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Synthesis of novel polyimide with highly enhanced thermal stability of second harmonic generation for electro-optic applications

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Summary

2,3-Bis-(3,4-dicarboxyphenylcarboxyethoxy)-1-(2,2-dicyanovinyl)benzene dianhydride (**4**) was prepared and reacted with 1,4-phenylenediamine to yield novel Y-type polyimide **5** containing 2,3-dioxybenzylidenemalononitrile group as NLO-chromophores, which constitute parts of the polymer backbones. The resulting polyimide **5** was soluble in polar solvents such as acetone and *N,N*-dimethylformamide. Polymer **5** showed a thermal stability up to 330 °C in thermogravimetric analysis thermogram with T_g value obtained from differential scanning calorimetry thermogram near 190 °C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer films at the 1064 nm fundamental wavelength was around $3.15\text{x } 10^{-9}$ esu. The dipole alignment exhibited a thermal stability even at 20 °C higher than the glass-transition temperature, and there was no SHG decay below 210 °C because of the partial main chain character of polymer structure, which was acceptable for nonlinear optical device applications.

Introduction

A lot of efforts have been focused on the synthesis of nonlinear optical (NLO) materials in recent years because of their potential applications in the field of electro-optic devices [1]. NLO polymers are considered candidate materials, mainly because they offer many advantages such as light weight and good processability to form optical devices [2]. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically-induced dipole alignment is one of important considerations. Two approaches to minimize the randomization have been proposed. One is to use cross-linking method [3-6] and the other is to utilize polymers with high glass transition temperatures (T_g) such as polyimides [7-10]. Polyimide materials for NLO applications have attracted attentions because of their high T_g and high thermal stability. There are two types of NLO polyimides, which have been used either as host polymers for composite materials or as matrix polymer backbones for side-chain NLO chromophores. Aromatic copolyimides showed high T_g and high thermal stabilities of optical nonlinearity at elevated temperatures [8].

Polyimide whose NLO chromophore aligns transverse to the polymer backbone exhibited enhanced thermal stability of dipole alignment [9]. In general, 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. On the other hand, side-chain NLO polymers have the advantages such as good solubility, homogeneity and high loading level of NLO chromophores relative to the main-chain systems, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we reported novel polyimides containing dioxynitrostilbenyl group as NLO chromophores [11-13]. The resulting polymers exhibited high thermal stability of second harmonic generation (SHG). The high thermal stability of optical nonlinearity stemmed from the stabilization of dipole alignment of the NLO chromophore, which was a part of the polymer backbone. In this work we prepared novel polyimide containing 2,3-dioxybenzylidenemalononitrile groups as NLO-chromophores. We selected the latter because they have a large dipole moment and are rather easy to synthesize. Furthermore 2,3-dioxybenzylidenemalononitrile groups constitute novel Y-type NLO polyimides (Fig. 1b), and these Y-type NLO polyimides have not yet been presented in the literature. Thus, we prepared another new polyimide, 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 namely, stable dipole alignment and good solubility. After confirming the structure of the resulting polymers we investigated their properties such as thermal stability and second harmonic generation (SHG) activity. We now report the results of the initial phase of the work.

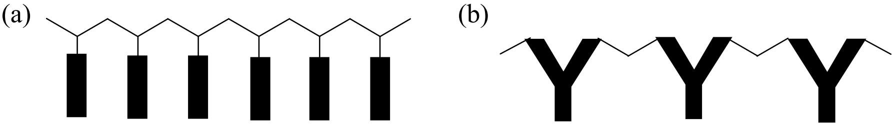


Figure 1. (a) Side chain NLO polymers and (b) Y-type NLO polymers.

Experimental

Materials

The reagent-grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2,3-Dihydroxybenzaldehyde, 2-chloroethyl vinyl ether, trimellitic anhydride chloride, and 1,4-phenylenediamine (PDA) were used as received. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium hydride, followed by distillation under reduced pressure. *m*-Cresol was dried over calcium chloride, and then over 4° molecular sieves, and it was distilled under reduced pressure before use.

