Synthesis and Nonlinear Optical Properties of Novel Y-Type Polyester Containing Tricyanovinylthiazolylazoresorcinoxy Group with Enhanced Thermal Stability of Dipole Alignment

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ABSTRACT: Novel Y-type polyester **4** containing 5-methyl-4-{5-(1,2,2-tricyanovinyl)-2-thiazolylazo}resorcinoxy groups as nonlinear optical (NLO) chromophores, which are parts of the polymer backbone, was prepared, and its NLO properties were investigated. Polyester **4** is soluble in common organic solvents such as *N,N*-dimethylformamide and dimethylsulfoxide. Polymer **4** shows a thermal stability up to 250 °C from thermogravimetric analysis with glass-transition temperature obtained from differential scanning calorimetry of approximately 94 °C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer film at 1560-nm fundamental wavelength is 8.12×10^{-9} esu. The dipole alignment exhibits a thermal stability even at 6 °C higher than glass-transition temperature (T_g), and no significant SHG decay is observed below 100 °C due to the partial main-chain character of polymer structure, which is acceptable for NLO device applications. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1784–1790, 2011

KEYWORDS: atomic force microscopy; differential scanning calorimetry; dipole alignment; NLO; polyester; second harmonic generation; thermogravimetric analysis

INTRODUCTION Materials with nonlinear optical (NLO) properties have been extensively studied because of their potential applications in the field of electro-optic devices including ultrafast optical switches, high-speed optical modulators, and high-density optical data storage media.[1–5] It is well known that organic and inorganic materials with high dipolar electronic systems exhibit large NLO effects. Organic materials display higher optical nonlinearity and faster response time than their inorganic counterparts; among the organic materials, NLO polymers are receiving great attention of late, mainly because they offer many advantages such as mechanical endurance, light weight, low cost, chemical resistance, and good processability in terms of their use in electro-optic devices. A potential NLO polymer must contain highly polarizable conjugated electronic systems and has to be mechanically very strong and thermally stable with a 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 considerations; in this context, two approaches to minimize the randomization have been proposed, namely the use of cross-linked systems[6–10] and the utilization of polymers with high glass transition temperature (T_g) such as polyimides.[11–17] Various polyesters with NLO chromophores in the main chain[18,19] or side chain[20,21] have been prepared and their NLO properties studied. Polyesters with amino-sulfone azobenzene chromophores in the main chain generate strong and stable reversible birefringence.[18] NLO polyesters containing azobenzene mesogens in the main chain exhibit high thermal and temporal stabilities.[19] Polyesters containing cyanophenylazoaniline moiety in the side chain show good temporal stability of second-order nonlinearity.[20] Main-chain NLO polymers usually 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 films. Side-chain NLO polymer systems have the advantages such as good solubility, homogeneity, and high loading level of NLO chromophores, but they often suffer from poor stability of dipole alignments at high temperatures. Recently, we prepared novel polyesters containing dioxynitrostilbene,[22,23] dioxybenzylidenemalononitrile,[24–26] dioxybenzylidenecyanoacetate,[27,28] and tricyanovinylthienyl groups[29,30] as NLO chromophores. The resulting polymers exhibit enhanced thermal stability of second harmonic generation (SHG), which stems from the stabilization of dipole alignment of the NLO chromophores.

In this work reported here, we prepared a new Y-type polyester containing 5-methyl-4-{5-(1,2,2-tricyanovinyl)-2-thiazolylazo}resorcinoxy groups as NLO chromophores. We selected the latter, because they were expected to have large NLO activities. Furthermore, these 5-methyl-4-{5-(1,2,2-tricyanovinyl)-2-thiazolylazo}resorcinoxy groups can be

