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SYNTHESIS AND ELECTRO-OPTIC PROPERTIES OF NOVEL Y-TYPE POLYURETHANES HAVING DIOXYBENZYLIDENEMALONONITRILE

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3,4-Di-(2'-hydroxyethoxy)benzylidenemalononitrile (3) was prepared and condensed with 2,4-toluenediisocyanate and 3,3'-dimethoxy-4,4'-biphenylene-diisocyanate to yield unprecedented novel Y-type polyurethanes (4–5) containing 3,4-dioxybenzylidenemalononitrile group as a NLO-chromophore, which is a part of the polymer main chain. The resulting polyurethanes 4–5 were soluble in common organic solvents such as acetone and DMF. Polymers 4–5 showed a thermal stability up to 280°C in TGA thermograms with T_g values from DSC thermograms in the range of 148–152°C. The SHG coefficients (d_{33}) of poled polymer films were around 5.96×10^{-9} esu. These poled polymer films exhibited greater thermal stabilities of dipole alignments even at 20°C higher than T_g due to the partial main chain character of the polymer structure, which is acceptable for NLO device applications.

Keywords: 3,4-Di-(2'-hydroxyethoxy)benzylidenemalononitrile; AFM; NLO; polyurethanes; poling; SHG coefficient

INTRODUCTION

Nonlinear optical (NLO) materials based on organic compounds have been extensively studied in recent years because of their potential applications in the field of telecommunications, optical switching, etc [1]. One of the current challenges is to design novel NLO polymers having optimized properties. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is important considerations. Two approaches to minimize the randomization have

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been proposed. One is to use crosslinking method [2] and the other is to use high T_g polymers such as polyimides [3]. Polyurethane matrix forms extensive hydrogen bond between urethane linkage and increases rigidity preventing the relaxation of induced dipoles [4]. Polyurethanes with hemicyanine [5–6] in the side chain, or having transverse NLO chromophore to main chain exhibit enhanced thermal stability [7]. In this work we prepared novel Y-type polyurethanes (Fig. 1c) containing 3,4-dioxybenzylidenemalononitrile groups as NLO-chromophores, which are parts of polymer backbones. The resulting polymers are mid type of side chain- and main chain NLO polymers, and are expected to have both of the merits of the two types; stabilization of dipole alignment and good solubility. After confirming the structure of the resulting polymers we investigated their NLO properties and thermal stability. We also compared their properties with those of benzylidenecyanoacetate derivatives [6].

EXPERIMENTAL

Materials

Synthetic methods of diol **3** and polymers **4–5** are summarized in Scheme 1 and Scheme 2. Diol **3**: Mp = 108–110°C. ^1H NMR (acetone- d_6) δ 2.78–2.87