Film preparation and SHG measurement

The polymer film was prepared from a 10 wt% polymer DMF solution deposited on an indium-tin oxide (ITO) covered glass. The film was spin-cast at room temperature in the range 1200 - 1600 rpm. The alignment of the NLO chromophore of the polymers was carried out by corona poling. The poling was performed in a wire-to plane geometry under *in situ* conditions. The discharging wire to plane distance was 1.0 cm. As the temperature was raised gradually to 5-10 °C higher than T_g, 6.5 kV of corona voltage was applied and kept at that temperature for 30 min. The refractive index of the sample was measured by the optical transmission technique [14]. A continuum PY61 mode-locked Nd:YAG laser (λ=1064 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 (1064 nm). 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 the function of an 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 from the measurement of the SHG signal at 0.5 ° intervals with a rotation stage. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [15].

*2,3-Di-(2'-vinyloxyethoxy)benzaldehyde (**1**)*

2,3-Dihydroxybenzaldehyde (13.8 g, 0.10 mol), anhydrous potassium carbonate (36 g, 0.36 mol), and 2-chloroethyl vinyl ether (26.6 g, 0.25 mol) were dissolved in 200 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 100 °C for 40 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**. Mp=48-50 °C. ^{1}H NMR ($CDCl_3$) δ 3.95-4.47 (m, 12H, 2 CH_2=, 2 -O-CH_2-CH_2-O-), 6.44-6.57 (m, 2H, 2 =CH-O-), 7.09-7.19 (m, 2H, aromatic), 7.42-7.48 (m, 1H, aromatic), 10.48 (s, 1H, -CHO). IR (KBr) 3098, 3076 (w, =C-H), 2953, 2883 (s, C-H), 1682 (vs, C=O), 1618 (vs, C=C) cm^{-1}.

*2,3-Di-(2'-vinyloxyethoxy)benzylidenemalononitrile (**2**)*

Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,3-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 8.11g (83% yield) of **2**. Mp=60-62 °C. ^{1}H NMR ($CDCl_3$) δ 3.90-4.42 (m, 12H, 2 CH_2=, 2 -O-CH_2-CH_2-O-), 6.45-6.57 (m, 2H, 2 =CH-O-), 7.13-7.20 (d, 2H, aromatic), 7.80-7.87 (t, 1H, aromatic), 8.47 (s, 1H, Ph-CH=). IR (KBr) 3116, 3059 (w, =C-H), 2941, 2885 (m, C-H), 2233 (s, CN), 1618, 1572 (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, 66.16; H, 5.4; N, 8.65.

2,3-Di-(2'-hydroxyethoxy)benzylidenemalononitrile (3)

Aqueous hydrochloric acid (1.5 mol L^{-1}, 30 mL) was slowly added to a solution of 2,3-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 5.85 g (82% yield) of **3**. Mp=116-118 °C. ^{1}H NMR (acetone-d_6) δ 3.75-3.96 (m, 4H, 2 -CH_2-OH), 4.12-4.25 (m, 4H, 2 -O-CH_2-), 4.26-4.34 (t, 2H, -OH), 7.21-7.29 (t, 1H, aromatic), 7.37-7.44 (d, 1H, aromatic), 7.72-7.78 (d, 1H, aromatic), 8.75 (s, 1H, -Ph-CH=). IR (KBr) 3360, 3256 (s, O-H), 3044 (w, =C-H), 2941 (m, C-H), 2222 (m, CN), 1572 (vs, 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, 61.23; H, 5.22; N, 10.13.

2,3-Bis(3,4-dicarboxyphenylcarboxyethoxy)-1-(2,2-dicyanovinyl)benzene dianhydride (4)

