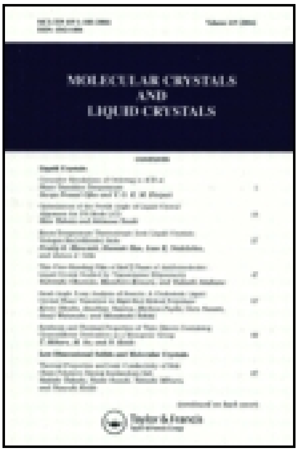

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Synthesis and Properties of Novel Nonlinear Optical Polyurethane Containing Nitrophenylazocatecholic Group

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*A novel Y-type polyurethane **3** containing 4-(4-nitrophenylazo)catecholic groups as nonlinear optical (NLO) chromophores was prepared and characterized. Polyurethane **3** is soluble in common organic solvents such as acetone and DMF. Polymer **3** shows a thermal stability up to 270°C from TGA thermogram and the* T_g *value obtained from DSC thermogram is around 96°C. The second harmonic generation (SHG) coefficient* (d_{33}) *of poled polymer film at 1064 nm fundamental wavelength is* 4.58×10^{-9} *esu. The dipole alignment exhibits a thermal stability even at 4°C higher than* T_g*, and there is no 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; polyurethane; SHG coefficient; thermogravimetric analysis (TGA)

Introduction

Recent years, nonlinear optical (NLO) materials have been extensively studied for their potential applications in the field of telecommunications, optical signal processing, optical switching, etc [1–3]. Among them, 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. In the developments of NLO polymers, stabilization of electrically induced dipole alignment is one of important considerations. Two approaches to minimize the randomization have been proposed namely the use of cross-linking methods [4] and to utilize high T_g polymers such as polyimides [5]. Polyurethane matrix forms extensive hydrogen bond between urethane linkages, with increased rigidity preventing the relaxation of induced dipoles. Polyurethanes with a NLO chromophore, whose dipole moment is aligned transverse to the main chain backbone, showed enhanced thermal stability [6]. Polyurethane with a thiophene ring having a tricyanovinyl group in the polymer side chain showed enhanced thermal stability [7]. In general, main-chain NLO polymers exhibit good thermal stability of dipole alignments, but they often do not dissolve in organic solvents. Side-chain NLO polymers have good solubility, but they often suffer

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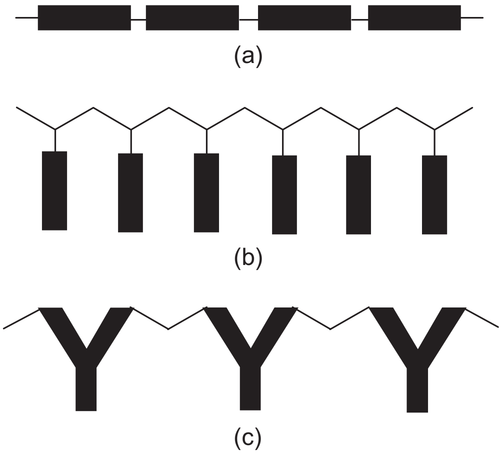


Figure 1. Main chain NLO polymers (a), Side chain NLO polymers (b), and Y-type NLO polymers (c).

from poor stability of dipole alignments at high temperatures. Recently we reported novel NLO polyurethanes containing dioxynitrostilbene [8] or dioxybenzylidenemalononitrile [9], which exhibit enhanced thermal stability of dipole alignments. In this work reported here, we have prepared a new polyurethane containing 4-(4-nitrophenylazo)catecholic groups as NLO chromophores. We selected the latter because it was expected to have a large dipole moment. Furthermore, these groups can be incorporated into novel Y-type NLO polyurthanes (see Fig. 1c). The structure of NLO chromophores and these Y-type NLO polyurethanes have not yet been described in the literature. Thus we formulated a new type of NLO polyurethane, in which the pendant NLO chromophores are components of the polymer backbone. This mid-type NLO polymer is expected to have both the merits of 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 properties such as thermal stability and second harmonic generation activity. We now report the results of the initial phase of the work.

