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Preparation of novel polyimides with high thermal stability of dipole alignment for electro-optic applications

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Summary

3,4-Bis-(3,4-dicarboxyphenylcarboxyethoxy)-1-(2,2-dicyanovinyl)benzene dianhydride (**4**) was prepared and reacted with 1,4-phenylenediamine and 4,4'-oxydianiline to yield novel Y-type polyimides **5-6** containing 3,4-dioxybenzylidenemalononitrile groups as NLO-chromophores, which constitute parts of the polymer backbones. The resulting polyimides **5-6** were soluble in polar solvents such as acetone and *N,N*-dimethylformamide. Polymers **5-6** showed a thermal stability up to 330°C in thermogravimetric analysis thermograms with T_g values obtained from differential scanning calorimetry thermograms in the range of 181-190°C. The second harmonic generation (SHG) coefficients (d_{33}) of poled polymer films at the 1064 nm fundamental wavelength were around 4.73×10^{-9} esu. The dipole alignment exhibited a thermal stability even at 20°C higher than the glass-transition temperatures, there was no SHG decay below 200°C because of the partial main chain character of polymer structure, which was acceptable for nonlinear optical device applications.

Introduction

Recently, attention has been focused on the synthesis of nonlinear optical (NLO) materials 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 mechanical endurance, light weight, and good processability to form optical devices [2-3]. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically-induced dipole alignment is an important consideration. Two approaches to minimize the randomization have been suggested. One is to use cross-linking method [4-8] and the other is to utilize high glass transition temperature (T_g) polymers such as polyimides [9-14]. 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.

In general main-chain NLO polymers have good thermal stability of dipole alignments, but they often do not dissolve in organic solvents, and the intractability of them make them impossible to fabricate stable noncentrosymmetric films. Side-chain NLO polymer systems have the advantages such as good solubility, homogeneity and high level of NLO chromophore relative to the main-chain systems, but they often suffer from poor stability of dipole alignmentsat high temperatures. Recently we reported polyimides containing dioxynitrostilbenyl group as NLO chromophores [15-17]. 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 polyimides containing 3,4-dioxybenzylidenemalononitriles groups as NLO-chromophores. We selected 3,4-dioxybenzylidenemalononitriles groups as NLO-chromophore because they have a large dipole moment and are rather easy to synthesize. Furthermore 3,4-dioxybenzylidenemalononitriles groups constitute novel Y-type NLO polyimides (Fig. 1b), and these Y-type NLO polyimides have not been presented in the literature. Thus, we prepared another new type of 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: stabilization of dipole alignment and good solubility. After confirming the structure of the resulting polymers we investigated the properties such as thermal stability and second harmonic generation (SHG) activity. We now report the results of the initial phase of the work.

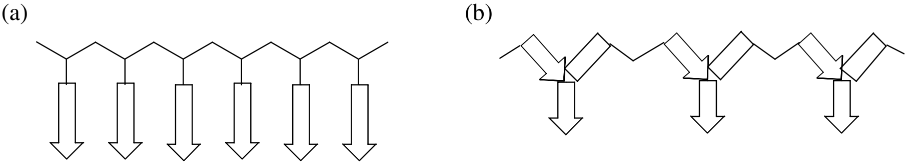


Figure 1. (a) Side chain NLO polymers and (b) Y-type NLO polymers.

Experimental

Materials

The reagent-grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 3,4-Dihydroxybenzaldehyde, 2-chloroethyl vinyl ether, trimellitic anhydride chloride, 1,4-phenylenediamine (PDA), and 4,4'-oxydianiline (ODA) 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 at a range from 1200 to 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 that temperature for 30 min. The refractive index of the sample was measured by the optical transmission technique [18]. SHG measurements were carried out 1 day after poling. 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 a 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 [19].

*3,4-Di-(2'-vinyloxyethoxy)benzaldehyde (**1**)*

Compound **1** was prepared from 3,4-dihydroxybenzaldehyde and 2-chloroethyl vinyl ether in dry DMF according to a literature procedure (20). Mp=56-57°C. ^{1}H NMR ($CDCl_3$) δ 4.04-4.36 (m, 12H, 2 CH_2=, 2 -O-CH_2-CH_2-O-), 6.50-6.62 (m, 4H, 2 =CH-O-, aromatic), 7.01-7.06 (d, 1H, aromatic), 7.45-7.42 (d, 2H, aromatic), 9.86 (s, 1H, -CHO). IR (KBr) 3099, 3080 (w, =C-H), 2952, 2872 (m, C-H), 1672 (vs, C=O), 1612 (vs, C=C), 1575 (s, C=C) cm^{-1}.

