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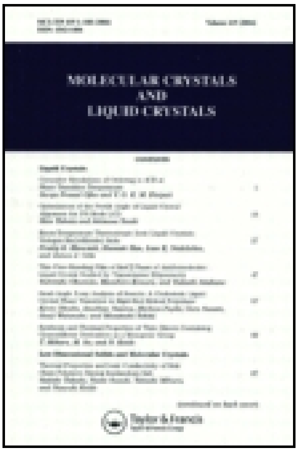

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# Synthesis and Nonlinear Optical Properties of Novel Y-type Polyester Containing Nitrophenylazoresorcinoxy Group

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*A new Y-type polyester (**3**) containing nitrophenylazoresorcinoxy groups as NLO chromophores, which are components of the polymer backbone was prepared. Polyester **3** is soluble in common organic solvents such as* N,N-*dimethylformamide and acetone. It shows a thermal stability up to 240°C from thermogravimetric analysis with glass-transition temperature (*$T_g$*) obtained from differential scanning calorimetry near 116°C. The second harmonic generation (SHG) coefficient (*$d_{33}$*) of poled polymer films at the 1064 nm fundamental wavelength is around* $4.63 \times 10^{-9}$ *esu. The dipole alignment exhibits a thermal stability even at 4°C higher than* $T_g$*, and no SHG decay was observed below 120°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

Recently nonlinear optical (NLO) materials are extensively studied because of their potential applications in the field of electro-optic devices, including high speed optical modulators and ultrafast optical switches [1–3]. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of important criteria [4]; in this context, two approaches to minimize the randomization have been proposed namely the use of cross-linking method [5] and the utilizing high glass-transition temperature ($T_g$) polymers such as polyimides [6]. Polyesters with amino-sulfone azobenzene chromophores in the main chain generate strong and stable reversible birefringence [7]. NLO polyesters containing azobenzene mesogens in the main chain exhibit high thermal and temporal stabilities [8]. Polyesters containing cyanophenylazoaniline moiety in the side chain show good temporal stability of second-order nonlinearity [9]. In general, polymers with the NLO chromophores in the main chain have good thermal stability of dipole alignments, but they often do not dissolve in organic solvents,

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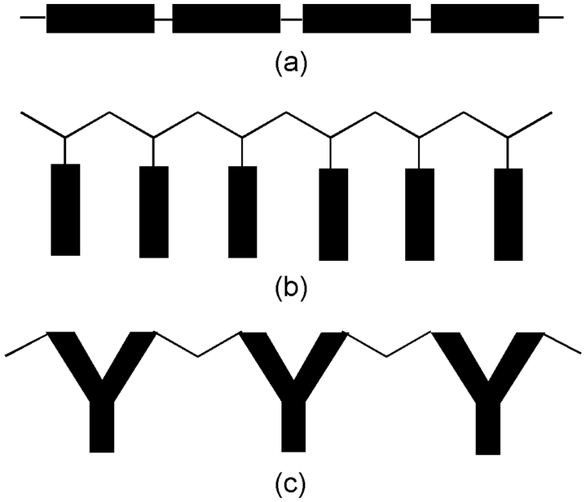


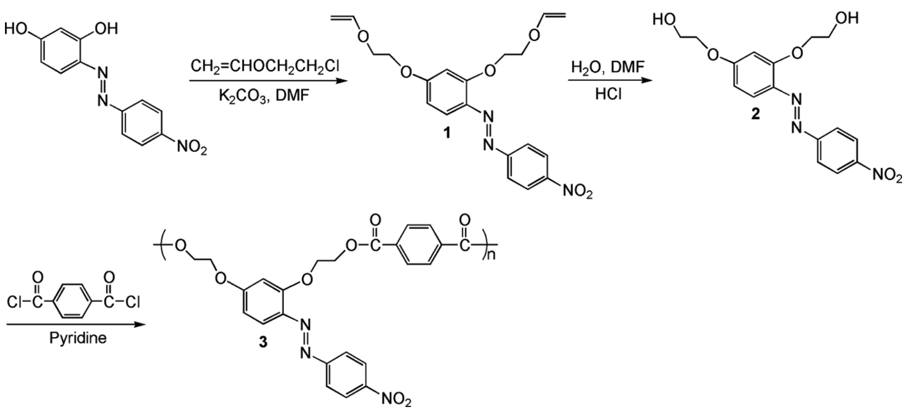
**Figure 1.** Main chain NLO polymers (a), Side chain NLO polymers (b), and Y-type NLO polymers (c).

and their intractability make them unusable to fabricate stable noncentrosymmetric films. Side chain NLO polymers have the advantages such as good solubility and homogeneity, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we reported novel NLO polyesters containing dioxynitrostilbenyl group [10] or dioxybenzylidenemalononitrile [11], which showed enhanced thermal stability of dipole alignments. In this work reported here, we prepared new Y-type polyester containing nitrophenylazoresorcinoxy groups as NLO chromophores. We selected the latter as NLO chromophores because they are expected to have high optical nonlinearities. Furthermore, these nitrophenylazoresorcinoxy groups constitute novel Y-type NLO polyesters (Fig. 1c), and these Y-type NLO polyesters have not yet been reported in the literature. Thus, we synthesized a new type of NLO polyester, in which the pendant NLO chromophores are parts of the polymer backbone. This Y-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 thermal and nonlinear optical properties.