Experimental

Materials

Synthetic method of polymer **3** is summarized in Scheme 1. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum to give 5.66 g (88% yield) of polymer **3**. Polymer **3**: $\eta_{\mathrm{inh}} = 0.31$ dL/g (c, 0.5 g/dL in DMSO at 25°C). ^{1}H NMR (DMSO-d_6) δ (ppm): 3.48 (s 6H, -OCH$_3$), 3.86–4.06 (m, 4H, 2 -O-CH$_2$-), 4.12–4.63 (m, 4H, 2 Ph-O-CH$_2$-), 7.18–7.51 (m, 4H, aromatic), 7.58–7.7.78 (m, 3H, aromatic), 7.82–8.13 (m, 2H, aromatic), 8.17–8.34 (m, 2H, aromatic), 8.39–8.51 (m, 1H, aromatic), 8.61–8.79 (t, 1H, aromatic), 8.92–9.18 (s, 2H, N-H). IR (KBr disk) (cm^{-1}): 3348 (m, N-H), 2883 (m, C-H), 1729 (s, C=O), 1589 (s, N=N), 1516, 1341 (vs, N=O) cm^{-1}. Anal. Calcd for $(C_{32}H_{29}N_5O_{10})_n$: C, 59.72; H, 4.54; N, 10.88. Found: C, 59.61; H, 4.46; N, 10.81.

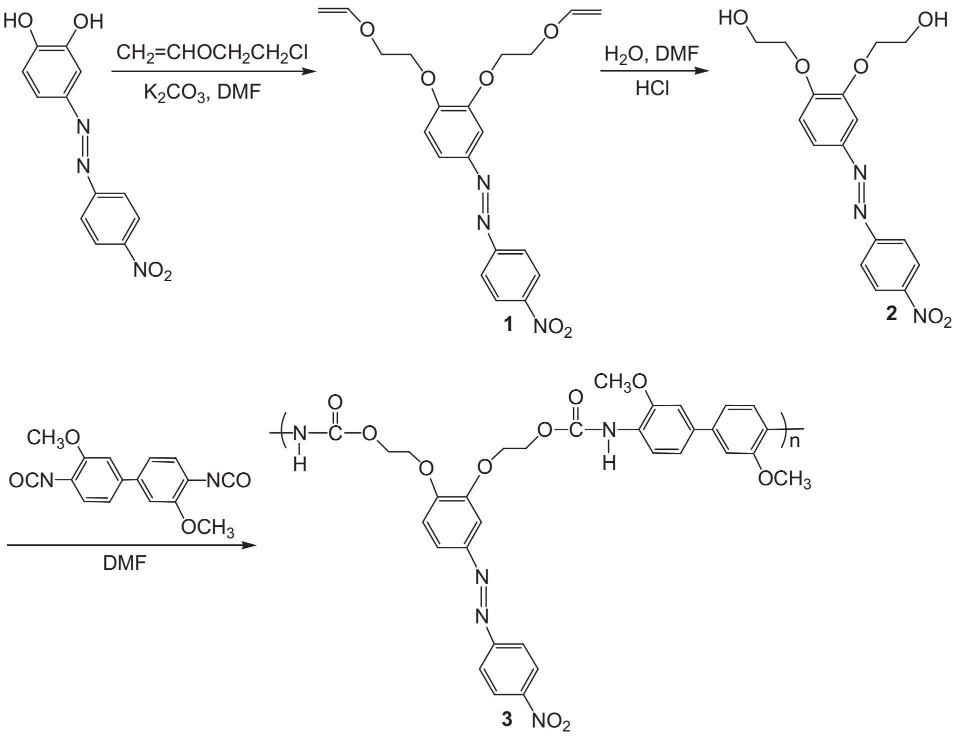
Measurements

IR, ^{1}H NMR, and UV-visible spectra were obtained with a Shimadzu FT IR-8201PC infrared spectrophotometer, Varian 300MHz NMR spectrometer, and Shimadzu UV-3100S spectrophotometer, respectively. T_g values were measured using 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 using 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 3

Synthetic method of polyurethane **3** is summarized in Scheme 1. Diol **2** was condensed with 3,3′-dimethoxy-4,4′-biphenylenediisocyanate in a dry DMF solvent to yield novel polyurethane **3** containing 4-(4-nitrophenylazo)catecholic group as NLO chromophore. The chemical structure of the polymer was confirmed by ^{1}H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structure. ^{1}H NMR spectrum



Scheme 1. Synthetic scheme and structure of polymer **3**.

