Synthesis and Properties of Novel Y-type Nonlinear Optical Polyester Containing Cyanovinylthiophene with Enhanced Thermal Stability of Second Harmonic Generation

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1-{2,4-Di-(2-hydroxyethoxy)phenyl}-2-(2-thienyl)ethene (**5**) was prepared and condensed with terephthaloyl chloride to yield polyester (**6**). Polymer **6** was reacted with tetracyanoethylene to give novel Y-type polyester (**7**) containing 1-(2,4-dioxyethoxy)phenyl-2-{5-(2,2,3-tricyanovinyl)-2-thienyl)}ethenyl groups as NLO-chromophores, which are parts the polymer backbones. Polymer **7** is soluble in common organic solvents such as acetone and *N,N*-dimethylformamide. It showed thermal stability up to 300 °C in thermogravimetric analysis with glass-transition temperature obtained from differential scanning calorimetry near 134 °C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer film at the 1560 nm fundamental wavelength was around 6.74 x 10^{-9} esu. The dipole alignment exhibited high thermal stability up to the glass-transition temperature (T_g), and there was no SHG decay below 135 °C because of the partial main-chain character of polymer structure, which is acceptable for NLO device applications.

Key Words: NLO, Polyester, Differential scanning calorimetry (DSC), Atomic force microscopy (AFM), Second harmonic generation (SHG)

Introduction

Nonlinear optical (NLO) materials have been extensively studied in recent years because of their potential applications in the field of telecommunications, optical signal processing, optical switching, etc.[1-3] The organic materials seem to be superior because of their higher nonlinear optical activity and faster response time than the inorganic ones. Among the organic materials, NLO polymers are receiving great attention, mainly because they offer many advantages such as mechanical endurance, light weight, chemical resistance, 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 creteria; in this context, two approaches to minimize the randomization have been proposed namely the use of cross-linking[4-7] and the utilization of high T_g polymers such as polyimides.[8] Various polyesters with the NLO-chromophores in the main chain[9] or in side chain[10-12] were prepared and investigated. Main-chain NLO polymers have good thermal stability of dipole alignments, but they often do not dissolve in organic solvents, and their intractability make them unusable to fabricate stable noncentrosymmetric films. Side-chain NLO polymer systems have the advantages such as good solubility, homogeneity and high loading level of NLO chromophore, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we have prepared novel NLO polyesters[13-16] with enhanced thermal stability of dipole alignment by modification of polymer structure.

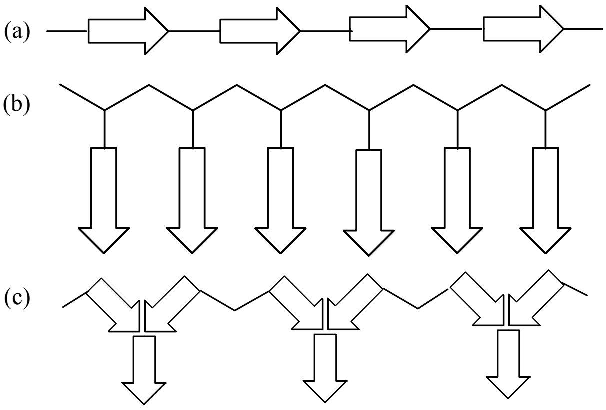


Figure 1. (a) Main-chain NLO polymers, (b) side-chain NLO polymers, and (c) Y-type NLO polymers.

In this work we prepared a novel Y-type polyester containing 1-(2,4-dioxyethoxy)phenyl)-2-{5-(2,2,3-tricyanovinyl)-2-thienyl)}ethenyl group as a NLO-chromophore. We selected the latter because it has large dipole moment. Furthermore 1-(2,4-dioxyethoxy)phenyl)-2-{5-(2,2,3-tricyanovinyl)-2-thienyl)}ethenyl groups constitute novel Y-type NLO polyesters (Fig. 1c), and these Y-type NLO polyesters have not yet been reported in the literature. Thus, we synthesized a new type of NLO polyester, in which the pendant NLO chromophores are components of the polymer backbones. This mid-type NLO polymer is expected to have both the merits of 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 solubility, T_g, thermal stability, surface morphology of polymer films, second harmonic generation (SHG) activity and relaxation of dipole alignment.

