Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 22 Sep 2010

To cite this article: Dong-Seon Won, Ga-Young Lee & Ju-Yeon Lee (2008): Preparation of Novel Y-Type Nonlinear Optical Polyimides with High Thermal Stability of Second Harmonic Generation, Molecular Crystals and Liquid Crystals, 491:1, 231-239

To link to this article: http://dx.doi.org/10.1080/15421400802330531

Mol. Cryst. Liq. Cryst., Vol. 491, pp. 231–239, 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802330531

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Preparation of Novel Y-Type Nonlinear Optical Polyimides with High Thermal Stability of Second Harmonic Generation

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2,4-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 2,4-dioxybenzylidenemalononitrile groups as NLO-chromophores, which constitute parts of the polymer backbone. The resulting polyimides 5-6 are soluble in polar solvents such as dimethylsulfoxide 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 179–188°C. The second harmonic generation (SHG) coefficients (d_{33}) of poled polymer films at the 1064 nm fundamental wavelength were around 6.32×10^{-9} esu. The dipole alignment exhibited exceptionally high thermal stability even at 20°C higher than T_g, there was no SHG decay below 200°C because of the partial main chain character of polymer structure, which is acceptable for nonlinear optical device applications.

Keywords: differential scanning calorimetry (DSC); NLO; polyimides; relaxation of dipole alignment; SHG coefficient; thermogravimetric analysis (TGA)

INTRODUCTION

Recently, attention has been focused on the synthesis of nonlinear optical (NLO) polymers because of their potential applications in the field of electro-optic devices [1–4]. In the developments of NLO polymers for applications, stabilization of electrically induced dipole

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund, KRF-2007-313-C00498).

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alignment is one of the important considerations. Two approaches to minimize the randomization have been proposed namely the use of cross-linking methods [5–8] and the utilization of high T_g polymers such as polyimides [9–12]. Polyimides as NLO materials have many advantages such as their high T_g and high thermal stability. There are two types of NLO polyimides, which have been used either as polymer hosts for composite materials or as polymer backbones for side-chain NLO chromophores. Side-chain polymer systems have the advantages such as good solubility, homogeneity and high loading level of NLO chromophores, but they tend to lose nonlinear optical activity at lower temperature by randomization of NLO chromophores. Main-chain NLO polymershave 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. Recently we reported novel Y-type NLO polyimides containing dioxynitrostilbenyl group [13–14]. In this work we prepared novel polyimides containing 2,4-dioxybenzylidenemalononitrile groups as NLO-chromophores. We selected 2,4-dioxybenzylidenemalononitrile because they have large dipole moments and are rather easy to

