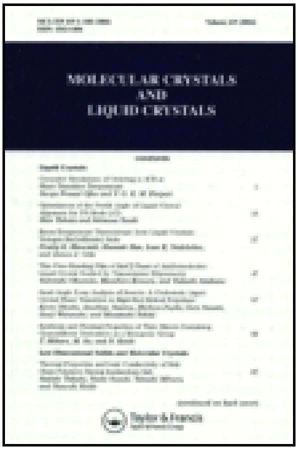

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Synthesis Of Novel T-Type Polyurethanes Containing 2,5-Dioxynitrostilbenyl Group As A Nlo Chromophore and Their Properties

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SYNTHESIS OF NOVEL T-TYPE POLYURETHANES CONTAINING 2,5-DIOXYNITROSTILBENYL GROUP AS A NLO CHROMOPHORE AND THEIR PROPERTIES

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2,5-Di-(2′-hydroxyethoxy)-4′-nitrostilbene (**2**) *was prepared and condensed with 2,4-toluenediisocyanate, 3,3′-dimethoxy-4,4′-biphenylenediisocyanate and 1,6-hexamethylenediisocyanate to yield novel T-type polyurethanes* **3–5** *containing the NLO-chromophore 2,5-dioxynitrostilbenyl group, which constitutes a part of the polymer backbone. Polymers* **3–5** *were soluble in common organic solvents such as acetone and DMSO. Polymers* **3–5** *showed a thermal stability up to 280°C in TGA thermograms with T_gs of 79–159°C in DSC thermograms. The SHG coefficients (d_{33}) of poled polymer films were around 5.4×10^{-9} esu, and they exhibited greater thermal stabilities of dipole alignments even at 10°C higher than T_g due to the partial main chain character of the polymer structure.*

Keywords: AFM; 2,5-Di-(2′-hydroxyethoxy)-4′-nitrostilbene; nonlinear optical (NLO); polyurethane; SHG coefficient (d_{33}); thermal stability

INTRODUCTION

Nonlinear optical (NLO) polymers have been extensively studied over the past decade because of their potential applications in the field of telecommunications, optical switching, etc [1]. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is important considerations. Two

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approaches to minimize the randomization have been proposed. One is to use crosslinking method and the other is to use high T_g polymers such as polyimides [2]. Physically crosslinked systems via hydrogen bonds have the advantages such as homogenity and good processibility relative to the chemically crosslinked systems. Polyurethane matrix forms extensive hydrogen bond between urethane linkage and increases rigidity preventing the relaxation of induced dipoles [3–4]. Polyurethanes functionalized with thiophene chromophore [5] in side chain or having transverse NLO chromophore to main chain [6] exhibit good thermal stability. In this work we prepared novel T-type polyurethanes (Fig. 1c) containing the NLO chromophore 2,5-dioxynitrostilbene, which is a part of polymer backbone. These mid-type NLO polymers are expected to have both of the merits of main chain- and side chain NLO polymers. After confirming the structure of the resulting polymers we investigated the properties such as T_g, thermal stability, and second order NLO activity.