Results and Discussion

Synthesis and Characterization of Polymer 7. 2,4-Di-(2'-vinyloxyethoxy)benzaldehyde (**1**) was prepared by the reaction of 2-chloroethyl vinyl ether with 2,4-dihydroxybenaldehyde. 2-Bromomethylthiophene (**2**) was prepared by the bromonation of 2-methylthiophene with N-bromosuccinimide. Diethyl 2-thiophenylmethylphosphonate (**3**) was prepared by Arbuzov reaction from compound **2** and triethyl phosphite. 1-{2,4-Di-(2-vinyloxyethoxy)phenyl}-2-(2-thienyl)ethene (**4**) was prepared by Horner-Emmons olefination with compounds **1** and **3** in DMF. Diol **5** was prepared by acid-catalyzed hydrolysis of **4**. Monomer **5** was condensed with terephthaloyl chloride in a dry pyridine to yield polyester **6**. The polymerization yield was 92%. Polymer **6** was reacted with tetracyanoethylene in anhydrous DMF[17] to yield polyester **7** containing 1-(2,4-dioxyethoxy)phenyl)-2-{5-(2,2,3tricyanovinyl)-2-thienyl)}ethenyl group as a NLO-chromophore. The synthetic route for polymer **7** is presented in Scheme 1. The resulting polymer was further purified by Soxhlet extraction with methanol as a solvent. The chemical structure of the polymer was confirmed by ^{1}H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structure. ^{1}H NMR spectra of the polymers showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The IR spectrum of polymer **7** showed strong carbonyl peaks near 1722 cm^{-1} indicating the presence of ester bond. The IR spectrum of the same polymer sample also showed strong absorption peak near 2219 cm^{-1} indicating the presence of nitrile group. These results are consistent with the proposed structures, indicating that the tricyanovinyl groups are introduced well to thiophene ring. The molecular weights were determined by GPC using polystyrene as the standard and THF as an eluent. The number average molecular weight (M_n) of the polymer **7**, determined by GPC, was 17800 (M_w/M_n = 1.98). The structural feature of this polymer is that it has pendant NLO chromophores, which are parts of the polymer main chains. Thus the resulting polymer **7** is a mid type of side chain- and main chain NLO polymers, and is expected to have both of their merits. 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 was 0.30-0.32 dL/g. Polymer **7** showed strong absorption near 550 nm by the NLO-chromophore 1-(2,4-dioxyethoxy)phenyl)-2-{5-(2,2,3-tricyanovinyl)-2-thienyl)}ethenyl group. Having well defined polyester (**7**), we

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

Polymer	T_g[a] (°C)	Degradation temp, °C[b]			Residue at 800 °C (wt%)[b]
		5 wt%-loss	20 wt%-loss	40 wt%-loss	
7	134	323	402	589	49.8

[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 TA Q50 thermogravimetric analyzer with a heating rate of 10 °C/min under nitrogen atmosphere.

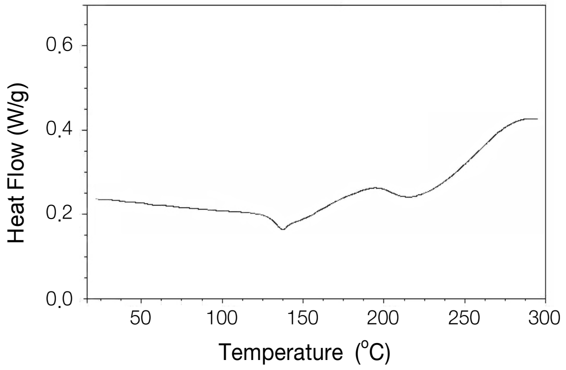
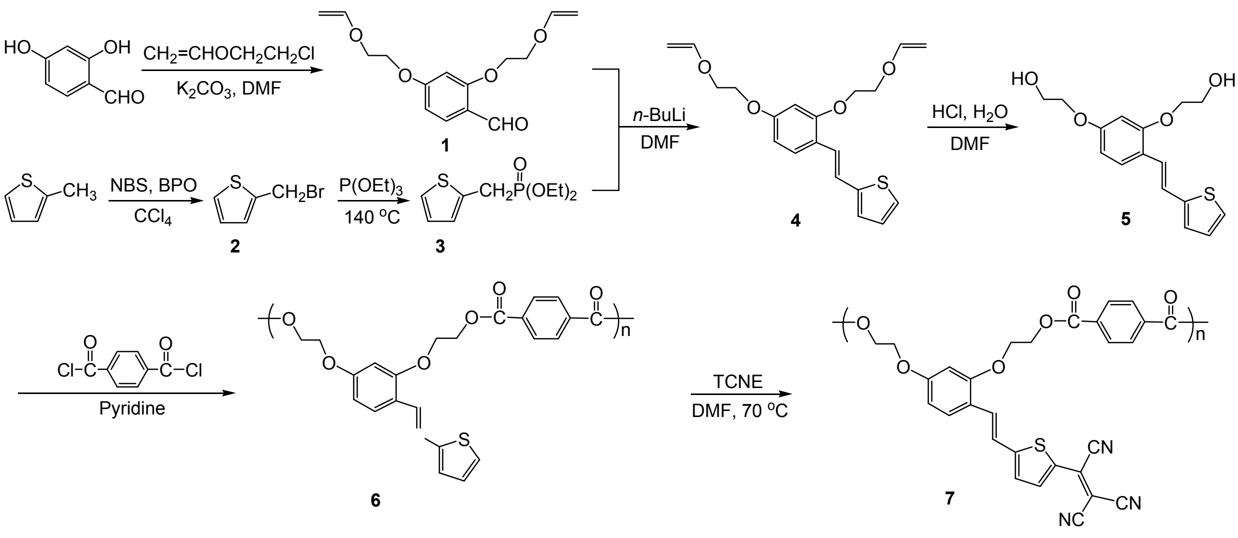