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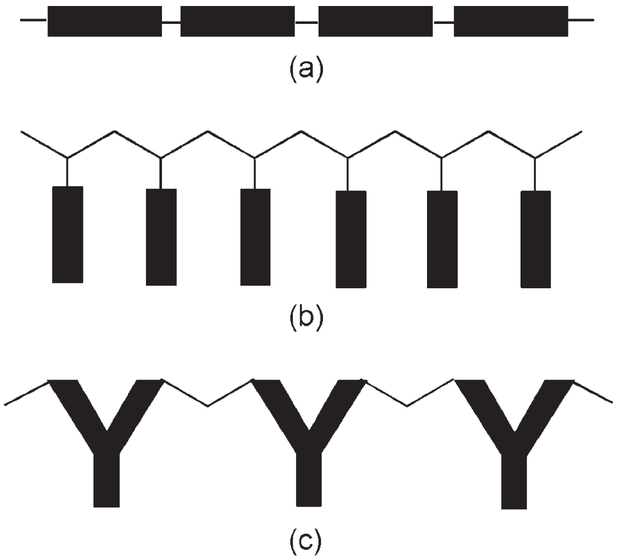


FIGURE 1 Main Chain NLO polymers (a), side chain NLO polymers (b), and Y-type NLO polymers (c).

incorporated into novel Y-type NLO polyesters [see Fig. 1(c)]. The structure of NLO chromophores and these Y-type NLO polyesters have not yet been described in the literature. Thus, we synthesized a new type of NLO polyester, in which the pendant NLO chromophores are parts of the polymer backbone. This Y-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 such as solubility, T_g, thermal stability, surface morphology of polymer films, SHG activity, and relaxation of dipole alignment.

EXPERIMENTAL

Materials

Reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 5-Methyl-4-(2-thiazolylazo)resorcinol 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.

Instrumentation

Infrared (IR) spectra were obtained with a Shimadzu FT IR-8201PC IR spectrophotometer. ^{1}H NMR and ^{13}C 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 (TGA) with a heating rate of 10 °C min^{-1} 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 using gel permeation chromatography [GPC; styragel HR5E4E columns; tetrahydrofuran (THF) solvent]. 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 using a Cannon-Fenske viscometer.

Film Preparation and SHG Measurements

The polymer film was prepared from a 10 wt % polymer solution in DMF deposited on an indium-tin oxide-covered glass. Before film casting, the polymer solution was filtered through 0.45 μm Teflon® membrane filter. The films were spin cast at room temperature in the range 1000–1200 rpm. The films were dried for 12 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 10 mm. As the temperature was raised gradually to 5–10 °C higher than T_g, a corona voltage of 6.5 kV was applied, and the temperature was maintained 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.[31] The transmittance of thin film gives information on the thickness, refractive index, and extinction coefficient of the film. Thus, we can determine these parameters by analyzing the transmittance. SHG measurement was carried out 1 day after poling. The IR fundamental radiation of the 1.56-μm was generated using an 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 were about 7 ns and 6 mm, respectively. The OPO that we used has a well-established design. It consists of a $LiNbO_3$ crystal (12 × 15 × 50 mm^3) cut at about 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^{-1}) 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.[32]

Preparation of 5-Methyl-4-(2-thiazolylazo)resorcinoxy Ethyl Vinyl Ether (1)

5-Methyl-4-(2-thiazolylazo)resorcinol (23.5 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 purified by column chromatography (hexane/ethyl acetate = 2/1 by volume) yielded 33.0 g (yield 88%) of pure product **1**.

^{1}H NMR (acetone-d_6) δ 2.56 (d, 3H, —CH_3), 3.92–4.41 (m, 12H, 2 CH_2=, 2 —O—CH_2—CH_2—O—), 6.43–6.74 (m, 4H, 2 =CH—O—, aromatic), 7.62–7.65 (q, 1H, aromatic), 7.93–7.98 (m, 1H, aromatic). IR (KBr) 3112, (m, =C—H), 2922 (m, C—H), 1622 (vs, C = C) cm^{-1}. Anal. Calcd for $C_{18}H_{21}N_3O_4S$: C, 57.58; H, 5.64; N, 11.19; S, 8.54. Found: C, 57.65; H, 5.68; N, 11.14; S, 8.58.

