

## Synthesis and Properties of Novel T-type Nonlinear Optical Polyurethane Containing Tricyanovinylthienyl Group with Enhanced Thermal Stability of Dipole Alignment

You Jin Cho, Mi Sung Kim, and Ju-Yeon Lee\*

Institute of Basic Science, Department of Chemistry, Inje University, Gimhae 621-749, Korea. \*E-mail: chemlly@inje.ac.kr  
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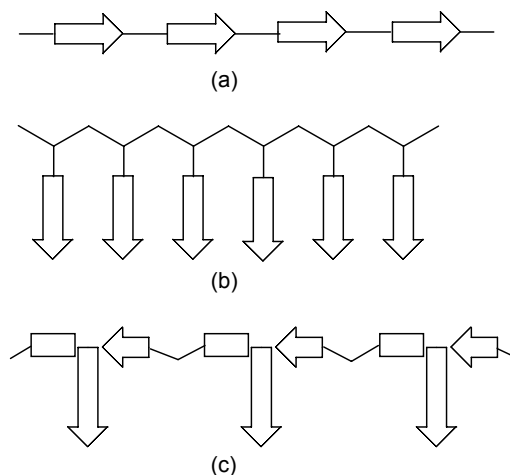
A novel T-type polyurethane **7** containing 1-(2,5-dioxyphenyl)-2-(5-(1,2,2-tricyanovinyl)-2-thienyl)ethenes as NLO chromophores, which constitute part of the polymer backbone, was prepared. Polyurethane **7** is soluble in common organic solvents such as DMF and DMSO. It shows a thermal stability up to 270 °C from TGA thermogram with  $T_g$  value obtained from DSC thermogram near 155 °C. The second harmonic generation (SHG) coefficient ( $d_{33}$ ) of poled polymer film at 1560 nm fundamental wavelength is  $3.56 \times 10^{-9}$  esu. Polymer **7** exhibits a thermal stability even at 5 °C higher than  $T_g$ , and no significant SHG decay is observed below 160 °C, which is acceptable for nonlinear optical device applications.

**Key Words:** Nonlinear optics, Polyurethane, Atomic force microscopy (AFM), Thermal stability, Second harmonic generation, Dipole alignment

### Introduction

Recently nonlinear optical (NLO) materials have been extensively studied because of their potential applications in the field of photonic devices, including ultrafast optical switches, high-speed optical modulators, and high-density optical data storage media.<sup>1-6</sup> The polymeric NLO materials seem to be superior because of their higher nonlinear optical activity, faster response time, low cost, and good processability to form electro-optic devices. A potential NLO polymer must contain highly polarizable conjugated dipolar electronic systems and they have to be mechanically very strong and thermally stable with high glass-transition temperature ( $T_g$ ). In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of important criteria; in this context, two approaches to minimize the randomization have been proposed, namely the use of cross-linking<sup>7-10</sup> and the utilization of high  $T_g$  polymers such as polyimides.<sup>11-16</sup>

A polyurethane matrix forms extensive hydrogen bonding between urethane linkages, with increased rigidity preventing the relaxation of induced.<sup>17-18</sup> Polyurethanes with a NLO chromophore, whose dipole moment is aligned transverse to the main chain backbone, show large second-order nonlinearity with good thermal stability.<sup>19-20</sup> Physically cross-linked systems *via* hydrogen bonds have the advantages such as homogeneity and good processability relative to chemically cross-linked systems, which suffer from significant optical loss and poor solubility. Recently we reported novel Y-type NLO polyurethanes with enhanced thermal stability of second harmonic generation.<sup>21-27</sup> The resulting polymers exhibit high thermal stability of second harmonic generation (SHG), which stems from the stabilization of dipole alignment of the NLO chromophore. In this work reported here, we have prepared a novel polyurethane containing 1-(2,5-dioxyphenyl)-2-(5-(1,2,2-tricyanovinyl)-2-thienyl)ethane groups as NLO chromophores. We selected the latter because they are expected to have large dipole moment. Furthermore, these 1-(2,5-dioxyphenyl)-2-(5-(1,2,2-tricyanovinyl)-2-thienyl)ethene groups constitute a novel T-

