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ORIGINAL PAPER

Synthesis of novel T-type nonlinear optical polyester with enhanced thermal stability of second harmonic generation for electro-optic applications

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Abstract 2,5-Di-(2′-hydroxyethoxy)benzylidenemalononitrile (**3**) was prepared and condensed with terephthaloyl chloride to yield novel T-type polyester (**4**) containing 2,5-dioxybenzylidenemalononitrile groups as NLO-chromophores, which are parts of the polymer backbones. The resulting polymer **4** was soluble in common organic solvents such as acetone and DMF and showed thermal stability up to 280 °C with T_g of 83 °C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer film at the 1,064 nm fundamental wavelength was around 4.46×10^{-9} esu. The dipole alignment exhibited high thermal stability even at 10 °C higher than T_g, and there was no SHG decay below 95 °C due to the partial main-chain character of polymer structure, which was acceptable for NLO device applications.

Keywords Nonlinear optical (NLO) · Polyester · AFM · SHG · Thermal stability

Introduction

Functional materials of nonlinear optical (NLO) activities are extensively studied in recent years because of their potential applications in the field of electro-optic devices. The organic materials are superior because of their higher nonlinear optical activity and faster response time than their inorganic counterparts; among 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 [1, 2]. A potential NLO

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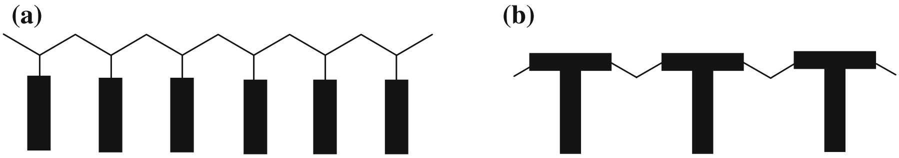


Fig. 1 **a** Side chain NLO polymers and **b** T-type NLO polymers

polymer must contain highly polarizable conjugated dipolar electronic systems and they have to be mechanically very strong and thermally stable with high T_g values. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is an important consideration; in this context, two approaches to minimize the randomization have been proposed. One is to use cross-linking method [3–6] and the other is to utilize high T_g polymers such as polyimides [7–10]. Polyesters with the NLO-chromophores in the main chain [11] or in side chain [12] have been prepared and their properties were 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 polymers have the advantages such as good solubility, homogeneity and high loading level of NLO chromophore relative to the main-chain systems, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we have prepared a couple of novel Y-type polyesters with enhanced thermal stability of dipole alignment through the stabilization of dipole alignment of the NLO chromophores [13–17]. In this work we prepared another novel polyester containing 2,5-dioxybenzylidenemalononitrile groups as NLO-chromophores. We selected the latter because they have a large dipole moment and are rather easy to synthesize. Furthermore, 2,5-dioxybenzylidenemalononitrile group constitutes novel T-type NLO polyester (Fig. 1b), and this T-type NLO polyester has not yet been reported in the literature. Thus, we synthesized a new type of NLO polyester, in which the pendant NLO chromophores are parts of the polymer backbones. These mid-type NLO polymers are expected to have the advantages of both main-chain and side-chain NLO polymers: stabilization of 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 film, second harmonic generation (SHG) activity and relaxation of dipole alignment. We now report the results of the initial phase of the work.

Experimental

Materials

The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2,5-Dihydroxybenzaldehyde and 2-chloroethyl vinyl ether were used as received. Terephthaloyl chloride (TPC) was purified by sublimation under vacuum. Malononitrile was recrystallized from water and distilled from phosphorus pentoxide. Piperidine was treated with potassium hydroxide and then distilled over barium oxide to remove trace amounts of water. *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 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 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.

