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Synthesis of Novel Y-Type Nonlinear Optical Polyurethane Containing Tricyanovinylthiophene with High Thermal Stability of Dipole Alignment

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A novel Y-type polyurethane **7** *containing 1-(2,4-dioxyethoxy)phenyl-2-{5-(1,2,2-tricyanovinyl)-2-thiophenyl)}ethenyl groups as nonlinear optical (NLO)-chromophores, which are components of the polymer backbones, was prepared. Polyurethane* **7** *is soluble in common organic solvents such as DMF and DMSO. It showed a thermal stability up to 280°C in TGA thermogram and the T_g value obtained from DSC thermogram was around 163°C. The second harmonic generation (SHG) coefficient (d_{33}) of poled polymer film at 1560 nm fundamental wavelength was around 3.72×10^{-9} esu. The dipole alignment exhibited a thermal stability up to near T_g, and there was no SHG decay below 150°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; polyurethane; relaxation of dipole alignment; SHG coefficient; thermogravimetric analysis (TGA)

INTRODUCTION

Recently there has been an extensive effort to synthesize novel nonlinear optical (NLO) materials because of their potential applications in the field of electro-optic devices [1–3]. Among them, NLO polymers are considered promising materials, mainly because they offer many advantages such as light weight and good processability to form optical devices. In the developments of NLO polymers, stabilization of

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electrically induced dipole alignment is one of important considerations [4]. Two approaches to minimize the randomization have been proposed, that is to use crosslinking method [5–6] and to utilize high T_g polymers such as polyimides [7–8]. Polyurethane matrix forms extensive hydrogen bond between urethane linkage and increases rigidity preventing the relaxation of induced dipoles. Polyurethanes with a NLO chromophore, whose dipole moment is aligned transverse to the main chain backbone, showed enhanced thermal stability [9–10]. A polyurethane with a thiophene ring having a tricyanovinyl group in the polymer side chain showed enhanced thermal stability [11–12]. In general, main-chain NLO polymers exhibit good thermal stability of dipole alignments, but they often do not dissolve in organic solvents. Side-chain NLO polymers have the advantages such as good solubility and high level of NLO chromophore, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we reported novel NLO polyurethanes containing dioxynitrostilbenyl group [13] and dioxybenzylidenemalononitrile [14] with enhanced thermal stability of dipole alignments. In this work we have prepared novel polyurethane containing 1-(2,4-dioxyethoxy) phenyl)-2-{5-(1,2,2-tricyanovinyl)-2-thiophenyl)}ethenyl groups as NLO-chromophores. We selected the latter because they have a large dipole moment. Furthermore, 1-(2,4-dioxyethoxy)phenyl)-2-{5-(1,2,2-tricyanovinyl)-2-thiophenyl)}ethenyl group constitutes a novel Y-type NLO polyurthane (see Fig. 1b), in which the structure of NLO chromophore, and this Y-type NLO polyurethane is not described in the literature. Thus we made a new type of NLO polyurethane, in which the pendant NLO-chromophores are components of the polymer backbones. These mid-type NLO polymers are expected to have the advantages of both main-chain and side-chain NLO polymers namely stable

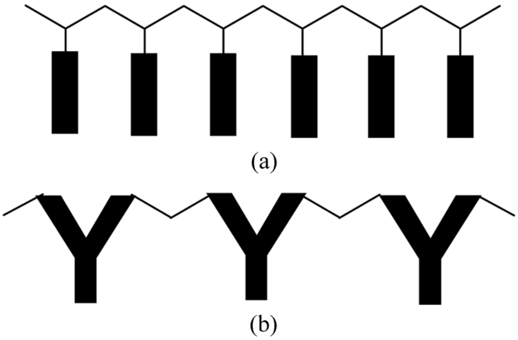


FIGURE 1 Side chain NLO polymers (a) and Y-type NLO polymers (b).

dipole alignment and good solubility. After confirming the structure of the resulting polymer, we investigated its properties such as thermal stability and second harmonic generation (SHG) activity (d_{33}). We now report the results of the initial phase of the work.

