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Synthesis and Nonlinear Optical Properties of Novel Y-Type Polyurethane Containing Cyanovinylthiazole

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A novel Y-type polyurethane **4** *containing 5-methyl-4-{5-(1,2,2-tricyanovinyl)-2-thiazolylazo}resorcinoxy groups as nonlinear optical (NLO)-chromophores, which constituted parts of the polymer backbones, was prepared and characterized. Polyurethane* **4** *is soluble in common organic solvents such as acetone and N,N-dimethylformamide. It showed a thermal stability up to 250°C in thermogravimetric analysis thermogram and the glass-transition temperature* (T_g) *obtained from differential scanning calorimetry thermogram was around 118°C. The second harmonic generation (SHG) coefficient* (d_{33}) *of poled polymer film at 1560 nm fundamental wavelength was around* 8.43×10^{-9} *esu. The dipole alignment exhibited a thermal stability even at 12°C higher than* T_g, *and there was no SHG decay below 130°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

There has been an extensive effort to synthesize novel nonlinear optical (NLO) polymers in recent years because of their potential applications in the field of electro-optic devices, including ultrafast optical switches and high-density optical data storage media [1–5]. The promise of NLO polymers lies in their light weight, low cost, and good processability to form electro-optical devices. In the developments of NLO polymers, stabilization of electrically induced dipole alignment is one of important considerations [6]. Two approaches have been proposed to minimize the randomization, that is to use crosslinking method [7–9] and to utilize high T_g polymers such as polyimides [10–12]. 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

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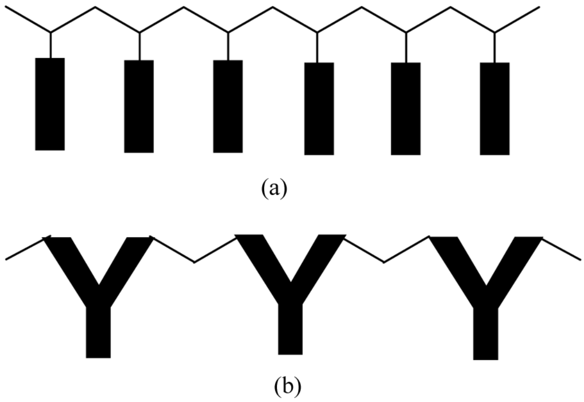

(a)
(b)

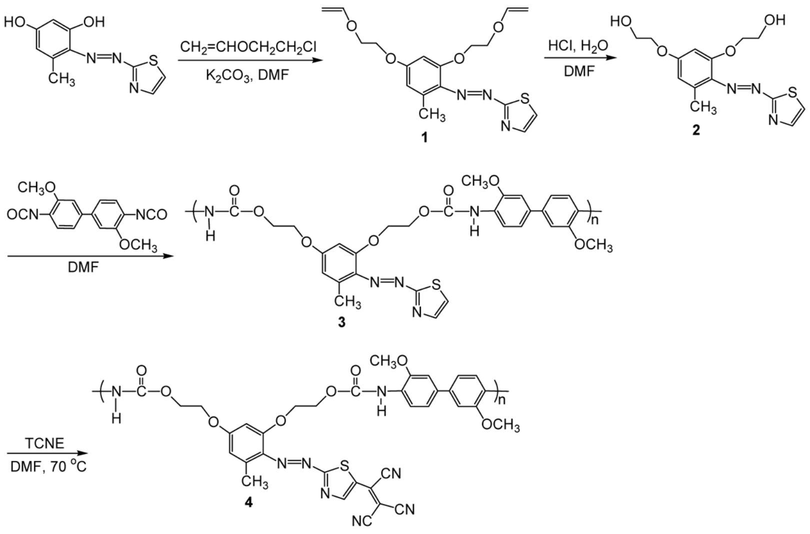
Figure 1. Side chain NLO polymers (a) and Y-type NLO polymers (b).

