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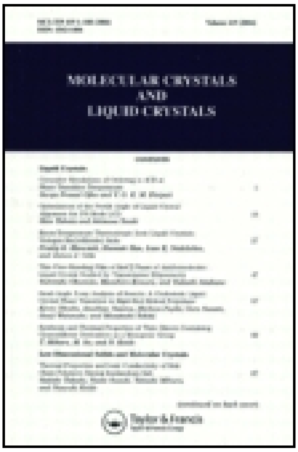

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Synthesis and Properties of Novel Nonlinear Optical Polyimide Containing Nitrophenylazoresorcinoxy Group

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*New Y-type polyimide (**4**) containing nitrophenylazoresorcinoxy groups as NLO chromophores, which are components of the polymer backbone, was prepared and characterized. Polyimide **4** is soluble in common organic solvents such as N,N-dimethylformamide and dimethylsulfoxide. It shows a thermal stability up to 290°C in thermogravimetric analysis with glass-transition temperature (T_g) obtained from differential scanning calorimetry near 128°C. The second harmonic generation (SHG) coefficient* (d_{33}) *of poled polymer film at the 1064 nm fundamental wavelength is around* 5.46×10^{-9} *esu. The dipole alignment exhibits a thermal stability up to* T_g, *and there is no SHG decay below 130°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; polyimide; SHG coefficient; thermogravimetric analysis (TGA)

Introduction

Syntheses of effective nonlinear optical (NLO) materials are very important due to their potential applications in the fields of optical data storage and optical information processing. NLO polymers have several advantages superior to conventional inorganics, such as ultrafast response, wide response wave band, high optical damage threshold, and easy fabrication [1–3]. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of important considerations; in this context, two approaches to minimize the randomization have been proposed, namely the use of cross-linked systems [4,5] and the utilization of polymers with high glass transition temperature (T_g) such as polyimides [6,7]. Polyimides for NLO applications have attracted attentions because of their high T_g and high thermal stability. There are two types of NLO polyimides, which have been used either as host polymers for composite materials or as matrix polymer backbones for side-chain NLO chromophores. Recently we prepared novel NLO polyimides containing dioxynitrostilbenyl groups [8] and dioxybenzylidenemalononitrile [9], which showed high thermal stability. In this work reported here,

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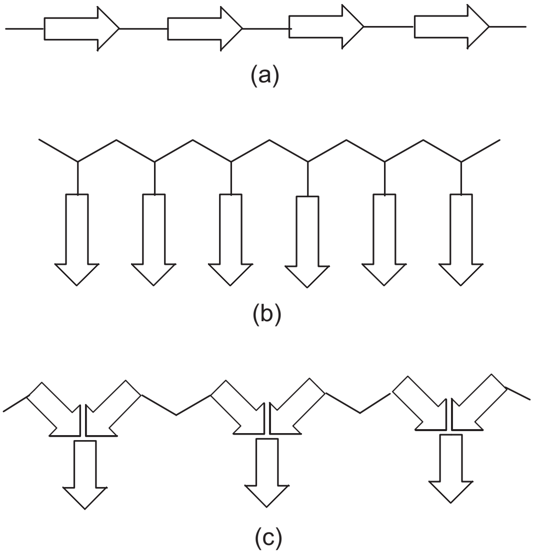