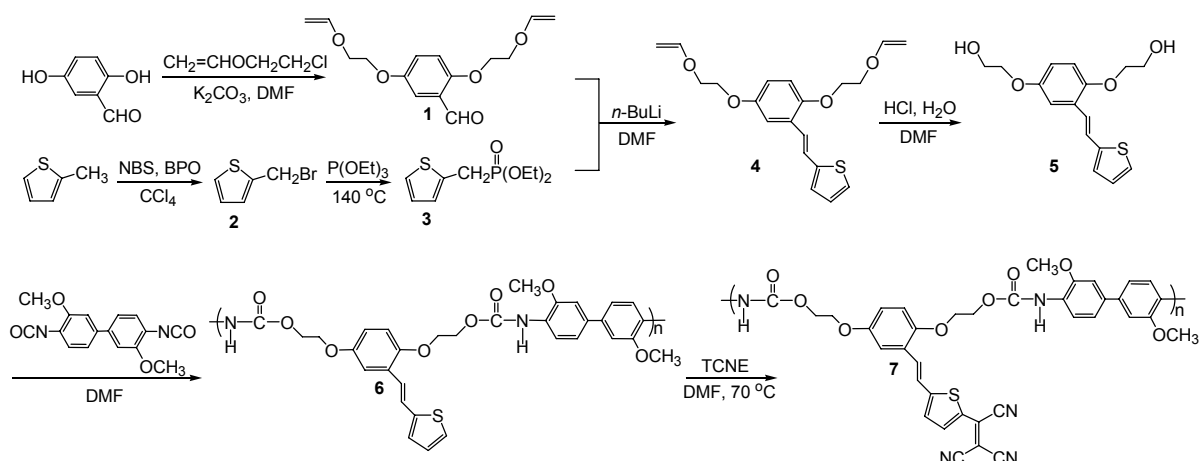


**Figure 1.** Schematic structures of NLO polymers with chromophores located (a) main-chain, (b) side-chain, and (c) main/side chain (T-type).

type NLO polyurethane (see Fig. 1c), in which the structure of NLO chromophores and this T-type NLO polyurethane is not described in the literature. Thus, we synthesized a new type of NLO polyurethane, in which the pendant NLO chromophores are components of the polymer backbone. This mid-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 properties: solubility,  $T_g$ , thermal stability, surface morphology of polymer films, second harmonic generation activity and relaxation of dipole alignment.

### Results and Discussion

**Synthesis and Characterization of Polymer.** Compound **1** was prepared by the reaction of 2-chloroethyl vinyl ether with 2,5-dihydroxybenzaldehyde. Compound **2** was prepared by the bromination of 2-methylthiophene with *N*-bromosuccinimide.



Scheme 1. Synthetic scheme and structure of polymer 7

Compound **3** was prepared by Arbusov reaction from compound **2** and triethyl phosphite. Compound **4** was prepared by Horner-Emmons olefination with compounds **1** and **3**. Compound **5** was prepared by acid-catalyzed hydrolysis of **4** in DMF. Polyurethane **6** was prepared by the polyaddition reaction between diol **5** and 3,3'-dimethoxy-4,4'-biphenylenediisocyanate (DMBPI) in a dry DMF solvent. The polymerization yield was 88 - 90%. Polymer **6** was reacted with tetracyanoethylene (TCNE) in anhydrous DMF<sup>18</sup> to yield polyurethane **7** containing 1-(2,5-dioxyphenyl)-2-(5-(1,2,2-tricyanovinyl)-2-thienyl)ethene groups as NLO chromophores. The synthetic route for polymer **7** is presented in Scheme 1. The resulting polymer was purified by Soxhlet extraction for 2 days with methanol as a solvent.

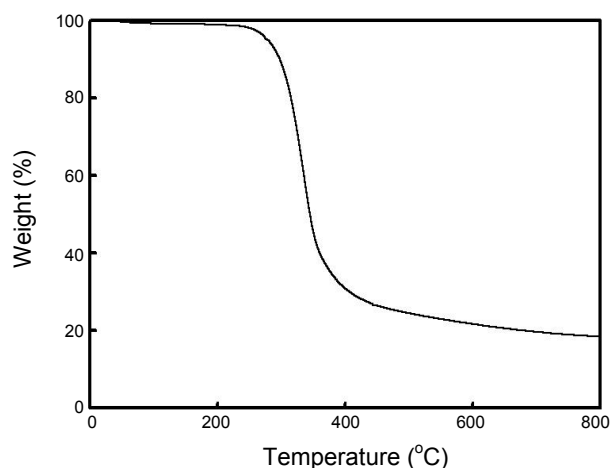
The chemical structure of the polymer was identified using <sup>1</sup>H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structure. <sup>1</sup>H NMR spectrum of the polymer had a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The signal at 8.54 - 9.17 ppm assigned to the amine proton indicates the formation of urethane linkage. The IR spectrum of polymer **7** shows a strong absorption peak near 2219 cm<sup>-1</sup> indicating the presence of nitrile group. The spectrum also shows a strong carbonyl peak near 1701 cm<sup>-1</sup> indicating the presence of urethane bond. These results are consistent with the proposed structure, indicating that the tricyanovinyl groups are introduced well to the thiophene rings. The molecular weights were determined by GPC with polystyrene as the standard and THF as the eluent. The number average molecular weight (*M<sub>n</sub>*) of the polymer **7**, determined using GPC, is 16800 (*M<sub>w</sub>*/*M<sub>n</sub>* = 1.91). The polymer **7** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity is in the range 0.30 - 0.32 dL/g. Polymer **7** shows strong absorption near 549 nm due to the NLO chromophore 1-(2,5-dioxyphenyl)-2-(5-(1,2,2-tricyanovinyl)-2-thienyl)ethene group.

