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

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To cite this article: Mi Young Song, Byeongman Jeon & Ju-Yeon Lee (2013) Synthesis and Properties of Novel Nonlinear Optical Polyurethane Containing Dicyanovinylnitroresorcinoxy Group, Molecular Crystals and Liquid Crystals, 581:1, 83-88

To link to this article: http://dx.doi.org/10.1080/15421406.2013.808557

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Mol. Cryst. Liq. Cryst., Vol. 581: pp. 83–88, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.808557

Synthesis and Properties of Novel Nonlinear Optical Polyurethane Containing Dicyanovinylnitroresorcinoxy Group

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Novel X-type polyurethane ***5*** *containing 4-(2′,2′-dicyanovinyl)-6-nitroresorcinoxy groups as nonlinear optical (NLO) chromophores, which constitute part of the polymer backbone, was prepared and characterized. Polyurethane* ***5*** *is soluble in common organic solvents such as acetone and N,N-dimethylformamide. It shows thermal stabilities up to 280°C from thermogravimetric analysis with glass transition temperature obtained from differential scanning calorimetry near 120°C. The second harmonic generation (SHG) coefficient* (d_{33}) *of poled polymer film at 1064 nm fundamental wavelength is* 6.12×10^{-9} *esu. Polymer* ***5*** *exhibits a high thermal stability even at 5°C higher than* T_g*, and no significant SHG decay is observed below 125°C, which is acceptable for nonlinear optical device applications.*

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

Introduction

Second-order nonlinear optical (NLO) polymers have been focused during the past decades due to their several advantages for photonic applications, such as high-speed optical switches and electro-optic modulators [1–4]. 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 [5] and to utilize high T_g polymers such as polyimides [6]. Polyurethane matrix forms extensive hydrogen bond between urethane linkages, with increased rigidity preventing the relaxation of induced dipoles [7,8]. 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 dioxybenzylidenemalononitrile [9] with enhanced thermal stability of dipole alignments. In this work, we have prepared novel polyurethane containing 4-(2′,2′-dicyanovinyl)-6-nitroresorcinoxy groups as NLO

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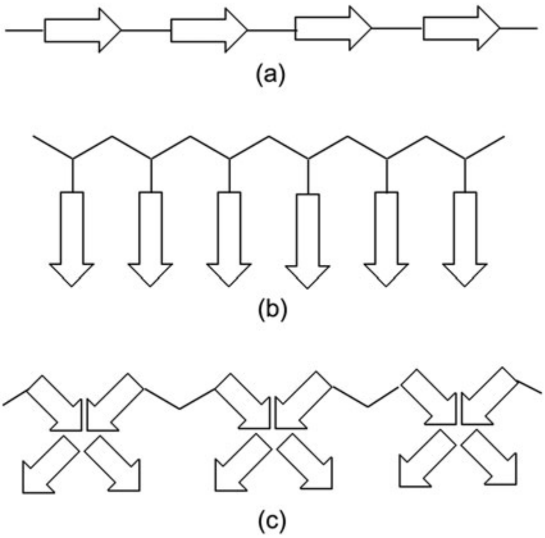


Figure 1. Main chain NLO polymers (a), side chain NLO polymers (b), and X-type NLO polymers (c).

chromophores. We selected the latter as NLO chromophores because they are expected to have higher optical nonlinearities than those without nitro group due to a quadruple conjugation and planarity of the dipole moments. Furthermore, these 4-(2′,2′-dicyanovinyl)-6-nitroresorcinoxy groups can be incorporated into novel X-type NLO polyurethane (see Fig. 1c), and this NLO polyurethane has not yet been described in the literature. This X-type NLO polymer, similar to the Y-type, 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 electro-optic properties. We now report the results of the initial phase of the work.

Experimental

Materials

A representative synthetic procedure for polymer **5** was as follows. Compounds **1–3** and polymer **4** was prepared according to a procedure similar to that reported already [9]. Polymer **4** (4.42 g, 0.01 mol) was dissolved in 22 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 (9 mL) and sulfuric acid (9 mL) were added dropwise to the solution and stirred for 24 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, giving 4.38 g (90% yield) of polymer **5**. Inherent viscosity (η_{inh}) = 0.30 dL/g (c = 0.5 g/dL in DMSO at 25°C). ^{1}H NMR (DMSO-d_6) δ 1.08–1.48 (d, 8H, -$(CH_2)_4$-), 2.88–3.03 (s, 4H, 2 –NH-CH_2-), 4.08–4.45 (m, 8H, 2 -O-CH_2-CH_2-O-), 5.68 (s, 2H, 2 N-H), 6.75–8.26 (m, 3H, aromatic). IR (KBr) 3332 (m, N-H), 2935 (m, C-H), 2223 (m, CN), 1697 (s, C=O), 1609 (s, C=C) cm^{-1}. Anal. Calcd for $(C_{22}H_{25}N_5O_8)_n$: C, 54.21; H, 5.17; N, 14.36. Found: C, 54.32; H, 5.11; N, 14.28.