## Experimental

### *Materials*

Synthetic method of polymer **3** is summarized in Scheme 1. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum, yielding 4.29 g (90% yield) of polymer **3**. Inherent viscosity ($\eta_{inh}$) = 0.30 dL/g (c, 0.5 g/dL in DMSO at 25°C). $^1$H NMR (DMSO-$d_6$) $\delta$ (ppm): $\delta$ 4.45–4.87 (m, 8H, 2 -O-$CH_2$-$CH_2$-O-), 6.68–6.82 (s, 1H, aromatic), 6.85–7.10 (s, 1H, aromatic), 7.58–8.33 (s, 9H, aromatic). IR (KBr disc) (cm$^{-1}$): 3085 (w, =C-H), 2926 (m, C-H), 1721 (vs, C=O), 1600 (s, N=N), 1521, 1342 (vs, N=O), 1180 (m, N=N). Anal. Calcd for $(C_{24}H_{19}N_3O_8)_n$: C, 60.38; H, 4.01; N, 8.80. Found: C, 60.48; H, 4.09; N, 8.72.



**Scheme 1.** Synthetic scheme and structure of polymer **3**.

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### *Measurements*

Infrared (IR) spectra were obtained with a Shimadzu FT IR-8201PC infrared spectrophotometer. $^1$H NMR spectra were obtained with a Varian 300 MHz NMR spectrometer. UV-visible absorption spectra were obtained with a Shimadzu UV-3100S spectrophotometer. $T_g$ values were measured using a TA 2920 differential scanning calorimeter DSC in a nitrogen atmosphere. A TA Q50 thermogravimetric analyzer with a heating rate of 10°C min$^{-1}$ 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 using gel permeation chromatography (GPC; styragel HR5E4E columns; tetrahydrofuran (THF) solvent). The refractive index of the sample was measured using the optical transmission technique [12]. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [13]. SHG coefficients ($d_{33}$) were derived from the analysis of measured Maker-fringes.

## Results and Discussion

### *Synthesis and Characterization of Polymer 3*

The synthetic route for polymer **3** is presented in Scheme 1. Polyester **3** was synthesized through the reaction of monomer **2** containing NLO chromophore with stoichiometric amounts of terephthaloyl chloride in pyridine. The chemical structure of the resulting polymer was confirmed by $^1$H NMR, IR spectra, and elemental analysis. The chemical shifts in $^1$H NMR spectrum of the polymer are consistent with the proposed polymer structure. The signal at 4.45–4.87 is assigned to the ethylene protons attached to oxygen. The aromatic protons are shown in the range 6.68–8.33 ppm. The IR spectrum of polymer **3** shows strong carbonyl peaks near 1721 cm$^{-1}$ indicating the presence of ester bond. The spectrum also shows strong absorption peaks near 1521 and 1342 cm$^{-1}$ due to nitro group indicating the presence of nitroazobenzene unit. These results are consistent with the proposed structure, indicating that the NLO chromophores remained intact during the polymerization. The number average molecular weight ($M_n$) of the polymer **3,** determined by GPC, was 18800 ($M_w/M_n = 1.97$). The structural feature of this

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polymer is that it has pendant NLO chromophores, which are parts of the polymer main chain. Thus the resulting polymer **3** is mid type of side-chain and main-chain NLO polymer, and is expected to have both of their merits. The polymer **3** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity value is 0.30 dL/g. Polymer **3** shows strong absorption near 398 nm due to the NLO chromophore nitrophenylazoresorcinoxy group.

### *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. Polymer **3** shows a thermal stability up to 240°C from its TGA thermogram. The 10% weight loss degradation temperature ($T_d$) of polymer **3** is near 262°C. $T_g$ value of the polymer **3** measured by DSC is around 116°C. This $T_g$ value is higher than those of the polyesters containing dioxynitrostilbene, which are in the range 90–95°C [10] or dioxybenzylidenemalononitrile, which is near 83°C [11].