The striking feature of this polymerization system is that it gives unprecedented T-type NLO polymers, in which the pendant NLO chromophores are part of the polymer backbone. These mid-type NLO polymers are expected to have the advan-

tages 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 well defined T-type polyurethane **7**, we investigated its properties.

**Thermal Properties of Polymer.** The thermal behavior of the polymer was investigated using thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature. The results are summarized in Table 1. The TGA thermogram of the polymer **7** is shown in Fig. 2. Polymer **7** has a thermal stability up to 270 °C according to its TGA thermogram. The *T<sub>g</sub>* value of the polymer **7** measured using DSC is near 155 °C. This *T<sub>g</sub>* value is higher than those of the polyurethanes containing dioxynitrostilbene, which is near 151 °C<sup>23</sup> or dioxymethylidenemalononitrile, which is near 146 °C.<sup>24</sup> However, the *T<sub>g</sub>* value is rather lower than that of the Y-type polyurethane, which is near 163 °C.<sup>27</sup> The TGA and DSC studies show that the decomposition temperature of the polymer **7** is higher than that of poling temperature. This indicates that corona poling at 160 °C for a short term is feasible without damaging the NLO chromophore.

**Film Morphology of Polymer.** 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 this temperature was maintained for 30 min. The poling was confirmed from UV-visible absorption spectra. The UV-visible spectra of the polymer **7** before and after poling are presented in Fig. 3. After electric poling, the dipole moments of the NLO chromophores were aligned and the UV-visible absorption of polymer **7** exhibits 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  $\Phi$  of polymer **7** is equal to 0.16 ( $\Phi = 1 - A_1/A_0$ ,  $A_1 = 0.7417$ ,  $A_0 = 0.8809$ , where  $A_0$  and  $A_1$  are the absorbances of the polymer film before and after poling). For the purpose of investigating the surface morphology of polymer film, domain structures of NLO chromophores for the thin-film samples were obtained using atomic force microscopy



**Figure 2.** TGA thermogram of polymer 7 obtained at a heating rate of 10 °C/min under nitrogen.

**Table 1.** Thermal Properties of Polymer 7

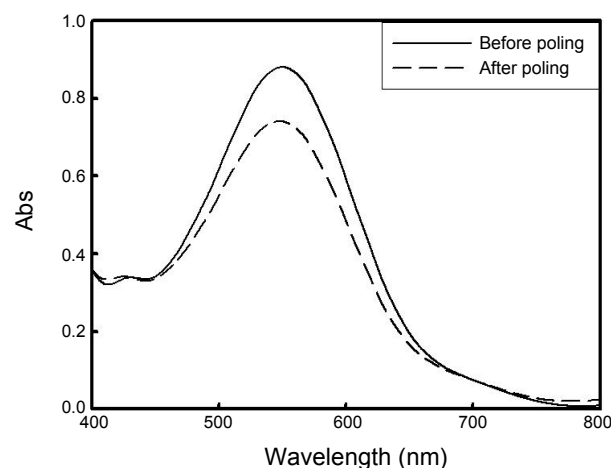
Polymer	$T_g^a$ (°C)	Degradation temp, °C <sup>b</sup>			Residue at 800 °C (wt %) <sup>b</sup>
		5 wt %- loss	20 wt %- loss	40 wt %- loss	
7	155	277	315	335	18.4

