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The design, synthesis and nonlinear optical properties of a novel, Y-type polyurethane containing tricyanovinylthiophene of high thermal stability

Han-Na Jang [a], Hyo Jin No [a], Ju-Yeon Lee [a,*], Bum Ku Rhee [b], Ki-Ho Cho [b], Hee-Dok Choi [b]

[a] *Institute of Basic Science, Department of Chemistry, Inje University, 607 Obang-dong, Gimhae 621-749, Republic of Korea*
[b] *Department of Physics, Sogang University, CPO Box 1142, Seoul 100-611, Republic of Korea*

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ABSTRACT

A novel, Y-type polyurethane containing 1-(2,4-dioxyethoxy)phenyl-2-{5-(2,2-dicyanovinyl)-2-thiophenyl}ethenes as nonlinear optical chromophores present within the polymer backbone, was prepared and characterized. The compound was soluble in common organic solvents and displayed thermal stability up to 260 °C and a glass transition temperature (T_g) of 163 °C. The second harmonic generation coefficient (d_{33}) of poled polymer films at the compound's fundamental wavelength of 1560 nm was $\sim 3.72 \times 10^{-9}$ esu. Dipole alignment exhibited high thermal stability up to the T_g, and there was no decay in d_{33} below 148 °C owing to the partial main-chain character of the polymer structure.

1. Introduction

Organic nonlinear optical (NLO) materials have been extensively studied recently because of their potential applications in the field of electro-optic devices [1–4]. Among the organic materials the NLO polymers are considered candidate materials, mainly because they offer many advantages such as mechanical endurance, light weight, chemical resistance, and good processability to form optical devices. One of the current tasks 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 one of important considerations; in this context, two approaches to minimize the randomization have been proposed namely the use of cross-linked system [5–9] and the utilization of polymers with high glass transition temperature (T_g) such as polyimides [10–16]. The polyurethane matrix forms extensive hydrogen bonding between urethane linkage and increases rigidity preventing the relaxation of induced dipoles. Polyurethanes functionalized with hemicyanine [17] and thiophene ring [18] in side chain showed an enhanced thermal stability of aligned dipoles. Polyurethanes with dipole moments aligning transverse to the main chain showed large second-order nonlinearity with good thermal stability [19,20]. Physically cross-linked systems via hydrogen bonds have the advantages such as homogenity and good processability relative to chemically cross-linked systems, which suffer from significant optical loss and poor solubility. Recently we prepared novel polyurethanes containing dioxybenzylidenemalononitrile [21] and dioxynitrostilbenyl group as NLO chromophores [22]. The resulting polymers exhibited high thermal stability of second harmonic generation (SHG). The high thermal stability of optical nonlinearity stemmed from the stabilization of dipole alignment of the NLO chromophores.

This work concerns the preparation of a novel polyurethane containing 1-(2,4-dioxyethoxy)phenyl-2-{5-(2,2,3-tricyano vinyl)-2-thiophenyl}ethenyl groups as NLO chromophores; the latter were selected on the basis of their large dipole moment. Furthermore, 1-(2,4-dioxyethoxy)phenyl-2-{5-(2,2,3-tricyano-vinyl)-2-thiophenyl}ethenyl groups constitute a novel Y-type NLO polyurthane (see Fig. 1c), in which the structure of NLO chromophores and this Y-type NLO polyurethane is not described in the literature. In this way, a novel type of NLO polyurethane, in which the pendant NLO chromophores are components of the polymer backbones, were prepared. This type of 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 such as T_g, thermal stability, surface morphology of polymer films, and second harmonic generation (SHG) activity (d_{33}).

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* Corresponding author. Tel.: +82 55 320 3221; fax: +82 55 321 9718.
E-mail address: chemljy@inje.ac.kr (J.-Y. Lee).