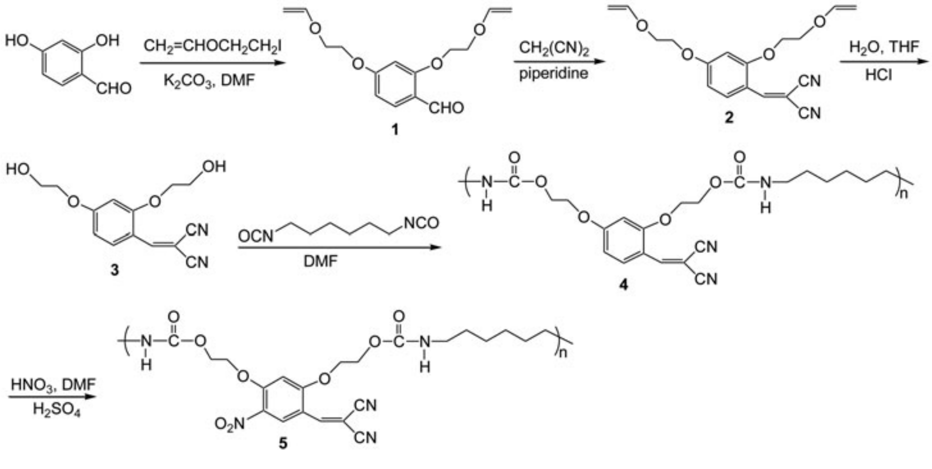
Measurements

IR, ^{1}H NMR, and UV-visible spectra were obtained with a Varian FT IR-1000 IR spectrophotometer, Varian VNMRS 500 MHz 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 5

The synthetic route for polymer **5** is presented in Scheme 1. Diol **3** was polyadded with 1,6-hexamethylenediisocyanate in a dry DMF solvent to yield polyurethane **4**. Polymer **4** was reacted with nitric acid and sulfuric acid in anhydrous DMF to yield novel polyurethane **5** containing 4-(2′,2′-dicyanovinyl)-6-nitroresorcinoxy groups as NLO chromophores. The chemical structure of the polymer was identified using ^{1}H NMR, IR spectra, and elemental analysis. The chemical shifts of the polymer **5** in ^{1}H NMR spectrum are consistent with the proposed polymer structure. The signal at 5.68 ppm assigned to the amine proton indicates the formation of urethane linkage. The IR spectrum of polymer **5** shows strong absorption peak near 2223 cm^{-1} indicating the presence of nitrile group. The spectrum also shows a strong carbonyl peak near 1697 cm^{-1} indicating the presence of urethane bond, and two



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

strong absorption bands due to the nitro group in the NLO chromophore appeared near 1568 cm^{-1} and 1276 cm^{-1}. These results are consistent with the proposed structure. 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 15,800 g mol^{-1} ($M_\mathrm{w}/M_\mathrm{n} = 1.95$). 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 0.30 dL/g. Polymer **5** shows strong absorption near 376 nm due to the NLO chromophore 4-(2′,2′-dicyanovinyl)-6-nitroresorcinoxy group. The striking feature of this polymerization system is that it gives unprecedented X-type NLO polymers, in which the pendant NLO chromophores are part of the polymer backbone. This X-type NLO polymer is expected to have the advantages of both main-chain and side-chain NLO polymers. Thus, we obtained new NLO polyurethane with side-chain and main-chain characteristics. Having obtained the well defined X-type polyurethane **5**, 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 (T_g). The TGA thermogram of the polymer **5** is shown in Fig. 2. Polymer **5** has a thermal stability up to 280°C according to its TGA thermogram. The T_g value of the polymer **5** measured using DSC is around 120°C. This T_g value is higher than that of the polyurethane **4**, which is near 117°C.

