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Synthesis and properties of novel X-type nonlinear optical polyester containing nitrophenylazonitroresorcinoxy group with highly enhanced SHG thermal stability

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ABSTRACT

New X-type polyester (**4**) containing nitrophenylazonitroresorcinoxy groups as NLO chromophores, which are components of the polymer backbone, was prepared and characterized. Polyester **4** is soluble in common organic solvents such as acetone and *N*,*N*-dimethylformamide. It shows a thermal stability up to 280 °C in thermogravimetric analysis with glass-transition temperature (T_g) obtained from differential scanning calorimetry near 120 °C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer film at the 1064 nm fundamental wavelength is around 2.13 pm/V. The dipole alignment exhibits a thermal stability even at 5 °C higher than T_g , and there is no SHG decay below 125 °C due to the partial main-chain character of polymer structure, which is acceptable for NLO device applications. © 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Nonlinear optical (NLO) polymers received a great attention in recent years because of their potential applications in the field of electro-optic devices including ultrafast optical switches, highspeed optical modulators, and high-density optical data storage media [1-8]. NLO polymers have many advantages superior to conventional inorganic ones such as light weight, low cost, ultrafast response, wide response wave band, high optical damage threshold, and good processability to form optical 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_{σ}). NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of important considerations; in this context, several approaches to minimize the randomization have been proposed, namely the use of cross-linked systems [9–13], the utilization of polymers with high glass transition temperature (T_g) such as polyimides [14–20], and H-shape polymers [2]. Host-guest polymer films doped with spindle-type

chromophores exhibit good thermal and temporal stability [1]. Polymers with H-type NLO chromophores exhibit a thermal stability and large optical nonlinearity [2]. Phenyltetraene chromophores-based inorganic—organic hybrid polymer films show a quite high thermal stability of optical nonlinearity [5].

Various polyesters with NLO chromophores in the main chain [21,22] or side chain [23,24] have been prepared and their NLO properties studied. Polyesters with amino-sulfone azobenzene chromophores in the main chain generate strong and stable reversible birefringence [21]. NLO polyesters containing azobenzene mesogens in the main chain exhibit high thermal and temporal stabilities [22]. Polyesters containing cyanophenylazoaniline moiety in the side chain show good temporal stability of second-order nonlinearity [23]. 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 polymers 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 NLO polyesters containing dioxynitrostilbene [25,26], dioxybenzylidenemalononitrile [27–29], dioxybenzylidenecyanoacetate [30,31], tricyanovinylthienylcatechol [32], tricyanovinylthienylresorcinol [33], tricyanovinylthiazolylazoresorcinol [34], and dioxynitroazobenzene





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[35,36] 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 new polyester containing nitrophenylazonitroresorcinoxy group as NLO chromophore. We selected the latter as NLO chromophore because it was expected to have high optical nonlinearities and thermal stability. Furthermore, this nitrophenylazonitroresorcinoxy group constitutes a novel X-type NLO polyester (Fig. 1c), and this X-type NLO polyester has not yet been reported in the literature. The X-type NLO polymer is expected to exhibit higher NLO activity and thermal stability due to a quadruple conjugation and planarity of the dipole moments than Y-type NLO polymer of double conjugation [35]. Thus, we synthesized a new type of NLO polyester, in which the pendant NLO chromophores are parts of the polymer backbone. This X-type NLO polymer is expected to have the merits of both main-chain (Fig. 1a) and side-chain (Fig. 1b) NLO polymers, namely stable dipole alignment and good solubility. After confirming the structure of the resulting polymer, we investigated its properties such as solubility, Tg, thermal stability, surface morphology of polymer films, second harmonic generation activity and relaxation of dipole alignment.

2. Experimental

2.1. Materials

Reagent-grade chemicals were purchased from Aldrich or AlfaAesar and purified by either distillation or recrystallization before use. All glassware was thoroughly dried under vacuum with a hot air gun before use. 4-(4-Nitrophenylazo)resorcinol, 2-chloroethyl vinyl ether, and bismuth (III) trifluoromethanesulfonate were used as supplied. Terephthaloyl chloride (TPC) was purified by sublimation under vacuum. *N*,*N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure.