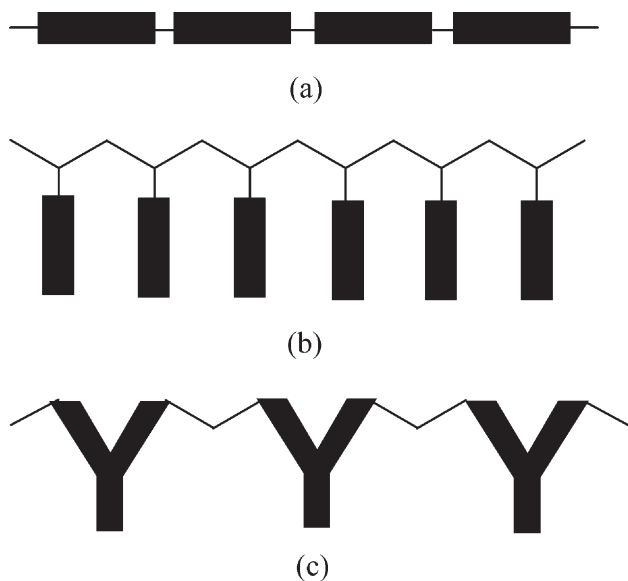
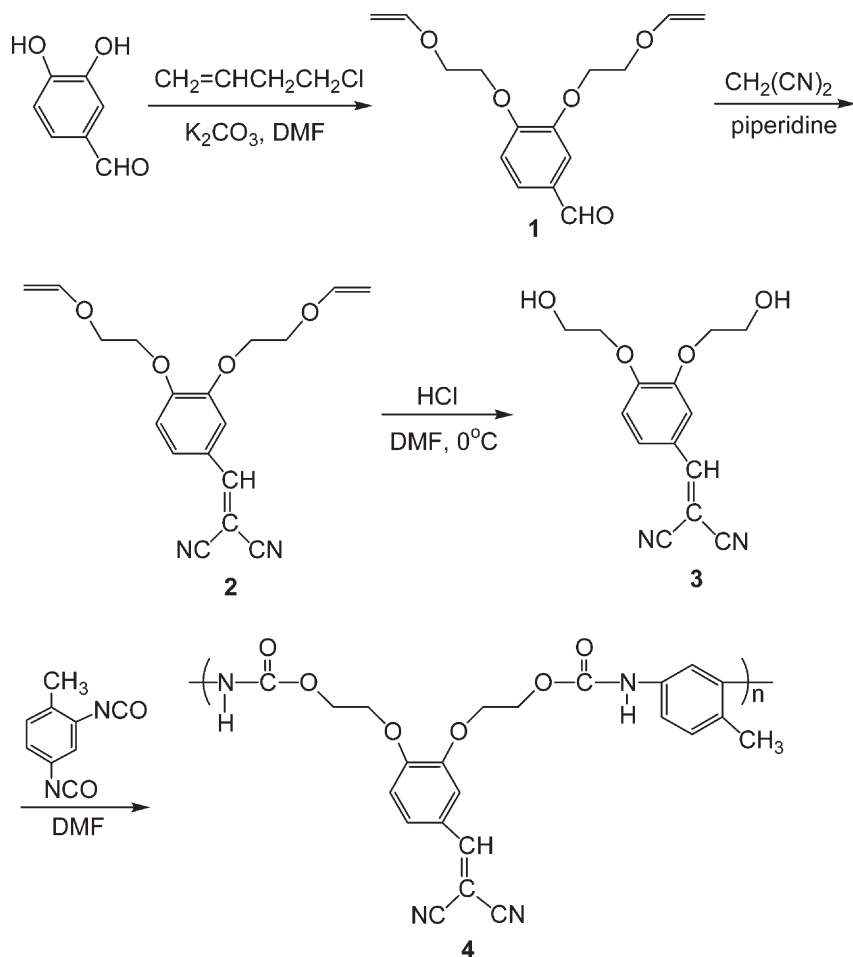
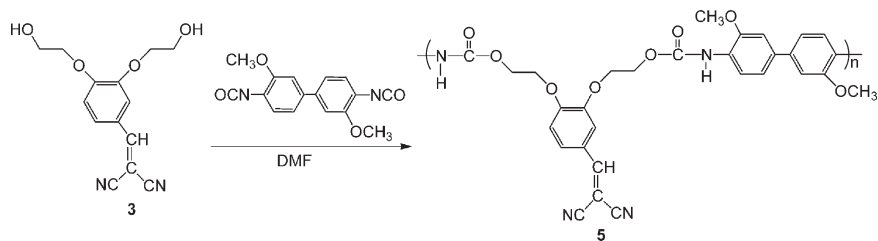


FIGURE 1 Main chain NLO polymers (a), side chain NLO polymers (b), and Y-type NLO polymers (c).

(d, 2H, -OH), 3.87–3.98 (m, 4H, 2 -CH₂-OH), 4.09–4.28 (m, 4H, 2 -O-CH₂-), 7.21–7.27 (d, 1H, aromatic), 7.63–7.65 (d, 1H, aromatic), 7.76 (d, 1H, aromatic), 8.14 (s, 1H, -Ph-CH=). IR (KBr) 3337 (s, O-H), 3045 (w, =C-H), 2930 (m, C-H), 2222 (s, CN), 1607, 1583 (s, C=C) cm⁻¹. Anal. Calcd for C₁₄H₁₄N₂O₄: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.40; H, 5.25; N, 10.28. Polymer **4**: η_{inh} = 0.30 dL/g (c, 0.5 g/dL in DMSO at 25°C). ¹H NMR (DMSO-*d*₆) δ 2.12–2.21 (m, 3H, -CH₃), 3.96–4.49 (m, 8H, 2 -O-CH₂-CH₂-O-), 6.94–8.56 (m, 7H, aromatic),



SCHEME 1 Synthetic method of polymer **4**.



SCHEME 2 Synthetic method of polymer **5**.