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 optical parametric oscillator. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. The SHG values

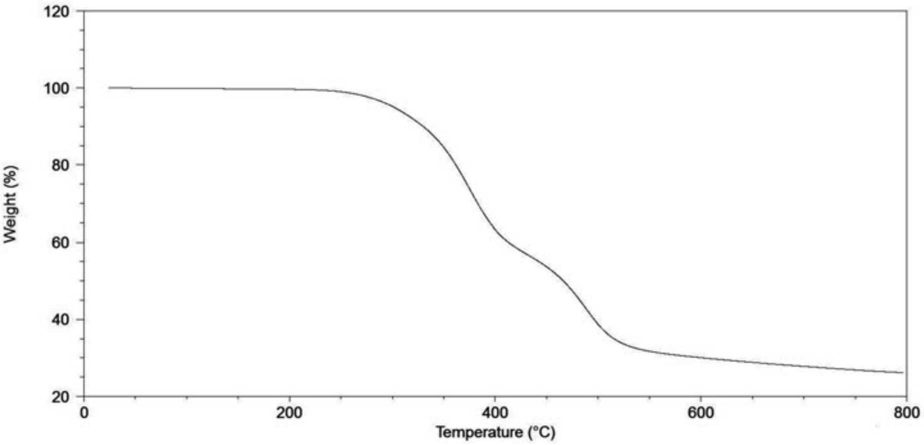


Figure 2. TGA thermogram of polymer **5** obtained at a heating rate of 10°C/min under nitrogen.

Table 1. Nonlinear optical properties of polymer **5**

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	d_{31}[b] (esu)	Film thickness[c] (μm)	n
5	376	6.12×10^{-9}	2.10×10^{-9}	0.52	1.628

[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].

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 **5** are summarized in Table 1. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure [11]. The values of d_{31} and d_{33} for polymer **5** are 2.10×10^{-9} and 6.12×10^{-9} esu, respectively. This d_{33} value is similar with those of the polyurethanes containing dioxybenzylidenemalononitrile, which are in the range $5.62 \times 10^{-9} \sim 7.71 \times 10^{-9}$ esu [9].

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 **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 high thermal stability even at 5°C higher than T_g, and no significant SHG decay is observed below 125°C. However, the SHG thermal stability of polymer **5** is somewhat

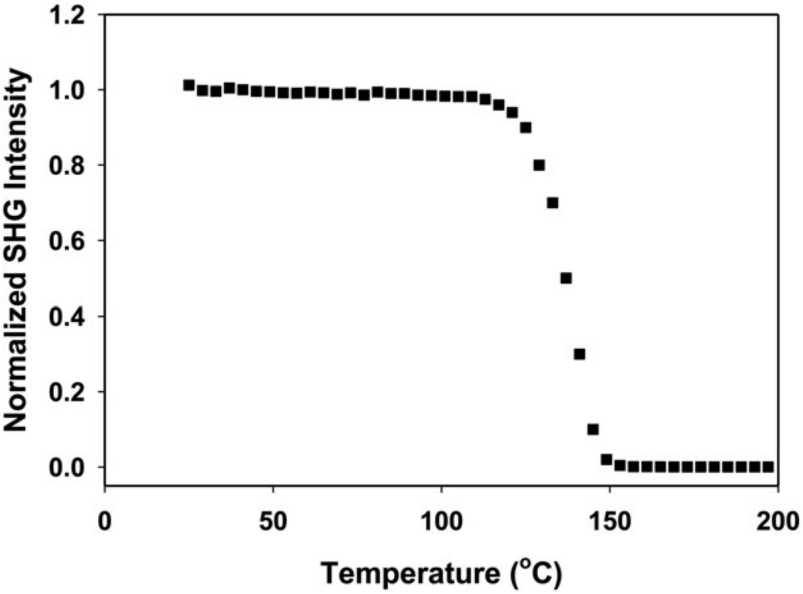


Figure 3. Normalized SHG signal of polymer **5** as a function of temperature at a heating rate of 4°C/min.

lower than that of the polyurethane [9] containing aromatic ring, which is probably due to a flexible hexamethylene group in the main chain. 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 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.

Conclusions

We synthesized novel X-type polyurethane **5** with pendant NLO chromophores, which are part of the polymer main chain. This X-type NLO polyurethane is soluble in common organic solvents. The resulting polymer **5** shows a thermal stability up to 280°C from TGA thermogram with T_g value near 120°C. The SHG coefficient (d_{33}) of corona-poled polymer film is 6.12×10^{-9} esu. Polymer **5** exhibits SHG stability up to 125°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.

Acknowledgment

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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