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

2.2. Instrumentation

Infrared (IR) spectra were obtained with a Varian FT IR-1000 IR spectrophotometer. ¹H NMR spectra were obtained with a Varian VNMRS 500 MHz NMR spectrometer. UV-visible absorption spectra were obtained with a SECOMAM Model UVIKON XS 99-90289 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 numberaverage molecular weight (M_n) and weight-average molecular weight (M_w) of the polymers were estimated using gel permeation chromatography (GPC; styragel HR5E4E columns; tetrahydrofuran (THF) solvent). AFM images were recorded with a Park Science Instrument Autoprobe CP, operated in a contact mode, which measures topography. Viscosity values were obtained using a Cannon-Fenske viscometer.

2.3. Film preparation and SHG measurements

Polymer films were prepared from a 10 wt% 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 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 using a 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 using the optical transmission technique [37]. 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 one day after poling. A continuum PY61 mode-locked Nd:YAG laser ($\lambda = 1064 \text{ nm}$) with pulse width of 40 ps and repetition rate of 10 Hz was used as the fundamental light source and Ycut quartz was used as reference. A poled polymer film was mounted on the rotator coupled to a step motor. The output signals from the photodiode and PMT were detected as a function of the incident angle. A 3-mm-thick Y-cut quartz crystal (a piece of quartz plate whose plane is perpendicular to the crystalline y-axis and the thickness of the plate is 3 mm and $d_{11} = 0.3 \text{ pm/V}$) was used as a reference for determining the relative 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 [38].

2.4. Synthesis

2.4.1. Preparation of 2,4-di-(2'-vinyloxyethoxy)-4'-nitroazobenzene (1)

4-(4-Nitrophenylazo)resorcinol (25.9 g, 0.10 mol), anhydrous potassium carbonate (82.9 g, 0.60 mol) and 2-chloroethyl vinyl ether (32.0 g, 0.30 mol) were dissolved in 400 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 90 °C for 24 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 300 mL of water, and extracted with



Scheme 1. Synthetic scheme and structure of polymer 4.

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 (ethyl acetate/hexane = 1/2 by volume). Thus obtained product was washed with 10% aqueous ethanol and dried in a vacuum oven yielded 30.3 g (76% yield) of pure product **1**. ¹H NMR (DMSO-*d*₆, δ): 4.02–4.49 (m, 12H, 2 CH₂=, 2 –O–CH₂–CH₂–O–), 6.56–6.63 (m, 2H, 2=CH–O–), 6.70–6.74 (m, 1H, aromatic), 6.89–6.91 (m, 1H, aromatic), 7.71–7.74 (d, 1H, aromatic), 7.95–7.98 (d, 2H, aromatic), 8.40–8.43 (d, 2H, aromatic). IR (KBr disc) (cm⁻¹): 3082 (w, =C–H), 2934 (m, C–H), 1600 (vs, N=N), 1583 (s, C=C), 1515, 1332 (vs, N=O), 1180 (m, N=N). Anal. Calcd for C₂₀H₂₁N₃O₆: C, 60.15; H, 5.30; N, 10.52. Found: C, 60.24; H, 5.26; N, 10.45.

2.4.2. Preparation of 2,4-di-(2'-hydroxyethoxy)-4'-nitroazobenzene (2)

Aqueous hydrochloric acid (1.5 mol L⁻¹, 30 mL) was slowly added to a solution of compound **1** (3.99 g, 10 mmol) in 50 mL of dry DMF with stirring under nitrogen at room temperature. The mixture was stirred at 50 °C for 6 h under nitrogen. The resulting solution was cooled to room temperature and poured into 100 mL of ice water, stirred, separated by suction, and washed with 50 mL of water. The obtained product was dried in a vacuum oven to give 2.78 g (80% yield) of pure **2**. ¹H NMR (DMSO-*d*₆, δ): 3.74–3.78 (t, 2H, –O–CH₂–), 3.79–3.83 (t, 2H, –O–CH₂–), 4.12–4.16 (t, 2H, Ph–O–CH₂–), 4.24–4.28 (t, 2H, Ph–O–CH₂–), 4.92–4.96 (t, 2H, 2–OH), 6.65–6.69 (d, 1H, aromatic), 6.84 (s, 1H, aromatic), 7.70–7.73 (d, 1H, aromatic), 7.96–7.99 (d, 2H, aromatic), 8.39–8.42 (d, 2H,

Table 1

Thermal	properties	of	polymer 4.	