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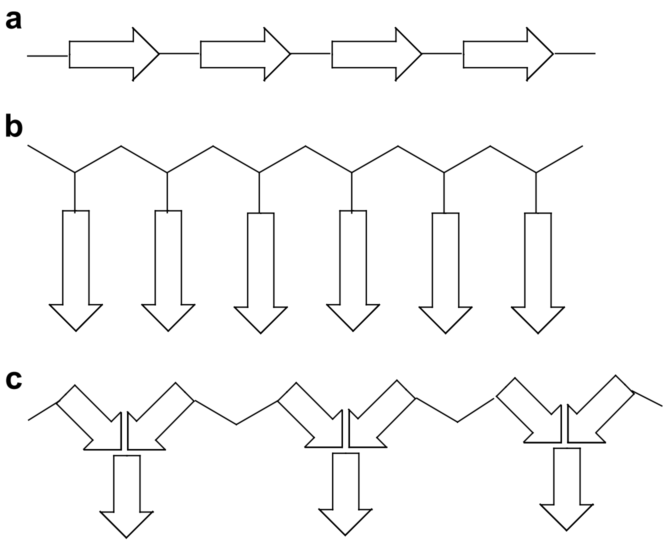


Fig. 1. (a) Main-chain NLO polymers, (b) side-chain NLO polymers, and (c) Y-type NLO polymers.

2. Results and discussion

2.1. Synthesis and characterization of polymer

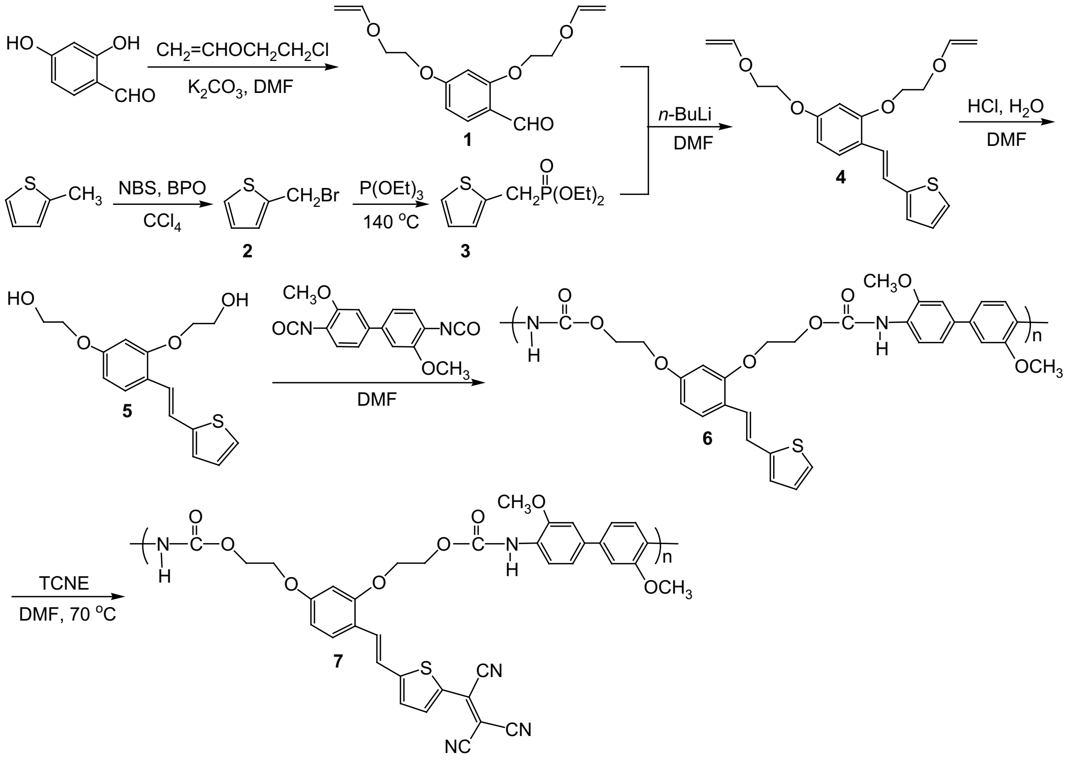
2,4-Di-(2′-vinyloxyethoxy)benzaldehyde (**1**) was prepared by the reaction of 2-chloroethyl vinyl ether (ed note: extremely flammable; reacts violently with water to produce extremely flammable gases; explosive when mixed with oxidizing substances) with 2,4-dihydroxybenzaldehyde. 2-Bromomethylthiophene (**2**) was prepared by the bromonation of 2-methylthiophene with *N*-bromosuccinimide. Diethyl 2-thiophenylmethylphosphonate (**3**) was prepared by the Arbuzov reaction of compound **2** with triethyl phosphite. 1-{2,4-Di-(2-vinyloxyethoxy)phenyl}-2-(2-thiophenyl)ethene (**4**) was prepared by Horner–Emmons olefination of compounds **1** and **3**. Compound **5** was prepared by the acid-catalyzed hydrolysis of **4** in DMF. The polyurethane **6** was prepared by the polyaddition reaction of the diol **5** and 3,3′-dimethoxy-4,4′-biphenylenediisocyanate in a dry DMF solvent. The polymerization yield was 87–88%. Polymer **6** was reacted with tetracyanoethylene in anhydrous DMF [18] to yield polyurethane **7** containing 1-(2,4-dioxyethoxy)phenyl-2-{5-(2,2,3-tricyanovinyl)-2-thiophenyl}ethenyl 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 by ^{1}H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structure. ^{1}H NMR spectrum (Fig. 2) of the polymer showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The signal at 8.53–9.12 ppm assigned to the amine proton indicates the formation of urethane linkage. The IR spectrum of polymer **7** showed strong absorption peak near 2219 cm^{-1} indicating the presence of nitrile group. The IR spectra of the same polymer sample also show a strong carbonyl peak near 1687 cm^{-1} indicating the presence of urethane bond. These results are consistent with the proposed structure, indicating that the tricyanovinyl groups are introduced well to thiophene ring. The molecular weights were determined by GPC with polystyrene as the standard and THF as the eluent. The number average molecular weight (M_n) of the polymer **7**, determined by GPC, was 19,200 ($M_w/M_n = 1.93$). The polymer **7** was soluble in common solvents such as acetone, DMF, and DMSO, but was not soluble in methanol and diethyl ether. The inherent viscosity values were in the range 0.30–0.32 L/g. Polymer **7** showed strong absorption near 581 nm by the NLO chromophore 1-(2,4-dioxyethoxy)phenyl-2-{5-(2,2,3-tricyanovinyl)-2-thiophenyl}ethenyl group. The striking feature of this polymerization system is that it gives unprecedented Y-type NLO polymers, in which the pendant NLO chromophores are part of the polymer backbones. These mid-type NLO polymers are expected to have the advantages 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 well defined Y-type polyurethane **7**, we investigated its properties.