Preparation of 5-Methyl-4-(2-thiazolylazo)resorcinoxyethanol (2)

Aqueous hydrochloric acid (1.5 mol L^{-1}, 12 mL) was slowly added to a solution of compound **1** (3.75 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 2.78 g (yield 86%) of **2**.

^{1}H NMR (acetone-d_6) δ 2.57 (s, 3H, —CH_3), 3.88–3.94 (m, 2H, —CH_2—O—), 4.21–4.27 (m, 2H, Ph-O—CH_2—), 6.42 (d, 1H, aromatic), 6.64 (d, 1H, aromatic), 7.65 (d, 1H, aromatic), 7.95 (d, 1H, aromatic). IR (KBr) 3312 (vs, O—H), 3084 (w, =C—H), 2943 (m, C—H), 1631 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{14}H_{17}N_3O_4S$: C, 52.00; H, 5.30; N, 12.99; S, 9.92. Found: C, 52.08; H, 5.36; N, 12.92; S, 9.96.

Synthesis of Polyester 3

A representative polycondensation reaction procedure was as follows. TPC (2.03 g, 10 mmol) and diol **2** (3.23 g, 10 mmol) were dissolved in 25 mL of anhydrous pyridine under nitrogen. The resulting solution was heated in an oil bath kept at 80 °C under a nitrogen atmosphere. After heating 20 h with stirring, the resulting polymerization solution was poured into 400 mL of methanol. The precipitated polymer was collected and reprecipitated from dimethylsulfoxide (DMSO) into methanol. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum, yielding 4.15 g (90% yield) of polymer **3**.

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 2.51 (s, 3H, —CH_3), 4.45–4.54 (m, 4H, 2 —O—CH_2—,) 4.62–4.68 (m, 4H, 2 —O—CH_2—OCO—), 6.55 (d, 1H, aromatic), 6.70 (d, 1H, aromatic), 7.80 (d, 1H, aromatic), 7.97 (d, 1H, aromatic), 8.07 (s, 4H, aromatic). IR (KBr) 3090 (w, =C—H), 2957 (w, C—H), 1718 (vs, C=O), 1626 (m, C=C) cm^{-1}. Anal. Calcd for $(C_{22}H_{27}N_3O_6S)_n$: C, 57.25; H, 5.90; N, 9.10; S, 6.95. Found: C, 57.33; H, 5.98; N, 9.17; S, 7.02.

Synthesis of Polymer 4

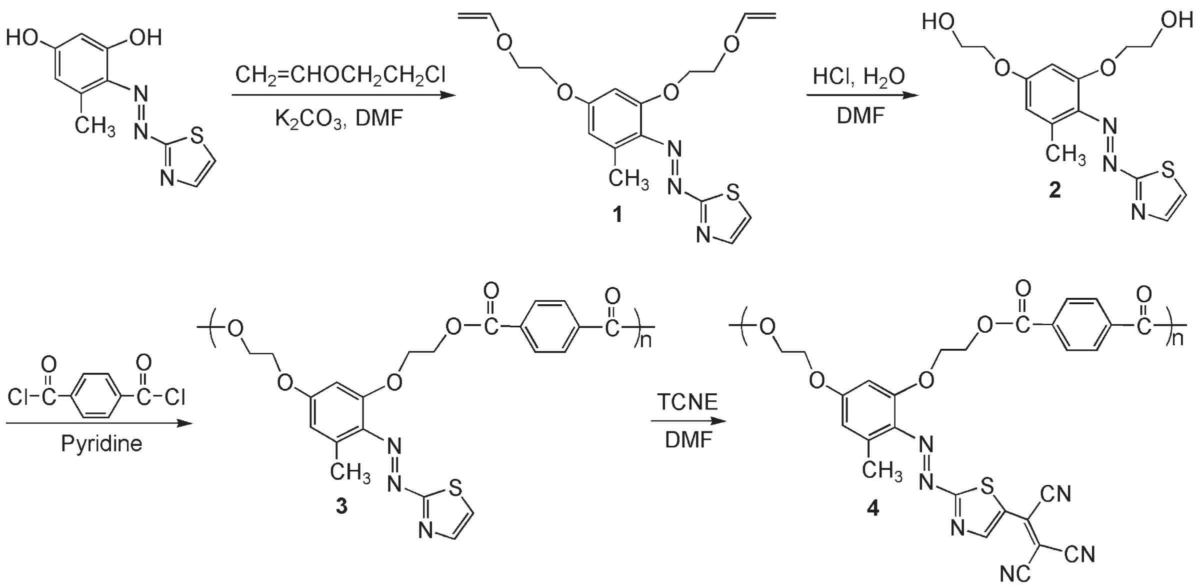
A representative reaction procedure was as follows. TCNE (1.28 g, 10 mmol) was added slowly to a solution of polymer **3** (5.27 g, 8.5 mmol) dissolved in 30 mL of DMF with stirring at room temperature under nitrogen. The resulting solution was heated in an oil bath kept at 70 °C for 16 h under a nitrogen 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 4.94 g (88% yield) of polymer **4**.