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

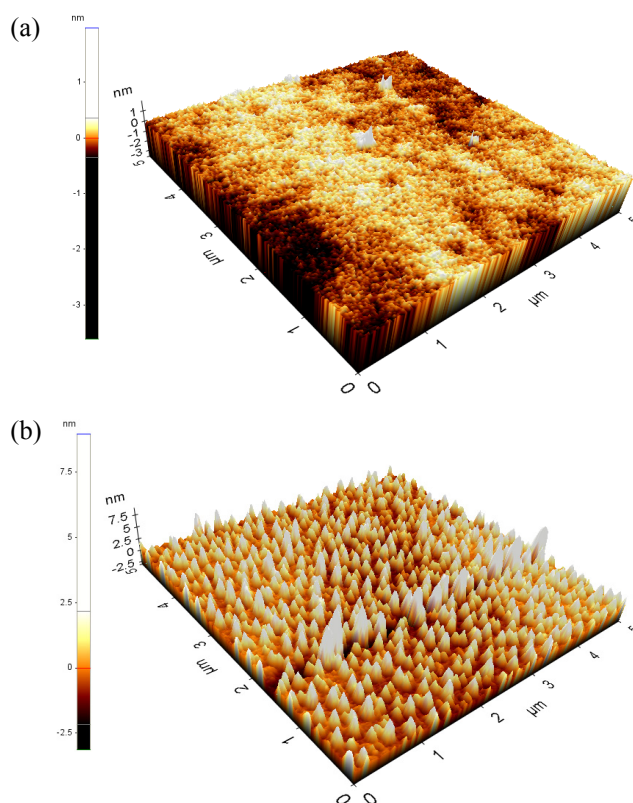
<sup>b</sup>Determined from TGA curves measured with a TA Q50 thermogravimetric analyzer with a heating rate of 10 °C/min under nitrogen atmosphere.

(AFM). Fig. 4 shows AFM scans of a spin-coated film of polymer 7 before and after poling. AFM images show that the surface of the film sample is flat and smooth (Fig. 4a). 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 (see Fig. 4b).

**Nonlinear Optical Properties of Polymer.** The NLO properties of polymer were studied using the SHG method. The refractive index of the sample was measured using the optical transmission technique.<sup>28</sup> The transmittance of thin film gives information on the thickness, refractive index and extinction coefficient. Thus, we could determine these parameters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of 1560 nm using a mode locked Nd-YAG laser and optical parametric oscillator (OPO). In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Fig. 5 shows the angular dependence of SHG signal for a poled sample of polymer 7. 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 at the samples. SHG coefficients ( $d_{33}$ ) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure.<sup>29</sup> Nonlinear optical properties of polymer 7 are summarized in Table 2. The values of  $d_{33}$  and  $d_{31}$  for polymer 7 are  $3.56 \times 10^{-9}$  and  $1.12 \times 10^{-9}$  esu, respectively. This  $d_{33}$  value is somewhat lower than that of the



**Figure 3.** UV-visible absorption spectra of a film of polymer 7 before and after poling.



**Figure 4.** AFM images of spin-coated film of polymer 7: (a) before corona-poling; (b) after corona-poling.

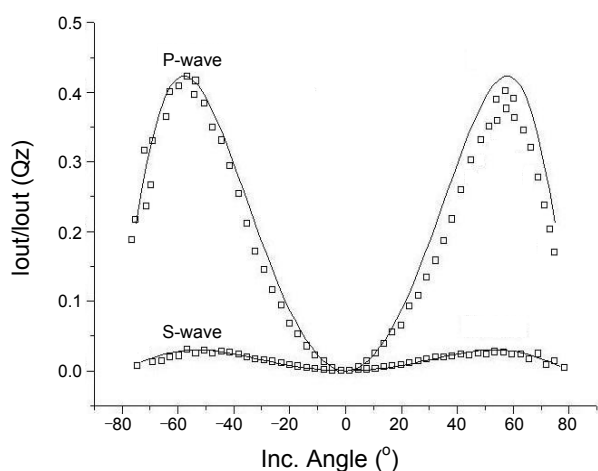
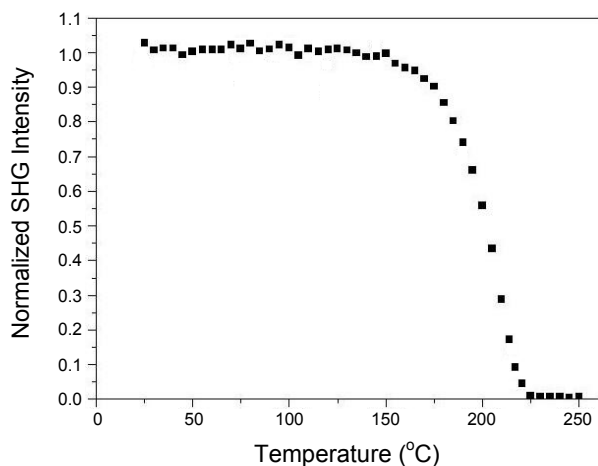
Y-type polyurethane and other NLO polyurethanes.<sup>19</sup> Since the second harmonic wavelength is at 780 nm, which is not in the absorptive region of the resulting polyester, there is not resonant contribution to this  $d_{33}$  value. In the isotropic model, the ratio of  $d_{33}/d_{31}$  is predicted to be about 3. Our  $d_{33}/d_{31}$  value of 3.2 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. Fig. 6 shows the dynamic thermal stability study of the NLO activity of a film of polymer 7. To investigate the real time NLO decay of the