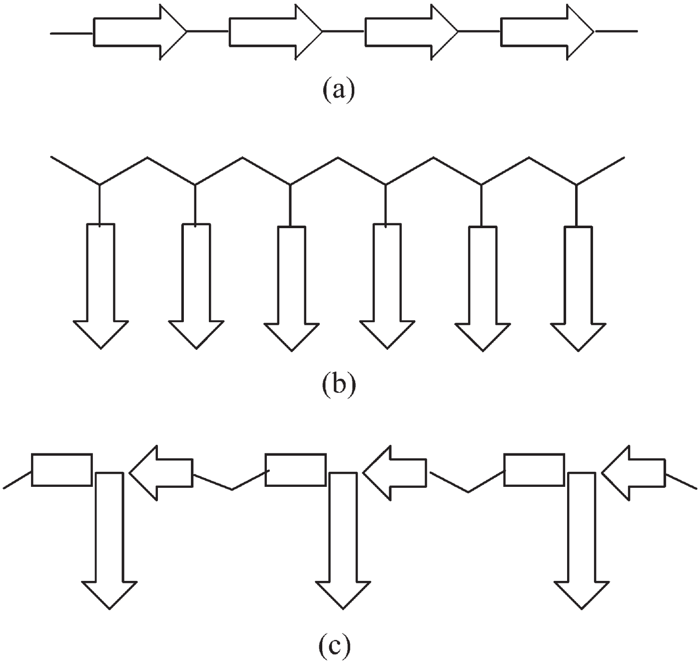


FIGURE 1 Main chain NLO polymers (a), side chain NLO polymers (b), and T-type NLO polymers (c).

EXPERIMENTAL

Materials

Diol **2** was prepared by the reaction of 2,5-dihydroxy-4′-nitrostilbene with iodoethanol. Polyurethanes **3–5** were prepared by polyaddition of diol **2** with 2,4-toluenediisocyanate (TDI), 3,3′-dimethoxy-4,4′-biphenylenediisocyanate (DMBPI) and 1,6-hexamethylenediisocyanate (HDI) according to a procedure similar to that reported already [3]. Polymer **3**: $\eta_{inh} = 0.25\,dL/g$ (c, 0.5 g/dL in DMSO at 25°C). ^1H NMR (DMSO-d_6) δ 1.90–2.28 (m, 3H, $-CH_3$), 4.15–4.52 (m, 8H, 2 $-O-CH_2-CH_2-O-$), 6.95–7.58 (m, 7H, aromatic), 7.83–8.05 (m, 2H, aromatic), 8.17–8.39 (m, 3H, aromatic), 8.87–9.12 (m, 2H, N−H). IR (KBr) 3394 (s, N−H), 2935, 2883 (m, C−H), 1713 (s, C=O), 1595 (s, C=C), 1520, 1344 (vs, N=O) cm^{-1}. UV/Vis (DMSO) $\lambda_{max} = 391$. Anal. Calcd for $(C_{27}H_{25}N_3O_8)_n$: C, 62.42; H, 4.85; N, 8.09. Found: C, 62.54; H, 4.97; N, 8.18. Polymer **4**: $\eta_{inh} = 0.23\,dL/g$ /g (c, 0.5 g/dL in DMSO at 25°C). ^1H NMR (DMSO−d_6) δ 3.25–3.39 (m, 6H, $-OCH_3$), 3.68–4.12 (m, 14H, 2 $-O-CH_2-CH_2-O-$, 2 $-OCH_3$), 6.84–7.49 (m, 10H, aromatic), 7.96–8.41 (m, 7H, aromatic), 8.85–9.08 (m, 2H, N−H). IR (KBr) 3383 (m, N−H), 2941 (m, C−H), 1716 (s, C=O), 1595 (s, C=C), 1525, 1344 (vs, N=O) cm^{-1}. UV/Vis (DMSO) $\lambda_{max} = 388$. Anal. Calcd for $(C_{34}H_{31}N_3O_{10})_n$: C, 63.64; H, 4.87; N, 6.55. Found: C, 63.75; H, 4.96; N, 6.63. Polymer **5**: $\eta_{inh} = 0.21$ dL/g (c, 0.5 g/dL in DMSO at 25°C). ^1H NMR (DMSO-d_6) δ 0.92–1.44 (m, 8H, $-(CH_2)_4-$), 2.76–3.12 (m, 4H, 2 $-NH-CH_2-$), 3.96–4.52 (m, 8H, 2 $-O-CH_2-CH_2-O-$), 5.66 (s, 2H, 2 N−H), 7.08–7.41 (d, 4H, aromatic), 7.81–8.03 (s, 2H, aromatic), 8.08–8.45 (s, 3H, aromatic). IR (KBr) 3325 (s, N−H), 2930, 2849 (s, C−H), 1707 (s, C=O), 1618,1572 (vs, C=C), 1350 (vs, N=O) cm^{-1}. UV/Vis (DMSO) $\lambda_{max} = 390$. Anal. Calcd for $(C_{26}H_{31}N_3O_8)_n$: C, 60.81; H, 6.08; N, 8.18. Found: C, 60.72; H, 6.16; N, 8.25.