### *Nonlinear Optical Properties of Polymer*

The NLO properties of polymer were studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer film was corona-poled. As the temperature was raised to 120°C, a corona voltage of 6.5 kV was applied and this temperature was maintained for 30 min. The poling was confirmed by UV-visible spectrum. After electric poling, the dipole moments of the NLO chromophores were aligned and the UV-visible absorption of polymer **3** exhibits a slight blue shift and a decrease in absorption due to birefringence. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. Nonlinear optical properties of polymer **3** are summarized in Table 1. 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 **3**. The SHG values were compared with those obtained from a Y-cut quartz plate. SHG coefficients ($d_{33}$, $d_{31}$) were derived from the analysis of measured Maker-fringes with the Pascal fitting program according to the literature procedure [13]. The measured values of $d_{33}$ and $d_{31}$ for polymer **3** are $4.63 \times 10^{-9}$ esu and $1.58 \times 10^{-9}$ esu, respectively. 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.

**Table 1.** Nonlinear optical properties of polymer **3**

| Polymer | $\lambda_{max}$[a] (nm) | $d_{33}$[b] (esu) | $d_{31}$[b] (esu) | Film thickness[c] (μm) | $n$ |
|---|---|---|---|---|---|
| **3** | 398 | $4.63 \times 10^{-9}$ | $1.58 \times 10^{-9}$ | 0.48 | 1.73 |

[a] Polymer film after poling.
[b] SHG coefficients ($d_{33}$) were derived from the analysis of measured Maker-fringes [13].
[c] Film thickness was determined by the optical transmission technique [12].

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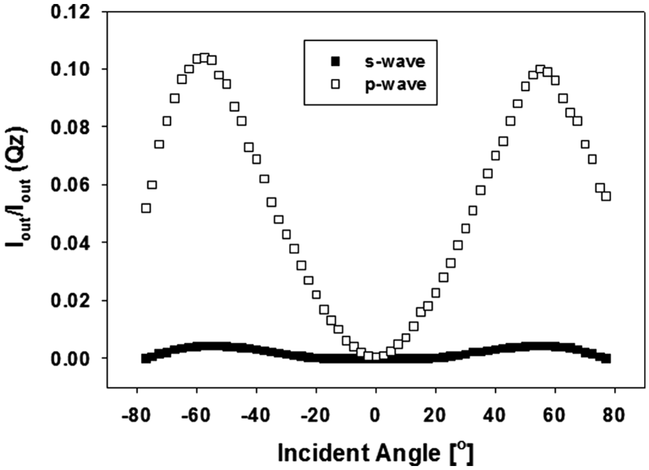

**Figure 2.** Angular dependence of SHG signal for a poled film of polymer **3**.

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 polymer **3**. 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 3.5°C/min from 25 to 200°C. The polymer film exhibits a thermal stability even at 4°C higher than $T_g$ and no significant SHG decay is observed below 120°C. In general, main-chain NLO polymers have good thermal stability of dipole alignments, but they often do not dissolve in organic solvents. Side-chain NLO polymer systems have good solubility, but they often suffer from poor stability of dipole alignments at high temperatures. The high thermal stability of second harmonic generation of polymer **3** is due to the stabilization of dipole alignment of NLO chromophore, which stems from the partial main

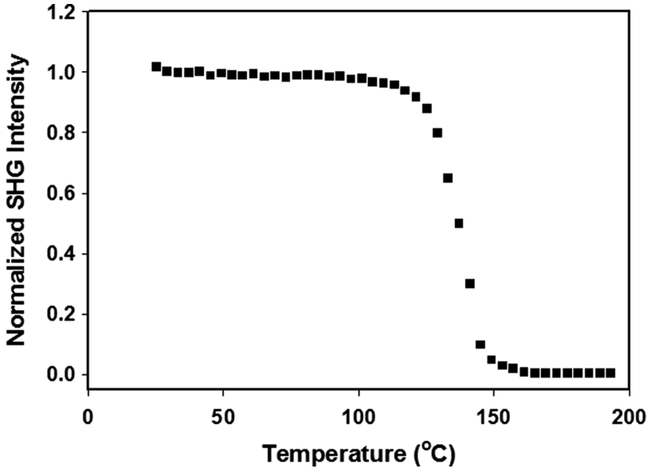

**Figure 3.** Normalized SHG signal of polymer **3** as a function of temperature at a heating rate of 3.5°C/min.

chain character of the polymer structure. Thus, we obtained a new type of NLO polyester having both the merits of main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility.

## Conclusions

A novel Y-type NLO polyester **3** with pendant NLO chromophores as parts of the polymer backbone was prepared and characterized. This Y-type polymer **3** is soluble in common organic solvents and shows a thermal stability up to 240°C with $T_g$ value around 116°C. The SHG coefficient ($d_{33}$) of corona-poled polymer film is $4.63 \times 10^{-9}$ esu. This polymer exhibits SHG stability even at 4°C higher than $T_g$ and no significant SHG decay is observed below 120°C. This high thermal stability of optical nonlinearity stems from the stabilization of dipole alignment of the NLO chromophores, which constitute parts of the polymer main chain

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