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 2.52 (s, 3H, —CH_3), 3.93–4.08 (m, 4H, 2 —CH_2—O—), 4.33–4.76 (m, 4H, 2 Ph-O—CH_2—), 7.15–7.43 (s, 4H, aromatic), 7.62–7.85 (m, 1H, aromatic), 8.16–8.28 (m, 1H, aromatic), 8.93–9.12 (d, 1H, aromatic). ^{13}C NMR (DMSO-d_6) δ 22.80, 60.43, 60.46, 64.90, 100.31, 110.01, 111.12, 116.93, 119.01, 128.74, 131.50, 133.85, 134.50, 148.92, 149.12, 153.09, 154.34, 173.44. IR (KBr) 3085 (w, =C—H), 2956 (m, C—H), 2220 (s, CN), 1719 (vs, C=O), 1590 (s, C=C) cm^{-1}. Anal. Calcd for $(C_{27}H_{26}N_6O_6S)_n$: C, 57.64; H, 4.66; N, 14.94; S, 5.70. Found: C, 57.73; H, 4.72; N, 14.86; S, 5.78.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymer

Compound **1** was prepared by the reaction of 2-chloroethyl vinyl ether with 5-methyl-4-(2-thiazolylazo)resorcinol. Diol **2** was prepared by acid-catalyzed hydrolysis of **2** in DMF. Polyester **3** was synthesized through the reaction of monomer **2** containing NLO chromophore with stoichiometric amount of TPC in pyridine (see Scheme 1). The polymerization yield was 90–92%. Polymer **3** was reacted with TCNE in anhydrous DMF[33] to yield polyester **4** containing 5-methyl-4-{5-(1,2,2-tricyanovinyl)-2-thiazolylazo}resorcinoxy groups as NLO chromophores. The synthetic route for polymer **4** 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 resulting polymer was confirmed using ^{1}H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structure. ^{1}H NMR spectrum of the polymer showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The ^{13}C NMR spectrum of the polymer **4** shows a signal at 117–119 ppm assigned to the cyano carbon, which indicates the presence of nitrile group. The IR spectrum of the polymer **4** shows a strong carbonyl peaks near 1719 cm^{-1} indicating the presence of ester bond. The spectrum also shows strong absorption peak near 2220 cm^{-1} indicating the presence of nitrile group.



SCHEME 1 Synthetic scheme and structure of polymer **4**.