Polymer	T_{g}^{a}	Degradation temp (°C) ^b			Residue at
(°C)	(°C)	5 wt%-loss	20 wt%-loss	40 wt%-loss	800 °C (%) ^b
4	120	298	325	421	36.1
PE ^c	116	241	284	388	34.2

 $^{\rm a}$ Determined from DSC curves measured on a TA 2920 differential scanning calorimeter with a heating rate of 10 $^{\circ}$ C/min under nitrogen atmosphere.

 $^{\rm b}$ Determined from TGA curves measured on a TA Q50 thermogravimetric analyzer with a heating rate of 10 $^\circ C/{\rm min}$ under nitrogen atmosphere.

^c Y-type polyester containing nitrophenylazoresorcinol [35].

aromatic). IR (KBr disc) (cm⁻¹): 3325 (m, O–H), 2948 (m, C–H), 1600 (vs, N=N), 1519, 1337 (vs, N=O). Anal. Calcd for C₁₆H₁₇N₃O₆: C, 55.33; H, 4.93; N, 12.10. Found: C, 55.25; H, 4.98; N, 12.15.

2.4.3. Preparation of 2,4-di-(2'-hydroxyethoxy)-5-nitro-4'nitroazobenzene (**3**)

Compound 2 (2.0 g, 5.76 mmol) was dissolved in 40 mL of dry 1,2-dichloroethane under nitrogen. To the resulted solution was added bismuth (III) trifluoromethanesulfonate (0.30 g, 0.46 mmol) and 60 wt% nitric acid (60%, 0.91 g, 8.64 mmol). The mixture was refluxed in an oil bath kept at 75 °C for 8 h under nitrogen. The resulting solution was cooled to room temperature, neutralized with 5 g of anhydrous sodium bicarbonate, diluted with 100 mL of water with stirring, extracted with 50 mL of diethyl ether three times, and separated. Rotary evaporation of solvent gave product, which was dissolved in 50 mL of dichloromethane, washed with water (100 mL) and saturated aqueous sodium bicarbonate (50 mL), dried with anhydrous sodium carbonate, filtered and concentrated by rotary evaporator. The combined product was purified by column chromatography (ethyl acetate/methanol = 1/2 by volume) gave 1.69 g (75% yield) of pure product **3**. ¹H NMR (DMSO- d_6 , δ): 3.78-3.82 (t, 2H, -O-CH₂-), 3.84-3.88 (t, 2H, -O-CH₂-), 4.37-4.40 (t, 2H, Ph-O-CH₂-), 4.43-4.46 (t, 2H, Ph-O-CH₂-), 5.02-5.04 (t, 1H, -OH), 5.05-5.07 (t, 1H, -OH), 7.17 (s, 1H, aromatic), 8.05-8.08 (d, 2H, aromatic), 8.28 (s, 1H, aromatic), 8.42–8.45 (d, 2H, aromatic). IR (KBr disc) (cm⁻¹): 3320 (m, O–H), 2943 (m, C-H), 1610 (vs, N=N), 1519, 1344 (vs, N=O). Anal. Calcd for C₁₆H₁₆N₄O₈: C, 48.98; H, 4.11; N, 14.28. Found: C, 48.92; H, 4.06; N, 14.22.

2.4.4. Preparation of polymer 4

A representative polycondensation reaction procedure was as follows. Terephthaloyl chloride (2.03 g, 10 mmol) and diol **3** (3.92 g, 10 mmol) were dissolved in 25 mL of anhydrous pyridine under nitrogen. The resulting solution was refluxed in an oil bath kept at 90 °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 DMSO into methanol. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum, yielding 4.70 g (90% yield) of polymer **4**. Inherent viscosity (η_{inh}) = 0.31 dL g⁻¹ (c, 0.5 g dL⁻¹ in DMSO at



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

25 °C). ¹H NMR (DMSO- d_6 , δ): 4.52–4.80 (m, 8H, 2 –O–CH₂–CH₂–O–), 6.76–7.12 (d, 1H, aromatic), 7.78–8.45 (m, 9H, aromatic). IR (KBr disc) (cm⁻¹): 3084 (w, =C–H), 2935 (m, C–H), 1723 (vs, C=O), 1520 (s, N=O), 1341 (vs, N=O), 1420 (m, N=N), 1182 (vs, N=N). Anal. Calcd for (C₂₄H₁₈N₄O₁₀)_n: C, 55.18; H, 3.47; N, 10.73. Found: C, 55.28; H, 3.56; N, 10.68.

