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# Synthesis and Nonlinear Optical Properties of Novel Polyester Containing Dicyanovinylnitroresorcinoxy Group

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*Novel X-type polyester containing 4-(2′,2′-dicyanovinyl)-6-nitroresorcinoxy groups as nonlinear optical (NLO) chromophores, which constitute parts of the polymer backbone, was prepared and characterized. Polyester is soluble in common organic solvents such as N,N-dimethylformamide and acetone. Polyester shows a thermal stability up to 300°C from thermogravimetric analysis with glass-transition temperature obtained from differential scanning calorimetry of near 108°C. The second harmonic generation (SHG) coefficient ($d_{33}$) of poled polyester film at the 1064 nm fundamental wavelength is 7.13 × $10^{-9}$ esu. The dipole alignment exhibits a thermal stability even at 7°C higher than glass-transition temperature ($T_g$), and no significant SHG decay is observed below 115°C due to the partial main-chain character of polymer structure, which is acceptable for NLO device applications.*

**Keywords** Differential scanning calorimetry (DSC); dipole alignment; NLO; polyester; SHG coefficient; thermogravimetric analysis (TGA)



## Introduction

Molecular design and synthesis of organic nonlinear optical (NLO) polymers are important because of their potential applications in the field of electro-optic devices such as optical switches and modulators [1–3]. In the developments of NLO polymers, stabilization of electrically induced dipole alignment is one of important considerations. Two approaches have been proposed to minimize the randomization, that is to use cross-linking method [4–5] and to utilize high $T_g$ polymers such as polyimides [6–7]. 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 films. Side-chain NLO polymers have good solubility, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we prepared novel Y-type polyesters containing dioxybenzylidenemalononitrile [8] or tricyanovinylthiazole [9] as NLO chromophores. In this work reported here, we prepared a new X-type polyester containing 4-(2′,2′-dicyanovinyl)-6-nitroresorcinoxy groups as NLO chromophores. We

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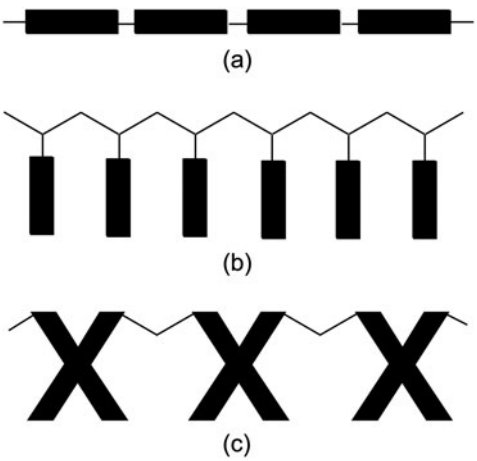



**Figure 1.** Main chain NLO polymers (a), side chain NLO polymers (b), and X-type NLO polymers (c).

selected the latter because they were expected to have large NLO activities. Furthermore these groups can be incorporated into novel X-type NLO polyesters (see Fig. 1c). The structure of NLO chromophores and these X-type NLO polyesters have not yet been described in the literature. This X-type NLO polymer is 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 polymer, we investigated its properties such as second harmonic generation activity and relaxation of dipole alignment. We now report the results of the initial phase of the work.

## Experimental

### *Materials*

A representative synthetic procedure for polyester **5** was as follows. Polymer **4** (4.04 g, 0.10 mol) was dissolved in 25 mL of DMF at room temperature and stirred for 30 min. The reaction mixture was cooled with ice bath, added 4 mL of sulfuric acid, and stirred for 30 min. A mixture of nitric acid (8 mL) and sulfuric acid (8 mL) were added dropwise to the solution and stirred for 24 hr at 0°C. The reaction mixture was poured to 500 mL of ice water and the precipitated polymer was separated with suction. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum, yielding 3.95 g (88% yield) of polyester **5**. $\eta_{inh} = 0.30$ dL/g (c, 0.5 g/dL in DMSO at 25°C). $^1$H NMR (DMSO-$d_6$) $\delta$ 4.39–4.56 (s, 4H, 2 -$CH_2$-O-), 4.61–4.78 (m, 4H, 2 Ph-O-$CH_2$-), 6.76–6.95 (m, 2H, aromatic), 7.94–8.07 (s, 4H, aromatic), 8.18–8.31 (s, 1H, aromatic). IR (KBr) 3032 (w, = C-H), 2956 (m, C-H), 2224 (s, CN), 1720 (vs, C=O), 1614, 1572 (s, C = C) cm$^{-1}$. Anal. Calcd for $(C_{22}H_{15}N_3O_8)_n$: C, 58.80; H, 3.36; N, 9.35. Found: C, 58.72; H, 3.42; N, 9.43.