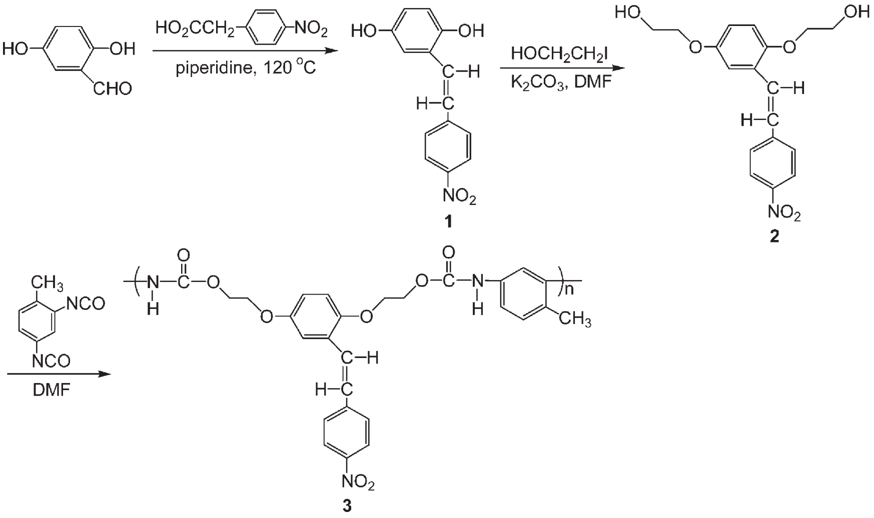
INSTRUMENTATION

IR, ^1H NMR, and UV-Vis spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer, Varian 300 MHz NMR spectrometer, and Shimadzu UV-3100S spectrophotometer, respectively. 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 measured 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, 170°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].

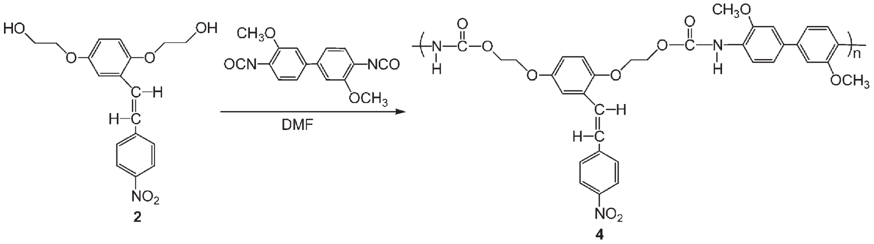
RESULTS AND DISCUSSION

Synthesis and Characterization of Polymers 3–5

2,5-Dihydroxy-4′ -nitrostilbene(**1**) was prepared by the condensation of 4-nitrophenylacetic acid with 2,5-dihydroxybenzaldehyde according to a literature procedure [8]. 2,5-Di-(2′-hydroxyethoxy)-4′-nitrostilbene(**2**) was prepared by the reaction of 2-iodoethanol with **1**. Polymers **3–5** were prepared by polyaddition reaction between **2** and TDI, DMBPI and HDI, respectively, in a dry DMF solvent (Scheme 1–3). The striking structural features of these polymers are that they have pendant NLO chromophores, which are part of their polymer main chains. Thus we found a new type of NLO polyurethanes. We expect that these mid-type NLO polymers can have both of the merits of main chain- and side chain NLO polymers. The chemical structures of the compounds were confirmed by ^{1}H NMR,



SCHEME 1 Synthetic method of polymer **3**.

