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Synthesis and properties of novel nonlinear optical polyester containing carbomethoxycyanovinylnitrocatecholic group

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ABSTRACT

A new X-type polyester **5** containing 4-(2'-carbomethoxy-2'-cyano)vinyl-5-nitrocatecholic groups as nonlinear optical (NLO) chromophores, which are parts of the polymer backbone, was prepared and studied its properties. Polyester **5** is soluble in common organic solvents such as acetone and dimethylsulfoxide. Polymer **5** shows a thermal stability up to 280°C from thermogravimetric analysis with glass-transition temperature (T_g) obtained from differential scanning calorimetry of near 110°C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer **5** film at the 1064 nm fundamental wavelength is 6.13 × 10⁻⁹ esu. The dipole alignment of polymer **5** exhibits a thermal stability up to T_g , and no significant SHG decay is observed below 110°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

Over the past few decades much effort have focused on nonlinear optical (NLO) materials with potential applications in electro-optic devices for optical information processing and optical data transmission [1-10]. Organic materials display higher optical nonlinearity and faster response time than their inorganic counterparts; among the organic materials, NLO polymers are receiving great attention of late, mainly because they offer many advantages such as mechanical endurance, light weight, low cost, chemical resistance, and ease of processing in terms of their use in electro-optic devices. A potential NLO polymer must contain highly polarizable conjugated electronic systems and has to be mechanically very strong and thermally stable with a high glass transition temperature (T_g). In the synthesis of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of important considerations. Several approaches to minimize the randomization have been developed, namely the use cross-linking method [11–14], utilization of high T_g polyimides [15–17], and host-guest polymers with spindle-type chromophores [18]. 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

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

prepared novel NLO polyesters containing dioxybenzylidenecyanoacetate [19], nitrophenylazoresorcinol [20], nitrophenylazocatechol [21], and dioxynitrobenzylidenemalononitrile [22] as NLO chromophores, which showed enhanced thermal stability of dipole alignment. In this work reported here, we prepared a new X-type polyester 5 containing 4-(2'-carbomethoxy-2'cyano)vinyl-5-nitrocatecholic groups as NLO chromophores. We selected the latter because they are expected to have higher optical nonlinearities due to nitro group and double conjugation. Furthermore these 4-(2'-carbomethoxy-2'-cyano)vinyl-5-nitrocatecholic groups can be incorporated into novel X-type NLO polyesters (see Fig. 1c). The structure of NLO chromophores and these X-type NLO polyesters have not yet been described in the literature. Thus, we synthesized a new type of NLO polyester 5, 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, namely stable dipole alignment and good solubility. After confirming the structure of the resulting polymer 5, we investigated its properties such as SHG 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 [19]. 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. The reaction mixture was cooled with ice bath, added 4 mL of sulfuric acid, and stirred for 30 min. A mixture of nitric acid (8 mL) and acetic acid (16 mL) were added dropwise to the solution and stirred for 20 hr at 0°C. 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 ¹H NMR spectrum was about 85%. $\eta_{inh} = 0.30$ dL g⁻¹ (c, 0.5 g⁻¹ dL in DMSO at 25°C). ¹H NMR (DMSO-*d*₆) δ 3.90 (s, 3H, -COOCH₃), 4.56– 4.68 (t, 8H, 2 -O-CH₂-CH₂-O-), 7.16–7.25 (s, 1H, aromatic), 7.59–7.64 (s, 1H, aromatic), 7.96–8.17 (m, 4H, aromatic), 8.83–8.86 (s, 1H, aromatic). IR (KBr) 3105 (w, = C-H), 2958 (m, C-H), 2224 (s, CN), 1725 (vs, C = O), 1596 (s, C = C), 1573, 1268 (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, 57.33; H, 3.82; N, 5.87.

Measurements

IR, ¹H 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. $T_{\rm g}$ 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⁻¹ up to 800°C was used for the thermal degradation study of polymers under nitrogen. The number average molecular weight ($M_{\rm n}$) and weight average molecular weight ($M_{\rm w}$) of the polymer were estimated by gel permeation chromatography (GPC; styragel HR5E4E columns; tetrahydrofuran (THF) solvent). 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 [23]. 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 [24].