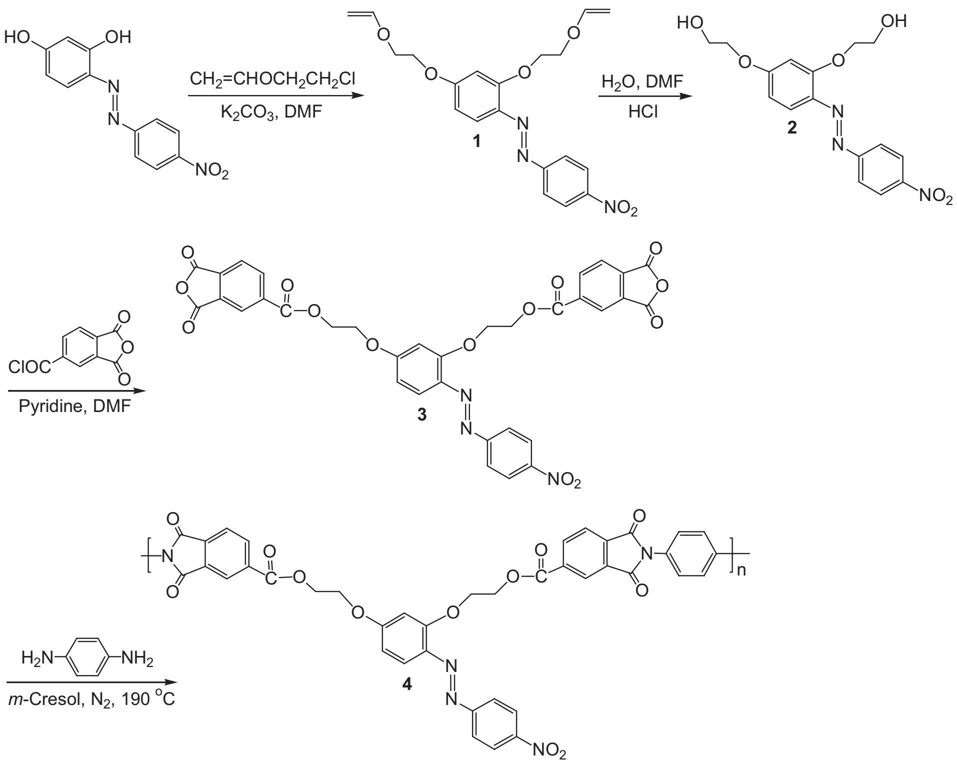
Figure 1. Main chain NLO polymers (a), Side chain NLO polymers (b), and Y-type NLO polymers (c).

we prepared new Y-type polyimide containing nitrophenylazoresorcinoxy groups as NLO chromophores. We selected the latter as NLO chromophores because they were expected to have high optical nonlinearities. Furthermore, these nitrophenylazoresorcinoxy groups constitute novel Y-type NLO polyimides (Fig. 1(c)), and these Y-type NLO polyimides have not yet been reported in the literature. This Y-type NLO polymer is expected to have the merits of both main-chain (Fig. 1(a)) and side-chain (Fig. 1(b)) NLO polymers, namely stable dipole alignment and good solubility. After confirming the structure of the resulting polymer, we investigated its NLO properties. We now report the results of the initial phase of the work.

Experimental

Materials

Polyimide **4** was synthesized through the reaction of monomer **3** containing NLO chromophore with equivalent amount of 1,4-phenylenediamine in *m*-cresol. 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 to give 6.90 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 4.08–4.86 (m, 8H, 2 $-O-CH_2-CH_2-O-$), 6.34–7.45 (m, 6H, aromatic), 7.56–7.68 (m, 2H, aromatic), 7.75–8.56 (m, 9H, aromatic). IR (KBr) 2960 (w, C$-$H), 1779 (m, C$=$O), 1723 (vs, C$=$O), 1612 (s, C$=$C), 1369 (s, C$-$N), 729 (s, imide ring) cm^{-1}. Anal. Calcd for $(C_{40}H_{25}N_5O_{12})_n$: C, 62.58; H, 3.28; N, 9.12. Found: C, 62.67; H, 3.36; N, 9.20.



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

Measurements

IR, ^{1}H NMR, and UV-visible spectra were obtained with a Shimadzu FT IR-8201PC infrared spectrophotometer, Varian 300 MHz NMR spectrometer, and Shimadzu UV-3100S 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 [10]. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [11].

Results and Discussion

Synthesis and Characterization of Polymer 4

The synthetic route for polymer **4** is presented in Scheme 1. The resulting polymer was purified by Soxhlet extraction with methanol as a solvent. The polymerization yield was 90%. The chemical structure of the polymer was identified using ^{1}H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structures. ^{1}H NMR spectrum of the polymer **4** has a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The IR spectrum of polymer **4** shows peaks near 1779 and 729 cm^{-1} that are characteristic bands of imide asymmetric carbonyl stretching and imide ring deformation, respectively. The spectrum also shows strong absorption peaks near 1723 cm^{-1} and 1369 cm^{-1} due to symmetric carbonyl stretching and C—N stretching of imide ring, respectively. These results are consistent with the proposed structures, indicating that the NLO chromophores 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 14,800 g mol^{-1} ($M_\mathrm{w}/M_\mathrm{n} = 1.78$). The polymer **4** is soluble in common solvents such as DMF and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity is 0.30 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. Having obtained the well defined Y-type polyimide **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** has a thermal stability up to 290°C according to its TGA thermogram. The T_g value of the polymer **4** measured using DSC is near 128°C. This T_g value is pretty lower than that of the polyimide containing dioxynitrostilbene, which is near 162°C [8], or dioxybenzylidenemalononitrile, which is near 188°C [9].