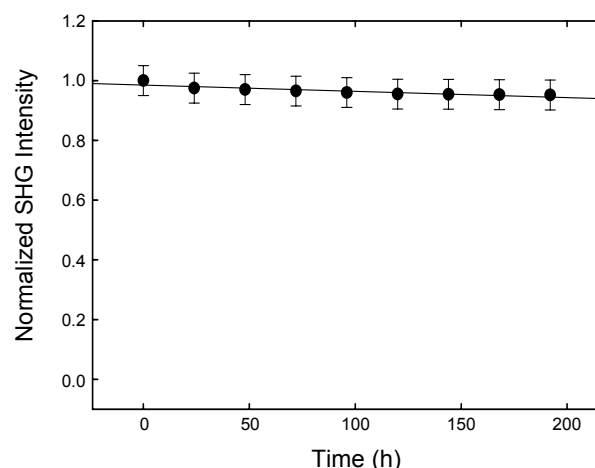
**Table 2.** Nonlinear Optical Properties of Polymer 7

Polymer	$\lambda_{\max}^a$ (nm)	$d_{33}^b$ (esu)	$\Phi^c$	$d_{31}^b$ (esu)	film thickness <sup>d</sup> ( $\mu\text{M}$ )	$n$
7	549	$3.56 \times 10^{-9}$	0.16	$1.12 \times 10^{-9}$	0.48	1.524

<sup>a</sup>Polymer film after corona poling. <sup>b</sup>SHG coefficients ( $d_{33}$ ) were derived from the analysis of measured Maker-fringes.<sup>29</sup> <sup>c</sup>Order parameter  $\Phi = 1 - A_1/A_0$ , where  $A_0$  and  $A_1$  are the absorbances of the polymer film before and after corona poling, respectively. <sup>d</sup>Film thickness was determined using the optical transmission technique.<sup>28</sup>

**Figure 5.** Angular dependence of SHG signal for a poled film of polymer 7.**Figure 6.** Normalized SHG signal of polymer 7 as a function of temperature at a heating rate of 4.5 °C/min.

SHG signal of the poled polymer films as a function of temperature, *in situ* SHG measurements were performed at a heating rate of 4.5 °C/min from 30 to 250 °C. The polymer film exhibited a greater thermal stability even at 5 °C higher than  $T_g$ , and no significant SHG decay was observed below 160 °C. In Fig. 7, we present the temporal stability of the polymer film in which there was no negligible decay of the SHG signal over hundreds of hours at 90 °C. In general, side-chain NLO polymers lose the

**Figure 7.** Normalized SHG signal of polymer 7 as a function of baking time at 90 °C in air.

thermal stability of dipole alignment around  $T_g$ . Stabilization of dipole alignment is a characteristic of main-chain NLO polymers. The high thermal stability of second harmonic generation of polymer 7 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 a new T-type of NLO polyurethane having the merits of both main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility.

## Conclusions

A novel T-type NLO polyurethane 7 with pendant NLO chromophores as part of the polymer backbone was prepared and characterized. This T-type polymer 7 is soluble in common organic solvents and shows a thermal stability up to 270 °C with  $T_g$  value around 155 °C. The SHG coefficient ( $d_{33}$ ) of corona-poled polymer film is  $3.56 \times 10^{-9}$  esu. The structural feature of this polymer is that it exhibits a high SHG thermal stability even at 5 °C higher than  $T_g$ , no SHG decay is observed below 160 °C. This high thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophores, which constitute part of the polymer backbone, and partly by hydrogen bonds between the neighboring urethane linkages. 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.

## Experimental Section

**Materials.** Reagent-grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2-Methylthiophene, triethyl phosphite, *n*-butyllithium, 2-chloroethyl vinyl ether, *N*-bromosuccinimide and 2,5-dihydroxybenzaldehyde were used as received. Tetracyanoethylene (TCNE) was purified by sublimation under vacuum. 3,3'-Dimethoxy-4,4'-biphenylenediisocyanate (DMBPI) was recrystallized from ethyl acetate. *N,N*-Dimethylformamide

(DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure.

**Measurements.** Infrared (IR) spectra were obtained with a Shimadzu FT IR-8201PC infrared spectrophotometer.  $^1\text{H}$  NMR spectra were obtained with a Varian 300 MHz NMR spectrometer. UV-visible absorption spectra were obtained with a Shimadzu UV-3100S spectrophotometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer.  $T_g$  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  $10\text{ }^\circ\text{C}/\text{min}$  up to  $800\text{ }^\circ\text{C}$  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). AFM images were recorded with a Park Science Instrument Autoprobe CP, operated in a contact mode, which measures topography. Viscosity values were obtained using a Cannon-Fenske viscometer.