Film preparation and SHG measurement

The polymer film was prepared from a 10 wt% by weight polymer solution in DMF 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 room temperature at a range from 1,000 to 1,200 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, 6.5 kV of corona voltage was applied and kept 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]. SHG measurement was carried out 1 day after poling. A continuum PY61 mode-locked Nd:YAG laser ($\lambda = 1{,}064$ nm) with pulse width of 40 ps and repetition rate of 10 Hz was used as the fundamental light source and Y-cut quartz was used as reference. A beam splitter and a photodiode were used to compensate for the intensity fluctuations of the fundamental beam (1,064 nm). The polarity of the fundamental laser beam was adjusted using a half-wave plate before it hit the 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].

2,5-Di-(2′-vinyloxyethoxy)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 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 24.5 g (88% yield) of pure product **1**. ^{1}H NMR ($CDCl_3$) δ 3.98–4.34 (m, 12H, 2 CH_2=, 2–O–CH_2–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) 3,096, 3,075 (w, =C–H), 2,941, 2,882 (s, C–H), 1,676 (vs, C=O), 1,624 (vs, C=C) cm^{-1}.

2,5-Di-(2′-vinyloxyethoxy)benzylidenemalononitrile (**2**)

Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,5-di-(2′-vinyloxyethoxy)benzaldehyde **1** (8.35 g, 30 mmol) and malononitrile (2.18 g, 33 mmol) in 170 mL of 1-butanol with stirring at 0 °C under nitrogen. After stirring for 4 h at 0 °C, the reaction mixture was cooled to −10 °C for crystallization. The product was filtered and washed successively with cold 1-butanol (80 mL), water (30 mL), and cold 1-butanol (20 mL). The obtained pale yellow product was recrystallized from 1-butanol to give 8.61 g (88% yield) of **2**. Mp = 72–74 °C. ^{1}H NMR ($CDCl_3$) δ 4.02–4.40 (m, 12H, 2 CH_2=, 2–O–CH_2–CH_2–O–), 6.46–6.58 (m, 2H, 2=CH–O–) 6.94–6.98 (d, 1H, aromatic), 7.18–7.23 (q, 1H, aromatic), 7.75–7.78 (d, 1H, aromatic), 8.31 (s, 1H, Ph–CH=). IR (KBr) 3,057 (w, =C–H), 2,941, 2,885 (m, C–H), 2,222 (s, CN), 1,624, 1,578 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{18}H_{18}N_2O_4$: C, 66.25; H, 5.56; N, 8.58. Found: C, 66.36; H, 5.64; N, 8.50.

2,5-Di-(2′-hydroxyethoxy)benzylidenemalononitrile (**3**)

Aqueous hydrochloric acid (1.5 mol L^{-1}, 30 mL) was slowly added to a solution of 2,5-di-(2′-vinyloxyethoxy)benzylidenemalononitrile (**2**) (8.48 g, 0.026 mol) in 60 mL of dry THF with stirring under nitrogen at 0 °C. The mixture was stirred at 80 °C for 8 h under nitrogen. The resulting solution was extracted with diethyl ether (80 mL) three times. The organic layer was washed successively with saturated sodium chloride, sodium hydrogen carbonate, and water, followed by drying with anhydrous magnesium sulfate. Rotary evaporation of diethyl ether gave crude product. The obtained pale yellow product was recrystallized from ethyl acetate to give 6.06 g (85% yield) of **3**. Mp = 138–140 °C. ^{1}H NMR (acetone-d_6) δ 3.74–3.94 (m, 4H, 2–CH$_2$–OH), 3.94–4.12 (m, 2H, –OH), 4.12–4.22 (m, 4H, 2 –O–CH$_2$–), 7.15–7.32 (m, 2H, aromatic), 7.75 (s, 1H, aromatic), 8.58 (s, 1H, –Ph–CH=). IR (KBr) 3,516, 3,233 (s, O–H), 3,045 (m, =C–H), 2,941 (m, C–H), 2,233 (m, CN), 1,576 (s, C=C) cm^{-1}. Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.41; H, 5.22; N, 10.28.