2.2. Thermal properties of polymer

The thermal behavior of the polymer was investigated by 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. In Fig. 3, TGA thermogram of the polymer **7** is presented. Polymer **7** showed a thermal stability up to 260 °C according to its TGA thermogram. The T_g value of the polymer **7** measured by DSC was near 163 °C. This is relatively a high value compared to those of common polyurethanes, which can probably be attributed to the rigid ring unit in the polymer pendant group. The TGA and DSC studies showed that the decomposition temperature of the polymer **7** was higher than the corresponding T_g value. This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

2.3. Nonlinear optical properties of polymer

The NLO properties of polymer were studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. As the temperature was raised gradually to 5–10 °C higher than T_g, 6.5 kV of corona voltage was applied and this temperature was maintained for 30 min. The poling was confirmed by UV–vis spectra. Fig. 4 shows the UV–vis absorption spectra of the polymer **7** before and after poling. After electric poling, the dipole moments of the NLO chromophores were aligned and UV–vis spectrum of polymer **7** 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 equal to 0.25 for polymer **7** ($\Phi = 1 - A_1/A_0$, where $A_0 = 0.956$ and $A_1 = 0.720$ are the absorbances of the polymer film before and after poling, respectively). For the purpose of investigating surface morphology of polymer films, domain structures of NLO chromophores for the thin-film samples were obtained using atomic force microscopy (AFM). Fig. 5 shows AFM scans of the spin-coated film before and after poling polymer **7**. AFM images show that the surface of the film sample is extremely flat and clean before poling (see Fig. 5a). 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 are aligned in the poling direction as shown in Fig. 5b. The refractive index of the sample was measured by the optical transmission technique [23]. The transmittance of thin film includes information on the thickness, refractive index and extinction coefficient of that. Thus, we could determine those 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. In order to determine the microscopic second-order susceptibility of the polymers, the angular SHG dependence was recorded. Fig. 6 shows the angular



