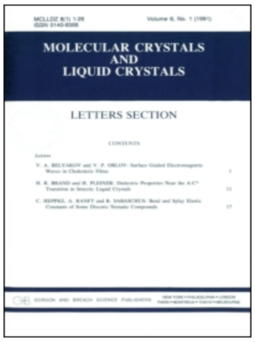

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Synthesis and properties of nonlinear optical novel polyurethane containing nitrothiazolylazoresorcinoxy group

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ABSTRACT

A new Y-type polyurethane (**4**) containing nitrothiazolylazoresorcinoxy groups as NLO chromophores, which are components of the polymer backbone was prepared. Polyurethane **4** is soluble in common organic solvents such as *N,N*-dimethylformamide and dimethylsulfoxide. It shows a thermal stability up to 240°C from thermogravimetric analysis with glass-transition temperature (T_g) obtained from differential scanning calorimetry near 126°C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer films at the 1064 nm fundamental wavelength is around 9.02×10^{-9} esu. The dipole alignment exhibits a thermal stability even at 4°C higher than T_g, and no SHG decay was observed 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; polyurethane; SHG coefficient; thermogravimetric analysis (TGA)

Introduction

Nonlinear optical (NLO) materials have drawn much attention because of their potential applications in the field of electro-optic devices, including high speed optical modulators and ultrafast optical switches [1–8]. Among them, the organic NLO polymers seem to be superior because of their higher nonlinear optical activity, faster response time, low cost, wide response wave band, high optical damage threshold, and good processability to form electro-optic devices. A potential NLO polymer must contain highly polarizable conjugated electronic systems and has to be mechanically very strong and thermally stable. Many attentions have been paid to the synthesis of new NLO polymers with not only high optical nonlinearity but also good thermal stability and good solubility. Several approaches to minimize the randomization of electrically induced dipole alignment have been proposed such as the use cross-linking methods [9–12], the utilization of high T_g polyimides [13–15], H-shape polymers [16], and dendronized hyperbranched polymers with suitable isolation group [17]. Polyurethane matrix forms extensive hydrogen bond between urethane linkages, with increased rigidity preventing the relaxation of induced dipoles [18–19]. Main-chain NLO polymers generally 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 nitrophenylazoresorcinoxy

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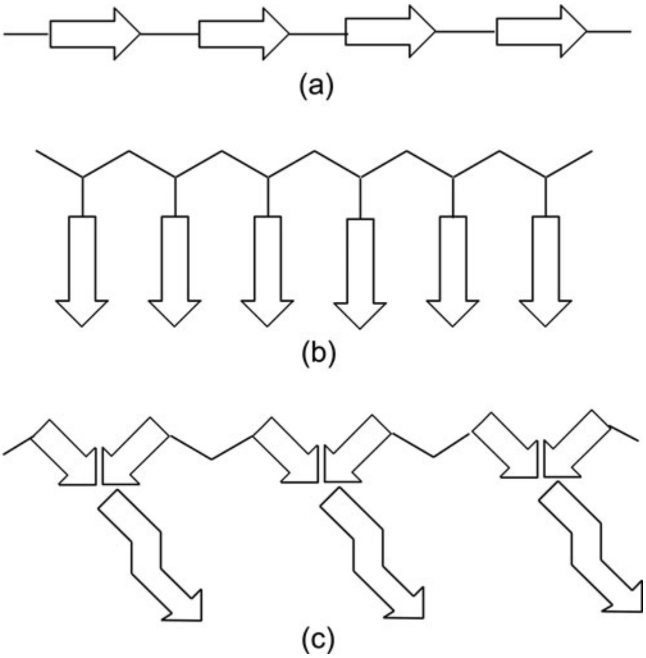


Figure 1. Main chain NLO polymers (a), Side chain NLO polymers (b), and Y-type NLO polymers (c).

group [20] with enhanced thermal stability of dipole alignments. In this work, we have prepared novel polyurethane containing 4-(5-nitro-2-thiazolylazo)resorcinoxy groups as NLO chromophores. We selected the latter as NLO chromophores because they are expected to have higher optical nonlinearities and thermal stability due to a double conjugation and nitro group. Furthermore, these 4-(5-nitro-2-thiazolylazo)resorcinoxy 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 new promising NLO polyurethane, in which the pendant NLO chromophores are components of the polymer backbone. 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 electro-optic properties. We now report the results of the initial phase of the work.