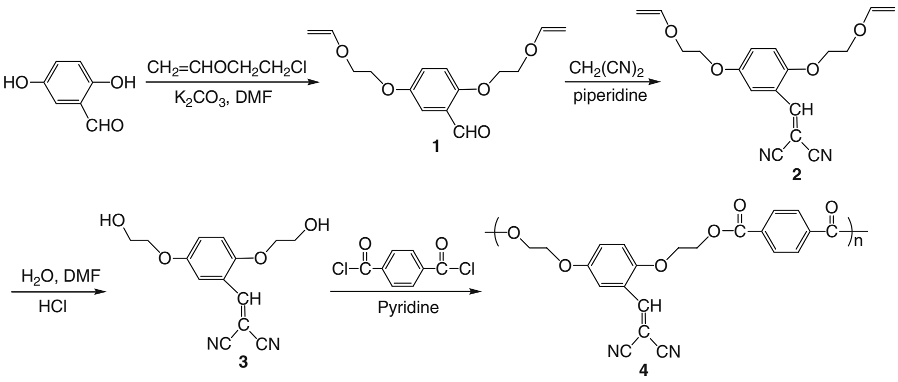
Synthesis of polyester **4**

A representative polycondensation procedure was as follows: TPC (2.03 g, 0.01 mol) and diol **3** (2.74 g, 0.01 mol) were dissolved in 30 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 25 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 diethyl ether and dried under vacuum, yielding 3.64 g (90% yield) of polymer **4**: $\eta_{\mathrm{inh}} = 0.28$ dL/g (c, 0.5 g/dL in DMSO at 25 °C). ^{1}H NMR (DMSO-d_6) δ 4.29–4.53 (d, 4H, 2–CH$_2$–O–), 4.56–4.72 (d, 4H, 2 Ph–O–CH$_2$–), 7.23–7.44 (d, 2H, aromatic), 7.52–7.62 (s, 1H, aromatic), 7.97–8.15 (d, 4H, aromatic), 8.32–8.44 (s, 1H, aromatic). IR (KBr) 3,048 (w, =C–H), 2,959 (m, C–H), 2,225 (s, CN), 1,723 (vs, C = O), 1,578 (s, C=C) cm^{-1}. Anal. Calcd for $(C_{22}H_{16}N_2O_6)_n$: C, 65.34; H, 3.99; N, 6.93. Found: C, 65.42; H, 4.05; N, 6.87.

Results and discussion

Synthesis and characterization of polymer **4**

2,5-Di-(2′-vinyloxyethoxy)benzaldehyde (**1**) was prepared by the reaction of 2-chloroethyl vinyl ether with 2,5-dihydroxybenaldehyde. 2,5-Di-(2′-vinyloxyethoxy)benzylidenemalononitrile (**2**) was prepared by the condensation reaction of **1** with malononitrile, and was hydrolyzed to yield acetaldehyde and diol **3**. Diol **3** was condensed with TPC in a dry DMF solvent to yield polyester **4** containing the NLO-chromophore 2,5-dioxybenzylidenemalononitrile group. The synthetic route for polymer **4** is presented in Scheme 1. The polymerization yield was 90%. The chemical structure of the resulting polymer was confirmed by ^{1}H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structures. ^{1}H NMR spectrum of the polymer showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structures. The IR spectrum of the same polymer sample showed a strong carbonyl peak near 1,723 cm^{-1} indicating the presence of ester bond. The same polymer sample also



Scheme 1 Synthetic scheme and structure of polymer **4**

showed a strong nitrile peak near 2,225 cm^{-1}. These results are consistent with the proposed structure, indicating that the NLO-chromophore remained intact during the polymerization. The molecular weights were determined by GPC using polystyrene as the standard and THF as eluent. The number average molecular weight (M_n) of the polymer **4** was determined to be 18,400 ($M_w/M_n = 1.94$). 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 (**4**) is mid type of side chain- and main chain NLO polymer, and is expected to have both of their merits. The polymer **4** was soluble in common solvents such as acetone, DMF, and DMSO, but was not soluble in methanol and diethyl ether. The inherent viscosity was around 0.28 dL/g.