**Film Preparation and SHG Measurement.** The polymer film was prepared from a 10 wt % DMF solution deposited on an indium-tin oxide (ITO) covered glass. Prior to film casting, the polymer solution was filtered through  $0.45\text{ }\mu\text{m}$  Teflon<sup>®</sup> membrane filter. The film was spin cast at  $60\text{ }^\circ\text{C}$  in the range 1200–1600 rpm. The films were dried for 48 h under vacuum at  $60\text{ }^\circ\text{C}$ . The alignment of the NLO chromophore of the polymer was carried out by corona poling method. The poling was performed in a wire-to plane geometry under in situ conditions. The discharging wire to plane distance was 1.0 cm. As the temperature was raised gradually to 5– $10\text{ }^\circ\text{C}$  higher than  $T_g$ , 6.5 kV of corona voltage was applied and kept at that temperature for 30 min. The films were cooled to room temperature in the presence of the electric field. Finally, the electric field was removed. The refractive index of the sample was measured by the optical transmission technique.<sup>28</sup> Second harmonic generation measurement was carried out one day after poling. The infrared fundamental radiation of the 1.56-micron was generated by using optical parametric oscillator (OPO) pumped by a Q-switched Nd:YAG laser operating at a repetition rate of 10 Hz. The pulse width and beam diameter of the pump laser are  $\sim 7\text{-ns}$  and 6 mm in diameter, respectively. The OPO that we used has a well-established design. It consists of a  $\text{LiNbO}_3$  crystal ( $12\text{ mm} \times 15\text{ mm} \times 50\text{ mm}$ ) cut at  $\sim 47\text{ deg}$  for type-I angle phase matching inside a 70-mm-long cavity with plane reflectors. The 3.346-micron output of the idler wave was eliminated by inserting a glass window in front of a sample. The electric field vector of the incident beam was either parallel (p-polarization) or perpendicular (s-polarization) to the plane of incidence. Only the p-polarized SH beam was made to enter a photomultiplier tube (PMT) by using a prism and a SH pass filter. An analyzer was used to confirm the polarization direction of the SH signal. A poled polymer film was mounted on the rotator coupled to a step motor. The output signals from the photodiode and PMT were detected as a function of the incident angle. A 3-mm-thick Y-cut quartz crystal (a piece of quartz plate whose plane is perpendicular to the crystalline y-axis and the thickness of the plate is 3 mm, and  $d_{11} = 0.3\text{ pm/V}$ ) was used as a reference for determining the relative in-

tensities of the SH signals generated from the samples. The Maker Fringe pattern was obtained by measuring the SHG signal at  $0.5^\circ$  intervals using a rotation stage. SHG coefficients ( $d_{33}$ ) were derived from the analysis of measured Maker-fringes.<sup>29</sup>

**2,5-Di-(2'-vinylxyethoxy)benzaldehyde (1).** 2,5-Dihydroxybenzaldehyde (13.8 g, 0.10 mol), anhydrous potassium carbonate (82.9 g, 0.60 mol), and 2-chloroethyl vinyl ether (26.6 g, 0.25 mol) were dissolved in 400 mL of dry DMF under nitrogen. The mixture was heated in an oil bath kept at  $80\text{ }^\circ\text{C}$  for 15 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 300 mL of water, and extracted with 300 mL of diethyl ether three times. The organic layer was washed with saturated aqueous sodium chloride solution, and dried with anhydrous magnesium sulfate. Rotary evaporation of diethyl ether gave crude product, which was recrystallized from 1-butanol yielded 24.5 g (88% yield) of pure product **1**.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.98–4.34 (m, 12H, 2  $\text{CH}_2=$ , 2 -O- $\text{CH}_2$ - $\text{CH}_2$ -O-), 6.45–6.58 (m, 2H, 2 =CH-O-), 6.92–6.99 (m, 1H, aromatic), 7.15–7.21 (m, 1H, aromatic), 7.33–7.36 (d, 1H, aromatic), 10.46 (s, 1H, -CHO). IR (KBr) 3096, 3075 (w, =C-H), 2941, 2882 (s, C-H), 1676 (vs, C=O), 1624 (vs, C=C)  $\text{cm}^{-1}$ .