3. Results and discussion

3.1. Synthesis and characterization of polymer

Compound **1** was prepared by the reaction of 2-chloroethyl vinyl ether with 4-(4-nitrophenylazo)resorcinol. Compound **2** was prepared by acid-catalyzed hydrolysis of **1** in DMF. Compound **2** was reacted with nitric acid and bismuth (III) trifluoromethanesulfonate in anhydrous 1,2-dichloroethane according to a literature procedure [39] to yield nitrated compound **3**. Monomer **3** was condensed with terephthaloyl chloride in a dry DMF solvent to yield X-type polyester **4** containing nitrophenylazonitroresorcinoxy groups as NLO chromophores. The synthetic route for polymer **4** is presented in Scheme 1. The resulting polymer was purified by Soxhlet extraction for two days with methanol as a solvent. The polymerization yield was 90%. The chemical structure of the resulting polymer was confirmed by ¹H NMR, IR spectra, and elemental



Fig. 3. DSC thermogram of polymer 4 at a heating rate of 10 °C/min under nitrogen.



Fig. 4. UV-Vis absorption spectra of a film of polymer 4 before and after poling.

analysis. Elemental analysis results fit the polymer structure. ¹H NMR spectrum of the polymer showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The IR spectrum of polymer 4 shows strong carbonyl peak near 1723 cm⁻¹ indicating the presence of ester bond. The spectrum also shows strong absorption peaks near absorptions at 1520 and 1341 cm⁻¹ due to nitro group and absorptions at 1420 and 1182 cm⁻¹ due to azo group indicating the presence of nitroazobenzene unit. These results are consistent with the proposed polymer 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 an eluent. The number average molecular weight (M_n) of the polymer **4**, determined by GPC, was 16,300 g mol⁻¹ ($M_{\rm w}$ / $M_{\rm n}=$ 1.94). The polymer **4** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity is in the range 0.30–0.31 dL g^{-1} . Polymer 4 shows strong absorption near 399 nm due to the NLO chromophore nitrophenylazonitroresorcinoxy group. The striking feature of this polymerization system is that it gives unprecedented X-type NLO polymer, in which the pendant NLO chromophores are parts of the polymer backbone. This X-type NLO polymer is expected to have the advantages of both main-chain and side-chain NLO polymers. Thus, we obtained a new type of NLO polyester with side-chain and main-chain characteristics. Having obtained the well-defined X-type polyester 4, we investigated its properties.

3.2. Thermal properties of polymer

The thermal behavior of the polymer was investigated by TGA and DSC to determine the thermal degradation pattern and glass transition temperature. The results are summarized in Table 1. The TGA and DSC thermograms of the polymer **4** are shown in Figs. 2 and 3, respectively. Polymer **4** has a thermal stability up to 280 °C according to its TGA thermogram. This thermal stability is much higher than that of the Y-type polyester containing nitrophenylazoresorcinol, which is near 240 °C [35]. The T_g value of the polymer **4** measured using DSC is near 120 °C. This T_g value is higher than that of the Y-type polyester [35] containing nitrophenylazoresorcinol, which is probably due to a nitro group and planarity of the dipole moments. These are also relatively high values 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 show that the decomposition



Fig. 5. AFM images of a spin-coated film of polymer 4: (a) before corona-poling; (b) after corona-poling.

Table 2	
Nonlinear optical properties of polymer 4 .	