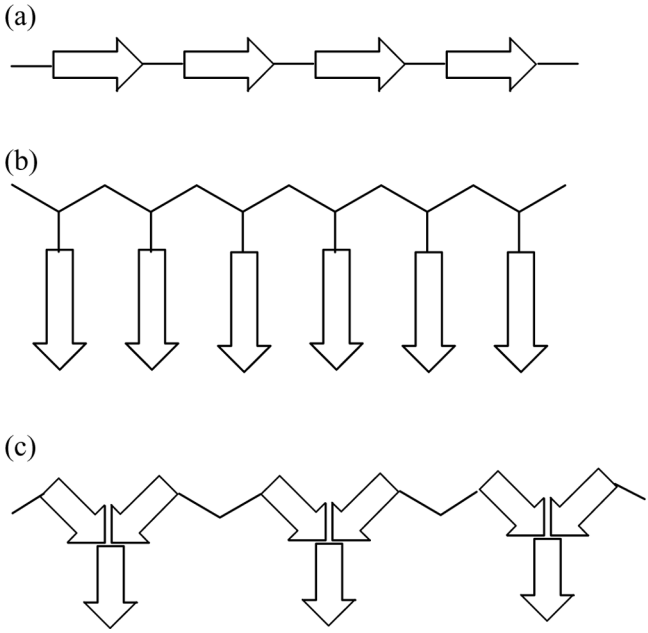


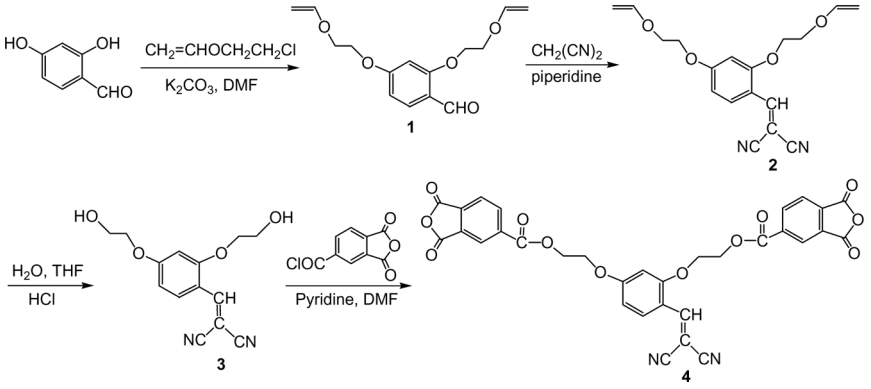
FIGURE 1 (a) Main Chain NLO polymers, (b) side chain NLO polymers, and (c) Y-type NLO polymers.

synthesize. Furthermore 2,4-dioxybenzylidenemalononitrile groups constitute novel Y-type NLO polyimides (Fig. 1c), and these Y-type NLO polyimides have not yet been presented in the literature. Thus, we synthesized another new type of NLO polyimide, in which the pendant NLO chromophores are parts of the polymer backbones. These mid-type NLO polymers are expected to have both the merits of 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 solubility, second harmonic generation (SHG) activity, and relaxation of dipole alignment. We now report the results of the initial phase of the work.

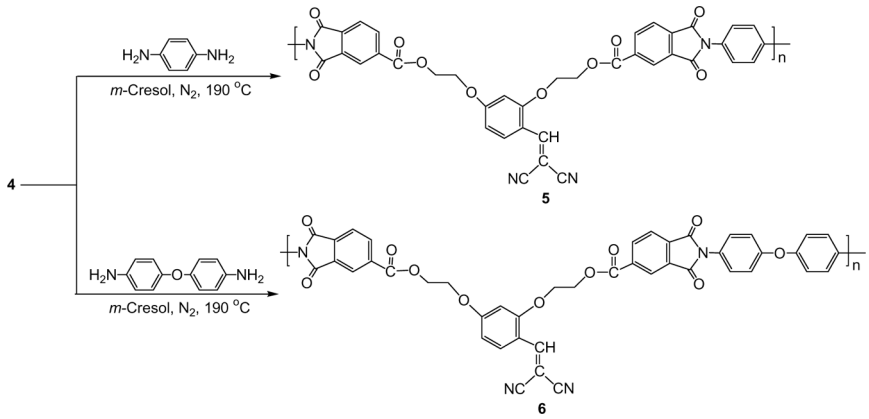
EXPERIMENTAL

Materials

Synthetic methods of dianhydride **4** and polymers **5-6** are summarized in Schemes 1 and 2. Compound **4**: ^{1}H NMR (DMSO-d_6) δ 4.38–4.82 (t, 8H, 2-O-CH_2-CH_2-O-), 6.82–6.95 (m, 2H, aromatic), 7.58–7.66 (m, 1H, benzylic), 7.73–7.82 (m, 2H, aromatic), 8.04–8.30 (m, 4H, aromatic), 8.67–8.72 (d, 1H, aromatic). IR (KBr) 3078 (w, =C-H), 2962 (w, C-H), 2226 (s, CN), 1780 (m, C=O, dianhydride), 1720 (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, 61.83 H, 2.97; N, 4.58. 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 4.24–4.82 (m, 8H, 2 -O-CH_2-CH_2-O-), 6.32–7.25 (m, 5H, benzylic, aromatic), 7.54–7.68 (s, 3H, aromatic), 7.92–8.55 (m, 6H, aromatic). IR (KBr) 3070 (w, =C-H), 2953 (w, C-H), 2201 (s, CN), 1779 (m, C=O),



SCHEME 1 Synthetic method of compound **4**.



SCHEME 2 Synthetic method of polymers **5-6**.

1727 (vs, C=O), 1610 (s, C=C), 1377 (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, 65.81; H, 3.25; N, 8.16. 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 4.23–4.81 (m, 8H, 2 -O-CH_2-CH_2-O-), 6.32–7.03 (m, 6H, benzylic, aromatic), 7.05–7.38 (m, 3H, aromatic), 7.40–7.58 (m, 4H, aromatic), 7.96–8.17 (m, 2H, aromatic), 8.20–8.49 (m, 3H, aromatic). IR (KBr) 3070 (w, −C-H), 2953 (w, C-H), 2205 (m, CN), 1779 (m, C=O), 1724 (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.

