHG thermal stability is higher than that of the Y-type polyester **4**, which is probably due to a nitro group and a quadruple conjugation. 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 **5** is due to the stabilization of dipole alignment of NLO chromophores, which stems from the partial main-chain character of the polymer structure. Thus, we obtained a new X-type NLO polyester having the advantages of both main-chain and side-chain NLO polymers, namely stable of dipole alignment and good solubility.

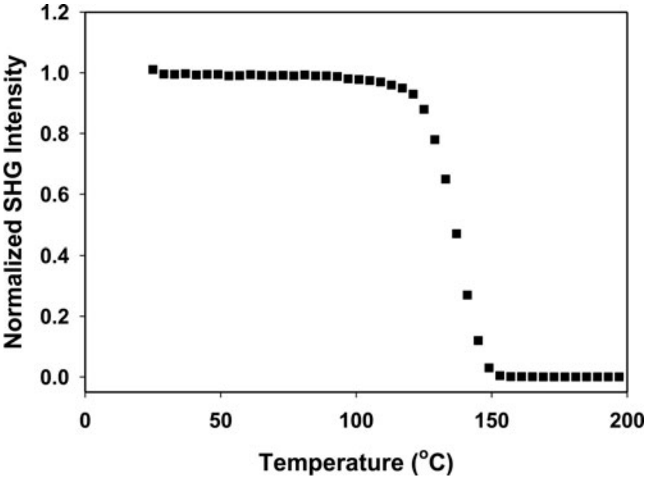


Figure 2. Normalized SHG signal of polyester **5** as a function of temperature at a heating rate of 4°C/min.

Conclusions

New X-type polyester **5** with pendant NLO chromophores as parts of the polymer main chain was synthesized. This X-type NLO polyester **5** is soluble in common organic solvents and displays a thermal stability up to 280°C with T_g values near 116°C. The SHG coefficient (d_{33}) of corona-poled polymer film is 4.25×10^{-9} esu. Polyester **5** exhibits SHG stability even at 4°C higher than T_g and no significant SHG decay is observed below 120°C. This high 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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