8.92–9.11 (m, 2H, N–H). IR (KBr) 3383 (s, N–H), 2953, 2883 (m, C–H), 2222 (m, CN), 1711, 1699 (s, C=O), 1562, 1534, 1512 (vs, C=C) cm^{-1} . UV/Vis (DMSO) $\lambda_{\text{max}}=371$. Anal. Calcd for $(\text{C}_{23}\text{H}_{20}\text{N}_4\text{O}_6)_n$: C, 61.60; H, 4.50; N, 12.49. Found: C, 61.68; H, 4.58; N, 12.58. Polymer **5**: $\eta_{\text{inh}}=0.25$ dL/g (c, 0.5 g/dL in DMSO at 25°C). ^1H NMR ($\text{DMSO}-d_6$) δ 3.79–4.48 (m, 14H, 2 $-\text{OCH}_3$, 2 $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$), 7.15–8.69 (m, 10H, aromatic), 8.91–9.06 (m, 2H, N–H). IR (KBr) 3383 (m, N–H), 2953, 2848 (m, C–H), 2222 (m, CN), 1726, 1711, 1699 (s, C=O), 1583, 1512 (vs, C=C) cm^{-1} . UV/Vis (DMSO) $\lambda_{\text{max}}=362$. Anal. Calcd for $(\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_8)_n$: C, 63.15; H, 4.59; N, 9.82. Found: C, 63.25; H, 4.66; N, 9.91.

Instrumentation

IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ^1H NMR spectra were obtained on a Varian 300 MHz NMR spectrometer. UV-Vis absorption spectra were measured on a Shimadzu UV-3100S spectrophotometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The glass transition temperatures (T_g) were measured on a TA 2920 differential scanning calorimeter in a nitrogen atmosphere. DuPont 951 thermogravimetric analyzer 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 polymers were estimated by gel permeation chromatography (GPC) (columns styragel HR5E4E; solvent THF). The alignment of the NLO-chromophore of the polymers was carried out by corona poling method (6.5 kV, 160°C, 30 min). Atomic force microscopy (AFM) images were recorded with a Park Science Instrument Autoprobe CP, operated in a contact mode, which measures topography. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [7].

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymers 4–5

3,4-Di-(2'-vinylxyethoxy)benzylidenemalononitrile (**2**) was prepared by the condensation reaction of **1** with malononitrile. Compound **2** was hydrolyzed to yield acetaldehyde and diol **3**. Polymers **4–5** were prepared by polyaddition reaction between a diol **3** and TDI and DMBPI, respectively (Scheme 1–2). The structural features of these polymers are that they have pendant NLO chromophores, which are part of their polymer backbones. Thus we found a new type of side chain NLO polyurethanes. These mid-type NLO polymers are expected to have both of the merits of main chain- and side chain NLO polymers. The chemical structures of the compounds were confirmed by ^1H NMR, IR spectra, and elemental analysis. The signal at 8.92–9.11 ppm of the ^1H NMR spectra assigned to the amine proton indicates the formation of urethane linkage. The IR spectra of the same polymer samples also show a strong carbonyl peaks near 1726, 1711, 1705 cm^{-1} indicating the presence of urethane bond. These results are consistent with the proposed structures. The number average molecular weight (M_n) of the polymers was determined to be 15300 ($M_w/M_n = 2.04$) for polymer **4**. Having well defined polyurethanes (**4–5**), we investigated their properties.

Electro-Optic Properties of Polymers 4–5

The polymers **4–5** was soluble in common solvents such as acetone, DMF and DMSO, but were not soluble in methanol and diethyl ether. The inherent viscosities were in the range of 0.25–0.30 dL/g. Polymers **4–5** showed strong absorption near 380 nm by the NLO-chromophore dioxynitrostilbenyl group. The thermal behaviors of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g). The results are summarized in Table I. Polymers **4–5** showed a thermal stability up to 280°C from their TGA thermograms. Glass transition temperature (T_g) values of the polymers **4–5** measured by DSC were around 148–152°C. According to our experimental results, these T_g values are higher than those of cyanoacetate derivatives.

To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. As the temperature was raised to 160°C, 6.5 kV of corona voltage was applied and kept 160°C for 30 min. The UV-Vis absorption spectra of the polymer sample **4** before and after the poling are presented in Figure 2. After the electric poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectrum of polymer

TABLE I Thermal Properties of Polymers 4–5

Polymer	T_g^a , °C	Degradation temp, °C ^b			Residue ^b at 800°C, %@
		5%-loss	20%-loss	40%-loss	
4	152	284	327	383	17.2
5	148	308	346	393	11.7

^aDetermined from DSC curves measured on a TA 2920 differential scanning calorimeter with a heating rate of 10°C/min under nitrogen atmosphere.