Experimental

Materials

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, yielding 5.98 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 3.78–4.06 (m, 10H, 2 –OCH_3, 2 –O–CH_2–), 4.38–4.63 (d, 4H, 2 Ph–O–CH_2–), 7.12–7.35 (m, 8H, aromatic), 8.13–8.25 (s, 2H, aromatic), 8.92-9.05 (s, 2H, N–H). IR (KBr) 3342 (s, N–H), 2953, 2835 (m, C–H), 1683 (s, C=O), 1595 (s, N=N), 1513, 1394 (vs, N=O) cm^{-1}. Anal. Calcd for $(C_{29}H_{26}N_6O_8S)_n$: C, 52.41; H, 3.94; N, 14.75; S, 4.83. Found: C, 52.52; H, 4.06; N, 14.82; S, 4.88.

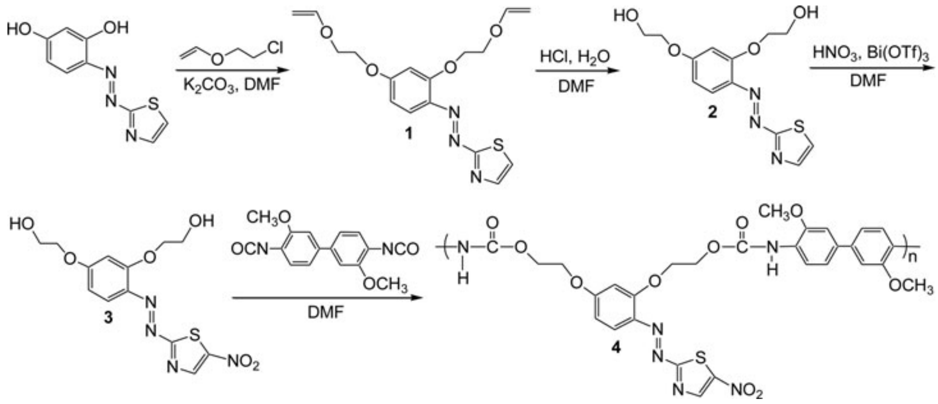
Measurements

Infrared (IR) spectra were obtained with a Varian FT IR-1000 IR spectrophotometer. ^{1}H NMR spectra were obtained with a Varian VNMRS 500MHz NMR spectrometer. UV-visible absorption spectra were obtained with a SECOMAM Model UVIKON XS 99-90289 spectrophotometer. T_g values were measured using a TA 2920 differential scanning calorimeter DSC in a nitrogen atmosphere. A TA Q50 thermogravimetric analyzer with a heating rate of 10°C min^{-1} up to 800°C was used for the thermal degradation of polymers under nitrogen. The refractive index of the sample was measured using the optical transmission technique [21]. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [22]. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.

Results and discussion

Synthesis and characterization of polymer 4

Monomer **3** was prepared by the reaction of compound **2** with nitric acid and bismuth (III) trifluoromethanesulfonate in anhydrous DMF according to a literature procedure [23]. Diol **3** was condensed with 3,3′-dimethoxy-4,4′-biphenylenediisocyanate in a dry DMF solvent to yield novel polyurethane **4** containing 4-(5-nitro-2-thiazolylazo)resorcinoxy group as NLO chromophore. 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. The ^{1}H NMR and IR spectra of the polymer **4** are shown in Fig. 2 and Fig. 3, respectively. 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 signal at 8.92-9.05 ppm of ^{1}N NMR spectrum of polymer **4** assigned to the amine proton indicates the formation of urethane linkage. The IR spectrum of polymer **4** shows strong carbonyl peaks near 1683 cm^{-1} indicating the presence of urethane bond. The spectrum also shows strong absorption peak near 1595 cm^{-1} due to azo group and absorptions at 1513 and 1394 cm^{-1} due to nitro group indicating the presence of nitrothiazole unit. These results are consistent with the proposed structure,



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

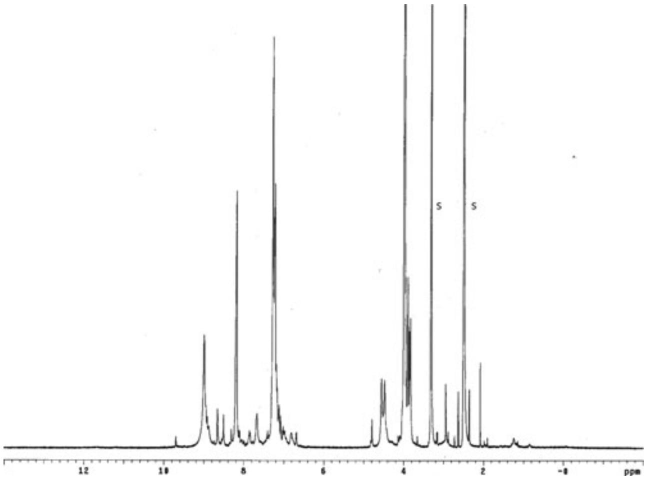


Figure 2. ^{1}H NMR spectrum of polymer **4** taken in DMSO-d_6 at room temperature.

