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Synthesis and Nonlinear Optical Properties of a Novel Polyester Containing Tricyanovinylthienyl Group

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A novel T-type polyester (7) containing 1-(2,5-dioxyphenyl)-2-{5-(1,2,2-tricyanovinyl)-2-thienyl}ethene groups as NLO-chromophores was synthesized and characterized. Polymer 7 was soluble in common organic solvents such as DMF and DMSO. It showed thermal stability up to 300°C in TGA with T_g *value obtained from DSC near 113°C. The second harmonic generation (SHG) coefficient (*d_{33}*) of poled polymer film at the 1560 nm fundamental wavelength was around* 4.42×10^{-9} *esu. The dipole alignment exhibited a greater thermal stability even at 10°C higher than* T_g*, and there was no SHG decay below 125°C due to the partial main-chain character of the polymer structure, which is acceptable for nonlinear optical device applications.*

Keywords Differential scanning calorimetry (DSC); NLO; polyester; relaxation of dipole alignment; 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 [1–6]. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of important criteria [7]; in this context, two approaches to minimize the randomization have been proposed namely the use of cross-linking method [8–10] and the utilizing high glass-transition temperature (T_g) polymers such as polyimides [11–14]. 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, 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

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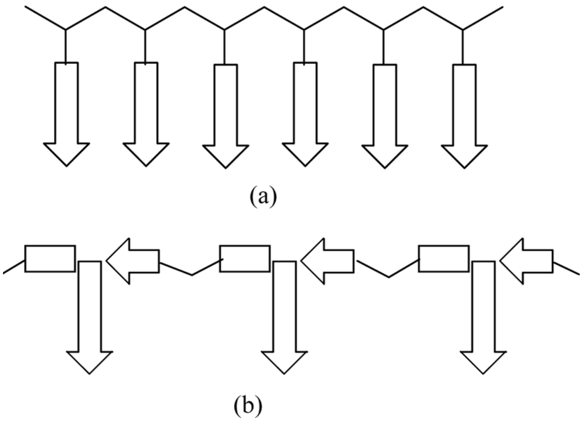


(a)

(b)

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

polyesters containing dioxynitrostilbenyl group [15] or dioxybenzylidenemalononitrile [16], which showed enhanced thermal stability of dipole alignments. In this work we prepared a novel T-type polyester containing 1-(2,5-dioxyphenyl)-2-{5-(1,2,2-tricyanovinyl)-2-thienyl}ethene groups as NLO chromophores. We selected the latter as a NLO chromophore because it has a large dipole moment. Furthermore, 1-(2,5-dioxyphenyl)-2-{5-(1,2,2-tricyanovinyl)-2-thienyl}ethene groups constitute novel T-type NLO polyesters (Fig. 1b), and these T-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 backbones. This T-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 solubility, thermal stability, second harmonic generation (SHG) activity, and relaxation of dipole alignment. We now report the results of the initial phase of the work.