Scheme 1. Synthetic scheme and structure of polymer **7**.

dependence of SHG signal in a poled 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 to the samples and recorded. Nonlinear optical properties of polymer **7** are summarized in Table 2. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure [24]. The values of d_{31} and d_{33} for polymer **7** were 1.19×10^{-9} esu and 3.72×10^{-9} esu, respectively. Since the second harmonic wavelength was at 780 nm, which is not in the absorptive region of the resulting polyurethane, there was no 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 3.1 is in good agreement with the predicted value.

To evaluate the high-temperature stability of the polymer, we studied the temporal stability of the SHG signal. In Fig. 7, we present

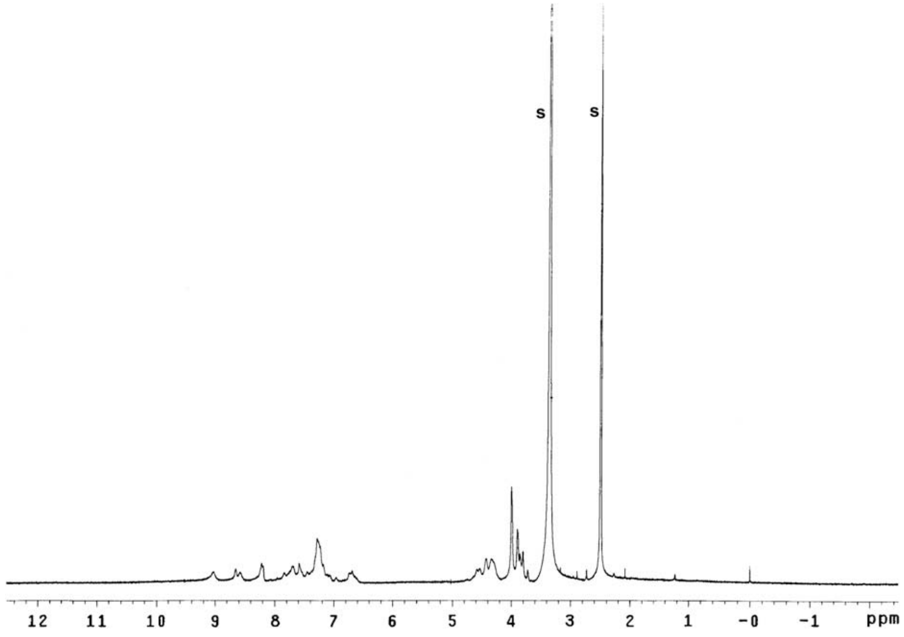


Fig. 2. ^{1}H NMR spectrum of polymer **7** taken in DMSO-d_6 at room temperature.

Table 1
Thermal properties of polymer **7**.

Polymer (°C)	T_g[a] (%)	Degradation temperature (°C)[b]			Residue at 800 °C[b]
		5 wt%-loss	20 wt%-loss	40 wt%-loss	
7	163	280	331	463	26.1

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

[b] Determined from TGA curves measured on a TA Q50 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen atmosphere.

the dynamic thermal stability study of the NLO activity of the film **7**. 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 30 to 220 °C. The polymer film exhibited a thermal stability up to near T_g and no significant SHG decay was observed below 148 °C. In general, side-chain NLO polymers lose the thermal stability of dipole alignment below T_g. Stabilization of dipole alignment is a characteristic of main-chain NLO polymers. The enhanced thermal stability of second harmonic generation of polymer **7** was due to the stabilization of dipole alignment of NLO chromophore, which stemmed from the partial main-chain character of the polymer structure. Thus, we obtained a new type of NLO polyurethane having the advantages of both main-chain and side-chain NLO polymers: stabilization of dipole alignment and good solubility.