*3,4-Di-(2'-vinyloxyethoxy)benzylidenemalononitrile (**2**)*

Compound **2** was prepared from compound **1** and malononitrile according to a literature procedure (20). Mp=66-68°C. ^{1}H NMR ($CDCl_3$) δ 4.02-4.39 (m, 12H, 2 CH_2=, 2 -O-CH_2-CH_2-O-), 6.47-6.58 (m, 2H, 2 =CH-O-), 6.96-7.03 (d, 1H, aromatic), 7.37-7.45 (d, 1H, aromatic), 7.58-7.69 (d, 2H, aromatic). IR (KBr) 3036 (w, =C-H), 2941, 2890 (m, C-H), 2222 (s, CN), 1636, 1618, 1583 (s, 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, 5.66; N, 8.48.

*3,4-Di-(2'-hydroxyethoxy)benzylidenemalononitrile (**3**)*

Compound **3** was prepared by hydrolysis of **2** according to a literature procedure (20). Mp: 108-110°C. ^{1}H NMR (acetone-d_6) δ 2.78-2.87 (d, 2H, -OH), 3.87-3.98 (m, 4H, 2 -CH_2-OH), 4.09-4.28 (m, 4H, 2 -O-CH_2-), 7.21-7.27 (d, 1H, aromatic), 7.63-7.65 (d, 1H, aromatic), 7.76 (d, 1H, aromatic), 8.14 (s, 1H, -Ph-CH=). IR (KBr) 3337 (s, O-H), 3045 (w, =C-H), 2930 (m, C-H), 2222 (s, CN), 1607, 1583 (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, 61.40; H, 5.25; N, 10.28.

*3,4-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 under at 50°C. The resulting solution was stirred for 12 hr at at room temperature. The resulting solution was diluted with 250 mL of water and stirred for 1 hr to dissolve pyridine hydrochloride. The product was filtered, and washed successively with water and methanol. Thus obtained deep brown product was dried at 50°C under vacuum to give pure 4. Yield: 4.73 g (76%). ^{1}H NMR (DMSO-d_6) 4.41-4.82 (t, 8H, 2 -O-CH_2-CH_2-O-), 6.78-6.86 (m. 2H, aromatic), 7.52-7.63 (m, 1H, benzylic), 7.70-7.78 (m, 2H, aromatic), 8.12-8.36 (m, 4H, aromatic), 8.58-8.67 (d, 1H, aromatic). IR (KBr) 3076 (w, =C-H), 2958 (w, C-H), 2225 (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, 61.85 H, 2.98; N, 4.56.