**2-Bromomethylthiophene (2).** Compound **2** was prepared according to a literature procedure.<sup>18</sup> 2-Methylthiophene (9.82 g, 0.10 mol), *N*-bromosuccinimide (17.80 g, 0.10 mol), and benzoylperoxide (0.24 g, 1.0 mmol) were dissolved in 80 mL of anhydrous carbon tetrachloride under a nitrogen atmosphere. The mixture was heated with vigorous stirring at  $80\text{ }^\circ\text{C}$  for 3 h under nitrogen and then cooled to room temperature. The succinimide produced was filtered out with suction and water (60 mL) was added to the filtrate, which was extracted with diethyl ether (60 mL) three times. The organic layer was washed successively with saturated aqueous sodium bicarbonate (60 mL) and sodium chloride solution (60 mL), which was dried with anhydrous potassium carbonate. After evaporation of solvent by rotary evaporator, the crude product was purified by distillation under reduced pressure to yield 11.95 g (75% yield) of **2**. Bp =  $45\text{--}46\text{ }^\circ\text{C}/5\text{ mmHg}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.75 (s, 2H,  $-\text{CH}_2\text{Br}$ ), 6.92 (m, 1H, aromatic), 7.09 (m, 1H, aromatic), 7.31 (m, 1H, aromatic). IR (KBr disc) 1673 (m, C=C), 1211 (s, C-S), 701 (vs, C-Br)  $\text{cm}^{-1}$ .

**Diethyl 2-Thienylmethylphosphonate (3).** 2-Bromomethylthiophene (5.97 g, 25 mmol) was added to triethyl phosphite (4.49 g, 27 mmol). The resulting mixture was heated at  $80\text{ }^\circ\text{C}$  for 12 h and then cooled to room temperature and then ethyl bromide produced was distilled off and water (60 mL) was added to the filtrate, which was extracted with diethyl ether (60 mL) three times. The organic layer was washed with sodium chloride solution (60 mL), which was dried with anhydrous potassium carbonate. After evaporation of solvent by rotary evaporator, the obtained crude product was purified by distillation under reduced pressure to yield 5.39 g (92% yield) of **3**. Bp =  $95\text{--}96\text{ }^\circ\text{C}/2\text{ mmHg}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.22 (t, 6H, 2  $-\text{CH}_3$ ), 3.31 (d, 2H, -Ar- $\text{CH}_2$ -PO-), 4.03 (m, 4H, 2 -O- $\text{CH}_2$ -), 6.91 (m, 2H, aromatic), 7.15 (m, 1H, aromatic). IR (KBr disc) 3123 (w, =CH), 2982 (m, C-H), 1674 (w, C=C), 1247 (s, P=O)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_9\text{H}_{15}\text{O}_3\text{PS}$ : C, 46.15; H, 6.45; S, 13.69. Found: C, 46.23; H, 6.49; S, 13.65.

**1-(2,5-Di-(2'-vinylxyethoxy)phenyl)-2-(2-thienyl)ethene (4).** Under nitrogen at  $0\text{ }^\circ\text{C}$ , *n*-butyllithium (18.75 mL, 30 mmol,

1.6 mol L<sup>-1</sup> in hexane) was added to the solution of compound **3** (5.86 g, 25 mmol) in 10 mL of anhydrous DMF and stirred for 30 min. To this reaction mixture was added compound **1** (5.56 g, 20 mmol) in 10 mL of anhydrous DMF slowly at 0 °C under nitrogen. The solution was stirred for 12 h at 0 °C under nitrogen. Water (60 mL) was added to the filtrate, which was extracted with diethyl ether (60 mL) three times. The organic layer was washed successively with saturated aqueous sodium bicarbonate (60 mL) and sodium chloride solution (60 mL), which was dried with anhydrous potassium carbonate. Evaporation of solvent by rotary evaporator gave crude product, which was purified by column chromatography (ethyl acetate/*n*-hexane = 1/4, vol/vol) to yield 5.24 g (74% yield) of **4**. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 3.96-4.08 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 4.17-4.33 (m, 6H, CH<sub>2</sub>=, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 6.54-6.66 (m, 2H, 2=CH-O-), 6.81-6.87 (q, 1H, -CH=), 6.97-7.01 (d, 1H, -CH=), 7.05-7.16 (m, 3H, aromatic), 7.23-7.27 (d, 1H, aromatic), 7.44-7.48 (d, 1H, aromatic), 7.51-7.57 (d, 1H, aromatic). IR (KBr disc) 3108 (w, =C-H), 2928, 2873 (m, C-H), 1618 (vs, C=C) cm<sup>-1</sup>. Anal. Calcd for C<sub>20</sub>H<sub>22</sub>O<sub>4</sub>S: C, 67.01; H, 6.19; S, 8.95. Found: C, 67.08; H, 6.25; S, 8.89.