Figure 2. DSC thermogram of polymer **7** at a heating rate of 10 °C/min under nitrogen.



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

investigated its properties.

Thermal Properties of the 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. 2, DSC thermogram of the polymer **7** is presented. Polymer **7** showed a thermal stability up to 300 °C from its TGA thermogram. T_g value of the polymer **7** measured by DSC was around 134 °C. This is relatively high value compared to those of common polyesters, 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 polyester **7** was higher than the corresponding T_g. This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

Nonlinear Optical Properties of the 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 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 absorption spectra. The UV-Vis 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-Vis spectrum of polymer **7** 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 Φ of polymer **7** was equal to 0.18 ($\Phi = 1 - A_1/A_0$, $A_1 = 0.7307$, $A_0 = 0.8890$, where A_0 and A_1 are the absorbances of the polymer film before and after poling). For the purpose of investigating surface morphology of polymer film, domain structures of NLO-chromophores for the thin-film sample were obtained with atomic force microscopy (AFM). Fig. 4 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 flat and smooth. 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 (see Fig. 4).

The refractive index of the sample was measured by the optical transmission technique.[18] The transmittance of thin film includes information on the thickness, refractive index and extinction coefficient of that. So 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. Nonlinear optical properties of polymer **7** are summarized in Table 2. 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 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.

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

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	Φ[c]	d_{31}[b] (esu)	film thickness[d] (μm)	*n*
7	550	6.74×10^{-9}	0.18	1.92×10^{-9}	0.47	$n_1 = 1.520$ $n_2 = 1.545$

[a] Polymer film after corona poling. [b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.[19] [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.[18]

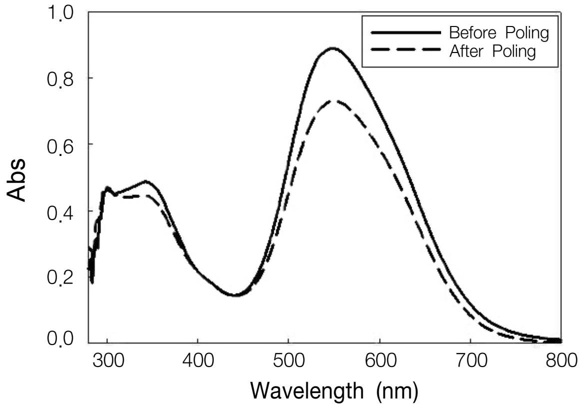


Figure 3. UV-Vis absorption spectra of a film of polymer **7** before and after poling.