^bDetermined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

4 exhibited a decrease in absorption due to birefringence. From the absorbance change, the order parameter of the poled film could be estimated, which is related to the poling efficiency. The estimated order parameter value, Φ , was 0.13 ($\Phi = 1-A_1/A_0$, A_0 and A_1 are the absorbances of the polymer film before and after poling) for the polymer 4.

Domain structures of NLO-chromophores for the poled thin-film samples were obtained using atomic force microscopy (AFM). AFM images

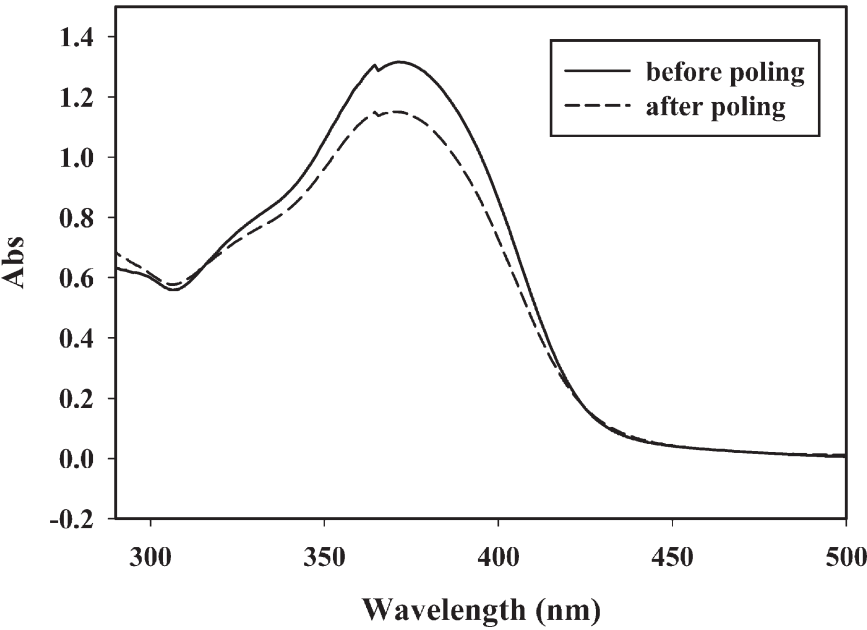


FIGURE 2 UV-Vis absorption spectra of a film of polymer 4 before and after poling.

TABLE II Nonlinear Optical Properties of Polymers 4–5

Polymer	λ_{max}^a (nm)	d_{33}^b (esu)	Φ^c	d_{31}^b (esu)	d_{33}/d_{31}
4	371	5.96×10^{-9}	0.13	2.03×10^{-9}	2.94
5	376	6.84×10^{-9}	0.21	2.36×10^{-9}	2.90
6	370	4.76×10^{-9}	0.11	1.63×10^{-9}	2.92

^a Polymer film after corona poling.

^b SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [10].

^c Order parameter $\Phi = 1 - A_1/A_0$, A_0 and A_1 are the absorbances of the polymer film before and after corona poling, respectively.

show that the surface of the film sample is extremely flat and clean. However, the morphology of the film was dramatically changed after poling, resulting in numerous hills and valleys in the surface structure, which were aligned the poling direction. The NLO properties were studied by the SHG method. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser [8]. The refractive index of

