Synthesis and Properties of Novel T-Type Polyurethanes Containing 2,5-Dioxynitrostilbenyl Group as a Nonlinear Optical Chromophore

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Received June 30, 2003

Functional materials of nonlinear optical (NLO) activities have been extensively studied over the past decade because of their potential applications in the field of telecommunications, optical switching, etc.[1] Among them, the NLO polymers are considered promising materials, mainly because they offer many advantages such as good processability to form optical devices.[2] 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 been proposed. One is to use crosslinking method[3-5] and the other is to use high T_g polymers such as polyimides.[6,7] Polyurethane matrix forms extensive hydrogen bond between urethane linkage and increases rigidity preventing the relaxation of induced dipoles. In this work we prepared new T-type polyurethanes containing dioxynitrostilbenyl group as a NLO-chromophore. We selected 2,5-dioxynitrostilbenyl group as NLO-chromophore because it will have a large dipole moment and is rather easy to synthesize. Furthermore 2,5-dioxynitrostilbenyl group constitutes a novel T-type NLO polyurthanes, in which the NLO chromophores are parts of polymer backbones (Fig. 1B). These T-type NLO polyurethanes are not shown in the literature. After confirming the structure of the resulting polymers we investigated the properties such as T_g and second harmonic generation (SHG) activity (d_{33}). We now report the results of the initial phase of the work.

2,5-Dihydroxy-4-nitrostilbene (**1**) was prepared by condensation of 4-nitrophenylacetic acid with 2,5-dihydroxy-benzaldehyde according to a literature procedure.[8] 2,5-Di-
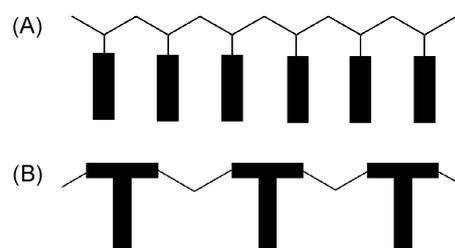
Figure 1. Side chain NLO polymers (A) and T-type NLO polymers (B).

(2-hydroxyethoxy)-4-nitrostilbene (**2**) was prepared by reaction of 2-iodoethanol with **1**. Polymer **3** was prepared by polyaddition reaction between a diol **2** and 2,4-toluene-diisocyanate (TDI) in a dry DMF solvent. Synthetic method of polymer **3** is summarized in Scheme 1. The chemical structures of the compounds were confirmed by ^{1}H NMR, IR spectra and elemental analysis. The signal at 8.32-8.43 ppm of the ^{1}H NMR spectra, assigned to the amide proton, indicates the formation of urethane linkage. The IR spectra of the same polymer samples also show a strong carbonyl peak near 1713 cm^{-1}, indicating the presence of urethane bond. Two strong absorption bands due to the nitro group in the NLO-chromophore of the stilbene unit appeared near 1520 cm^{-1} and 1350 cm^{-1}. These results are consistent with the proposed structures, indicating that the NLO-chromophore remained intact during the polymerization. We now have a novel T-type polyurethane (**3**) and investigate its property.

The polymer **3** was soluble in common solvents such as acetone, DMF and DMSO, but were not soluble in methanol
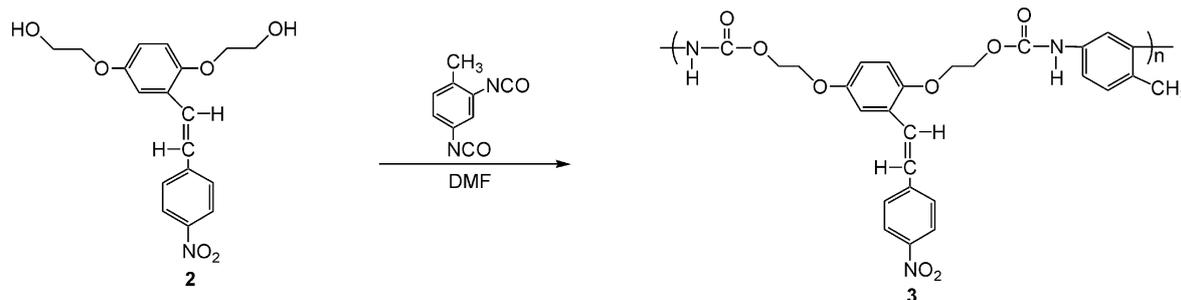
Scheme 1