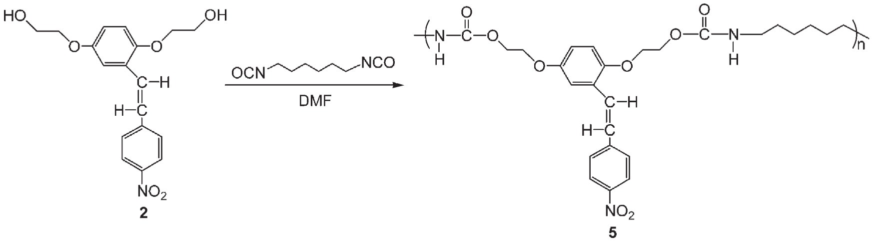


SCHEME 2 Synthetic method of polymer **4**.

IR spectra and elemental analyses. The signal at 8.85–9.08 ppm of the ^{1}H NMR spectra of polymer samples assigned to the amine proton indicates the formation of urethane linkage. The IR spectra of the same polymer samples also show a strong carbonyl peak near 1716 cm^{-1} indicating the presence of urethane bond. The number average molecular weights (M_n) of the polymers were determined to be 13300 ($M_w/M_n = 1.94$) for polymer **4**. Having well defined polyurethanes (**3–5**), we investigate their properties.

THERMAL BEHAVIORS OF POLYMERS 3–5

The polymers **3–5** were 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 0.23–0.26 dL/g. Polymers **3–5** showed strong absorption near 390 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 **3–5** showed a thermal stability up to 280°C from their TGA



SCHEME 3 Synthetic method of polymer **5**.

TABLE I Thermal Properties of Polymers **3–5**

		Degradation temp, °C[b]			
Polymer	T_g[a],°C	5%-loss	20%-loss	40%-loss	Residue[b] at 800°C,%
3	159	308	354	421	41.8
4	151	316	337	365	31.6
5	79	311	335	384	30.4

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

[b] Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

thermograms. DSC curves showed that T_g values of the polymers **3–5** were in the range of 79–159°C. Glass transition of polymer **5** is much lower than those of polymers **3–4** probably because of the flexible hydrocarbon chain in the polymer backbone.

NONLINEAR OPTICAL PROPERTIES OF POLYMERS 3–5

The NLO properties of polymers **3–5** were studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. As the temperature was raised to 170°C, 6.5 kV of corona voltage was applied and kept 170°C for 30 min. The UV-Vis absorption spectra of the polymer samples **3–5** before and after the poling were recorded. After the electric poling, the dipole moments of the NLO–chromophores were aligned and UV-Vis spectrum of polymers **3–5** 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 deduced to be 0.10–0.36 ($\Phi = 1 - A_1/A_0$, 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 using atomic force microscopy (AFM). Figure 2 shows AFM scans of the spin-coated film before and after poling for polymer **5**. 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 chromophores were aligned to the poling direction. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser [9]. The refractive index of the polymer sample was