3. Conclusions

We synthesized novel Y-type polyurethane **7** with pendant NLO chromophores, which are parts of the polymer main chains. This mid-type NLO polyurethane is soluble in common organic solvents. The resulting polymer **7** showed a thermal stability up to 260 °C from TGA thermograms with T_g value near 163 °C. The SHG coefficient (d_{33}) of corona-poled polymer film was 3.72×10^{-9} esu. The striking feature of this polymer is that it exhibits SHG stability up to near T_g and no SHG decay was observed below 148 °C. This high thermal stability of optical nonlinearity stemmed from the stabilization of dipole alignment of the NLO chromophore, which constituted a part of the polymer backbone. 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.

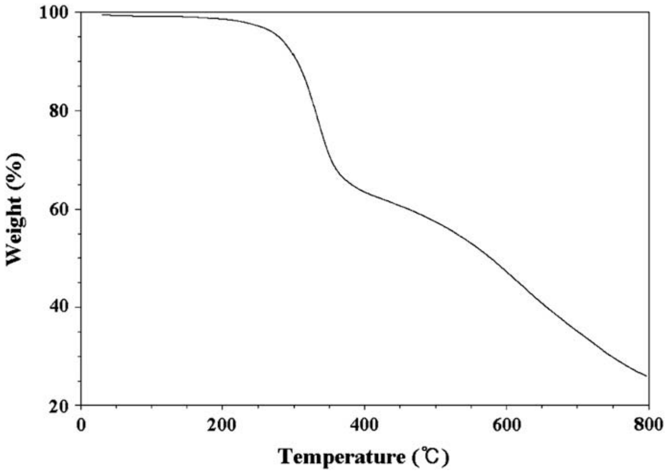


Fig. 3. TGA thermogram of polymer **7** at a heating rate of 10 °C/min under nitrogen.

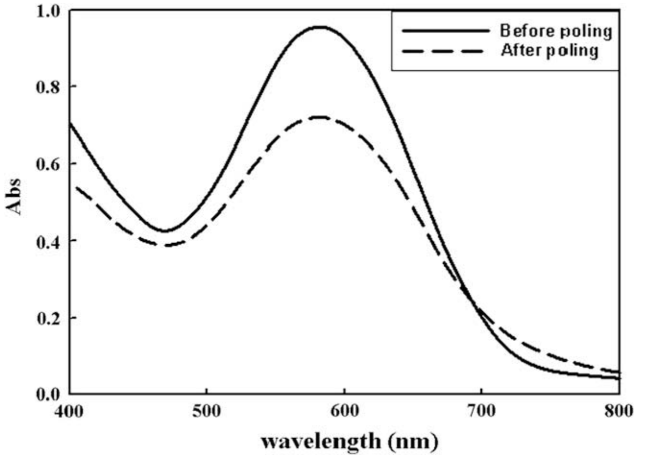


Fig. 4. UV–vis absorption spectra of a film of polymer **7** before and after poling.

4. Experimental

4.1. Materials

The 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 and 2,4-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