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-5-nitrocatecholic groups as NLO chromophores. The degree of nitration was about 85%. The chemical structure of the polymer was identified by ¹H NMR, IR spectra, and elemental analysis. ¹H NMR spectrum and elemental analysis results of the polymer are fit the polymer structure. The IR spectrum of polymer 5 shows strong carbonyl peaks near 1725 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 1573 cm⁻¹ and 1268 cm⁻¹. These results are consistent with the proposed structure, indicating that the NLO chromophores remained intact during the polymerization. The molecular weights were determined by GPC with polystyrene as the standard and THF as the eluent. The molecular weights were determined using GPC with polystyrene as the standard and THF as the eluent. M_n of the polymer 5, determined using GPC, is 15,400 g mol^{-1} ($M_w/M_n = 1.92$). The polymer 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



Scheme 1. Synthetic scheme and structure of polyester 5.

range 0.30-0.32 dL g⁻¹. Polymer **5** shows strong absorption near 362 nm due to the NLO chromophore 4-(2'-carbomethoxy-2'-cyano)vinyl-5-nitrocatecholic group. The striking feature of this polymerization system is that it gives unprecedented X-type NLO polymers, in which the pendant NLO chromophores are parts of the polymer backbone. These X-type NLO polymers are 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.

Thermal properties of polymer

The thermal behavior of the polymer was investigated using TGA and DSC to determine the thermal degradation pattern and T_g . The TGA thermogram of the polymer **5** is shown in Fig. 2. 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 110°C. This T_g value is higher than that of the Y-type polyester **4**, which is near 105°C [19].

Nonlinear optical properties of polymer

The NLO properties of polymer **5** 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 $5-10^{\circ}$ C higher than $T_{\rm g}$, 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. Figure 3 shows the UV-visible absorption spectra of the polymer **5** before and after poling. After electric poling, the dipole moments of the NLO chromophores were aligned and UV-visible absorption of polymer **5** exhibits a decrease in absorption due



Figure 2. TGA thermogram of polymer **5** obtained at a heating rate of 10°C min⁻¹ under nitrogen.

to birefringence. From the absorbance change, the order parameter of the poled films can be estimated, which is related to the poling efficiency. The estimated order parameter value Φ is equal to 0.19 for polymer 5 ($\Phi = 1$ -A₁/A₀, where A₀ = 1.2436 and A₁ = 1.0126 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. 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} value, both *s*-polarized and *p*-polarized IR laser were directed at the samples and recorded. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure [24]. The NLO properties of polymer **5** are summarized in Table 1. The values of d_{31} and d_{33} for polymer **5** are 2.18 × 10⁻⁹ esu and 6.13 × 10⁻⁹ esu, respectively. This d_{33} value is higher than that of Y-type polyester **4**, which is 5.78 × 10⁻⁹ esu [19].

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



Figure 3. UV-visible absorption spectra of a film of polymer 5 before and after poling.

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Polymer	λ _{max} (nm)	d ₃₃ ^b (esu)	Φ^{c}	d ₃₁ ^b (esu)	Film thickness ^d (μ m)	n
4 ^e 5	356 362	$\begin{array}{c} 5.78 \times 10^{-9} \\ 6.13 \times 10^{-9} \end{array}$	0.21 0.19	$\begin{array}{c} 2.07 \times 10^{-9} \\ 2.18 \times 10^{-9} \end{array}$	0.51 0.52	1.680 1.682

Table 1. Nonlinear optical properties of polyesters 4–5.

^aPolymer film after corona poling.

^bSHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [24].

^cOrder parameter $\Phi = 1-A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after corona poling, respectively.

^dFilm thickness was determined by the optical transmission technique [23].

^eY-type polyester containing 3,4-dioxybenzylidenecyanoacetate [19].



Figure 4. Normalized SHG signal of polymer 5 as a function of temperature at a heating rate of 4°C min⁻¹.

film of polymer **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 measurements were performed at a heating rate of 4°C min⁻¹ from 30 to 200°C. The polymer film exhibits a thermal stability up to T_g and no SHG decay is observed below 110°C. This SHG thermal stability is higher than that of the Y-type polyester **4** (100°C) [19], which is probably due to a nitro group and a double 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 polymer **5** 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 a new NLO polyester having both the merits of main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility.

Conclusions

We prepared a new X-type polyester 5 with pendant NLO chromophores which constitute part of the polymer main chain. The chemical structure of the polymer was confirmed by ¹H NMR, IR spectra, and elemental analysis. The X-type NLO polyester 5 is soluble in common organic solvents and shows a thermal stability up to 280°C from its TGA thermogram with T_g value measured using DSC near 110°C. The NLO properties of polymer 5 were studied using the SHG method. The SHG coefficient (d_{33}) of corona-poled polymer film is 6.13×10^{-9} esu. Polyester **5** exhibits SHG stability up to T_g and no significant SHG decay is observed below 110°C. This high thermal stability of optical nonlinearity is due to the stabilization of dipole alignment of NLO chromophore, which stems from the partial main-chain character of the polymer structure. We are now in the process of extending the polymerization system to the synthesis of other type of NLO polymers and the results will be reported elsewhere.

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