Compound **3** (2.74 g, 0.01 mol) was dissolved in dry DMF (20 mL) and pyridine (20 mL) at 50 °C under nitrogen. Trimellitic anhydride chloride (8.42 g, 0.04 mol) was added to the mixture with stirring at 50 °C. The resulting solution was stirred for 12 hr at room temperature. The resulting solution was diluted with 250 mL of water and stirred for 1 h to dissolve pyridine hydrochloride. The product was filtered, and washed successively with water and methanol. The obtained deep brown product was dried at 50 °C under vacuum to give pure **4**. Yield: 4.48 g (72%). ^{1}H NMR (DMSO-d_6) δ 4.35-4.73 (t, 8H, 2 -O-CH_2CH_2-O-), 7.23-7.35 (t, 1H, benzylic), 7.46-7.75 (m, 3H, aromatic), 7.97-8.28 (m, 3H, aromatic), 8.53 (s, 1H, aromatic), 8.71 (d, 2H, aromatic). IR (KBr) 3075 (w, =C-H), 2962 (w, C-H), 2224 (s, CN), 1780 (m, C=O, dianhydride), 1722 (vs, C=O, ester), 1608 (s, C=C) cm^{-1}. Anal. Calcd for $C_{32}H_{18}N_2O_{12}$: C, 61.74; H, 2.91; N, 4.50. Found: C, 61.65 H, 2.98; N, 4.59.

Synthesis of polyimide **5**

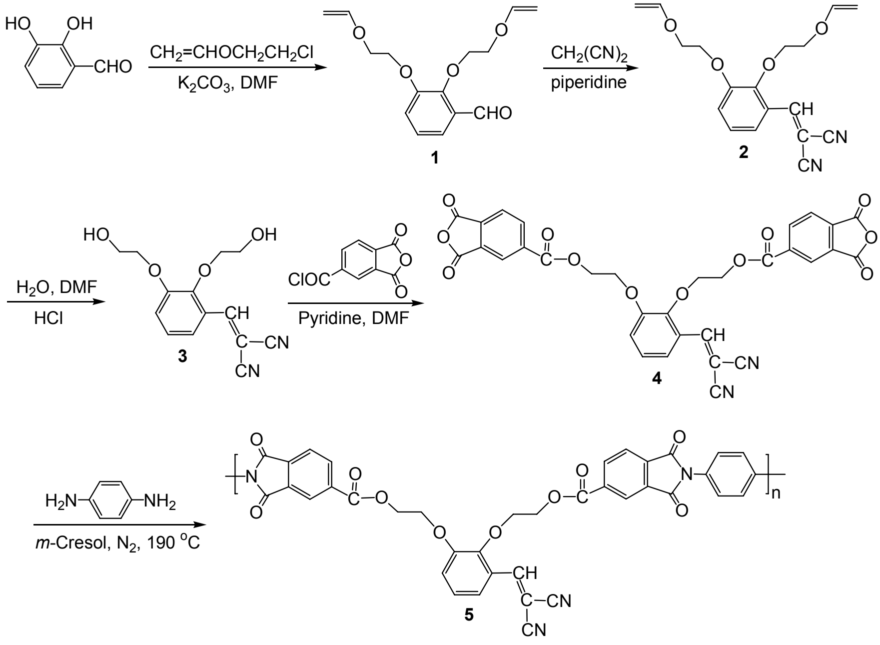
The polymerization was carried out in a drybox at room temperature. A representative synthetic procedure of polyimide **5** was as follows. Anhydride **4** (6.22 g, 0.01 mol) was added slowly to a solution of 1,4-phenylenediamine (1.08 g, 0.01 mol) in 60 mL of dry *m*-cresol over 1 h. The polymerization was allowed to continue at 50 °C for 12 h. The mixture was gradually elevated to 190 °C and then stirred for 12 h. The polymer solution was poured into 400 mL of methanol. The precipitated polymer was collected and further purified by extraction in a Soxhlet extractor with diethyl ether for two days. The final product was dried under vacuum to give 6.31 g (91% yield) of polymer **5**. Inherent viscosity (η_{inh}): 0.30 dL g^{-1} (c = 0.5 g dL^{-1} in *m*-cresol at 25 °C). ^{1}H NMR (DMSO-d_6) δ 4.05-4.86 (m, 8H, 2 -O-CH_2-CH_2-O-), 6.23-6.68 (m, 3H, benzylic, aromatic), 6.73-7.18 (m, 2H, aromatic), 7.35-7.72 (m, 3H, aromatic), 7.80-

8.51 (m, 4H, aromatic), 8.96-9.23 (m, 2H, aromatic). IR (KBr) 3073 (w, =C-H), 2957 (w, C-H), 2211 (w, CN), 1780 (m, C=O), 1724 (vs, C=O), 1618 (s, C=C), 1379 (s, C-N), 725 (s, imide ring) cm^{-1}. Anal. Calcd for $(C_{38}H_{22}N_4O_{10})_n$: C, 65.71; H, 3.19; N, 8.07. Found: C, 65.78; H, 3.27; N, 8.15.