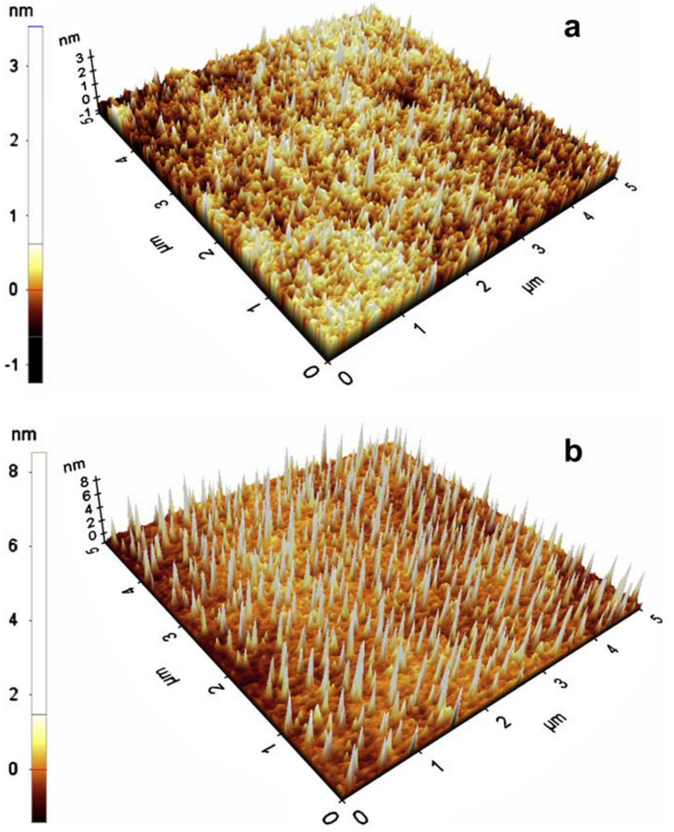


Fig. 5. AFM images of a spin-coated film of polymer **7**: (a) before corona poling; (b) after corona poling.

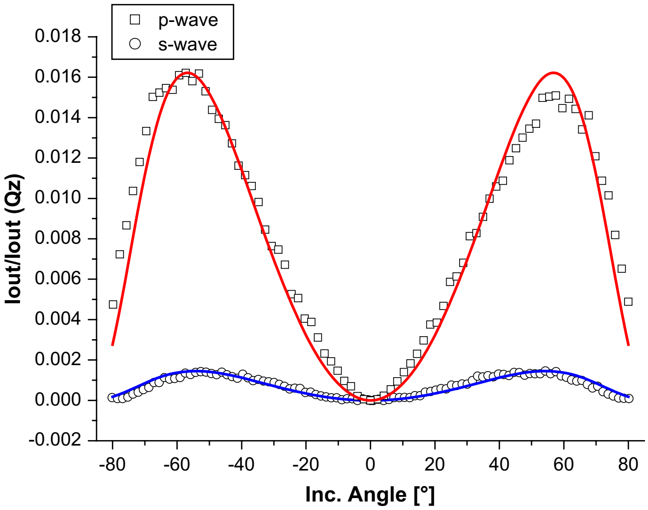


Fig. 6. Angular dependence of SHG signal in a poled film of polymer **7**.

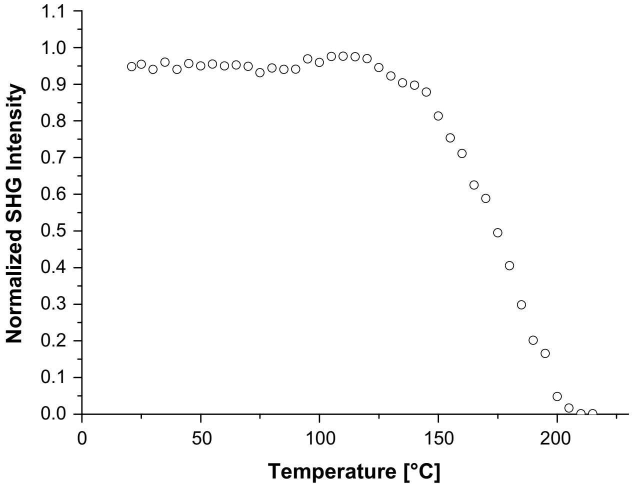


Fig. 7. Normalized SHG signal of polymer **7** as a function of temperature at a heating rate of 3.5 °C/min.

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

4.2. Instrumentation

IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ^{1}H 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. TA Q50 thermogravimetric analyzer with a heating rate of 10 °C/min 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 by gel permeation chromatography (GPC) (columns styragel HR5E4E; solvent THF). Atomic force microscopy (AFM) images were recorded with a Park Science Instrument Autoprobe CP, operated in a contact mode, which measures topography. Viscosity values were obtained by using a Cannon–Fenske viscometer.