Polymer **4** showed strong absorption near 408 nm by the NLO-chromophore 2,5-dioxybenzylidenemalononitrile group. We now have well defined polyester (**4**) and investigate 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 (T_g). The results are summarized

Table 1 Thermal properties of polymer **4**

Polymer	T_g (°C)[a]	Degradation temp. (°C)[b]			Residue at 800 °C, %[b]
		5 wt%-loss	20 wt%-loss	40 wt%-loss	
4	83	305	398	472	43.5

[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

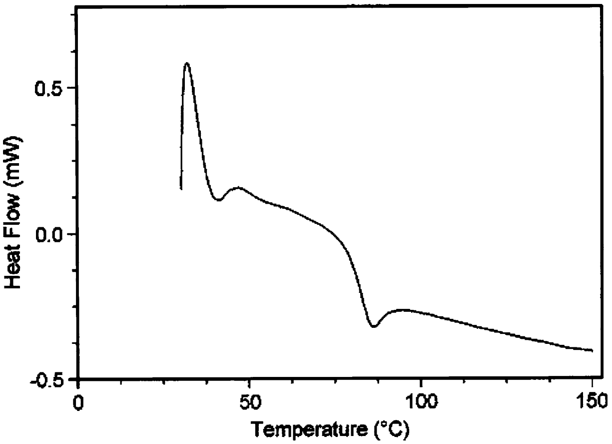


Fig. 2 DSC thermogram of polymer **4** at a heating rate of 10 °C/min under nitrogen

in Table 1. DSC thermogram of polymer **4** is presented in Fig. 2. Polymer **4** showed a thermal stability up to 280 °C according to its TGA thermogram. The T_g value of the polymer **4** measured by DSC was around 83 °C. The TGA and DSC studies showed that the decomposition temperature of the polyimide **5** 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.

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. The UV–Vis absorption spectra of polymer **4** 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 **4** exhibited a decrease in absorption

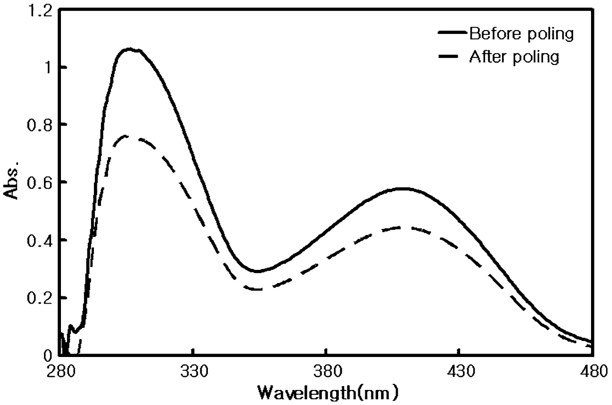


Fig. 3 UV–Vis absorption spectra of a film of polymer **4** before and after poling