Results and Discussion

*Synthesis and characterization of polyimide **5***

Compound **1** was prepared through the condensation of 2-chloroethyl vinyl ether with 2,3-dihydroxybenzaldehyde. Compound **2** was prepared by the condensation reaction of **1** with malononitrile, and was hydrolyzed to yield compound **3**. Dianhydride monomer **4** was prepared by the reaction of diol **3** with trimellitic anhydride acid chloride in dry DMF in the presence of pyridine. The chemical structures of the compounds were identified by ^{1}H NMR and IR spectra. All the analytical data confirmed the expected chemical structure. In the IR spectrum of **4**, a characteristic peak of nitrile group and a carbonyl group of dianhydride appeared at 2224 and 1780 cm^{-1}, respectively. IR spectra of the same sample also showed a strong carbonyl peak near 1722 cm^{-1} indicating the presence of aromatic ester bond. Polyimide **5** was synthesized through the reaction of aromatic dianhydride monomer **4** containing NLO-chromophore with stoichiometric amount of 1,4-phenylenediamine in *m*-cresol. The synthetic method of polymer **5** is summarized in Scheme 1. The polymerization yield was 91%. The striking feature of this polymer is that it had pendant NLO chromophores that were parts of the polymer main chain. Thus, we obtained a new type of NLO polyimide with side-chain and main-chain characteristics. The chemical structure of the resulting polymer was confirmed with ^{1}H NMR, IR spectra and elemental analysis.



^{1}H NMR spectrum of the polymer showed a signal broadening due to polymerization, but the chemical shifts were consistent with the proposed polymer structures. The IR spectrum supported the formation of polyimide. The IR spectra of the polymer sample showed peaks near 1780 and 725 cm^{-1} that were characteristic bands of imide asymmetric carbonyl stretching and imide ring deformation, respectively. IR spectrum of the same polymer sample also showed strong absorption peaks near 1724 cm^{-1} and 1379 cm^{-1} due to symmetric carbonyl stretching and C-N stretching of imide ring, respectively. These results are consistent with the proposed structures, indicating that the NLO-chromophores remained intact during the polymerization. The molecular weight was determined by GPC using polystyrene as the standard and THF as an eluent. The number average molecular weight (M_n) of the polymer was determined to be 21,600 (M_w/M_n=1.85) for polymer **5**. Polydispersities were in the range 1.75-1.89. Polyimide **5** was soluble in common solvents such as acetone, DMF, and DMSO, but it was not soluble in methanol and diethyl ether. The η_{inh} value was around 0.30 dL/g. Polymer **5** showed strong absorption near 338 nm by the NLO-chromophore 2,3-dioxybenzylidenemalononitrile group.

Thermal properties of the polymers

The thermal behavior of the polymer was investigated by thermogravimetric analysis and differential scanning calorimetry to determine the thermal degradation pattern and glass transition temperature (T_g). Polymer **5** showed a thermal stability up to 330 °C according to the TGA thermogram. T_g value of **5** measured by DSC was around 190 °C, as shown in Figure 2.