**1-(2,5-Di-(2-hydroxyethoxy)phenyl)-2-(2-thienyl)ethene (5).** Aqueous hydrochloric acid (1.5 mol L<sup>-1</sup>, 12 mL) was slowly added to a solution of compound **4** (3.58 g, 10 mmol) in 30 mL of dry DMF with stirring under nitrogen at 0 °C. The mixture was stirred at 0 °C for 5 h under nitrogen. The resulting solution was poured into 100 mL of ice water and stirred. The product obtained was separated by suction and washed with 30% aqueous ethanol. Thus obtained product was recrystallized from ethanol to give 2.69 g (yield 88%) of **5**. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 3.67-3.79 (m, 4H, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 3.95-4.01 (t, 4H, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 4.87 (t, 1H, -O-H), 4.94 (t, 1H, -O-H), 6.78-6.84 (q, 1H, -CH=), 6.94-6.97 (d, 1H, -CH=), 7.04-7.09 (m, 1H, aromatic), 7.15-7.24 (m, 3H, aromatic), 7.44-7.55 (q, 2H, aromatic). IR (KBr disc) 3266 (s, O-H), 2932, 2864 (m, C-H), 1602 (m, C=C) cm<sup>-1</sup>. Anal. Calcd for C<sub>16</sub>H<sub>18</sub>O<sub>4</sub>S: C, 62.72; H, 5.92; S, 10.47. Found: C, 62.80; H, 5.96; S, 10.53.

**Synthesis of Polyurethane 6.** A representative polyaddition reaction procedure was as follows. Dimethoxy-4,4'-biphenylenediisocyanate (DMBPI) (2.96 g, 0.01 mol) was added slowly to a solution of 3.06 g of diol **5** (0.01 mol) in 25 mL of anhydrous DMF. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 80 °C. After heating 15 h with stirring the polymerization tube was opened and the viscous polymer solution was poured into 400 mL of cold water. The precipitated polymer was collected and re-precipitated from DMSO into methanol. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum to give 5.43 g (90% yield) of polymer **6**. Inherent viscosity (η<sub>inh</sub>) = 0.30 dL/g (c = 0.5 g dL<sup>-1</sup> in DMSO at 25 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 3.79-3.92 (m, 4H, 2 Ph-O-CH<sub>2</sub>-), 3.99 (s, 6H, 2 -OCH<sub>3</sub>), 4.18-4.53 (t, 4H, 2 -CH<sub>2</sub>-OCO-), 6.88 (m, 1H, vinylic), 6.98 (m, 1H, vinylic), 7.12-7.36 (m, 8H, aromatic), 7.51-7.57 (d, 1H, aromatic), 7.67-7.78 (q, 1H, aromatic), 8.18-8.21 (d, 2H, aromatic), 8.54-8.63 (d, 1H, N-H), 8.95-9.06 (s, 1H, N-H). IR (KBr disc) 3397 (s, N-H), 2937 (m, C-H), 1702 (s, C=O), 1591 (s, C=C) cm<sup>-1</sup>. Anal. Calcd for (C<sub>32</sub>H<sub>30</sub>N<sub>2</sub>O<sub>8</sub>S)<sub>n</sub>: C, 63.77; H, 5.02; N, 4.65; S, 5.32. Found: C, 63.86;

H, 5.09; N, 4.74; S, 5.41.

**Synthesis of Polyurethane 7.** A representative reaction procedure was as follows. Tetracyanoethylene (1.28 g, 10 mmol) was added slowly to a solution of polymer **6** (5.12 g, 8.5 mmol) dissolved in 15 mL of DMF with stirring at room temperature under nitrogen. The resulting solution was heated in an oil bath kept at 70 °C for 20 h under a nitrogen atmosphere. The resulting polymerization solution was cooled to room temperature and poured into 400 mL of methanol. The precipitated polymer was collected and re-precipitated from DMSO into methanol. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum to give 6.33 g (90% yield) of polymer **7**. Inherent viscosity (η<sub>inh</sub>) = 0.31 dL/g (c = 0.5 g dL<sup>-1</sup> in DMSO at 25 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 3.85-4.13 (m, 8H, -O-CH<sub>2</sub>-, 2 -OCH<sub>3</sub>), 4.26-4.65 (m, 6H, -O-CH<sub>2</sub>-, 2 -O-CH<sub>2</sub>-OCO-), 6.91-7.15 (m, 2H, -CH=CH-), 7.15-7.92 (m, 10H, aromatic), 8.25-8.32 (d, 1H, aromatic), 8.54-8.72 (t, 1H, N-H), 9.03-9.17 (s, 1H, N-H). IR (KBr disc) 3398 (s, N-H), 2940 (m, C-H), 2219 (m, CN), 1701 (s, C=O), 1592 (s, C=C) cm<sup>-1</sup>. Anal. Calcd for (C<sub>37</sub>H<sub>29</sub>N<sub>5</sub>O<sub>8</sub>S)<sub>n</sub>: C, 63.15; H, 4.15; N, 9.95; S, 4.56. Found: C, 63.27; H, 4.23; N, 9.86; S, 4.48.

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