These results are consistent with the proposed structures, indicating that the tricyanovinyl groups are attached well to the thiazole rings. The molecular weights were determined using GPC with polystyrene as the standard and THF as the eluent. M_n of the polymer **4**, determined using GPC, is 17,200 g mol^{-1} (M_w/M_n = 1.94). The inherent viscosity is 0.30–0.32 dL g^{-1}. Polymer **4** shows strong absorption near 394 nm due to the 5-methyl-4-{5-(1,2,2-tricyanovinyl)-2-thiazolylazo}resorcinoxy group NLO chromophore. The structural feature of this polymer is that it has pendant NLO chromophores, which are parts of the main chain polymer. Thus, the resulting polymer **4** is mid type of side-chain and main-chain NLO polymer, and is expected to have both of their merits. The polymer **4** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. Having obtained the well-defined polyester **4**, we investigated its properties.

Thermal Properties of Polymers

The thermal behavior of the polymer was investigated using TGA and DSC to determine the thermal degradation pattern and glass transition temperature. The results are summarized in Table 1. The TGA thermogram of the polymer **4** is shown in Figure 2. Polymer **4** shows a thermal stability up to 250 °C from its TGA thermogram. T_g value of polymer **4** measured using DSC is approximately 94 °C. This T_g value is similar with those of the polyesters containing dioxynitrostilbene, which are in the range 90–95 °C,[34] but is higher than those with dioxybenzylidenemalononitrile, which are in the range 83–94 °C.[25,26] The TGA and DSC studies show that the decomposition temperature of the polyester **4** is 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 Polymer

The NLO properties of polymer were studied using 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, a corona voltage of 6.5 kV was applied, and this temperature was maintained for 30 min. The poling was confirmed from UV–visible spectra. After electric poling, the dipole moments of the NLO chromophores were aligned and UV–visible absorption of polymer **4** exhibits a decrease in absorption due to alignment of the chromophores perpendicular to the substrate plain. From the absorbance change, the order parameter of the poled films can be estimated, which is related to the poling efficiency. The estimated order parameter value Φ is equal to 0.15 for polymer **4** ($\Phi = 1 - A_1/A_0$, where A_0 =

TABLE 1 Thermal Properties of Polymer **4**

		Degradation Temperature (°C)[b]				
Polymer	T_g[a] (°C)	5 wt % Loss	10 wt % Loss	20 wt % Loss	40 wt % Loss	Residue[b] at 800 °C (%)
4	94	252	271	286	317	31.0

[a] Determined from DSC curves measured with a TA 2920 differential scanning calorimeter with a heating rate of 10 °C min^{-1} under nitrogen atmosphere.
[b] Determined from TGA curves measured with a TA Q50 thermogravimetric analyzer with a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

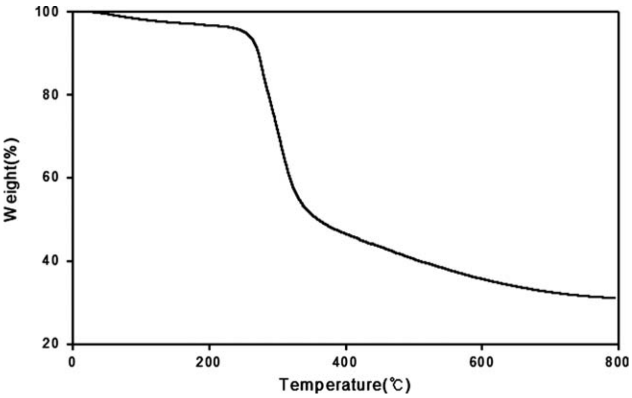


FIGURE 2 TGA thermogram of polymer **4** obtained at a heating rate of 10 °C min^{-1} under nitrogen.

1.5515 and $A_1 = 1.3226$ are the absorbances of the polymer film before and after poling, respectively).

For the purpose of investigating surface morphology of polymer film, domain structures of NLO chromophores for the thin-film samples were obtained with AFM. Figure 3 shows AFM scans of a spin-coated film of polymer **4** before and after poling. AFM images show that the surface of the film sample is extremely flat and smooth before poling [Fig. 3(a)]. 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, as shown in Figure 3(b).