### *Measurements*

IR, $^1$H NMR, and UV-visible spectra were obtained with a Varian FT IR-1000 IR spectrophotometer, Varian VNMRS 500MHz NMR spectrometer, and SECOMAM Model

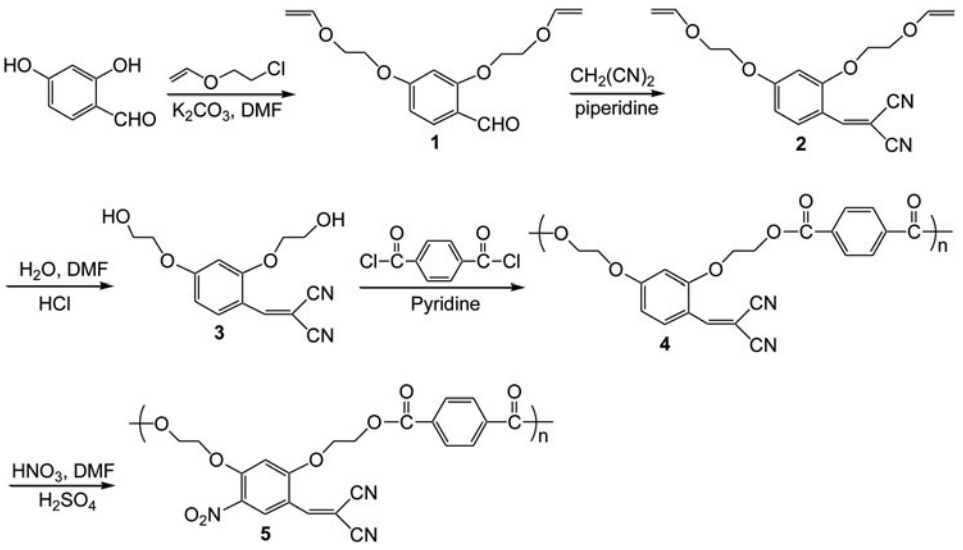
UVIKON XS 99–90289 spectrophotometer, respectively. $T_g$ values were measured on a TA 2920 differential scanning calorimeter (DSC) in a nitrogen atmosphere. TA Q50 thermogravimetric analyzer (TGA) with a heating rate of 10°C/min up to 800°C was used for the thermal degradation study of polymers under nitrogen. The number average molecular weight ($M_n$) and weight average molecular weight ($M_w$) of the polymer were estimated by gel permeation chromatography (GPC) (columns styragel HR5E4E; solvent THF). The alignment of the NLO chromophore of the polymer was carried out by corona poling method. The refractive index of the polymer sample was measured by the optical transmission technique [10]. 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. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [11].



## Results and Discussion

### *Synthesis and Characterization of Polymer 4*

The synthetic route for polyester **5** is presented in Scheme 1. Diol **3** was condensed with terephthaloyl chloride (TPC) in a dry DMF solvent to yield polyester **4**. Polymer **4** was reacted with nitric acid and sulfuric acid in anhydrous DMF to yield X-type polyester **5** containing 4-(2′,2′-dicyanovinyl)-6-nitroresorcinoxy groups as NLO chromophores. The chemical structure of the polymer was identified by $^1$H NMR, IR spectra, and elemental analysis. $^1$H NMR spectrum and elemental analysis results of the polymer are fit the polymer structure. The IR spectrum of polyester **5** shows strong carbonyl peaks near 1720 cm$^{-1}$ indicating the presence of ester bond. The spectrum also shows strong absorption peak near 2224 cm$^{-1}$ indicating the presence of nitrile group, and two strong absorption bands due to the nitro group in the NLO chromophore appeared near 1572 cm$^{-1}$ and 1268 cm$^{-1}$. These results are consistent with the proposed structure. The molecular weights were determined




