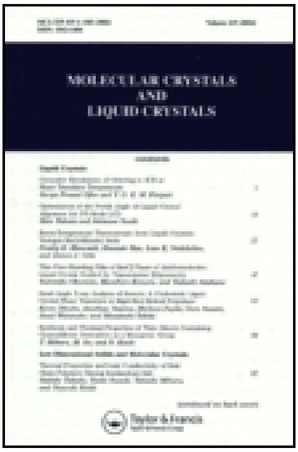

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 27 Sep 2012.

To cite this article: Mi Sung Kim, Mi Young Song, Byeongman Jeon & Ju-Yeon Lee (2012): Synthesis and Nonlinear Optical Properties of Novel Y-type Polyurethane Containing Nitroazobenzene Group, Molecular Crystals and Liquid Crystals, 568:1, 111-116

To link to this article: http://dx.doi.org/10.1080/15421406.2012.710302

Mol. Cryst. Liq. Cryst., Vol. 568: pp. 111–116, 2012
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.710302

Synthesis and Nonlinear Optical Properties of Novel Y-type Polyurethane Containing Nitroazobenzene Group

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*Novel Y-type polyurethane **3** containing 4-(4-nitrophenylazo)resorcinoxy groups as nonlinear optical (NLO) chromophores, which constitute part of the polymer backbone, was prepared and characterized. Polyurethane **3** is soluble in common organic solvents such as acetone and N,N-dimethylformamide. It shows thermal stabilities up to 270°C from thermogravimetric analysis with glass transition temperature obtained from differential scanning calorimetry of 102°C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer film at 1064 nm fundamental wavelength is 4.92×10^{-9} esu. Polymer **3** exhibits a high thermal stability even at 8°C higher than T_g, and no significant SHG decay is observed below 110°C, which is acceptable for nonlinear optical device applications.*

Keywords Differential scanning calorimetry (DSC); dipole alignment; NLO; polyurethane; SHG coefficient; thermogravimetric analysis (TGA)

Introduction

During the past decades, second-order nonlinear optical (NLO) polymers have focused due to their several advantages for photonic applications, such as high-speed optical switches and electro-optic modulators [1–3]. 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, that is to use 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 [6–7]. In general, main-chain NLO polymers exhibit good thermal stability of dipole alignments, but they often have poor solubility in organic solvents and difficulty in poling. Side-chain NLO polymers have good solubility, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we reported novel NLO polyurethanes containing dioxynitrostilbene [8] or dioxybenzylidenemalononitrile [9] with enhanced thermal stability of dipole alignments. In this work, we have prepared novel polyurethane containing 4-(4-nitrophenylazo)resorcinoxy groups as NLO chromophores.

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We selected the latter as NLO chromophores because they are expected to have high optical nonlinearities. Furthermore, these 4-(4-nitrophenylazo)resorcinoxy groups can be incorporated into novel Y-type NLO polyurthane, and this NLO polyurethane has not yet been described in the literature. This Y-type NLO polymer is expected to have the merits of both main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility. After confirming the structure of the resulting polymer, we investigated its properties. We now report the results of the initial phase of the work.

Experimental

Materials

A representative polyaddition reaction procedure was as follows. 3,3′-Dimethoxy-4,4′-biphenylenediisocyanate (2.96 g, 0.01 mol) was added slowly to a solution of 3.47 g of diol **2** (0.01 mol) in 25 mL of anhydrous DMF. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 80°C. After heating 12 h with stirring the polymerization tube was opened and the viscous polymer solution was poured into 400 mL of cold water. The precipitated polymer was collected and re-precipitated from dimethylsulfoxide (DMSO) into methanol. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum to give 5.79 g (90% yield) of dark orange colored polymer **3**. Inherent viscosity (η_{inh}): 0.32 dL g^{-1} (c, 0.5 g dL^{-1} in DMSO at 25°C). ^{1}H NMR (DMSO-d_6) δ 3.42 (s 6H, -OCH_3), 3.86–4.07 (m, 4H, 2 -O-CH_2-), 4.43–4.67 (m, 4H, 2 Ph-O-CH_2-), 6.76–6.83 (s, 1H, aromatic), 7.18–7.36 (m, 5H, aromatic), 7.73–7.81 (d, 2H, aromatic), 7.93–8.05 (d, 2H, aromatic), 8.25–8.35 (t, 3H, aromatic), 8.63–8.74 (d, 2H, N-H). IR (KBr) 3401 (m, N-H), 2943 (m, C-H), 1729 (s, C = O), 1591 (s, N = N), 1514, 1339 (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, 59.82; H, 4.62; N, 10.82.