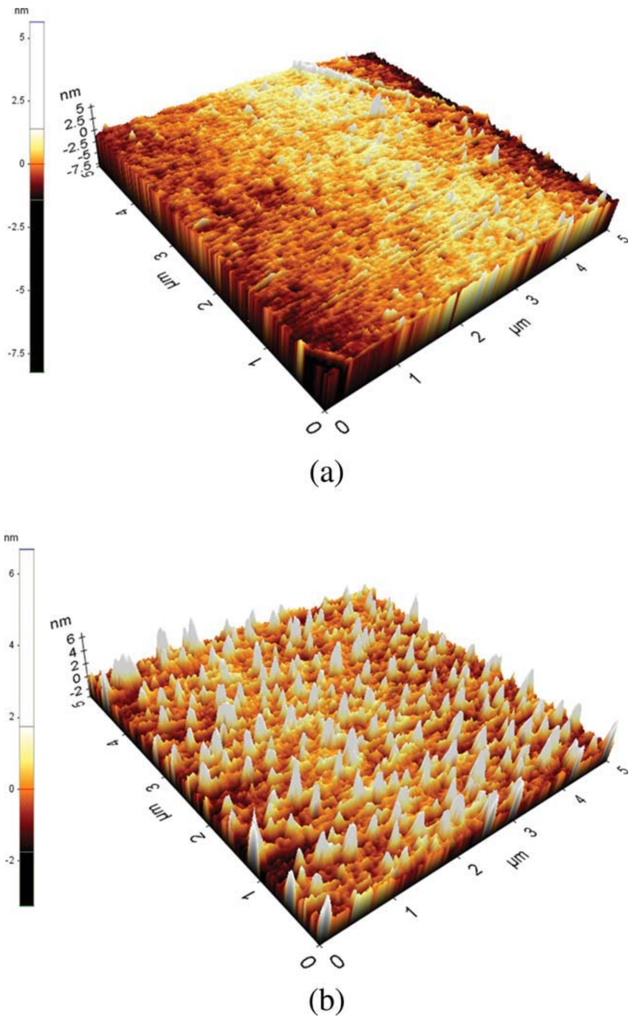


FIGURE 3 AFM images of spin-coated film of polymer **4**: (a) before corona-poling and (b) after corona-poling.

The refractive index of the sample was measured using the optical transmission technique.[31] 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. To determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Figure 4 shows the angular dependence of SHG signal for a poled sample of polymer **4**. 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 and recorded. SHG coefficients (d_{33}) were derived from the analysis of measured Maker fringes with the Pascal fitting program according to the literature procedure.[32] The NLO properties of polymer **4** are summarized in Table 2. The values of d_{31} and d_{33} for polymer **4** are 2.56×10^{-9} esu and 8.12×10^{-9} esu, respectively. As the second harmonic wavelength is at 780 nm, which is not in the absorptive region of the resulting polyester, there is 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 3.17 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. Figure 5 shows the dynamic thermal stability study of the NLO activity of a film of polymer **4**. To investigate the real time NLO decay of the SHG signal of the poled polymer film as a

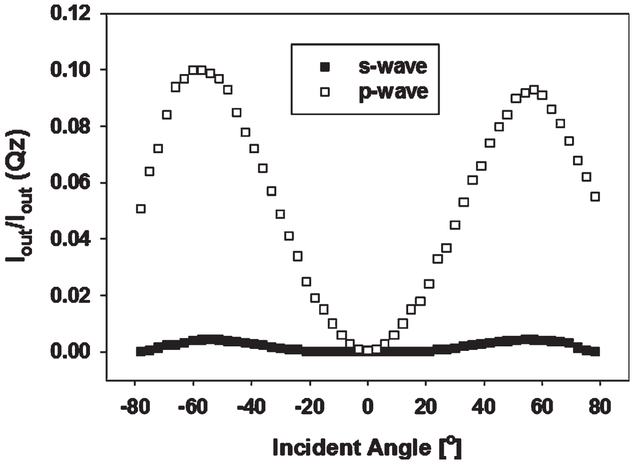


FIGURE 4 Angular dependence of SHG signal for a poled film of polymer **4**.