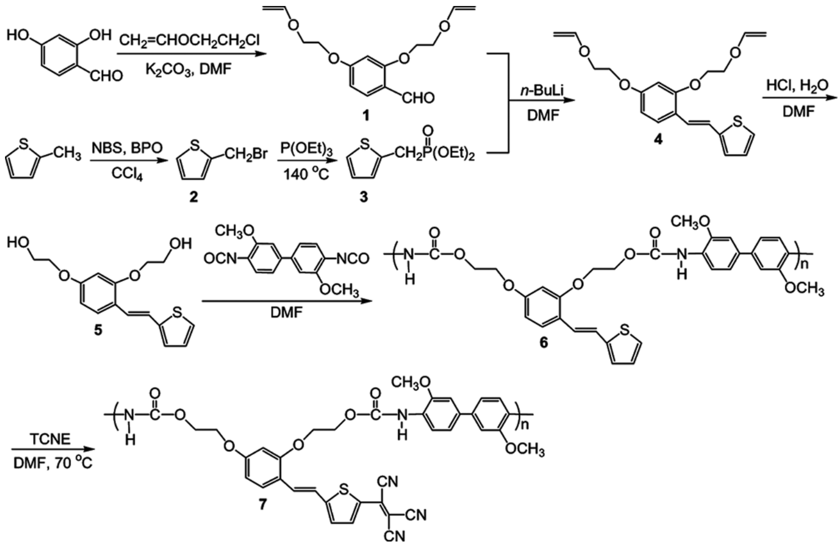
EXPERIMENTAL

Materials

Synthetic method of polymer **7** is summarized in Scheme 1. Polymer **7**: $\eta_{inh} = 0.30$ dL/g (c, 0.5 g/dL in DMSO at 25°C). ^{1}H NMR (DMSO-d_6) δ 3.73–4.13 (m, 8H, -O-CH$_2$-, 2 –OCH$_3$), 4.21–4.68 (m, 6H, -O-CH$_2$-, 2-O-CH$_2$-OCO-), 6.59–6.75 (m, 1H, aromatic), 7.02–7.88 (m, 11H, aromatic), 8.18–8.35 (d, 1H, aromatic), 8.53–8.71 (d, 1H, N-H), 8.95–9.12 (s, 1H, N-H). IR (KBr) 3397 (s, N-H), 2939 (m, C-H), 2219 (m, CN), 1687 (s, C = O), 1595 (s, C = C) cm^{-1}. Anal. Calcd for $(C_{37}H_{29}N_5O_8S)_n$: C, 63.15; H, 4.15; N, 9.95; S, 4.56. Found: C, 63.24; H, 4.18; N, 9.88; S, 4.62.

Measurements

IR, ^{1}H NMR, and UV-Vis spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer, Varian 300 MHz NMR



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

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. 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 [15]. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [16].

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymer 7

Synthetic method of polyurethane **7** is summarized in Scheme 1. Polymer **6** was prepared by the polyaddition reaction between a diol **5** and 3,3′-dimethoxy-4,4′-biphenylenediisocyanate. Polymer **6** was reacted with tetracyanoethylene in anhydrous DMF [11–12] to yield polyurethane **7** containing 1-(2,4-dioxyethoxy)phenyl)-2-{5-(1,2,2-tricyanovinyl)-2-thiophenyl)}ethenyl group as a NLO-chromophore. 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 absorption peak near 2219 cm^{-1} indicating the presence of nitrile group. The IR spectrum of the same polymer sample also showed a strong carbonyl peak near 1687 cm^{-1} indicating the presence of urethane bond. These results are consistent with the proposed structure, indicating that the tricyanovinyl groups are introduced well to thiophene ring. The number average molecular weight (M_n) of the polymer **7**, determined by GPC, was 18200 ($M_w/M_n = 1.93$). The polymer **7** was soluble in common solvents such as DMF and DMSO, but was not soluble in methanol and diethyl ether. The inherent viscosity value was 0.30 dL;g. Polymer **7** showed strong absorption near 581 nm by the NLO-chromophore 1-(2,4-dioxyethoxy)phenyl)-2-{5-(1,2,2-tricyanovinyl)-2-thiophenyl)}ethenyl group. The striking feature of this polymerization system is that it gives unprecedented

Y-type NLO polymer, 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. Thus, we obtained a new type of NLO polyurethane with side-chain and main-chain characteristics.