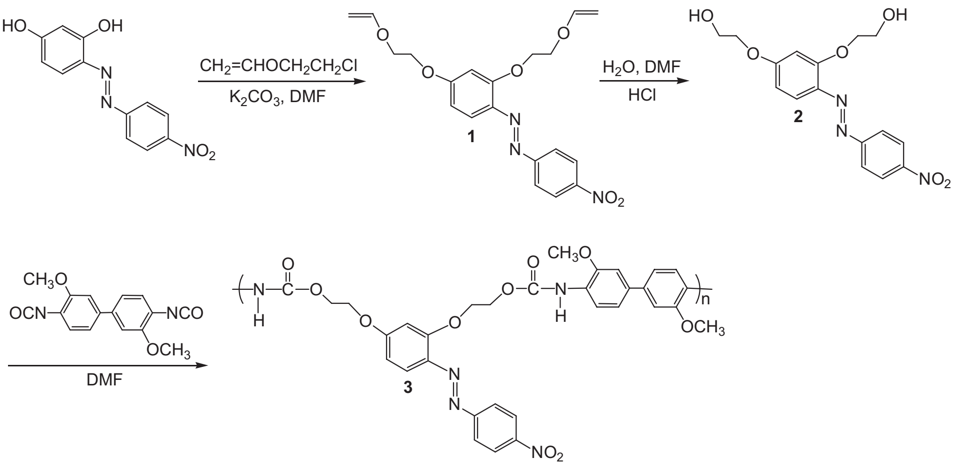
Measurements

IR, ^{1}H NMR, and UV-visible spectra were obtained with a Varian FT IR-1000 IR spectrophotometer, Varian 300MHz 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 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 3

The synthetic route for polymer **3** is presented in Scheme 1. The chemical structure of the polymer was identified using ^{1}H NMR, IR spectra, and elemental analysis. ^{1}H NMR



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

spectrum of the polymer **3** has a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The signal at 8.63–9.08 ppm of ^{1}N NMR spectrum of polymer **3** 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. These results are consistent with the proposed structure. The molecular weight (M_n) of the polymer **3**, determined using GPC, is 17600 g mol^{-1} ($M_w/M_n = 1.88$). The polymer **3** is soluble in common solvents such as acetone and DMF, but is not soluble in methanol and diethyl ether. Polymer **3** shows strong absorption near 399 nm due to the 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 glass transition temperature. The TGA thermogram of the polymer **3** is shown in Fig. 2. Polymer **3** has a thermal stability up to 270°C according to its TGA thermogram. The T_g value of the polymer **3** measured using DSC is near 102°C. This T_g value is lower than those of the polyurethanes containing dioxynitrostilbene, which are in the range 143-150°C [12-13] or dioxybenzylidenemalononitrile, which are in the range 135-159°C [14–15].

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. The film was transparent and dark orange colored. As the temperature was raised gradually to 5–10°C

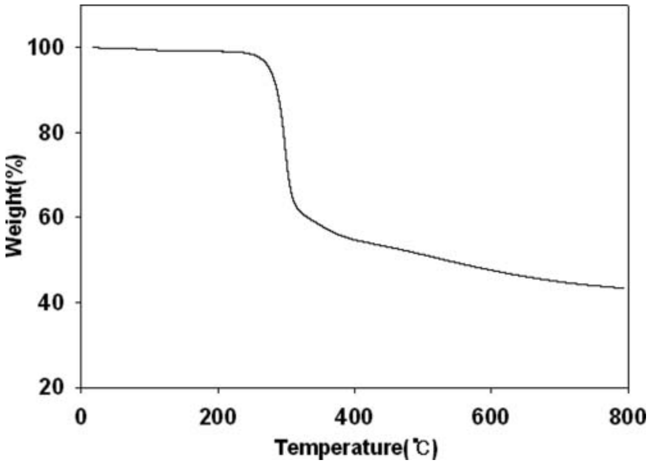


Figure 1. TGA thermogram of polymer **3** obtained at a heating rate of 10°C min^{-1} under nitrogen.