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. SHG measurements were performed at a fundamental wavelength of 1064 nm with a mode locked Nd-YAG laser and OPO. 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 for a poled sample of polymer **4**. The SHG values were compared with those obtained from a Y-cut quartz plate. To calculate the d_{31} and d_{33} values, both *s*-polarized and *p*-polarized IR laser were directed at the samples. The NLO properties of polymer **4** are summarized in Table 1. SHG coefficients (d_{33}) were derived from the analysis of measured

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

Polymer	d_{33}[a] (esu)	d_{31}[a] (esu)	film thickness[b] (μm)	n	M_n[c]	M_w[c]
4	5.46×10^{-9}	1.72×10^{-9}	0.54	1.682	14,800	26,300

[a] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [11].
[b] Film thickness was determined by the optical transmission technique [10].
[c] Measured by gel permeation chromatography (GPC) in THF using polystyrene standard.

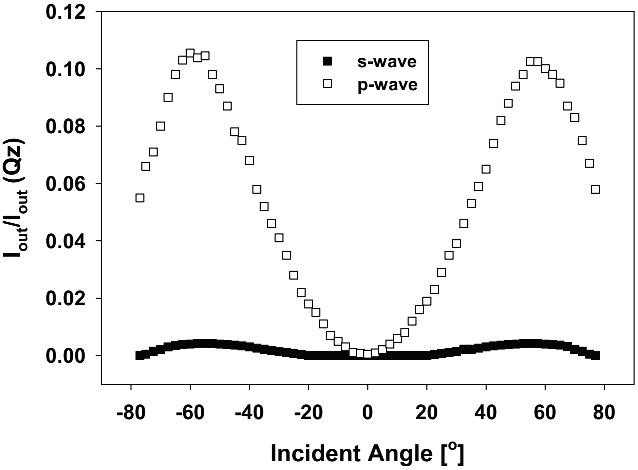


Figure 2. Angular dependence of SHG signal for a poled film of polymer **4**.

Maker-fringes with the Pascal fitting program according to the literature procedure [11]. The values of d_{33} and d_{31} for polymer **4** are 5.46 × 10^{-9} and 1.72 × 10^{-9} esu, respectively. This d_{33} value is higher than that of the polyimide containing dioxynitrostilbene [8], but is similar with that of polyimide with dioxybenzylidenemalononitrile [9]. However, the d_{33} value is rather smaller than those of conventional polymers [1,2].

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 measurement was 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 significant SHG decay is observed below 130°C. However,

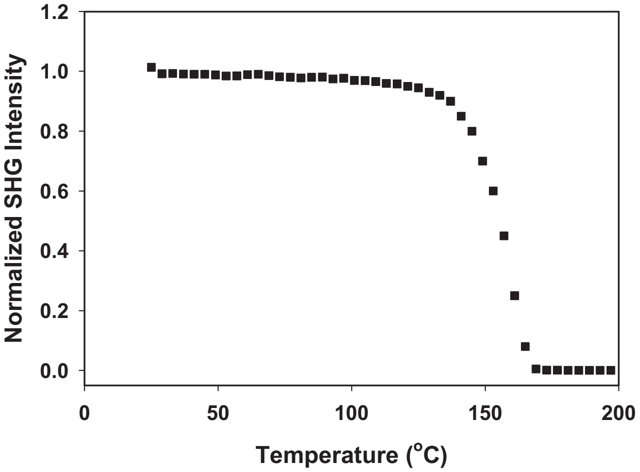


Figure 3. Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 4°C/min.

the SHG thermal stability is lower than that of the polyimide containing dioxynitrostilbene, which is in the range 180–190°C [8] or dioxybenzylidenemalononitrile, which is in the range 190–200°C [9]. This lower SHG thermal stability of the polymer **4** is probably due to the lower T_g value. 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 **4** 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 type of NLO polyimide with quite stable dipole alignment and good solubility.

Conclusions

New Y-type polyimide **4** with pendant NLO chromophores as parts of the polymer main chain was synthesized. This Y-type NLO polyimide **4** is soluble in common organic solvents and displayed a thermal stability up to 290°C with a T_g of 128°C. The SHG coefficient (d_{33}) of corona-poled polymer film is 5.46×10^{-9} esu. Polymer **4** exhibits SHG stability up to glass transition temperature (T_g), and no SHG decay is observed below 130°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.

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