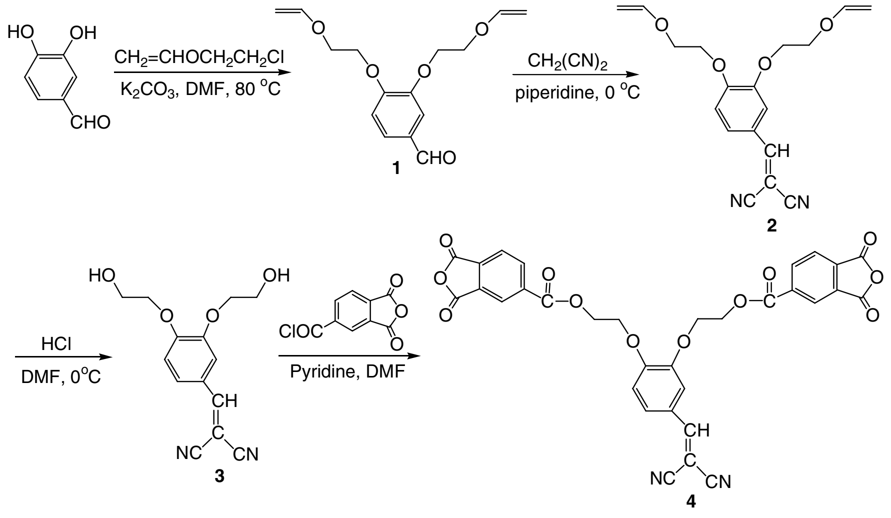
*Synthesis of polyimides **5-6***

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 6.24 g (90% yield) of polymer **5**. Inherent viscosity (η_{inh}): 0.27 dL g^{-1} (c = 0.5 g dL^{-1} in *m*-cresol at 25°C). ^{1}H NMR (DMSO-d_6) δ 4.25-4.81 (m, 8H, 2 -O-CH_2-CH_2-O-), 6.42-7.23 (m, 5H, benzylic, aromatic), 7.58-7.72 (s, 3H, aromatic), 7.85-8.62 (m, 6H, aromatic). IR (KBr) 3072 (w, =C-H), 2956 (w, C-H), 2220 (s, CN), 1780 (m, C=O), 1724 (vs, C=O), 1610 (s, C=C), 1378 (s, C-N), 726 (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, 65.80; H, 3.26; N, 8.15. Polymer **6**: η_{inh}: 0.28 dL g^{-1} (c = 0.5 g dL^{-1} in *m*-cresol at 25°C). ^{1}H NMR (DMSO-d_6) δ 4.23-4.80 (m, 8H, 2 -O-CH_2-CH_2-O-), 6.41-7.02 (m, 6H, benzylic, aromatic), 7.02-7.36 (m, 3H, aromatic), 7.41-7.56 (m, 4H, aromatic), 7.95-8.16 (m, 2H, aromatic), 8.18-8.46 (m, 3H, aromatic). IR (KBr) 3070 (w, =C-H), 2953 (w, C-H), 2221 (m, CN), 1779 (m, C=O), 1725 (vs, C=O), 1610 (s, C=C), 1379 (s, C-N), 728 (s, imide ring) cm^{-1}. Anal. Calcd for $(C_{44}H_{26}N_4O_{11})_n$: C, 67.18; H, 3.33; N, 7.12. Found: C, 67.27; H, 3.37; N, 7.19.

Results and Discussion

*Synthesis of monomer **4***

Compound **1** was prepared through the condensation of 2-chloroethyl vinyl ether with 3,4-dihydroxybenaldehyde. Compound **2** was prepared by the condensation reaction of **1** with malononitrile. Compound **3** was prepared by hydrolysis of **2**. 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 ^1H NMR, IR spectra and elemental analysis. All the analytical data confirmed the expected chemical structure. In the IR spectrum of **4**, a peak characteristic of a nitrile group and a carbonyl group of dianhydride appeared at 2225 and 1780 cm^{-1}, respectively. IR spectrum of the same sample also showed a strong carbonyl peak near 1722 cm^{-1} indicating the presence of aromatic ester bond.