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1728   *Bull. Korean Chem. Soc.* **2003**, Vol. 24, No. 12

Communications to the Editor

Table 1. Thermal Properties of Polymer **3**

Polymer	T_g, °C	Degradation temp, °C			Residue at 700 °C, %
		5%-loss	20%-loss	40%-loss	
3	159	308	354	421	41.8

and diethyl ether. The thermal behavior 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). Polymer **3** showed a thermal stability up to 300 °C from their TGA thermograms, as shown in Table 1. Glass transition temperature (T_g) value of the polymer **3** measured by DSC was around 159 °C. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled (170 °C, 6 kV, 30 min). After the electric poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectrum of polymer **3** exhibited a slight blue shift and 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 was deduced to be 0.25 ($\Phi = 1 - A_1/A_0$, A_0 and A_1 are the absorbances of the polymer film before and after poling). Domain structures of NLO-chromophores for the poled thin-film samples were obtained by using atomic force microscopy (AFM). Figure 2 shows AFM scans of the spin-coated film before and after poling for polymer **3**. AFM images show that the surface of the film sample is extremely flat and clean. However, this good quality film was dramatically changed after poling, resulting in numerous hills and valleys in the surface structure, which means that the NLO chromophores were aligned in the poling direction. The refractive index of the polymer sample was measured by the optical transmission technique.[9] The transmittance of thin film includes the information of the thickness, refractive index and extinction coefficient of that. The NLO properties were studied by the SHG method. NLO properties of polymer **3** are summarized in Table 2. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser.[10,11] 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 value of d_{31} and d_{33} for polymer **3** were 1.74×10^{-9} esu and 5.36×10^{-9} esu, respectively.

Since the second harmonic wavelength was at 532 nm, which is not in the absorptive region of the resulting

Table 2. Nonlinear Optical Properties of Polymer **3**

Polymer	$\lambda_{max}{}^a$	$d_{33}{}^b$	Φ^c	$d_{31}{}^b$	d_{33}/d_{31}
3	391	5.36×10^{-9}	0.25	1.74×10^{-9}	3.08

*[a]*Polymer film after corona poling. *[b]*SHG coefficients were derived from the analysis of measured Maker-fringes.[19] *[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.
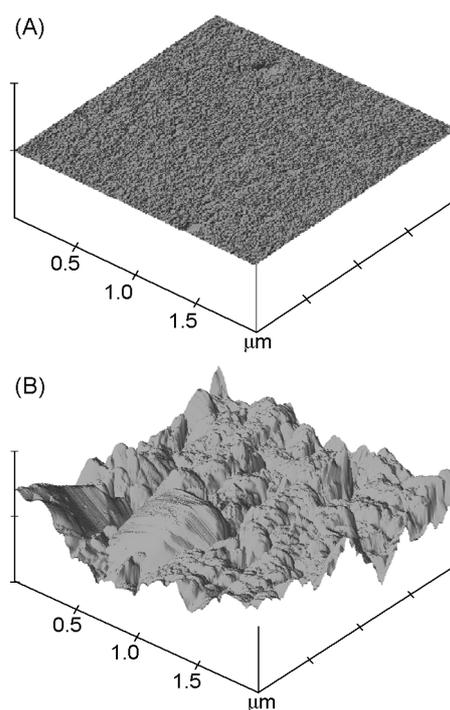
Figure 2. AFM images (3D) as spin-coated (A) followed by corona-poled (B) for a polymer film of **3**.

polyurethane, there was not resonant contribution to this d_{33} value. In the isotropic model, the ratio of d_{33}/d_{31} is predicted to be about 3. Our d_{33}/d_{31} value of 3.08 is in good agreement with the predicted value. To evaluate the high-temperature stability of the polymers, we studied the temporal stability of the SHG signal. The poled polymer film of **3** exhibited no negligible decay of the d_{33} signals up to 170 °C. These temporal thermal stabilities are probably due to the partial main chain character of polymer structure and hydrogen bonds between urethane linkage, which are acceptable for NLO device applications. 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.

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