Instrumentation

IR, ^{1}H NMR, and UV-Vis spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer, Varian 300 MHz NMR spectrometer, and Shimadzu UV-3100S spectrophotometer, respectively. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. T_g values were measured on a TA 2920 differential scanning calorimeter (DSC) in a nitrogen atmosphere. DuPont 951 thermogravimetric analyzer (TGA) with a heating rate of 10°C/min up to 800°C was used for the thermal degradation of polymers under nitrogen. The number average molecular weight (M_n) and weight average molecular weight (M_w) of the polymers were estimated by gel permeation chromatography (GPC) (columns styragel HR5E4E;

solvent THF). The alignment of the NLO-chromophore of the polymers was carried out by corona poling method. The refractive index of the polymer sample was measured by the optical transmission technique [15]. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [16].

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymers 5-6

Synthetic method of monomer **4** is summarized in Scheme 1. The polymers **5-6** were synthesized by reacting aromatic dianhydride monomer **4** containing NLO-chromophore with stoichiometric amounts of the corresponding aromatic diamine in *m*-cresol (Scheme 2). The polymerization yield was 88–92%. The resulting polymers were purified by Soxhlet extraction with diethyl ether as a solvent. The chemical structures of the resulting polymers were confirmed by ^{1}H NMR, IR spectra, and elemental analysis. ^{1}H NMR spectra of the polymers showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structures. The IR spectra of the polymer samples showed peaks near 1779 and 726 cm^{-1} that are characteristic bands of imide asymmetric carbonyl stretching and imide ring deformation, respectively. IR spectra of the same polymer samples also showed strong absorption peaks near 1727 cm^{-1} and 1377 cm^{-1} due to a symmetric carbonyl stretching and C-N stretching of imide ring, respectively. These results are consistent with the proposed structures, indicating that the NLO-chromophore remained intact during the imidization process. The number-average molecular weight (M_n) was determined by GPC to be 21600 ($M_w/M_n = 1.75$) for polymer **5**. Polydispersities were in the range of 1.67–1.79. The polyimides **5-6** were soluble in common solvents such as DMF and DMSO, but were not soluble in methanol and diethyl ether. The inherent viscosities were in the range of 0.28–0.30 dL/g. Polymers **5-6** showed strong absorption near 382 nm by the NLO-chromophore dioxybenzylidenemalononitrile group. The striking feature of these polymers was that they had pendant NLO chromophores that were parts of the polymer main chains. Thus, we obtained a new type of NLO polyimide with side chain and main chain characteristics. These mid-type NLO polymers were expected to have the advantage of both main-chain and side-chain NLO polymers. We now have well defined polymers **5-6** and investigate their properties.

TABLE 1 Thermal Properties of Polymers **5-6**

Polymer	T_g^a, °C	Degradation temp, °C[b]			Residue[b] at 800°C, wt%
		5 wt%-loss	20 wt%-loss	40 wt%-loss	
5	188	376	436	542	41.8
6	179	342	427	498	35.6

[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 DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

Thermal Properties of Polymers

The thermal behavior of the polymers was investigated by TGA and DSC to determine the thermal degradation pattern and T_g. The results are summarized in Table 1. Polymers **5-6** showed thermal stability up to 330°C from their TGA thermograms as shown in Table 1. T_g values of the polymers **5-6** measured by DSC were in the range 179–188°C. These are high values compared to those of polyimides containing 2,3-dioxynitrostilbene [13,14], but are rather low values 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 temperatures of the polyimides **5-6** were higher than the corresponding T_g values. This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

Nonlinear Optical Properties of Polymers

The NLO properties of polymers were studied by the SHG method. The spin-coated polymer films were corona-poled to induce noncentrosymmetric polar order. UV-Vis absorption spectra of the polymers before and after poling were recorded. After electric poling, the dipole moments of the NLO-chromophores were aligned and the UV-Vis spectra of polymers exhibited a slight blue shift and a decrease in absorption due to birefringence. The estimated order parameter value Φ was equal to 0.16 for polymer **6** ($\Phi = 1 - A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after poling). The decrease in absorbance after poling is an indicator of the dipole alignment. The refractive index of the sample was measured by the optical transmission technique [14]. SHG measurements were performed at a