**Scheme 1.** Synthetic scheme and structure of polyester **5**.

by GPC with polystyrene as the standard and THF as the eluent. $M_n$ of the polyester **5**, determined using GPC, is 16,200 ($M_w/M_n = 1.91$). The polyester **5** 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 0.30–0.32 dL/g. Polyester **5** shows strong absorption near 373 nm due to the 4-(2′,2′-dicyanovinyl)-6-nitroresorcinoxy group NLO chromophore. Thus, we obtained a new X-type of NLO polyester with side-chain and main-chain characteristics. Having obtained the well defined polyester **5**, we investigated its properties.

### *Thermal Properties of Polymer*

The thermal behavior of the polymer was investigated using TGA and DSC to determine the thermal degradation pattern and glass transition temperature ($T_g$). Polyester **5** shows a thermal stability up to 300°C from its TGA thermogram. $T_g$ value of polyester **5** measured using DSC is around 108°C. This $T_g$ value is higher than that of the polyester containing dioxybenzylidenemalononitrile, which is near 94°C [8].

### *Nonlinear Optical Properties of Polymer*

The NLO properties of polymers were studied using the SHG method. To induce non-centrosymmetric polar order, the spin-coated polymer films were corona-poled. As the temperature was raised gradually 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 poling was confirmed from UV-visible spectra. Polyester **5** shows strong absorption near 376 nm before electric poling. After electric poling, the dipole moments of the NLO chromophores were aligned and UV-visible absorption of polyester **5** exhibits a slight blue shift showing absorption near 373 nm, and a decrease in absorption due to birefringence, namely by the Pockelseffect, where an electric field induces molecules to line up asymmetrically, inducing anisotropy [12]. SHG measurements were performed at a fundamental wavelength of 1064 nm with 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 for a poled sample of polyester **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 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 [11]. The NLO properties of polyester **5** are summarized in Table 1. The values of $d_{31}$ and $d_{33}$ for polyester **5** are $2.41 \times 10^{-9}$ and $7.13 \times 10^{-9}$ esu, respectively. This $d_{33}$ value is higher than that of the polyester containing

**Table 1.** Nonlinear optical properties of polyester **5**

| Polymer | $\lambda_{max}$[a] (nm) | $d_{33}$[b] (esu) | $d_{31}$[b] (esu) | Film thickness[c] ($\mu$m) | $n$ |
|---|---|---|---|---|---|
| **5** | 373 | $7.13 \times 10^{-9}$ | $2.41 \times 10^{-9}$ | 0.51 | 1.573 |

[a]Polymer film after corona poling.
[b]SHG coefficients ($d_{33}$) were derived from the analysis of measured Maker-fringes [11].
[c]Film thickness was determined by the optical transmission technique [10].