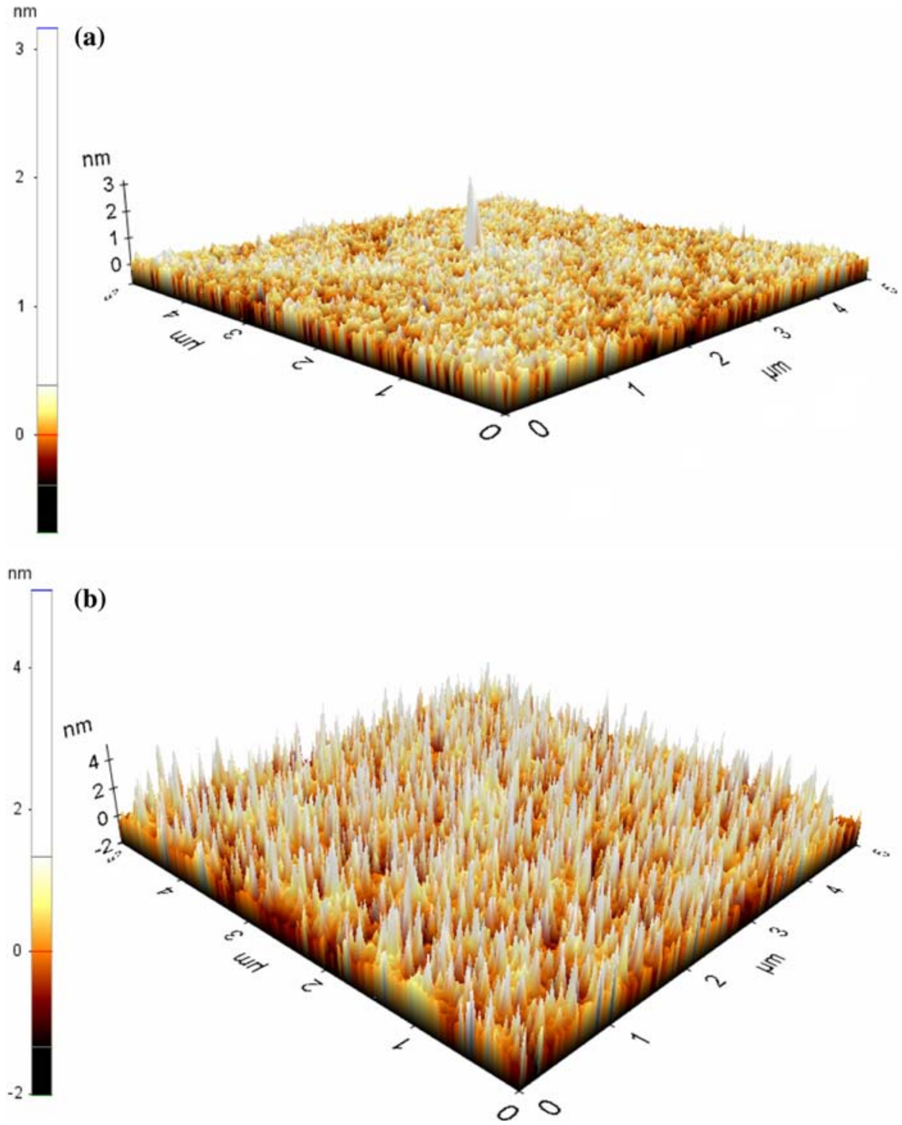


Fig. 4 AFM images of spin-coated film of polymer **4**: **a** before corona-poling, **b** after corona-poling

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 0.23 for polymer **4** ($\Phi = 1 - A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after poling, respectively).

Domain structures of NLO-chromophores for the poled thin-film sample were obtained with AFM. Figure 4 shows AFM scans of the spin-coated film before and after poling polymer **4**. AFM images show that the surface of the film sample is flat and clean. However, this good quality film was dramatically changed after poling,

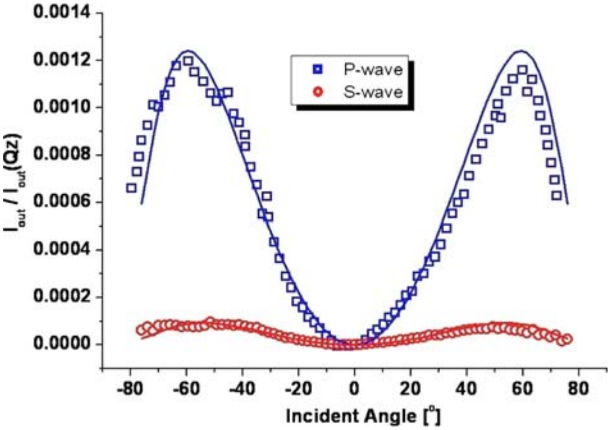


Fig. 5 Angular dependence of SHG signal in a poled film of polymer **4**

Table 2 Nonlinear optical properties of polymer **4**

Polymer	λ_{max} (nm)[a]	d_{33} (esu)[b]	Φ[c]	Film thickness (μm)[d]	d_{31} (esu)[b]
4	408	$(4.46 \pm 0.11) \times 10^{-9}$	0.23	0.54	$(1.55 \pm 0.05) \times 10^{-9}$