indicating that the NLO chromophores remained intact during the polymerization. The polymer **4** 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^{-1}. 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. Thus, we obtained a new type of NLO polyurethane with side-chain and main-chain characteristics. Having obtained the well-defined Y-type polyurethane **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** showed a thermal stability up to 240°C from its TGA thermogram. T_g value of the polymer **4** measured by DSC is around 126°C. This T_g value is higher than that of the polyester containing nitrophenylazoresorcinoxy group [20], which is near 102°C.

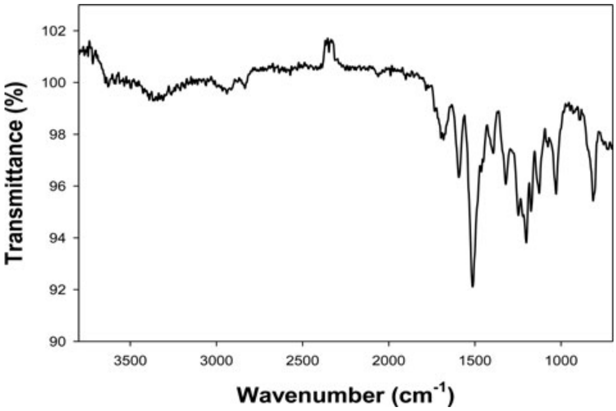


Figure 3. FT IR spectrum of polymer **4** taken at room temperature.

Table 1. Nonlinear optical properties of polymer **4**.

Polymer	d_{33}[a] (esu)	d_{31}[a] (esu)	film thickness[b] (μm)	n	d_{33}/d_{31}
4	9.02×10^{-9}	2.89×10^{-9}	0.52	1.556	3.12

[a] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [22].
[b] Film thickness was determined by the optical transmission technique [21].

Nonlinear optical properties of polymer

The NLO properties of polymer were studied by 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. The films were cooled to room temperature in the presence of the electric field. Finally, the electric field was removed. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. Nonlinear optical properties of polymer **4** are summarized in Table 1. 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). SHG coefficients (d_{33}, d_{31}) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure [22]. The measured values of d_{33} and d_{31} for polymer **4** are 9.02×10^{-9} esu and 2.89×10^{-9} esu, respectively. This d_{33} value is higher than that of the polyurethane containing nitrophenylazoresorcinol, which is near 4.92×10^{-9} esu [20].

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 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 measurements were performed at a heating rate of 4°C/min from 30 to 200°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 130°C. This SHG thermal stability is higher than that of the polyurethane containing nitrophenylazoresorcinol, which is near 100°C [20]. In general, main-chain NLO polymers have good thermal stability of dipole

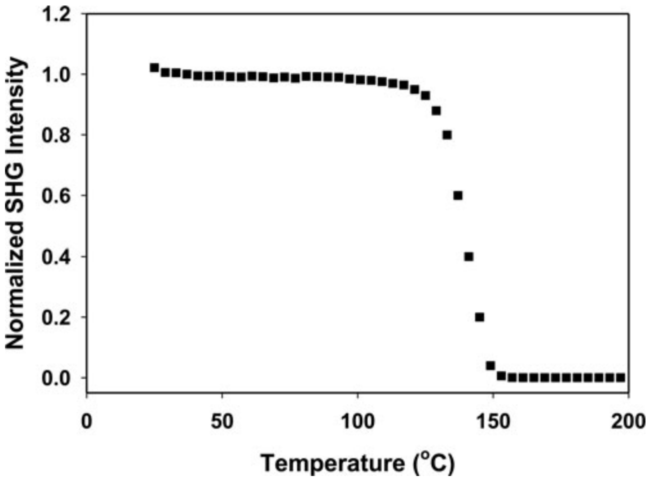


Figure 4. Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 4°C/min.

alignments, but they often do not dissolve in organic solvents, and their intractability make them unusable to fabricate stable films. Side-chain NLO polymer systems have good solubility and high loading level of NLO chromophores, but they often suffer from poor stability of dipole alignments at high temperatures. The high SHG thermal stability of polymer **4** is due to the stabilization of dipole alignment of NLO chromophore, which stems from the partial main chain character of the polymer structure and partly by hydrogen bonds between the neighboring urethane linkages. Thus, we obtained new NLO polyurethane having the merits of both main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility.