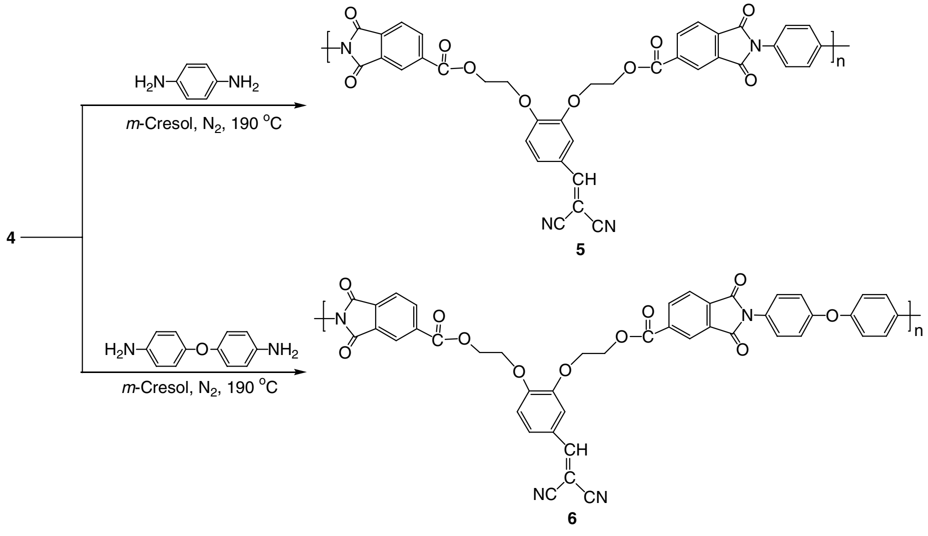


*Synthesis and characterization of polyimides **5-6***

Polyimides **5-6** were synthesized by the reaction of aromatic dianhydride monomer **4** containing NLO-chromophore with stoichiometric amounts of the corresponding aromatic diamine in *m*-cresol. The polymerization yield was 85-91%. The striking feature of these polymers is that they had pendant NLO chromophores that are parts of the polymer main chains. These mid-type NLO polymers were expected to have the advantages of both main-chain and side-chain NLO polymers. The chemical structures of the resulting polymers were confirmed with ^1H NMR, IR spectra and elemental analysis. The elemental analysis results fit the polymer structures. ^1H NMR spectra of the polymers showed a signal broadening due to polymerization, but the chemical shifts were consistent with the proposed polymer structures. The IR spectra supported the formation of polyimides. The IR spectra of the polymer samples showed peaks near 1780 and 726 cm^{-1} that were characteristic absorption bands of imide asymmetric carbonyl stretching and imide ring deformation, respectively. IR spectra of the same polymer samples also show strong absorption peaks near 1724 cm^{-1} and 1378 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 weights were determined by GPC with polystyrene as the standard and THF as the eluent. M_n was around 23200 (M_w/M_n = 1.71) for polymer **5**. Polyimides **5-6** were soluble in common solvents such as acetone, DMF, and DMSO, but they were not soluble in methanol and diethyl ether. The η_{inh} values were 0.26-0.30 dL g^{-1}. Polymers **5-6** showed strong absorption near 378 nm by the NLO-chromophore dioxybenzylidenemalononitrile group. Having well defined polymers **5-6**, we investigate their properties.

Thermal properties of the polymers

The thermal behavior of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g). Polymers **5-6** showed a thermal stability up to 330°C according to their TGA thermograms. The initial weight loss in the polymers begins at 330-360°C. T_g values of **5-6** measured by DSC were in the range of 181-190°C. These T_g values are higher than those of polyimides containing 2,3-dioxynitrostilbenyl groups as NLO-chromophores (16), but are rather low T_g values compared to those of common rigid polyimides and can probably attributed to the flexibility of the polymer backbone containing ether linkages. The TGA and DSC studies showed that the decomposition temperatures of the polyimides **5-6** were higher than the corresponding T_g's. 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 polymers were studied by the SHG method. We corona-poled the spin-coated polymer films to induce noncentrosymmetric polar order. The UV-Vis absorption spectra of the polymer **6** before and after poling are recorded. After electric poling, the dipole moments of the NLO-chromophores were aligned, and the UV-vis spectrum of polymer **6** 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, being related to the poling efficiency. The estimated order parameter value Φ was 0.23 for polymer **6**. 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 [18[. The transmittance of thin film includes on the information of 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. To determine the microscopic

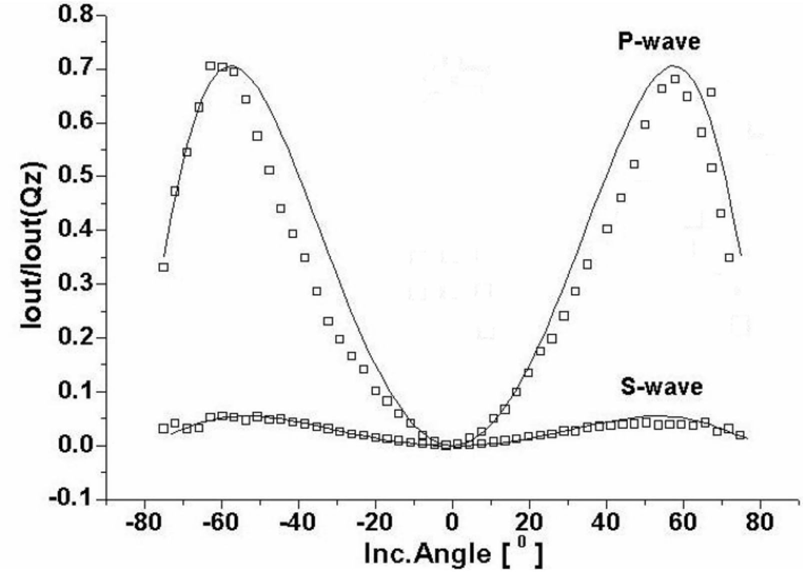


Figure 2. Angular dependence of SHG signal in a poled film of polymer 6.