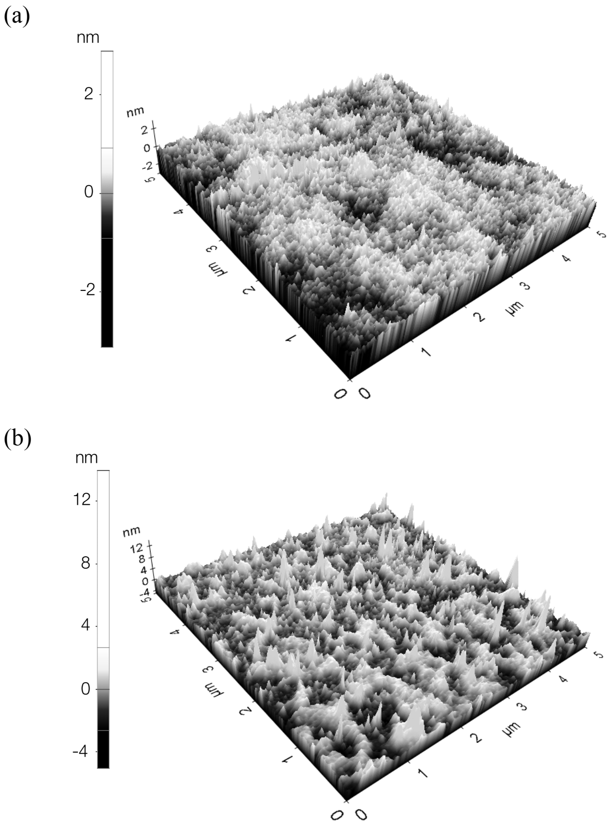


Figure 4. AFM images of spin-coated film of polymer **7**: (a) before corona-poling; (b) after corona-poling.

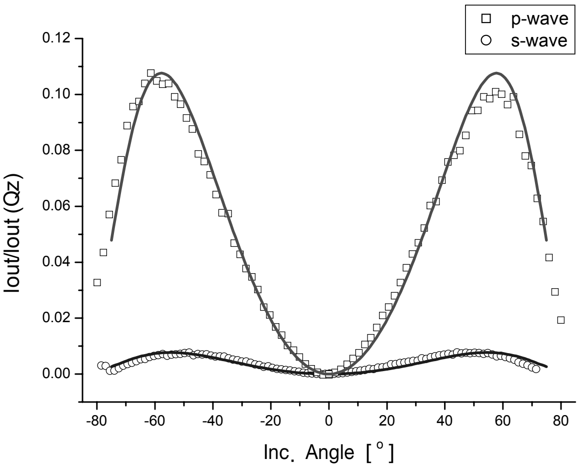


Figure 5. Angular dependence of SHG signal in a poled film of polymer **7**.

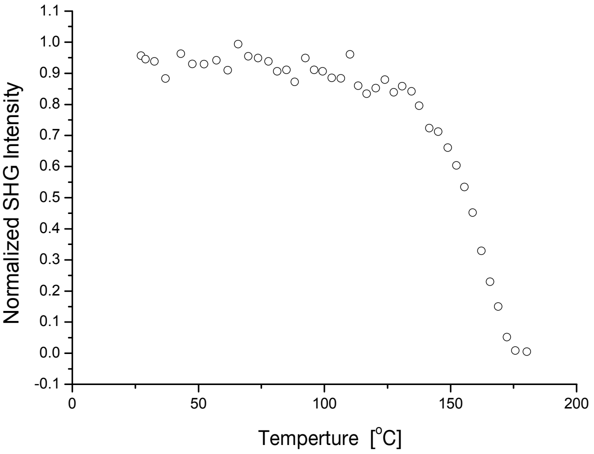


Figure 6. Normalized SHG signal of polymer **7** as a function of temperature at a heating rate of 3.5 °C/min.

SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure.[19] The values of d_{33} and d_{31} for polymer **7** were 6.74 x 10^{-9} esu and 1.92 x 10^{-9} esu, respectively. Since the second harmonic wavelength was at 780 nm, which is not in the absorptive region of the resulting polyester, 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 3.5 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. In Fig. 6, we present 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 films as a function of temperature, in situ SHG measurements were performed at a heating rate of 3.5 °C/min from 30 to 200 °C. The polymer film exhibited a thermal stability up to T_g and no significant SHG decay was observed below 135 °C. In general, side chain NLO polymers lose the thermal stability of dipole alignment around T_g. Stabilization of dipole alignment is a characteristic of main chain NLO polymers. The exceptional high 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 polyester having both the merits of main chain- and side-chain NLO polymers namely stabilization of dipole alignment and good solubility.

Conclusions

A novel Y-type NLO polyester **7** with pendant NLO chromophores as parts of the polymer backbones was prepared and characterized. This mid-type polymer **7** is soluble in common organic solvents and showed a thermal stability up to 300 °C with T_g value around 134 °C. The SHG coefficient (d_{33}) of corona-poled polymer film was 6.74 x 10^{-9} esu. The striking feature of this polymer is that it exhibits SHG stability up to T_g and no significant SHG decay was observed below 135 °C. This high thermal stability of optical nonlinearity stemmed from the stabilization of dipole alignment of the NLO-chromophore.

Experimental Section

Materials. The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2-Methylthiophene, triethyl phosphite, *n*-butyllithium, 2,4-dihydroxybenzaldehyde, N-bromosuccinimide, and 2-chloroethyl vinyl ether were used as received. Tetracyanoethylene (TCNE) and terephthaloyl chloride (TPC) were purified by sublimation under vacuum. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure.

