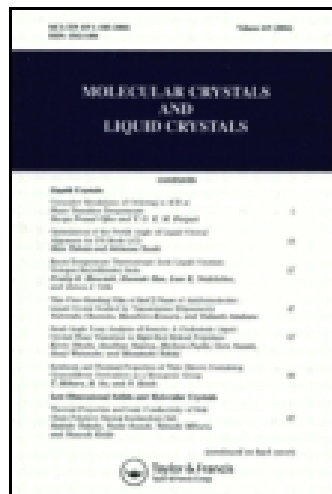


This article was downloaded by: [The Aga Khan University]

On: 14 December 2014, At: 23:40

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

Synthesis and Nonlinear Optical Properties of Novel Y-type Polyester Containing Nitrophenylazoresorcinoxy Group

You Jin Cho^a, Mi Sung Kim^a & Ju-Yeon Lee^a

^a Department of Chemistry, Institute of Basic Science, Inje University, Obang-dong, Gimhae, Korea

Published online: 16 May 2011.

To cite this article: You Jin Cho, Mi Sung Kim & Ju-Yeon Lee (2011) Synthesis and Nonlinear Optical Properties of Novel Y-type Polyester Containing Nitrophenylazoresorcinoxy Group, *Molecular Crystals and Liquid Crystals*, 539:1, 115/[455]-120/[460], DOI: [10.1080/15421406.2011.566074](https://doi.org/10.1080/15421406.2011.566074)

To link to this article: <http://dx.doi.org/10.1080/15421406.2011.566074>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Synthesis and Nonlinear Optical Properties of Novel Y-type Polyester Containing Nitrophenylazoresorcinoxy Group

YOU JIN CHO, MI SUNG KIM, AND JU-YEON LEE

Department of Chemistry, Institute of Basic Science, Inje University,
Obang-dong, Gimhae, Korea

A new Y-type polyester (3) containing nitrophenylazoresorcinoxy groups as NLO chromophores, which are components of the polymer backbone was prepared. Polyester 3 is soluble in common organic solvents such as N,N-dimethylformamide and acetone. It shows a thermal stability up to 240°C from thermogravimetric analysis with glass-transition temperature (T_g) obtained from differential scanning calorimetry near 116°C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer films at the 1064 nm fundamental wavelength is around 4.63×10^{-9} esu. The dipole alignment exhibits a thermal stability even at 4°C higher than T_g , and no SHG decay was observed below 120°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; polyester; SHG coefficient; thermogravimetric analysis (TGA)

Introduction

Recently nonlinear optical (NLO) materials are extensively studied because of their potential applications in the field of electro-optic devices, including high speed optical modulators and ultrafast optical switches [1–3]. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of important criteria [4]; in this context, two approaches to minimize the randomization have been proposed namely the use of cross-linking method [5] and the utilizing high glass-transition temperature (T_g) polymers such as polyimides [6]. Polyesters with amino-sulfone azobenzene chromophores in the main chain generate strong and stable reversible birefringence [7]. NLO polyesters containing azobenzene mesogens in the main chain exhibit high thermal and temporal stabilities [8]. Polyesters containing cyanophenylazoaniline moiety in the side chain show good temporal stability of second-order nonlinearity [9]. In general, polymers with the NLO chromophores in the main chain have good thermal stability of dipole alignments, but they often do not dissolve in organic solvents,

Address correspondence to Ju-Yeon Lee, Department of Chemistry, Institute of Basic Science, Inje University, 607 Obang-dong, Gimhae 621-749, Korea. Tel.: +82-55-320-3221; Fax: +82-55-321-9718; E-mail: chemlly@inje.ac.kr