[a] Polymer film after corona poling

[b] SHG coefficient (d_{33}) was derived from the analysis of measured Maker-fringe [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]

which resulted in numerous sharp hills and valleys in the surface structure, which were aligned in the poling direction, as shown in Fig. 4. The refractive index of the sample was measured by the optical transmission technique [18]. The transmittance of thin film includes the information on the thickness, refractive index and extinction coefficient of that. Thus, we can determine those parameters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of 1,064 nm using a mode locked Nd-YAG laser. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Figure 5 shows the angular dependence of SHG signal in a poled 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 to 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 [19]. Nonlinear optical properties of polymer **4** are summarized in Table 2. The values of d_{31} and d_{33} for polymer **4** were 1.55×10^{-9} and 4.46×10^{-9} esu, respectively. Since the second harmonic wavelength was at 532 nm, which is not in the absorptive region of the resulting polyurethane, there was not resonant contribution to this d_{33} value. In the isotropic

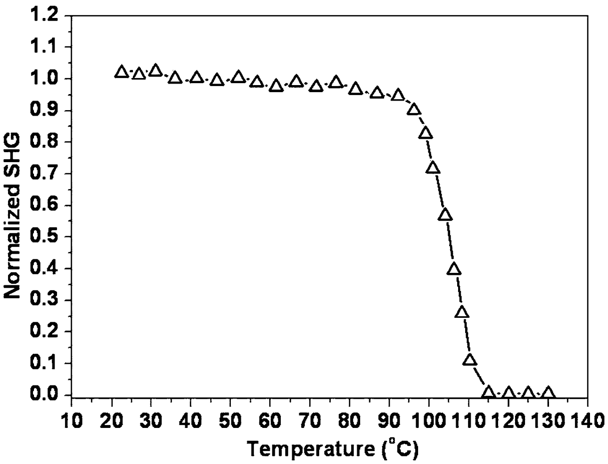


Fig. 6 Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 10 °C/min

model, the ratio of d_{33}/d_{31} is predicted to be about 3. Our d_{33}/d_{31} value of 2.88 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. 6, we present the dynamic thermal stability study of the NLO activity of the film **4**. 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 10 °C/min from 25 to 150 °C. The polymer film exhibited a thermal stability even at 10 °C higher than T_g and no SHG decay was observed below 95 °C. In general, side-chain NLO polymers lose the thermal stability of dipole alignment far below T_g. Stabilization of dipole alignment is a characteristic of main chain NLO polymers. The high thermal stability of second harmonic generation of polymer **4** 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 NLO polyester having the advantages of both main-chain and side-chain NLO polymers namely stable dipole alignment and good solubility.

Conclusions

We have synthesized novel T-type polyester **4** with pendant NLO chromophores, which are parts of the polymer main chains. This mid-type NLO polyester is soluble in common organic solvents. Polymer **4** showed thermal stability up to 280 °C according to TGA thermogram and had T_g near 83 °C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer film at the 1,064 nm fundamental wavelength was around 4.46×10^{-9} esu. The dipole alignment exhibited a thermal stability even at 10 °C higher than T_g, and there was no SHG decay below 95 °C because of the partial main chain character of polymer structure. This highly enhanced thermal stability of optical nonlinearity stemmed from the stabilization of dipole alignment of the NLO chromophore, which was a part of the polymer backbone.

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