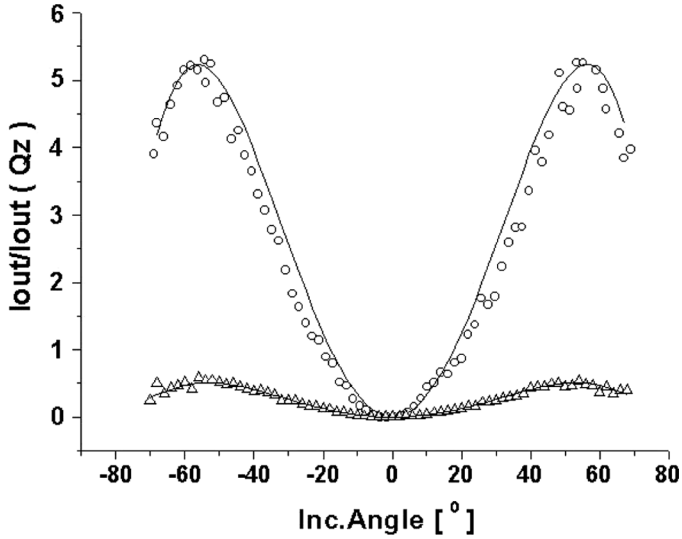


FIGURE 2 Angular dependence of SHG signal in a poled film of polymer **6**.

fundamental wavelength of 1064 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 2 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. To calculate 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 2. The values of d_{31} and d_{33} for polymer **6** were 2.28×10^{-9} and 6.32×10^{-9} esu, respectively. These values are somewhat higher

TABLE 2 Nonlinear Optical Properties of Polymers **5-6**

Polymer	$\lambda_{max}{}^a$ (nm)	$d_{33}{}^b$ (esu)	ϕ^c	Film thickness^d (μm)	$d_{31}{}^b$ (esu)	d_{33}/d_{31}
5	382	5.48×10^{-9}	0.24	0.32	1.94×10^{-9}	2.82
6	381	6.32×10^{-9}	0.16	0.30	2.28×10^{-9}	2.77

[a]Polymer film after corona poling.

[b]SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [16].

[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 [15].

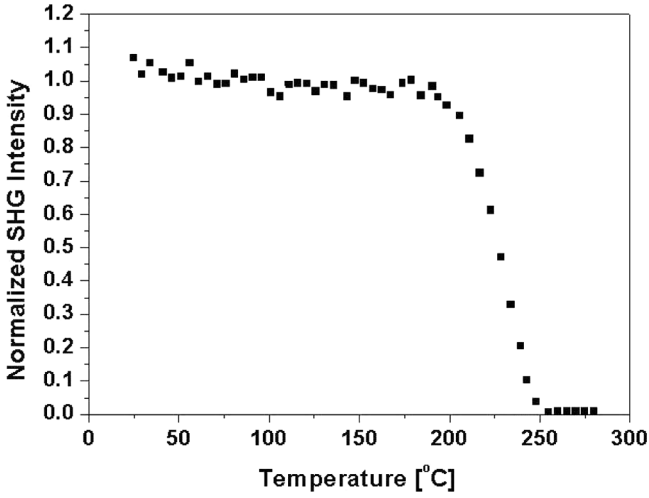


FIGURE 3 Normalized SHG signal of polymer **6** as a function of temperature at a heating rate of 10°C/min.

than those of polyimides containing 2,3-dioxynitrostilbene as NLO chromophores. 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 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, in situ SHG measurements were performed at a heating rate of 10°C/min from 30 to 250°C. The poled film of polymers **5-6** exhibited a thermal stability even at 20°C higher than T_g and no significant SHG decay was observed below 200°C, which is acceptable for NLO device applications. These thermal stability of SHG are higher than those of polymers with 2,3-dioxynitrostilbenyl groups. Side-chain NLO polymers usually lose thermal stability of dipole alignment below T_g. Stabilization of dipole alignment is a characteristic of main-chain NLO polymers. The exceptionally high thermal stability of second harmonic generation of polymers **5-6** was probably 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 advantage of both main chain- and side-chain NLO polymers: stabilization of dipole alignment and good solubility.

CONCLUSIONS

Novel, Y-type polyimides (**5-6**) with pendant NLO chromophores as parts of polymer main chains were synthesized. These mid-type NLO polyimides **5-6** are soluble in common organic solvents and showed thermal stability up to 320°C and T_g values in the range 179–188°C. The SHG coefficients (d_{33}) of corona-poled polymer films were around 6.32×10^{-9} esu. The striking feature of these polymers is that they exhibit SHG stability up to 20°C higher than T_g and no SHG decay was observed below 200°C. The high thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophore, which was a part of the polymer backbone.

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