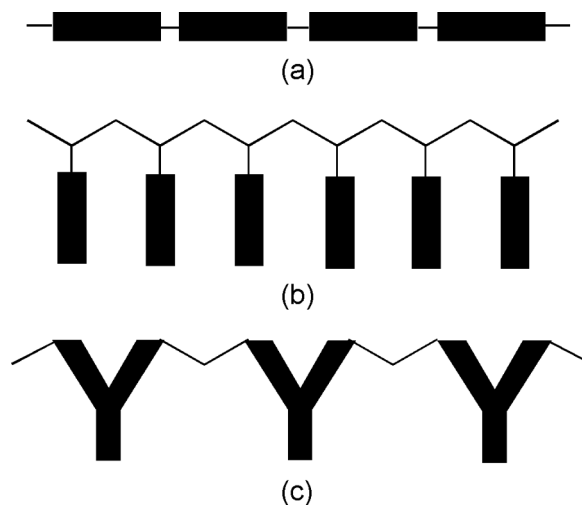


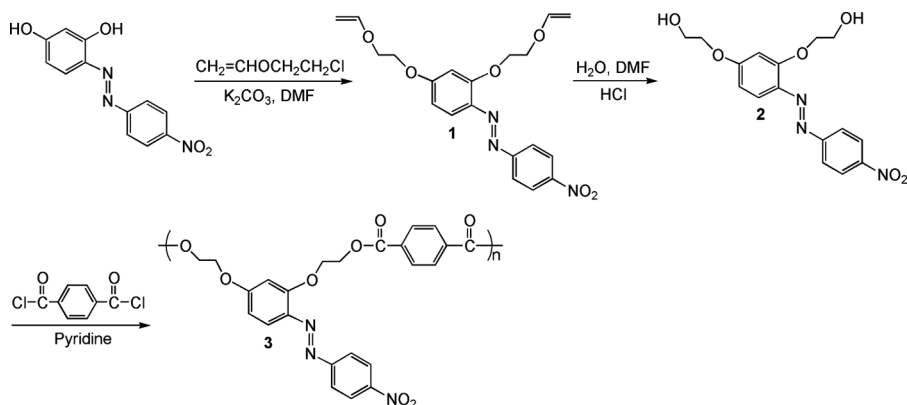
Figure 1. Main chain NLO polymers (a), Side chain NLO polymers (b), and Y-type NLO polymers (c).

and their intractability make them unusable to fabricate stable noncentrosymmetric films. Side chain NLO polymers have the advantages such as good solubility and homogeneity, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we reported novel NLO polyesters containing dioxynitrostilbenyl group [10] or dioxybenzylidenemalononitrile [11], which showed enhanced thermal stability of dipole alignments. In this work reported here, we prepared new Y-type polyester containing nitrophenylazoresorcinoxy groups as NLO chromophores. We selected the latter as NLO chromophores because they are expected to have high optical nonlinearities. Furthermore, these nitrophenylazoresorcinoxy groups constitute novel Y-type NLO polyesters (Fig. 1c), and these Y-type NLO polyesters have not yet been reported in the literature. Thus, we synthesized a new type of NLO polyester, in which the pendant NLO chromophores are parts of the polymer backbone. This Y-type NLO polymer is expected to have the advantages 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 thermal and nonlinear optical properties.

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, yielding 4.29 g (90% yield) of polymer **3**. Inherent viscosity (η_{inh}) = 0.30 dL/g (c, 0.5 g/dL in DMSO at 25°C). ^1H NMR (DMSO- d_6) δ (ppm): δ 4.45–4.87 (m, 8H, 2 -O-CH₂-CH₂-O-), 6.68–6.82 (s, 1H, aromatic), 6.85–7.10 (s, 1H, aromatic), 7.58–8.33 (s, 9H, aromatic). IR (KBr disc) (cm⁻¹): 3085 (w, =C-H), 2926 (m, C-H), 1721 (vs, C=O), 1600 (s, N=N), 1521, 1342 (vs, N=O), 1180 (m, N=N). Anal. Calcd for (C₂₄H₁₉N₃O₈)_n: C, 60.38; H, 4.01; N, 8.80. Found: C, 60.48; H, 4.09; N, 8.72.



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

Measurements

Infrared (IR) spectra were obtained with a Shimadzu FT IR-8201PC infrared spectrophotometer. ^1H NMR spectra were obtained with a Varian 300 MHz NMR spectrometer. UV-visible absorption spectra were obtained with a Shimadzu UV-3100S 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 $10^\circ\text{C min}^{-1}$ up to 800°C was used for the thermal degradation of polymers under nitrogen. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the polymers were estimated using gel permeation chromatography (GPC; styragel HR5E4E columns; tetrahydrofuran (THF) solvent). The refractive index of the sample was measured using the optical transmission technique [12]. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [13]. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.