Polymer	λ _{max} a (nm)	d33 ^b (pm/V)	Φ^{c}	Film thickness ^d (µm)	d ₃₁ ^b (pm/V)	n
4	397	2.13	0.32	0.50	0.72	$n_1 = 1.712$
PE ^e	398	1.94	0.28	0.48	0.66	$n_2 = 1.725$ $n_1 = 1.724$
						$n_2 = 1.736$

^a Polymer film after corona poling.

^b SHG coefficients (d_{33}) were derived from the analysis of measured Makerfringes [38].

 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 [37].

^e Y-type polyester containing nitrophenylazoresorcinol [35].

temperature of the polymer **4** is higher than the corresponding T_g value. This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

3.3. Nonlinear optical properties of polymer

The NLO properties of polymers were studied using the SHG method. To induce noncentrosymmetric polar order, the spincoated 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 films were cooled to room temperature in the presence of the electric field. Finally, the electric field was removed. The poling was confirmed from UV–visible spectra. The UV–visible absorption spectra of the polymer **4** before and after poling are presented in



Fig. 6. Angular dependence of SHG signal in a poled film of polymer 4.

Fig. 4. Polyester **4** shows strong absorption near 399 nm before electric poling. After electric poling, the dipole moments of the NLO chromophores were aligned and the UV–visible spectrum of polymer **4** exhibits a slight blue shift showing absorption near 397 nm, and a decrease in absorption due to birefringence, namely by the Pockels effect, where an electric field induces molecules to line up asymmetrically, inducing anisotropy [40]. 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 is equal to 0.32 for polymer **4** ($\Phi = 1 - A_1/A_0$, where $A_0 = 1.0184$ and $A_1 = 0.6922$ are the absorbances of the polymer film before and after poling, respectively).

For the purpose of investigating the surface morphology of polymer film, domain structures of NLO chromophores for the thinfilm samples were obtained using atomic force microscopy (AFM). Fig. 5 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 quite flat and smooth before poling (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 were aligned in the poling direction (Fig. 5b).

The refractive index of the sample was measured using the optical transmission technique [37]. The transmittance of thin film gives information on the thickness, refractive index and extinction coefficient. So we could determine these parameters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. Nonlinear optical properties of polymer **4** are summarized in Table 2. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Fig. 6 shows the angular dependence of SHG signal for a poled polymer 4. The SHG values were compared with those obtained from a Y-cut guartz plate. To calculate the d_{31} and d_{33} values, both s-polarized and p-polarized IR laser were directed at the samples. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure [38]. The values of d_{33} and d_{31} for polymer **4** are 2.13 pm/V and 0.72 pm/V, respectively. This d_{33} value is higher than that of the Y-type polyester containing nitrophenylazoresorcinol, which is near 1.94 pm/V [35]. Since the second harmonic wavelength is at 532 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 2.95 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. Fig. 7 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 function of temperature. *in situ* SHG measurements were performed at a heating rate of 4 °C/min from 30 to 200 °C. The dipole alignment exhibits a thermal stability even at 5 °C higher than T_g , and there is no SHG decay below 125 °C due to the partial main-chain character of the polymer structure. This SHG thermal stability is higher than that of the Y-type polyester containing nitrophenylazoresorcinol, which is near 120 °C [35]. In Fig. 8, we present the temporal stability of the polymer film in which there was no negligible decay of the SHG signal over hundreds of hours. We measured normalized SHG signal of polymer 4 as a function of baking time at 80 °C, which is enough for electrooptic device applications. In general, side chain NLO polymers lose the thermal stability of dipole alignment below Tg. Stabilization of dipole alignment is a characteristic of main chain NLO polymers. The high thermal stability of second harmonic generation of







Fig. 8. Normalized SHG signal of polymer 4 as a function of baking time at 80 °C in air.

polymer **4** at high temperature 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 the merits of both main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility.

4. Conclusion

New X-type polyester **4** containing pendant NLO chromophore, which constitutes a part of the polymer main chain, was synthesized and characterized. This X-type NLO polyester **4** is soluble in common organic solvents and displayed a thermal stability up to 280 °C with a T_g of 120 °C. The SHG coefficient (d_{33}) of corona-poled polymer film is 2.13 pm/V. Polymer **4** exhibits SHG stability even at 5 °C higher than glass transition temperature (T_g), and no SHG decay is observed below 125 °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.

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