Conclusions

A novel Y-type NLO polyurethane **4** with pendant NLO chromophores as parts of the polymer backbone was prepared and characterized. This Y-type polymer **4** is soluble in common organic solvents and shows a thermal stability up to 240°C with T_g valuearound 126°C. The SHG coefficient (d_{33}) of corona-poled polymer film was 9.02×10^{-9} esu. This polymer exhibits SHG stability even at 4°C higher than T_g and no significant SHG decay is observed below 130°C. This high thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophores and partly by hydrogen bonds between the neighboring urethane linkages.

Acknowledgments

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References

[1] Burland, D. M., Miller, R. D., & Walsh, C. (1994). *Chem. Rev.*, *94*, 31.
[2] Ikeda, T., Tadaki, Y., Funajima, R., Tatewaki, Y., & Okada, S. (2011). *Mol. Cryst. Liq. Cryst.*, *539*, 142.
[3] Ganapayya, B., Jayarama, A., & Dharmaprakash, S. M. (2013). *Mol. Cryst. Liq. Cryst.*, *571*, 87.
[4] Jeon, B., Song, M. Y., Kim, H. J., & Lee, J.-Y. (2013). *Mol. Cryst. Liq. Cryst.*, *581*, 89.
[5] Song, M. Y., Jeon, B., Kim, H. J., & Lee, J.-Y. (2013). *J. Polym. Sci. Part A: Polym. Chem.*, *51*, 275.
[6] Lee, J.-H., Choe, K. Y., & Lee, J.-Y. (2014). *Mol. Cryst. Liq. Cryst.*, *599*, 72.
[7] Dos Santos, R. T., Longo Jr, L. S., & Alves, S. (2014). *Mol. Cryst. Liq. Cryst.*, *596*, 1.
[8] Khoo, I. C., Chen, C.-W., Hong, K. L., Lin, T.-H., & Zhao, S. (2014). *Mol. Cryst. Liq. Cryst.*, *594*, 31.
[9] Han, K. S., Park, S. K., Shim, S. Y., Jahng, W. S., & Kim, N. J. (1998). *Bull. Kor. Chem. Soc.*, *19*, 1165.
[10] Lee, J. W., & Kawatsuki, N. (2009). *Mol. Cryst. Liq. Cryst.*, *498*, 59.
[11] Mori, Y., Nakaya, K., Piao, X., Yamamoto, K., Otomo, A., & Yokoyama, S. (2012). *J. Polym. Sci. Part A: Polym. Chem.*, *50*, 1254.
[12] Sato, Y., Inada, S., Araki, T., Tatewaki, Y., & Okada, S. (2014). *Mol. Cryst. Liq. Cryst.*, *597*, 73.
[13] Tsutsumi, N., Morishima, M., & Sakai, W. (1998). *Macromolecules*, *31*, 7764.
[14] Liu, J.-G., Nakamura, Y., Shibasaki, Y., Ando, S., & Ueda, M. (2007). *J. Polym. Sci. Part A: Polym. Chem.*, *45*, 5606.
[15] Hoang, M. A., Kim, M. H., Cho, M. J., Kim, K. H., Kim, K. N., Jin, J.-I., & Choi, D. H. (2008). *J. Polym. Sci. Part A: Polym. Chem.*, *46*, 5064.
[16] Li, Z., Qui, G., Ye, C., Qin, J., & Li, Z. (2012). *Dyes. Pigm.*, *94*, 16.
[17] Wu, W., Qin, J., & Li, Z. (2013). *Polymer*, *17*, 4351.
[18] Moon, K. J., Shim, H. K., Lee, K. S., Zieba, J., & Prasad, P. N. (1996). *Macromolecules*, *29*, 861.

[19] Woo, H. Y., Shim, H.-K., & Lee, K.-S. (2000). *Polym. J.*, *32*, 8.
[20] Kim, M. S., Song, M. Y., Jeon, B., & Lee, J.-Y. (2012). *Mol. Cryst. Liq. Cryst.*, *568*, 111.
[21] Cisneros, J. I. (1998). *Appl. Opt.*, *37*, 5262.
[22] Herman, W. N., & Hayden, L. M. (1995). *J. Opt. Soc. Am. B.*, *12*, 416.
[23] Zhu, W., Liu, Y., Niu, G., Wang, Q., Li, J., Zhu, X., Li, Y., Xue, H., & Yang, G. (2012). *Catal. Commun.*, *29*, 145.