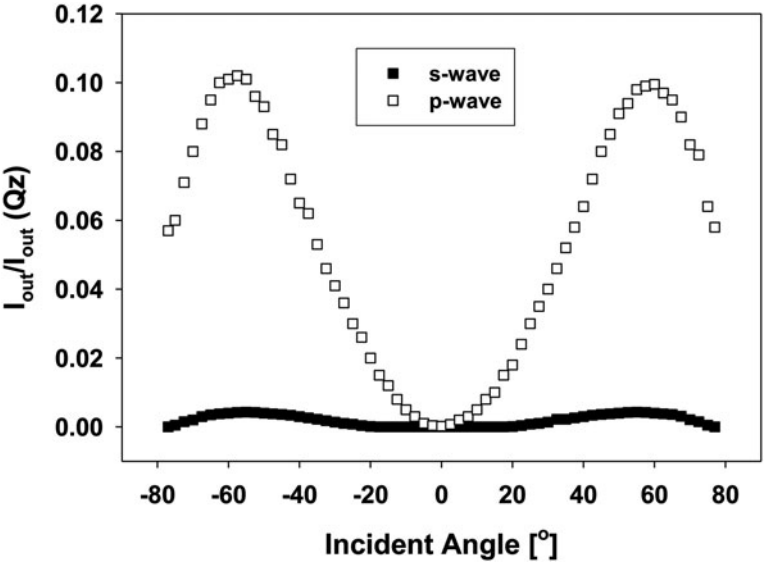



**Figure 2.** Angular dependence of SHG signal for a poled film of polyester **5**.

dioxybenzylidenemalononitrile, which is $6.48 \times 10^{-9}$ esu [8]. Since the second harmonic wavelength is at 532 nm, which is not in the absorptive region of the resulting polyester, there is 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. Figure 3 shows the dynamic thermal stability study of the NLO activity of a film of polyester **5**. To investigate the real time NLO decay of the SHG

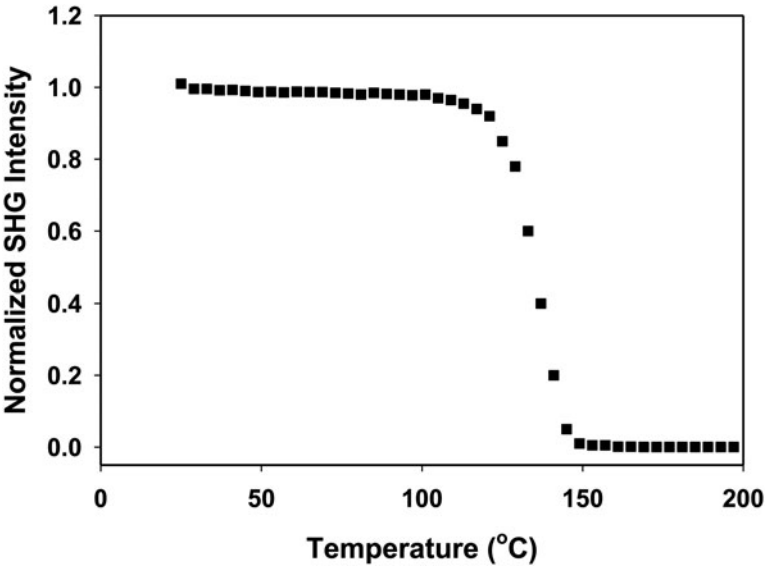



**Figure 3.** Normalized SHG signal of polyester **5** as a function of temperature at a heating rate of **4** °C/min.

signal of the poled polymer film as a function of temperature, *in situ* SHG measurement was performed at a heating rate of 4°C/min from 30 to 200°C. The polymer film exhibits a high thermal stability even at 7°C higher than $T_g$, and no significant SHG decay is observed below 115°C. This SHG thermal stability is higher than that of the polyester containing dioxybenzylidenemalononitrile [8]. In general, side-chain NLO polymers lose the thermal stability of dipole alignment below $T_g$. Stabilization of dipole alignment is a characteristic of main-chain NLO polymers. The enhanced thermal stability of second harmonic generation of polyester **5** is due to the stabilization of dipole alignment of NLO chromophores, which stems from the partial main-chain character of the polymer structure. Thus, we obtained a new X-type NLO polyester having the advantages of both main-chain and side-chain NLO polymers, namely stable of dipole alignment and good solubility.

## Conclusions

New X-type polyester **5** with pendant NLO chromophores as parts of the polymer main chain was synthesized. This X-type NLO polyester **5** is soluble in common organic solvents and displays a thermal stability up to 300°C with $T_g$ values near 108°C. The SHG coefficient ($d_{33}$) of corona-poled polymer film is $7.13 \times 10^{-9}$ esu. Polyester **5** exhibits SHG stability even at 7°C higher than $T_g$ and no significant SHG decay is observed below 115°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.

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