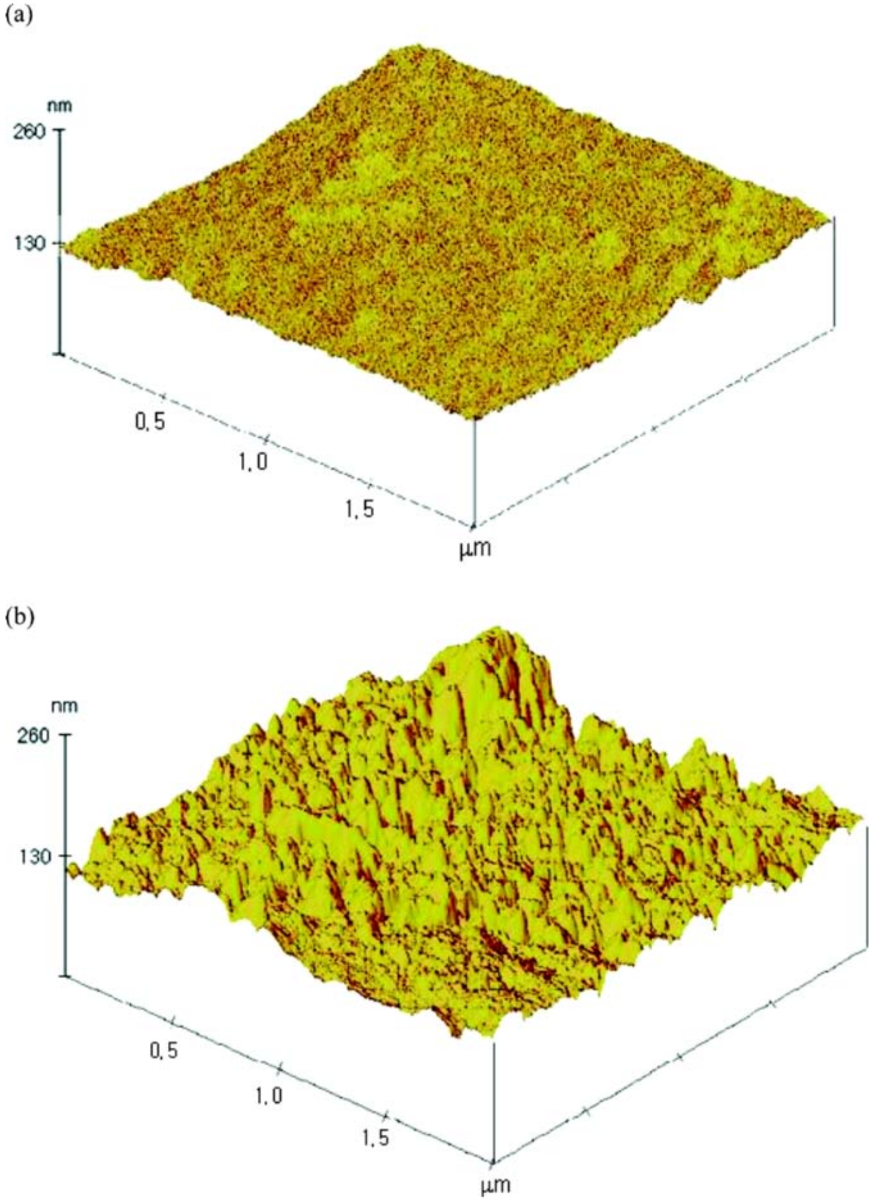


FIGURE 2 AFM images of spin-coated film of polymer **5**: (a) before corona-poling; (b) after corona-poling.

TABLE II Nonlinear Optical Properties of Polymers **3–5**

Polymer	$\lambda_{\max}{}^{a}$ (nm)	$d_{33}{}^{b}$ (esu)	Φ^{c}	$d_{31}{}^{b}$ (esu)	d_{33}/d_{31}
3	391	5.36×10^{-9}	0.25	1.74×10^{-9}	3.08
4	388	4.64×10^{-9}	0.10	1.35×10^{-9}	3.44
5	390	4.93×10^{-9}	0.36	1.75×10^{-9}	2.82

[a] Polymer film after corona poling.

[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [11].

[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.

measured by the optical transmission technique [10]. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. The SHG coefficient d_{33} was calculated through the method developed by Herman *et al.* [11]. The values of d_{33} and d_{31} for polymer **3** were 5.36×10^{-9} and 1.74×10^{-9} esu, respectively. 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 the d_{33} value.

According to our experimental results, these d_{33} values are lower than those of 3,4-derivatives. In the isotropic model, the ratio of d_{33}/d_{31} is predicted to be about three. Our d_{33}/d_{31} value of 2.82–3.44 is in good agreement with the predicted value. 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 from 30°C to 250°C. The poled film of polymer **3** exhibited greater thermal stability and there was little decay of the d_{33} signal up to 170°C. In general, side chain NLO polymers loose thermal stability of dipole alignment below T_g. However, our T-type NLO polymer films showed thermal stabilities of dipole alignments even at 10°C above T_g. Stabilization of dipole alignment is a characteristic of main chain NLO polymers. Thus, we obtained novel 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 structure and extensive hydrogen bonds between urethane linkage.

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