Results and Discussion

Synthesis and Characterization of Polymer 3

The synthetic route for polymer **3** is presented in Scheme 1. Polyester **3** was synthesized through the reaction of monomer **2** containing NLO chromophore with stoichiometric amounts of terephthaloyl chloride in pyridine. The chemical structure of the resulting polymer was confirmed by ^1H NMR, IR spectra, and elemental analysis. The chemical shifts in ^1H NMR spectrum of the polymer are consistent with the proposed polymer structure. The signal at 4.45–4.87 is assigned to the ethylene protons attached to oxygen. The aromatic protons are shown in the range 6.68–8.33 ppm. The IR spectrum of polymer **3** shows strong carbonyl peaks near 1721 cm^{-1} indicating the presence of ester bond. The spectrum also shows strong absorption peaks near 1521 and 1342 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 number average molecular weight (M_n) of the polymer **3**, determined by GPC, was 18800 ($M_w/M_n=1.97$). The structural feature of this

polymer is that it has pendant NLO chromophores, which are parts of the polymer main chain. Thus the resulting polymer **3** is mid type of side-chain and main-chain NLO polymer, and is expected to have both of their merits. 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 value is 0.30 dL/g. Polymer **3** shows strong absorption near 398 nm due to the NLO chromophore nitrophenylazoresorcinoxy group.

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 **3** shows a thermal stability up to 240°C from its TGA thermogram. The 10% weight loss degradation temperature (T_d) of polymer **3** is near 262°C. T_g value of the polymer **3** measured by DSC is around 116°C. This T_g value is higher than those of the polyesters containing dioxynitrostilbene, which are in the range 90–95°C [10] or dioxybenzylidenemalononitrile, which is near 83°C [11].

Nonlinear Optical Properties of Polymer

The NLO properties of polymer were studied by the SHG method. To induce non-centrosymmetric polar order, the spin-coated polymer film was corona-poled. As the temperature was raised to 120°C, a corona voltage of 6.5 kV was applied and this temperature was maintained for 30 min. The poling was confirmed by UV-visible spectrum. After electric poling, the dipole moments of the NLO chromophores were aligned and the 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. Nonlinear optical 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 in a poled polymer **3**. The SHG values were compared with those obtained from a Y-cut quartz plate. 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 [13]. The measured values of d_{33} and d_{31} for polymer **3** are 4.63×10^{-9} esu and 1.58×10^{-9} esu, respectively. Since the second harmonic wavelength is at 532 nm, which is not in the absorptive region of the resulting polyester, there is not resonant contribution to this d_{33} value.

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	398	4.63×10^{-9}	1.58×10^{-9}	0.48	1.73

^aPolymer film after poling.

^bSHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [13].

^cFilm thickness was determined by the optical transmission technique [12].

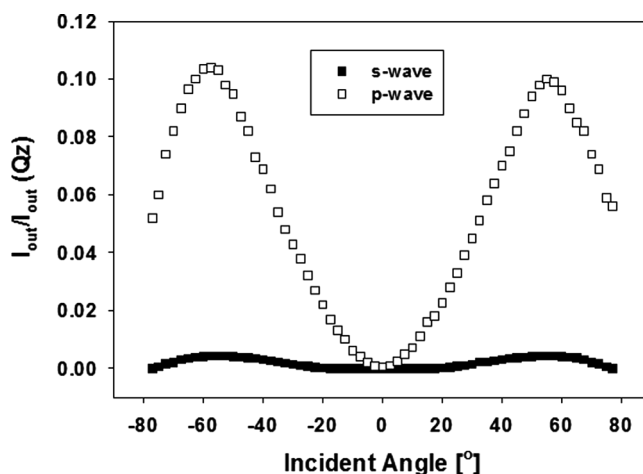


Figure 2. Angular dependence of SHG signal for a poled film of polymer 3.