Thermal Properties of Polymer

The thermal behavior of the polymer was investigated by TGA and DSC to determine the thermal degradation pattern and T_g. Polymer **7** showed a thermal stability up to 280°C according to its TGA thermogram. The T_g value of the polymer **4** measured by DSC was around 163°C. The TGA and DSC studies showed that the decomposition temperature of the polyurethane **7** was higher than the corresponding T_g value. 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 films were corona-poled. As the temperature was raised gradually to 165°C, 6.5 kV of corona voltage was applied and this temperature was maintained for 30 min. The UV-Vis absorption spectra of the polymers before and after the poling were recorded. After electric poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectrum 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 of polymer **7** was equal to 0.25. SHG measurements were performed at a fundamental wavelength of 1560 nm using a mode locked Nd-YAG laser. NLO properties of polymer **7** are summarized in Table 1. In

TABLE 1 Nonlinear Optical Properties of Polymer **7**

Polymer	$\lambda_{max}{}^{a}$(nm)	$d_{33}{}^{b}$(esu)	Φ^{c}	$d_{31}{}^{b}$(esu)	Film thickness^{d} (μm)	n
7	581	3.72×10^{-9}	0.25	1.19×10^{-10}	0.50	1.56

[a] Polymer film.

[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].

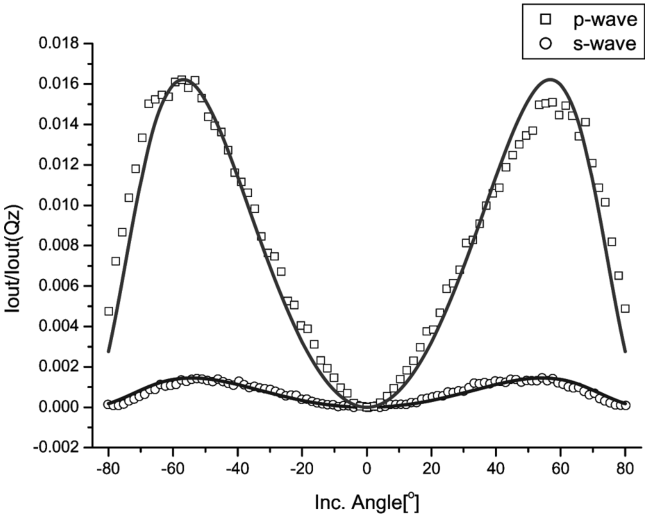


FIGURE 2 Angular dependence of SHG signal in a poled film of polymer **7**.

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}) were derived from the analysis of measured Maker-fringes with Pascal fitting program according to the literature procedure [16]. The preliminary measured values of d_{33} and d_{31} for polymer **7** were 3.72×10^{-9} and 1.19×10^{-10} esu, respectively. Since the second harmonic wavelength was at 780 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 **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 3.5°C/min from 25°C to 250°C. The polymer film exhibited a thermal stability up to near T_g and no significant SHG decay was observed below 150°C, as shown in Figure 3. In general, side chain NLO polymers lose thermal stability of dipole alignment below T_g. Stabilization of dipole alignment is a characteristic of main chain NLO polymer. The enhanced thermal stability of SHG of polymer **7** is due to the stabilization of dipole

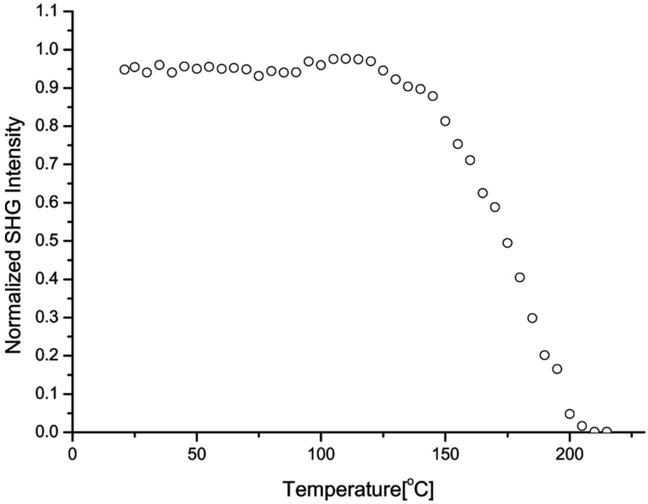


FIGURE 3 Normalized SHG signal of polymer **7** as a function of temperature at a heating rate of 3.5°C/min.

alignment of NLO chromophore, which stems from the partial main chain character of the polymer structure and partly by hydrogen bonds between the neighboring urethane linkages. Thus, we obtained a new type of NLO polyurethane having both of the merits of main chain- and side-chain NLO polymers namely stabilization of dipole alignment and good solubility.

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