TABLE 2 Nonlinear Optical Properties of Polymer **4**

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	Φ[c]	d_{31}[b] (esu)	Film Thickness[d] (μm)	*n*
4	394	8.12×10^{-9}	0.15	2.56×10^{-9}	0.51	1.532

[a] Polymer film after corona poling.

[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker fringes.[32]

[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 using the optical transmission technique.[31]

function of temperature, *in situ* SHG measurements were performed at a heating rate of 3.5 °C min^{-1} from 30 to 200 °C. The polymer film exhibits a thermal stability even at 6 °C higher than T_g, and no SHG decay is observed below 100 °C for polymer **4**. In Figure 6, we present the temporal stability of the polymer film in which there was no negligible decay of the SHG signal over hundreds of hours. 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 SHG of polymer **4** is due to the stabilization of dipole alignment of NLO chromophore, which stems 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 stable dipole alignment and good solubility.

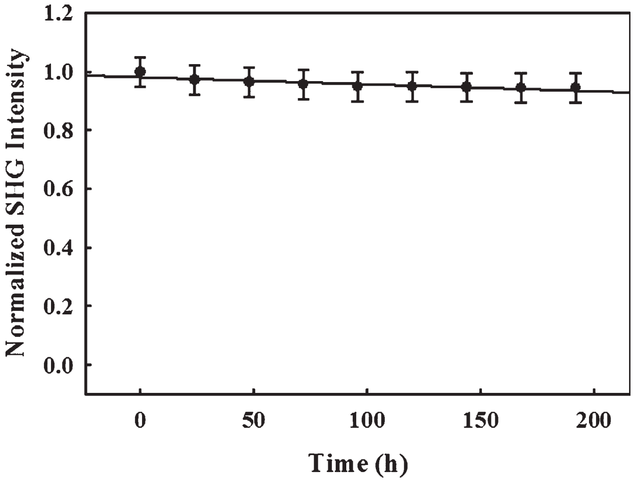


FIGURE 6 Normalized SHG signal of polymer **4** as a function of baking time at 60 °C in air.

CONCLUSION

New Y-type polyester **4** with pendant NLO chromophores as parts of the main chain polymer was synthesized. This Y-type NLO polyester **4** is soluble in common organic solvents and displays a thermal stability up to 250 °C with T_g values near 94 °C. The SHG coefficient (d_{33}) of corona-poled polymer film is 8.17×10^{-9} esu. Polymer **4** exhibits SHG stability even at 6 °C higher than T_g, and no significant SHG decay is observed below 100 °C. This high-thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophores, which are parts 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.

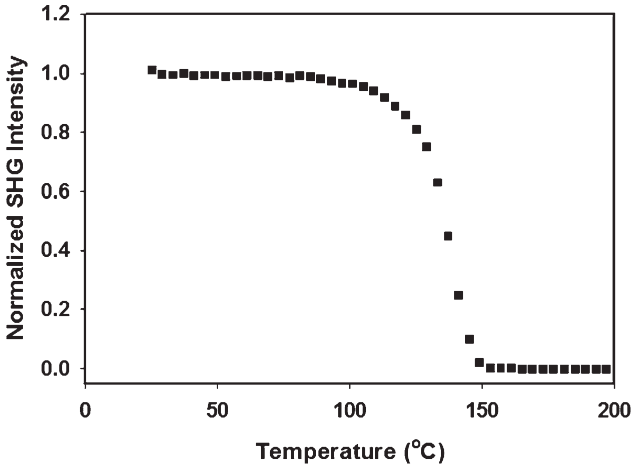


FIGURE 5 Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 3.5 °C min^{-1}.

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