of the polymer has a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The signal at 8.92–9.18 ppm assigned to the amine proton indicates the formation of urethane linkage. The IR spectrum of polymer **3** shows strong carbonyl peaks near 1729 cm^{-1} indicating the presence of urethane bond. The spectrum also shows strong absorption peak near 1589 cm^{-1} due to azo group and absorptions at 1516 and 1341 cm^{-1} due to nitro group indicating the presence of nitroazobenzene unit. These results are consistent with the proposed structure, indicating that the NLO chromophores remained intact during the polymerization. The molecular weights were determined using GPC with polystyrene as the standard and THF as the eluent. M_n of the polymer **3**, determined using GPC, is 14,200 g mol^{-1} ($M_w/M_n = 1.98$). The polymer **3** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity is 0.31 dL g^{-1}. Polymer **3** shows strong absorption near 384 nm due to the 4-(4-nitrophenylazo)catecholic group NLO chromophore. The striking feature of this polymerization system is that it gives unprecedented Y-type NLO polymers, in which the pendant NLO chromophores are part of the polymer backbone. These Y-type NLO polymers are expected to have the advantages of both main-chain and side-chain NLO polymers. Having obtained the well defined Y-type polyurethane **3**, we investigated its properties.

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. Polymer **3** shows a thermal stability up to 270°C according to its TGA thermogram. The T_g value of the polymer **3** measured using DSC is around 96°C. This T_g value is lower than that of the polyurethane containing dioxynitrostilbene, which is near 143°C [8] or dioxybenzylidenemalononitrile, which is near 146°C [9].

Nonlinear optical properties of polymer

The NLO properties of polymer were studied using the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer film was 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. After electric poling, the dipole moments of the NLO chromophores were aligned and UV-visible absorption of polymer **3** exhibits a slight blue shift and 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 **3** 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 for a poled sample of polymer **3**. The SHG values were compared with those obtained from a Y-cut quartz plate. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with Pascal fitting program according to the literature procedure [11]. The values of d_{33} and d_{31} for polymer **3** are 4.58×10^{-9} and 1.45×10^{-9} esu, respectively. These SHG values are smaller than those of the polyurethanes containing 3,4-dioxynitrostilbene [8] or 2,4-dioxybenzylidenemalononitrile [9], as shown in Table 1. The lower SHG values of polymer **3** are probably due to the easy *cis-trans* isomerization of diazo linkage.

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

Table 1. Nonlinear Optical Properties of Polymer 3

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	d_{31}[b] (esu)	film thickness[c] (μm)	n
3	384	4.58×10^{-9}	1.45×10^{-9}	0.50	1.72
4[d]	383	3.64×10^{-8}	1.28×10^{-8}	0.45	1.70
5[e]	382	5.62×10^{-9}	1.95×10^{-9}	0.42	1.61

[a] Polymer film after corona poling.
[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [11].
[c] Film thickness was determined using the optical transmission technique [10].
[d] Polyurethane containing 3,4-dioxynitrostilbene [8].
[e] Polyurethane containing 2,4-dioxybenzylidenemalononitrile [9].

activity of a film of polymer **3**. 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 30°C to 250°C. The polymer film exhibits a greater thermal stability even at 4°C higher than T_g, and no significant SHG decay is observed below 100°C, as shown in Figure 3. In general, side chain NLO polymers lose thermal stability of dipole alignment below T_g. Stabilization of dipole alignment is a characteristic of main chain NLO polymer. The enhanced thermal stability of SHG of polymer **3** is due to the stabilization of dipole alignment of NLO chromophore, which stems