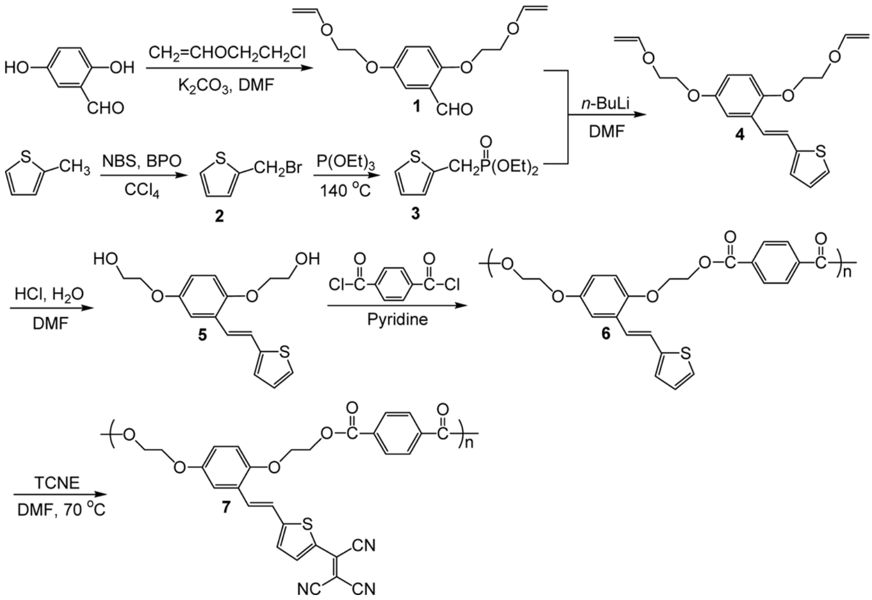
Experimental

Materials

Synthetic method of polymer **7** is summarized in Scheme 1. Polymer **7**: $\eta_{\mathrm{inh}} = 0.28$ dL/g (c, 0.5 g/dL in DMSO at 25°C). ^{1}H NMR (DMSO-d_6) δ (ppm): 4.26–4.45 (s, 4H, 2 -CH$_2$-O-), 4.54–4.78 (d, 4H, 2 Ph-O-CH$_2$-), 6.84–7.72 (m, 6H, -CH=CH-, aromatic), 7.85–8.23 (m, 5H, aromatic). IR (KBr disc) (cm^{-1}): 3085 (w, =C-H), 2954 (m, C-H), 2219 (s, CN), 1720 (vs, C=O), 1627 (s, C=C). Anal. Calcd for $(C_{29}H_{19}N_3O_6S)_n$: C, 64.80; H, 3.55; N, 7.81.; S, 5.97. Found: C, 64.88; H, 3.61; N, 7.76; S, 5.93.

Measurements

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



Scheme 1. Synthetic scheme and structure of polymer **7**.

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. TA Q50 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 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 [17]. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [18].

Results and Discussion

Synthesis and Characterization of Polymer 7

The synthetic route for polymer **7** is presented in Scheme 1. Diol **5** was condensed with terephthaloyl chloride in a dry pyridine to yield polyester **6**, and it was reacted with tetracyanoethylene in anhydrous DMF [19] to yield polyester **7** containing the NLO chromophore 1-(2,5-dioxyphenyl)-2-{5-(1,2,2-tricyanovinyl)-2-thienyl}ethene group. The resulting polymer was purified by Soxhlet extraction for 2 days with methanol as a solvent. The chemical structure of the polymer was confirmed by ^{1}H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structure. ^{1}H NMR spectrum of the polymer showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The IR spectrum of polymer **7** showed strong carbonyl peak near 1720 cm^{-1}, indicating the presence of ester bond. The IR spectrum of the same polymer sample showed strong absorption peak near 2219 cm^{-1}, indicating the presence of nitrile group. These results are consistent with the proposed structure, indicating that the tricyanovinyl groups are attached well to thiophene ring. The number average molecular weight (M_n) of the polymer **7**, determined by GPC, was 17200 ($M_w/M_n = 1.94$). The structural feature of this polymer is that it has pendant NLO chromophores, which are parts of the polymer main chain. Thus the resulting polymer **7** is mid type of side chain- and main chain NLO polymers, and is expected to have both of their merits. The polymer **7** was soluble in common solvents such as acetone, DMF, and DMSO, but was not soluble in methanol and diethyl ether. The inherent viscosity value was 0.28 dL/g. Polymer **7** showed strong absorption near 527 nm by the NLO chromophore 1-(2,5-dioxyethoxy)phenyl)-2-{5-(1,2,2-tricyanovinyl)-2-thienyl)}ethene group. Having well defined polyester **7**, we investigated its properties.

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 **7** showed a thermal stability up to 300°C from its TGA thermogram. T_g value of the polymer **7** measured by DSC was around 113°C. This T_g value is higher than those of the polyesters containing dioxynitrostilbene, which are in the range 90–95°C [15] or dioxybenzylidenemalononitrile, which is near 83°C [16]. The TGA and DSC studies show that the decomposition temperature of the polyester **7** is higher than the corresponding T_g. This indicates that high-temperature poling for a short term is feasible without damaging the NLO chromophore.

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, 6.5 kV of corona voltage was applied and this temperature was maintained for 30 min. The poling was confirmed by UV-Vis spectrum. After electric poling, the dipole moments of the NLO chromophores were aligned and the UV-Vis spectra of polymer **7** 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 **7** ($\Phi = 1 - A_1/A_0$, where $A_0 = 1.9642$ and $A_1 = 1.7354$ are the absorbances of the polymer film before and after poling, respectively). The refractive index of the sample was measured by the optical transmission technique [17]. SHG measurements were performed at a fundamental wavelength of 1560 nm using a mode locked Nd-YAG laser. Nonlinear optical properties of polymer **7** 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 **7**. 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 [18]. The measured values of d_{33} and d_{31} for polymer **7** were 4.42×10^{-9} esu and 1.51×10^{-9} esu, respectively. These values are higher than those of the polyesters containing dioxynitrostilbene [15], and are similar with those of the polyesters containing dioxybenzylidenemalononitrile [16]. If we increase the length

Table 1. Linear and nonlinear optical properties of polymer **7**

Polymer	λ_{max}[a](nm)	d_{33}[b](esu)	Φ[c]	d_{31}[b](esu)	Film thickness[d] (μm)	n
7	527	4.42×10^{-9}	0.12	1.51×10^{-9}	0.51	1.51

[a] Polymer film after poling.