4.3. Film preparation and SHG measurements

The polymer film was prepared from a 10 wt% by weight DMF solution deposited on an indium–tin oxide (ITO) covered glass. Prior to film casting, the polymer solution was filtered through 0.45 μm Teflon® membrane filter. The film was spin cast at 60 °C in the range 1200–1600 rpm. The films were dried for 48 h under vacuum at 60 °C. The alignment of the NLO chromophore of the polymers 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 °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 [23]. Second harmonic generation measurement was carried out one day after poling. The infrared fundamental radiation of the 1.56 μm 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 ~7 ns and 6 mm in diameter, respectively. The OPO that we used has a well-established design. It consists of a $LiNbO_3$ crystal (12 mm × 15 mm × 50 mm) cut at ~47° for type-I angle phase matching inside a 70-mm-long cavity with plane reflectors. The 3.346 μm 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 $d_{11} = 0.3$ pm/V) was used as a reference for determining the relative intensities of the SH signals generated from the samples. The Maker-fringe pattern was obtained by measuring the SHG signal at 0.5° intervals using a rotation stage. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [24].

Table 2
Nonlinear optical properties of polymer **7**.

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	Φ[c]	Film thickness[d] (μm)	d_{31}[b] (esu)	*n*
7	581	3.72×10^{-9}	0.25	0.50	1.19×10^{-9}	$n_1 = 1.510$ $n_2 = 1.542$

[a] Polymer film after corona poling.
[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [24].
[c] 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.
[d] Film thickness was determined by the optical transmission technique [23].

4.4. Preparation of 2,4-di-(2′-vinyloxyethoxy)benzaldehyde (**1**)

2,4-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 refluxed in an oil bath kept at 80 °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 25.0 g (yield 90%) of pure product **1**. Mp = 68–69 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): 4.03–4.35 (m, 12H, 2 CH_2=, 2 –O–CH_2–CH_2–O–), 6.50–6.62 (m, 4H, 2=CH–O–, aromatic), 7.82–7.86 (d, 1H, aromatic), 10.35 (s, 1H, –CHO). IR (KBr disc) (cm^{-1}): 3100, 3082 (w, =C–H), 2954, 2875 (m, C–H), 1674 (vs, C=O), 1615 (vs, C=C), 1575 (s, C=C).

*4.5. Preparation of 2-bromomethylthiophene (**2**)*

Compound **2** was prepared according to a literature procedure [18]. 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 refluxed with vigorous stirring at 80 °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 = 45–46 °C/5 mm Hg. ^{1}H NMR ($CDCl_3$) δ (ppm): 4.75 (s, 2H, –CH_2Br), 6.92 (m, 1H, aromatic), 7.09 (m, 1H, aromatic), 7.31 (m, 1H, aromatic). IR (KBr disc) (cm^{-1}): 1673 (m, C=C), 1211 (s, C–S), 701 (vs, C–Br).

*4.6. Preparation of diethyl 2-thiophenylmethylphosphonate (**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 °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 = 95–96 °C/2 mm Hg. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.22 (t, 6H, 2 –CH_3), 3.31 (d, 2H, –Ar–CH_2–PO–), 4.03 (m, 4H, 2 –O–CH_2–), 6.91 (m, 2H, aromatic), 7.15 (m, 1H, aromatic). IR (KBr disc) (cm^{-1}): 3123 (w, =CH), 2982 (m, C–H), 1674 (w, C=C), 1247 (s, P=O). Anal. Calcd for $C_9H_{15}O_3PS$: C, 46.15; H, 6.45; S, 13.69. Found: C, 46.23; H, 6.49; S, 13.65.

*4.7. Preparation of 1-{2,4-di-(2-vinyloxyethoxy)phenyl}-2-(2-thiophenyl)ethene (**4**)*

Under nitrogen at 0 °C, *n*-butyllithium (18.75 ml, 30 mmol, 1.6 M in hexane) was added dropwise 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 5.38 g (75% yield) of **4**. Mp = 70–72 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.96–4.12(m, 6H, CH_2=, –O–CH_2–CH_2–O–), 4.22–4.33(m, 6H, CH_2=, –O–CH_2–CH_2–O–), 6.50–6.78 (m, 4H, 2 =CH–O–, –CH=CH–), 6.98–7.08 (m, 3H, aromatic), 7.31–7.42 (m, 2H, aromatic), 7.52 (d, 1H, aromatic). IR (KBr disc) (cm^{-1}): 3123 (w, =C–H), 2930, 2873 (m, C–H), 1602 (vs, C=C). Anal. Calcd for $C_{20}H_{22}O_4S$: C, 67.01; H, 6.19; S, 8.95. Found: C, 67.09; H, 6.24; S, 8.90.