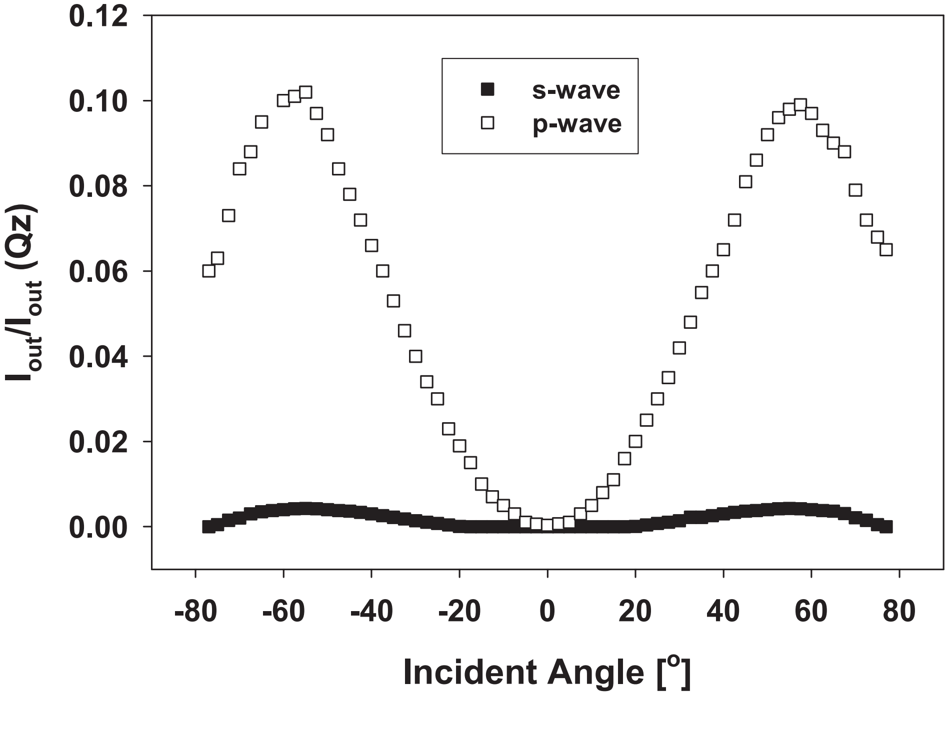


Figure 2. Angular dependence of SHG signal for a poled film of polymer **3**.

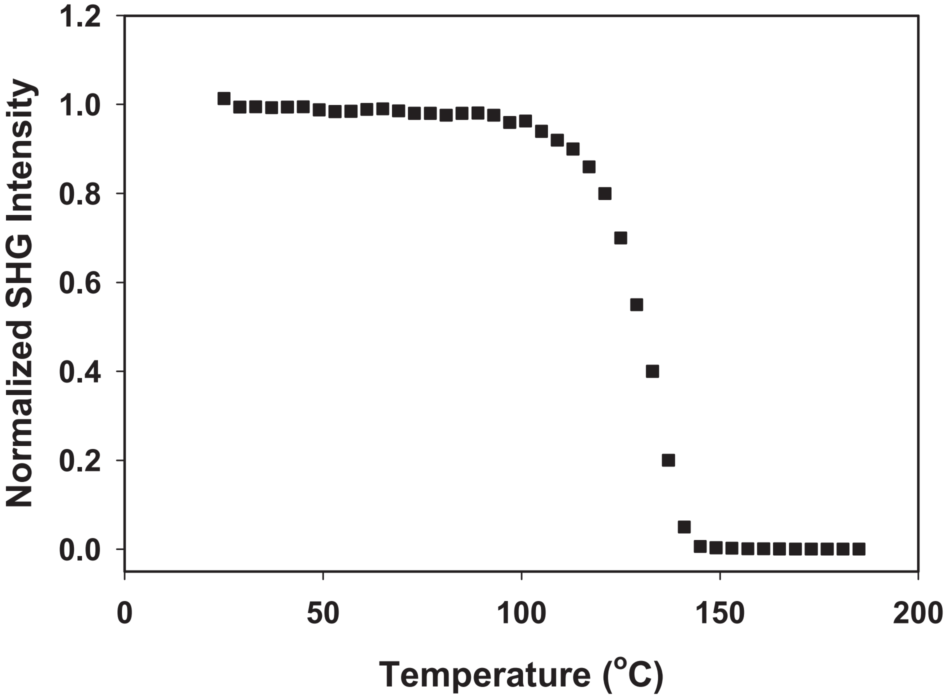


Figure 3. Normalized SHG signal of polymer **3** as a function of temperature at a heating rate of 4°C/min.

from the partial main chain character of the polymer structure and partly by hydrogen bonds between the neighboring urethane linkages.

Conclusions

A novel Y-type NLO polyurethane **3** with pendant NLO chromophores as part of the polymer backbone was prepared. This Y-type polymer **3** is soluble in common organic solvents and shows a thermal stability up to 270°C with T_g value around 96°C. The SHG coefficient (d_{33}) of corona-poled polymer film is 4.58×10^{-9} esu. The polymer exhibits a SHG thermal stability even at 4°C higher than T_g, and no SHG decay is observed below 100°C. This enhanced thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophores, which constitute part of the polymer main chain.

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