higher than T_g, a corona voltage of 6.5 kV was applied and this temperature was maintained for 30 min. The poling was confirmed from UV-visible spectra. Figure 2 shows the UV-visible absorption spectra of the polymer film deposited on a slide glass before and after poling. 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 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. 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 **3** are summarized in Table 1. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with

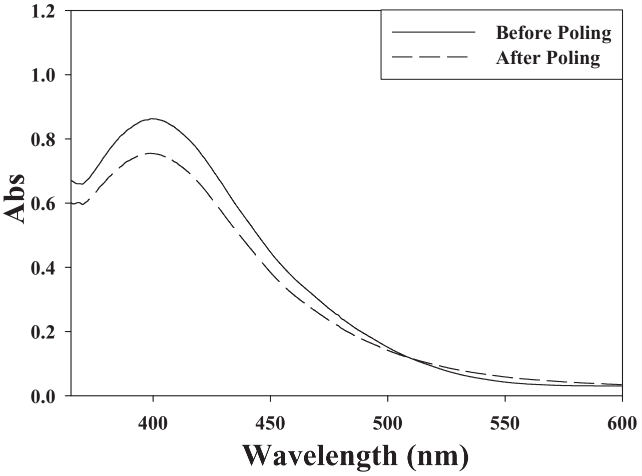


Figure 2. UV-visible absorption spectra of a film of polymer **3** before and after poling.

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	399	4.92×10^{-9}	1.65×10^{-9}	0.52	1.716

[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 by the optical transmission technique [10].

the Pascal fitting program according to the literature procedure [11]. The values of d_{31} and d_{33} for polymer **3** are 1.65×10^{-9} and 4.92×10^{-9} esu, respectively. These SHG values are smaller than those of the polyurethanes containing 3,4-dioxynitrostilbene [12] or 2,4-dioxybenzylidenemalononitrile [14], but are larger than those of the polyurethanes containing 2,3-dioxynitrostilbene [13].

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 **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 measurement was performed at a heating rate of 4°C min^{-1} from 30 to 200°C. The polymer film exhibits a high thermal stability even at 8°C higher than T_g, and no significant SHG decay is observed below 110°C. 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 **3** 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 polyurethane with stable dipole alignment and good solubility.

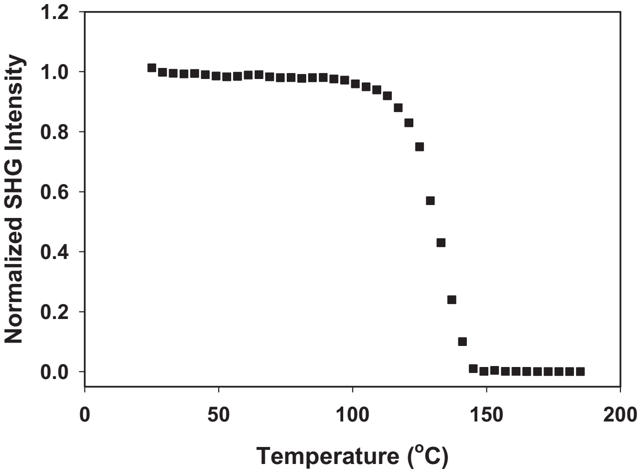


Figure 3. Normalized SHG signal of polymer **3** as a function of temperature at a heating rate of 4°C/min.

Conclusions

We synthesized novel Y-type polyurethane **3** with pendant NLO chromophores, which are part of the polymer main chain. This Y-type NLO polyurethane is soluble in common organic solvents. The resulting polymer **3** shows a thermal stability up to 270°C from TGA thermogram with T_g value near 102°C. The SHG coefficient (d_{33}) of corona-poled polymer film is 4.92×10^{-9} esu. Polymer **3** exhibits SHG stability up to 110°C. This high thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophores, which constitute part of the polymer backbone.

Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 2011-0026534).

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