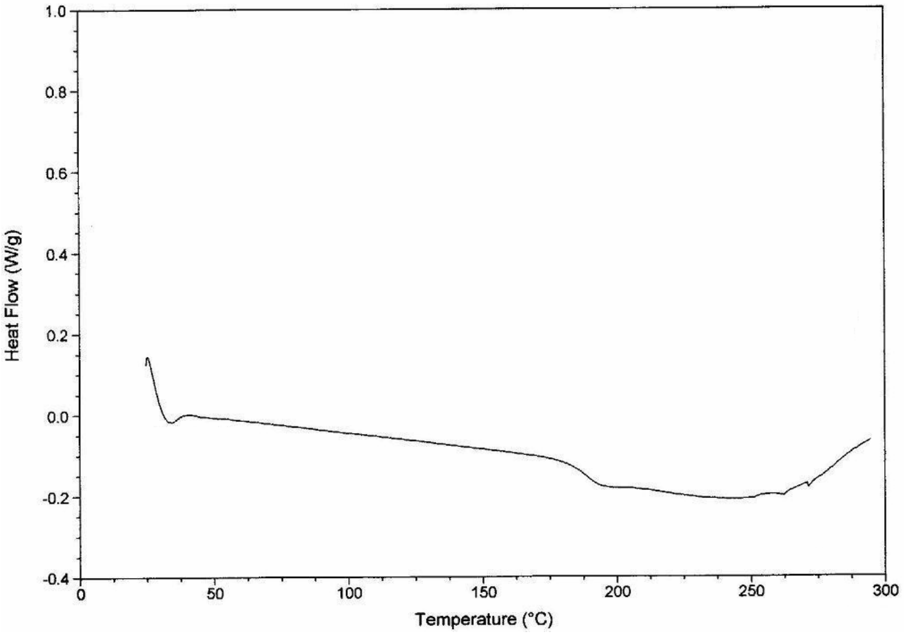


Figure 2. DSC thermogram of polymer **5** at a heating rate of 10 °C/min under nitrogen.

This is rather low T_g value compared to those of common rigid polyimides, which can probably be attributed to the flexibility of the polymer backbone containing ether linkages. 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 polymers

The NLO properties of polymer were studied by the SHG method. We corona-poled the spin-coated polymer film to induce noncentrosymmetric polar order. As the temperature was raised gradually to 5-10 °C higher than T_g, 6.5 kV of corona voltage was applied and this temperature was maintained for 30 min. The UV-Vis absorption spectra of the polymer **5** before and after poling were recorded. After electric poling, the dipole moments of the NLO-chromophores were aligned and the UV-Vis spectrum of polymer **5** 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 was equal to 0.12 for polymer **5** ($\Phi = 1-A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after poling, respectively). The decrease in absorbance after poling was an indicator of the dipole alignment. The refractive index of the sample was measured by the optical transmission technique [14]. The transmittance of thin film includes information on the thickness and refractive index and its extinction coefficient. Thus, we could determine these parameters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of 1064 nm with a mode-locked Nd-YAG laser.

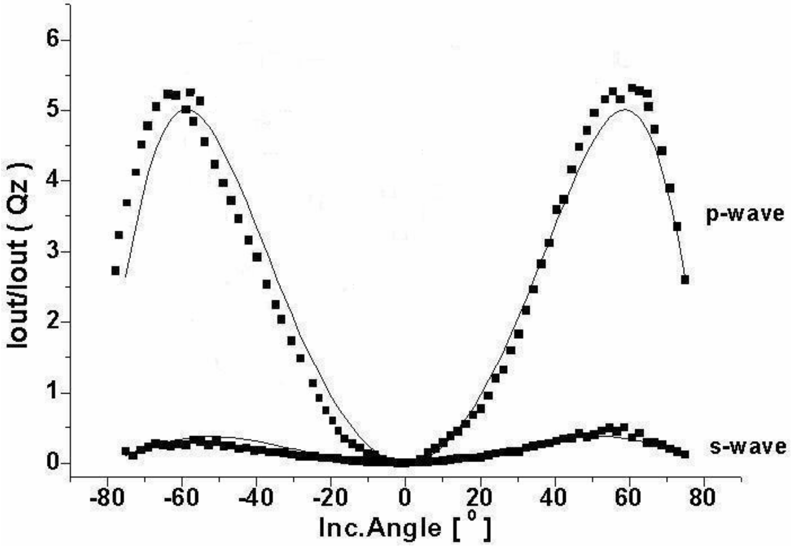


Figure 3. Angular dependence of SHG signal in a poled film of polymer **5**.