[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [18].

[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 [17].

of the NLO chromophores, the SHG values would be improved. Since the second harmonic wavelength was at 780 nm, which is not in the absorptive region of the resulting polyester, 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 3, we present the dynamic thermal stability study of the NLO activity of the film **7**. 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 4°C/min from 25 to 220°C. The polymer film exhibited a greater thermal stability even at 10°C higher than T_g and no significant SHG decay was observed below 125°C. This thermal stability is higher than those of the polyesters containing dioxynitrostilbene [15] or dioxybenzylidenemalononitrile [16], which exhibits SHG thermal stability up to 100°C. 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 polymer systems have the advantages such as good solubility and high loading level of NLO chromophores, but they often suffer from poor stability of dipole alignments at high temperatures. The exceptional high thermal stability of second harmonic generation of polymer **7** is due to the stabilization of dipole alignment of NLO chromophore,

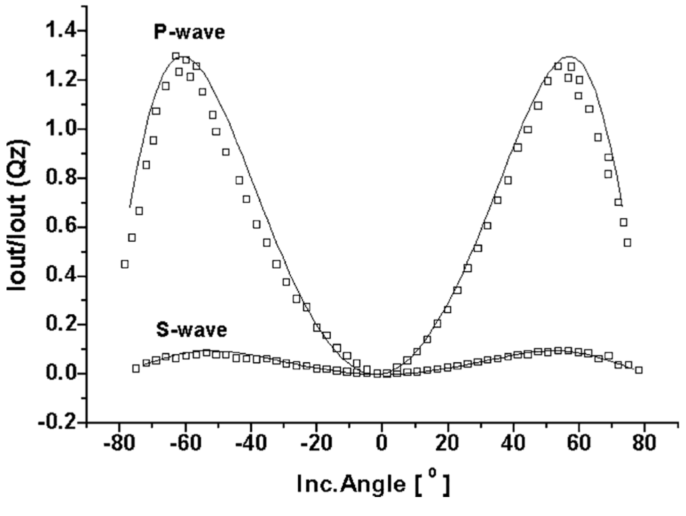


Figure 2. Angular dependence of SHG signal for a poled film of polymer **7**.

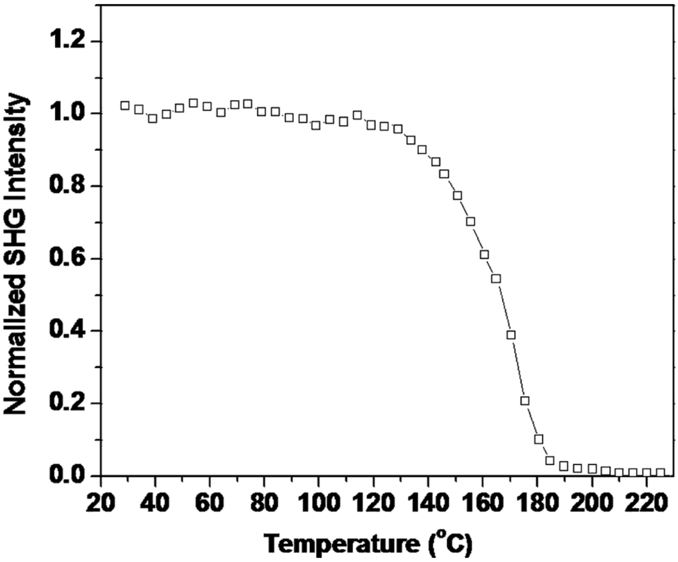


Figure 3. Normalized SHG signal of polymer **7** as a function of temperature at a heating rate of 4°C/min.

which stems from the partial main 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 T-type NLO polyester **7** with pendant NLO chromophores as parts of the polymer backbones was prepared and characterized. This T-type polymer **7** is soluble in common organic solvents and showed a thermal stability up to 300°C with T_g value around 113°C. The SHG coefficient (d_{33}) of corona-poled polymer film was 4.42×10^{-9} esu. This polymer exhibits SHG stability even at 10°C higher than T_g and no significant SHG decay was observed below 125°C. This high thermal stability of optical nonlinearity stemmed from the stabilization of dipole alignment of the NLO chromophore, which constituted a part of the polymer main chain.

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