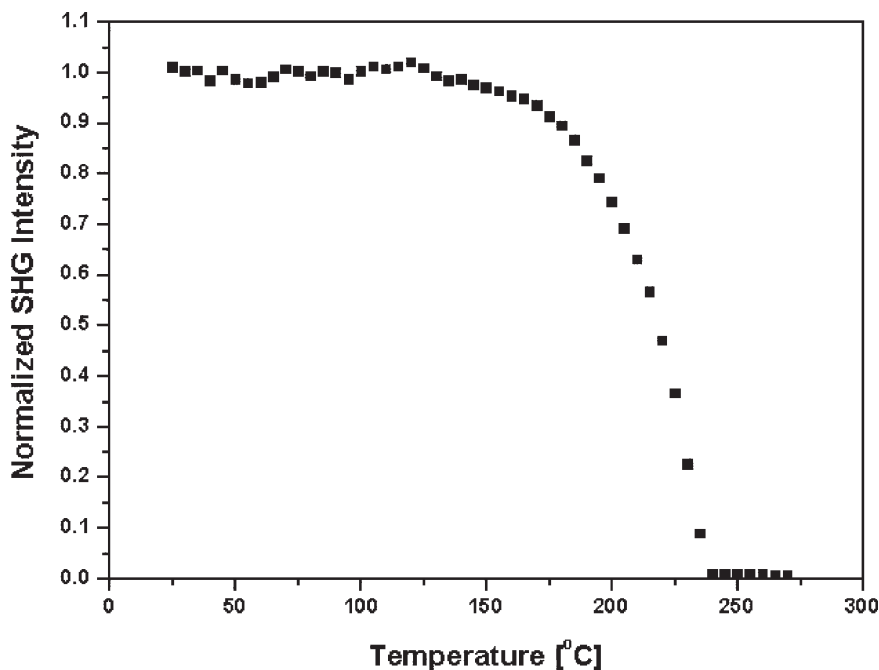


FIGURE 3 Normalized SHG intensity of polymer 4 as a function of temperature at a heating rate of 10°C/min.

the polymer sample was measured by the optical transmission technique [9]. 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 to the samples and recorded. The SHG coefficient d_{33} was calculated through the method developed by Herman et al. [10]. The SHG measurements revealed a d_{33} value of 5.96×10^{-9} esu for polymer **4**. NLO properties of polymers **3–5** are summarized in Table II. Since the second harmonic wavelength was at 532 nm, which is not in the absorptive region of the resulting polyurethane, there was not resonant contribution to this d_{33} value. According to our experimental results, these d_{33} values are a bit lower than those of benzylidenecyanoacetate derivatives. To evaluate the high-temperature thermal stability of the polymers, we studied the temporal stability of the SHG signal. In Figure 3 we present the dynamic thermal stability study of the NLO activity of the film **4**. To investigate the real time NLO decay of the SHG signal of the poled polymer films as a function of temperature, in situ SHG measurements were performed at a heating rate of 10°C/min from 30°C to 250°C. The poled film of polymer **4** exhibited greater thermal stability and there was little decay of the d_{33} signal up to 175°C, as shown in Figure 3. This excellent thermal stability of optical nonlinearity is due to the stabilization of dipole alignment of NLO chromophore. In general, side chain NLO polymers loose thermal stability of dipole alignment around T_g . On the contrary of these common side chain NLO polymers, Y-type NLO polymer **4** showed a thermal stability of SHG even at 20°C above T_g . Stabilization of dipole alignment is a characteristic of main chain NLO polymers. Thus, we obtained novel Y-type NLO polymers having both of the merits of main chain- and side chain NLO polymers; stabilization of dipole alignment and good solubility. These good temporal thermal stabilities are probably due to the partial main chain character of the polymer structures. We are now in the process of extending the polymerization system to the synthesis of other type of NLO polymers and the results will be reported elsewhere.

REFERENCES

- [1] Chelma, D. S. & Zyss, J. (1987). *Nonlinear optical properties of organic molecules and crystals*, Academic Press: New York, vol 1.
- [2] Chen, M., Dalton, L. R., Yu, L. P., Shi, Y. Q., & Steier, W. H. (1992). *Macromolecules*, **25**, 4032.
- [3] Tsutsumi, N., Morishima, M., & Sakai, W. (1998). *Macromolecules*, **31**, 7764.
- [4] Kim, P.-S., Kim, M.-R., Sung, G.-Y., Kim, K.-H., Ha, C.-H., Kwak, & Lee, J.-K. (2002). *Mol. Cryst. Liq. Cryst.*, **377**, 277.

- [5] Moon, K. J., Shim, H. K., Lee, K. S., Zieba, Z., & Prasad, P. N. (1996). *Macromolecules*, *29*, 861.
- [6] Lee, J.-Y., Park, E.-J., Kang, T.-S., Lee, H., Yoon, K., Byun, N., Rhee, B., Jung, C., & Joo, M. (2002). *Mol. Cryst. Liq. Cryst.*, *377*, 269.
- [7] Tsutumi, N., Matsumoto, O., & Sakai, W. (1997). *Macromolecules*, *30*, 4584.
- [8] Jephagnon, J. & Kurtz, S. K. (1970). *J. Appl. Phys.*, *40*, 1667.
- [9] Cisneros, J. (1998). *Appl. Opt.*, *37*, 5262.
- [10] Herman, W. N. & Hayden, L. M. (1995). *J. Opt. Soc. Am. B*, *12*, 416.