*4.8. Preparation of 1-{2,4-di-(2-hydroxyethoxy)phenyl}-2-(2-thiophenyl)ethene (**5**)*

Aqueous hydrochloric acid (1.5 M, 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 crude product obtained was separated by suction and washed with 30% aqueous ethanol to give 2.60 g (yield 85%) of **5**. ^{1}H NMR (DMSO-d_6): δ (ppm): 3.65–3.82 (m, 4H, –O–CH_2–CH_2–O–), 3.93–4.08 (m, 4H, –O–CH_2–CH_2–O–), 4.86 (t, 1H, –O–H), 4.94 (t, 1H, –O–H), 6.50–6.58 (m, 2H, –CH=CH–), 6.99–7.08 (m, 3H, aromatic), 7.30–7.41 (m, 2H, aromatic), 7.53 (d, 1H, aromatic). IR (KBr disc) (cm^{-1}): 3366 (s, O–H), 2938, 2875 (m, C–H), 1606 (s, C=C). Anal. Calcd for $C_{16}H_{18}O_4S$: C, 62.72; H, 5.92; S, 10.47. Found: C, 62.81; H, 5.98; S, 10.54.

*4.9. Synthesis of polyurethane **6***

A representative polycondensation 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 12 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 reprecipitated from DMSO into methanol. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum to give 5.30 g (88% yield) of polymer **6**. Inherent viscosity (η_{inh}) = 0.31 dL g^{-1} (c = 0.5 g dL^{-1} in DMSO at 25 °C). ^{1}H NMR (DMSO-d_6) δ (ppm): 3.74–4.13 (m, 8H, –O–CH_2–, 2 –OCH_3), 4.21–4.58 (t, 6H, –O–CH_2–, 2 –O–CH_2–OCO–), 6.57–6.74 (m, 1H, aromatic), 7.92–7.78 (m, 12H, aromatic), 8.18 (d, 1H, aromatic), 8.53–8.68 (d, 1H, N–H), 8.93–9.10 (s, 1H, N–H). IR (KBr disc) (cm^{-1}): 3387 (s, N–H), 2937 (m, C–H), 2233 (m, CN), 1687 (s, C=O), 1596 (s, C=C). Anal. Calcd for $(C_{32}H_{30}N_2O_8S)_n$: C, 63.77; H, 5.02; N, 4.65; S, 5.32. Found: C, 63.72; H, 5.08; N, 4.68; S, 5.25.

*4.10. Synthesis of polymer **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 12 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 reprecipitated 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_{inh}) = 0.32 dL g^{-1} (c = 0.5 g dL^{-1} in DMSO at 25 °C). ^{1}H NMR (DMSO-d_6) δ (ppm): 3.73–4.13 (m, 8H, –O–CH_2–, 2 –OCH_3), 4.21–4.68 (m, 6H, –O–CH_2–, 2 –O–CH_2–OCO–), 6.59–6.75 (m, 1H, aromatic), 7.02–7.88 (m, 11H, aromatic), 8.18–8.35 (d, 1H, aromatic), 8.53–8.71 (d, 1H, N–H), 8.95–9.12 (s, 1H, N–H). IR (KBr disc) (cm^{-1}): 3397 (s, N–H), 2939 (m, C–H), 2219 (m, CN), 1687 (s, C=O), 1595 (s, C=C). Anal. Calcd for $(C_{37}H_{29}N_5O_8S)_n$: C, 63.15; H, 4.15; N, 9.95; S, 4.56. Found: C, 63.24; H, 4.18; N, 9.88; S, 4.62.

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