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 measurements were performed at a heating rate of 3.5°C/min from 25 to 200°C. The polymer film exhibits a thermal stability even at 4°C higher than T_g and no significant SHG decay is observed below 120°C. In general, main-chain NLO polymers have good thermal stability of dipole alignments, but they often do not dissolve in organic solvents. Side-chain NLO polymer systems have good solubility, but they often suffer from poor stability of dipole alignments at high temperatures. The high thermal stability of second harmonic generation of polymer 3 is due to the stabilization of dipole alignment of NLO chromophore, which stems from the partial main

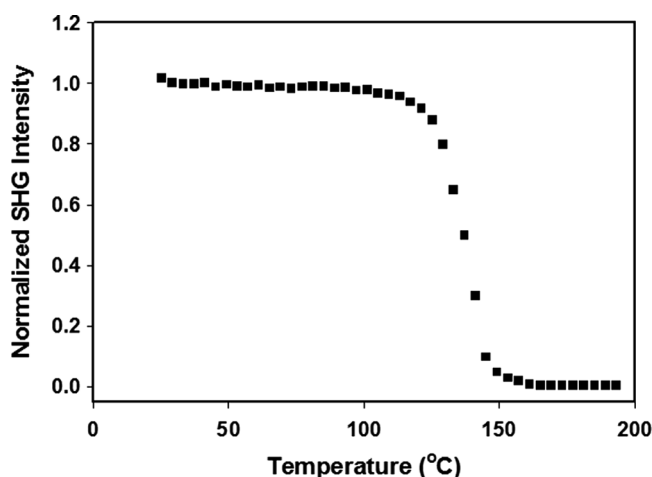


Figure 3. Normalized SHG signal of polymer 3 as a function of temperature at a heating rate of 3.5°C/min.

chain character of the polymer structure. Thus, we obtained a new type of NLO polyester having both the merits of main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility.

Conclusions

A novel Y-type NLO polyester **3** with pendant NLO chromophores as parts of the polymer backbone was prepared and characterized. This Y-type polymer **3** is soluble in common organic solvents and shows a thermal stability up to 240°C with T_g value around 116°C. The SHG coefficient (d_{33}) of corona-poled polymer film is 4.63×10^{-9} esu. This polymer exhibits SHG stability even at 4°C higher than T_g and no significant SHG decay is observed below 120°C. This high thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophores, which constitute parts of the polymer main chain

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. 2010-0020951).

References

- [1] Burland, D. M., Miller, R. D., & Walsh, C. (1994). *Chem. Rev.*, 94, 31.
- [2] Nie, X., Xianyu, H., Wu, T. X., & Wu, S.-T. (2008). *Mol. Cryst. Liq. Cryst.*, 489, 194.
- [3] Lee, S. K., Cho, M. J., Jin, J.-I., & Choi, D. H. (2007). *J. Polym. Sci. Part A: Polym. Chem.*, 45, 531.
- [4] Rau, I. (2008). *Mol. Cryst. Liq. Cryst.*, 485, 862.
- [5] Lee, J. W., & Kawatsuki, N. (2009). *Mol. Cryst. Liq. Cryst.*, 498, 59.
- [6] Tsutsumi, N., Morishima, M., & Sakai, W. (1998). *Macromolecules*, 31, 7764.
- [7] Xu, Z. S., Drnoyan, V., Natansohn, A., & Rochon, R. (2000). *J. Polym. Sci. Part A: Polym. Chem.*, 38, 2245.
- [8] Sandhya, K. Y., Pillai, C. K. S., Sato, M., & Tsutsumi, N. (2003). *J. Polym. Sci. Part A: Polym. Chem.*, 41, 1527.
- [9] Nemoto, N., Miyata, F., Nagase, Y., Abe, J., Hasegawa, M., & Shirai, Y. (1996). *Macromolecules*, 29, 2365.
- [10] Lee, J.-Y., & Kim, W.-T. (2007). *Mol. Cryst. Liq. Cryst.*, 471, 347.
- [11] Won, D.-S., Lee, G.-Y., & Lee, J.-Y. (2008). *Dyes Pigments*, 78, 225.
- [12] Cisneros, J. I. (1998). *Appl. Opt.*, 37, 5262.
- [13] Herman, W. N., & Hayden, L. M. (1995). *J. Opt. Soc. Am. B*, 12, 416.