Measurements. IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ^{1}H NMR spectra were obtained on a Varian 300MHz NMR spectrometer. UV-Vis absorption spectra were measured on a Shimadzu UV-3100S spectrophotometer. Mass spectra were obtained on a Agilent Technologies G2708DA mass spectrometer. 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). 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.

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 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, 6.5kV 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.[18] 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 ~ 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 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 $d_{11} = 0.3$ 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.[19]

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). MS *m/z* 278 (M$^+$). Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52. Found: C, 64.79; H, 6.58.

Preparation of 2-bromomethylthiophene (2). Compound **2** was prepared according to a literature procedure.[17] 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 mmHg. ^{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). MS *m/z* 177 (M$^+$). Anal. Calcd for C_5H_5BrS: C, 33.92; H, 2.85; S, 18.11. Found: C, 33.98; H, 2.88; S, 18.06.

Preparation of 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 °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 mmHg. ^{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). ^{13}C NMR (DMSO-d_6) δ (ppm): 15.86, 15.94, 26.47, 28.38, 61.89, 61.98, 124.28, 124.32, 126.56, 126.60, 126.83, 126.94, 131.98. IR (KBr disc) (cm^{-1}): 3123 (w, =CH), 2982 (m, C-H), 1674 (w, C=C), 1247 (s, P=O). MS *m/z* 234 (M$^+$). 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.

Preparation of 1-{2,4-di-(2-vinyloxyethoxy)phenyl}-2-(2-thienyl)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). ^{13}C NMR (DMSO-*d*$_6$) δ(ppm): 66.35, 66.38, 66.76, 67.13, 87.24, 87.30, 100.11, 106.64, 118.34, 120.36, 122.61, 124.33, 125.68, 127.66, 127.87, 143.46, 151.74, 152.07, 156.69, 159.15. IR (KBr disc) (cm^{-1}): 3123 (w, =C-H), 2930, 2873 (m, C-H), 1602 (vs, C=C). MS *m/z* 358 (M^+). 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.

Preparation of 1-{2,4-di-(2-hydroxyethoxy)phenyl}-2-(2-thienyl)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.

Synthesis of polyester 6. Terephthaloyl chloride (2.03 g, 10 mmol) and diol **5** (3.06 g, 10 mmol) were dissolved in 25 mL of anhydrous pyridine under nitrogen. The resulting solution was refluxed in an oil bath kept at 80 °C under a nitrogen atmosphere. After heating 24 h with stirring the resulting polymerization solution was 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, yielding 4.01 g (92% yield) of polymer **6**. 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): 4.26-4.45 (s, 4H, 2 -CH_2-O-), 4.58-4.75 (d, 4H, 2 Ph-O-CH_2-), 6.52-6.78 (m, 2H, -CH=CH-), 6.87-7.06 (m, 3H, aromatic), 7.23-7.35 (m, 1H, aromatic), 7.44-7.56 (s, 1H, aromatic), 7.91-8.13 (m, 5H, aromatic). IR (KBr disc) (cm^{-1}): 3069 (w, =C-H), 2956 (m, C-H), 1722 (vs, C=O), 1606 (s, C=C). Anal. Calcd for $(C_{24}H_{20}O_6S)_n$: C, 66.04; H, 4.62; S, 7.35. Found: C, 66.15; H, 4.66; S, 7.39.

Synthesis of polyester 7. Tetracyanoethylene (1.28 g, 10 mmol) was added slowly to a solution of polymer **6** (3.71 g, 8.5 mmol) dissolved in 30 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, yielding 4.10 g (90% yield) of polymer **7**. Inherent viscosity (η_{inh}) = 0.30 dL g^{-1} (c = 0.5 g dL^{-1} in DMSO at 25 °C). ^{1}H NMR (DMSO-*d*$_6$) δ (ppm): 4.26-4.52 (m, 4H, 2 -CH_2-O-), 4.52-4.78 (m, 4H, 2 Ph-O-CH_2-), 6.53-7.72 (m, 6H, -CH=CH-, aromatic), 7.90-8.13 (m, 5H, aromatic). IR (KBr disc) (cm^{-1}): 3086 (w, =C-H), 2958 (m, C-H), 2219 (s, CN), 1721 (vs, C=O), 1596 (s, C=C). Anal. Calcd for $(C_{29}H_{19}N_3O_6S)_n$: C, 64.80; H, 3.55; N, 7.81.; S, 5.97. Found: C, 64.88; H, 3.62; N, 7.76; S, 6.03.

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