We recorded the angular SHG dependence to determine the microscopic second-order susceptibility of the polymer. Figure 3 shows the angular dependence of SHG signal in a poled polymer **5**. The SHG values were compared with those obtained from a Y-cut quartz plate. For the calculation of the d_{31} and d_{33} values, both *s*-polarized and *p*-polarized IR laser were directed to the samples and recorded. Nonlinear optical properties of polymer **5** are summarized in Table 1. SHG coefficient (d_{33}) was derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure [15]. The values of d_{31} and d_{33} for polymer **5** were 1.36 x 10^{-9} esu and 3.15 x 10^{-9} esu, respectively. Since the second harmonic wavelength was at 532 nm, which is not in the absorptive region of the resulting polymer, there was not resonant contribution to this d_{33} value. To evaluate the high-temperature stability of the polymer, we studied the temporal stability of the SHG signal. In Figure 4, we present the dynamic thermal stability study of the NLO activity of the film **5**. To investigate the real-time NLO decay of the SHG signal of the poled polymer films as a function of temperature, we performed *in situ* SHG measurements at a heating rate of 10 °C/min from 30 to 300 °C. The polymer film exhibited a thermal stability even at 20 °C higher than T_g and no significant SHG decay was observed below 210 °C. In general, side-chain NLO polymers lose the thermal stability of dipole alignment below T_g. The stabilization of dipole alignment is a characteristic of main-chain NLO polymers. The exceptionally high thermal stability of SHG of polymer **5** 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 polyimide having the advantages of both main-chain and side-chain NLO polymers: the stabilization of dipole alignment and good solubility.

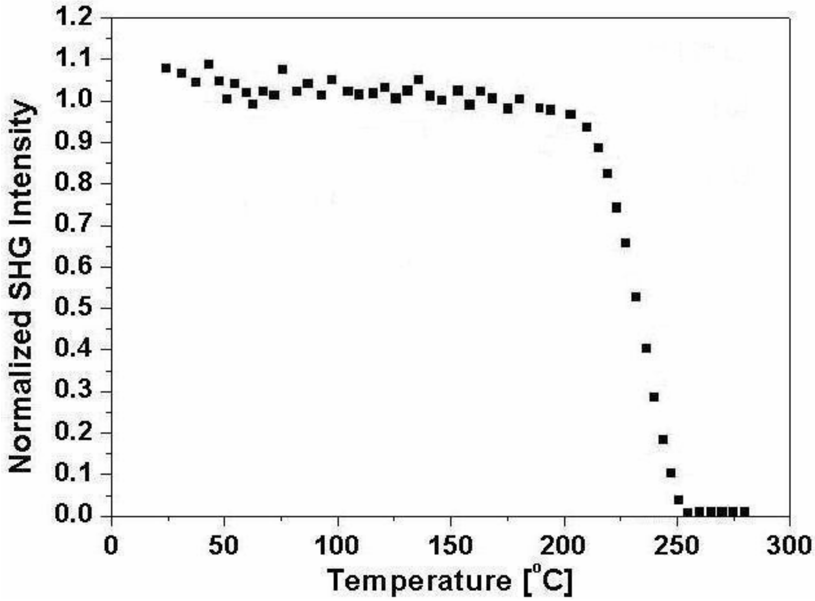


Figure 4. Normalized SHG signal of polymer **5** as a function of temperature at a heating rate of 10 °C/min.

Table 1. Nonlinear Optical Properties of Polyimide **5**

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	Φ[c]	film thickness[d] (μm)	d_{31}[b] (esu)
5	338	$(3.15\pm0.12)\times10^{-9}$	0.12	0.52	$(1.36\pm0.05)\times10^{-9}$

[a] Polymer film after corona poling.
[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [15].
[c] Order parameter $\Phi = 1\text{-}A_1/A_0$, 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 [14].

Conclusions

We synthesized novel Y-type polyimide (**5**) with pendant NLO chromophores, which are parts of the polymer main chains. This mid-type NLO polyimide is soluble in common organic solvents. Polymer **5** showed thermal stability up to 330 °C according to TGA thermogram and had T_g value around 190 °C. The SHG coefficients (d_{33}) of corona-poled polymer films were 3.15×10^{-9} esu. The striking feature of this polymer was that it exhibit SHG stability up to 20 °C higher than T_g and no SHG decay was observed below 210 °C. This exceptionally high thermal stability of optical nonlinearity stemmed from the stabilization of dipole alignment of the NLO chromophore, which was a part of the polymer backbone. We are now in the process of extending the polymerization system to the synthesis of other type of NLO polymers and the results will be reported elsewhere.

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