second-order susceptibility of the polymer, we recorded the angular SHG dependence. Figure 2 shows the angular dependence of SHG signal in a poled polymer **6**. 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 polymers **5-6** are summarized in Table 1. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with Pascal fitting program according to the literature procedure [19]. The values of d_{31} and d_{33} for polymer **6** were 1.62 x 10^{-9} and 4.73 x 10^{-9} esu, respectively. Because of the second harmonic wavelength was at 532 nm, which was not in the absorptive region of the resulting polymer, there was not resonant contribution to this d_{33} value. In the isotropic model, the ratio of d_{33}/d_{31} is predicted to be about 3. Our d_{33}/d_{31} value of near 2.92 is in good agreement with the predicted value. To evaluate the high-temperature stability of the polymers, we studied the temporal stability of the SHG signal. In Figure 3, we present the dynamic thermal stability study of the NLO activity of the film **6**. 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°C to 300°C.

The polymer film exhibited a greater thermal stability even at 20°C higher than T_g and no significant SHG decay was observed below 200°C. In general, side-chain NLO polymers lose thermal stability of dipole alignment around T_g. The stabilization of dipole alignment is a characteristic of main-chain NLO polymers. The exceptionally high thermal stability of SHG of polymers **5-6** 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 merits of both main-chain and side-chain NLO polymers: the stabilization of dipole alignment and good solubility.

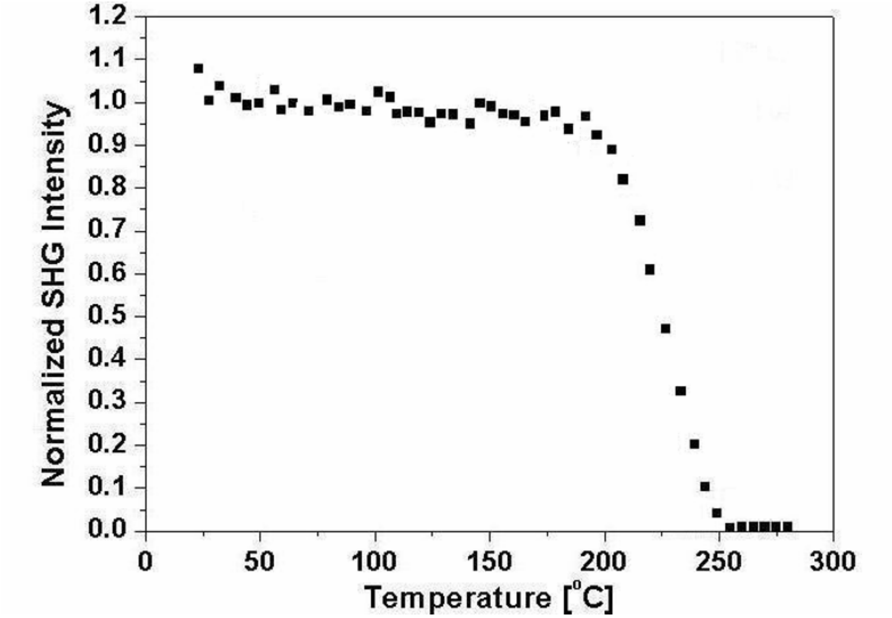


Figure 3. Normalized d_{33} of polymer **6** as a function of temperature at a heating rate of 10°C/min.

Table 1. Nonlinear Optical Properties of Polyimides **5-6**

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	Φ[c]	film thickness[d] (μm)	d_{31}[b] (esu)
5	376	$(4.42\pm0.16)x10^{-9}$	0.17	0.32	$(1.56\pm0.10)x10^{-9}$
6	378	$(4.73\pm0.15)x10^{-9}$	0.23	0.35	$(1.62\pm0.07)x10^{-9}$

[a] Polymer film after corona poling.

[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [19].

[c] Order parameter $\Phi = 1\text{-}A_1/A_0$, 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 [18].

Conclusions

We have synthesized novel Y-type polyimides (**5-6**) with pendant NLO chromophores, which were parts of the polymer main chains. These mid-type NLO polyimides were soluble in common organic solvents. Polymers **5-6** showed thermal stability up to 330°C according to TGA thermograms and had T_g values in the range of 181-190°C. The SHG coefficients (d_{33}) of corona-poled polymer films were 4.73 x 10^{-9} esu. The striking feature of these polymers was that they exhibit SHG stability up to 20°C higher than T_g and no SHG decay was observed below 200°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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