[13,14]. Polyurethane with a thiophene ring having a tricyanovinyl group in the polymer side chain showed enhanced thermal stability [15,16]. Recently we reported novel NLO polyurethanes containing dioxynitrostilbene [17] or dioxybenzylidenemalononitrile [18] with enhanced thermal stability of dipole alignments. In this work we have prepared a novel polyurethane containing 5-methyl-4-{5-(1,2,2-tricyanovinyl)-2-thiazolylazo}resorcinoxy groups as NLO chromophores. We selected the latter because they are expected to have a large NLO activity. Furthermore, it 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. 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 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 **4** is summarized in Scheme 1. A representative synthetic procedure was as follows. Tetracyanoethylene (1.28 g, 10 mmol) was added slowly to a solution of polymer **3** (5.27 g, 8.5 mmol) dissolved in 15 mL of DMF with stirring at room temperature under nitrogen. The resulting solution was heated in an oil bath kept at 70°C for 12 h under a nitrogen atmosphere. The resulting polymerization solution was cooled to room temperature and poured into 400 mL of methanol. The precipitated polymer was collected and reprecipitated from DMSO into methanol. The polymer was further purified by extraction in a Soxhlet extractor with methanol and dried under vacuum to give 6.49 g (90% yield) of polymer **4**. Inherent viscosity (η_{inh}) = 0.30 dL g^{-1} (c = 0.5 g dL^{-1} in DMSO at 25°C). ^{1}H NMR (DMSO-d_6) δ (ppm): 2.53 (s, 3H, $-CH_3$), 3.83–4.01 (m, 10H, 2 $-OCH_3-$, 2 $-O-CH_2-$,) 4.35–4.70 (q, 4H, 2 $-O-CH_2-OCO-$), 6.51 (s, 1H, aromatic), 6.68 (s, 1H, aromatic), 7.16–7.29 (m, 4H, aromatic), 7.64–7.73 (d, 1H, aromatic), 7.67–7.98 (t, 1H,



Scheme 1. Synthetic scheme and structure of polymer **4**.

aromatic), 8.15–8.33 (t, 1H, aromatic), 8.65 (s, 1H, N–H), 8.97–9.07 (d, 1H, N–H). IR (KBr disc) (cm^{-1}): 3392 (s, N–H), 2940 (m, C–H), 2200 (m, CN), 1687 (s, C=O), 1594 (s, C=C). Anal. Calcd for $(C_{35}H_{28}N_8O_8S)_n$: C, 58.33; H, 3.91; N, 15.55; S, 4.45. Found: C, 58.42; H, 3.98; N, 15.46; S, 4.38.

Measurements

IR, ^1H 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. 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 [19]. Second harmonic generation (SHG) measurements were made using a Maker fringe technique [20].

Results and Discussion

Synthesis and Characterization of Polymer 4

5-Methyl-4-(2-thiazolylazo)resorcinol was purchased from Aldrich and used as received. Polyurethane **3** was prepared by the polyaddition reaction between a diol **2** and 3,3′-dimethoxy-4,4′-biphenylenediisocyanate in a dry DMF solvent. Polymer **3** was reacted with tetracyanoethylene in anhydrous DMF [15,16] to yield polyurethane **4** containing 5-methyl-4-{5-(1,2,2-tricyanovinyl)-2-thiazolylazo}resorcinoxy groups as NLO-chromophores. The synthetic route for polymer **4** is presented in Scheme 1. The resulting polymer was purified by Soxhlet extraction for 2 days with methanol solvent. The chemical structure of the polymer was identified 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 signal at 8.65–9.07 ppm assigned to the amine proton indicates the formation of urethane linkage. The IR spectrum of polymer **4** showed strong absorption peak near 2200 cm^{-1} indicating the presence of nitrile group. The IR spectra of the same polymer sample also show 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 molecular weights were determined by GPC with polystyrene as the standard and THF as the eluent. The number average molecular weight (M_n) of the polymer **4**, determined by GPC, was 18400 ($M_w/M_n = 1.96$). The polymer **4** was soluble in common solvents such as acetone, DMF, and DMSO, but was not soluble in methanol and diethyl ether. The inherent viscosity values were in the range 0.30–0.31 dL/g. Polymer **4** showed strong absorption near 422 nm by the NLO-chromophore 5-methyl-4-{5-(1,2,2-tricyanovinyl)-2-thiazolylazo}resorcinoxy group. The striking feature of this polymerization system is that it gives unprecedented Y-type NLO polymers, in which the pendant NLO chromophores are part of the polymer backbones. These Y-type NLO polymers are expected to have the advantages of both main-chain and side-chain NLO polymers. 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, homogeneity and high loading level of NLO chromophores relative to the main-chain systems, but they often suffer from poor stability of dipole alignments at high temperatures. Thus, we obtained a new type of NLO polyurethane with side-chain and main-chain characteristics. Having well defined Y-type polyurethane **4**, 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 T_g. Polymer **4** showed a thermal stability up to 250°C according to its TGA thermogram. The T_g value of the polymer **4** measured by DSC was around 118°C. This T_g value is lower than those of the polyurethanes containing dioxybenzylidenemalononitrile, which are in the range 145–159°C [17] or dioxynitrostilbene, which are in the range 142–143°C [18]. The TGA and DSC studies showed that the decomposition temperature of the polyurethane **4** 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 film was corona-poled. As the

Table 1. Nonlinear optical properties of polymer **4**

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	Φ[c]	d_{31}[b] (esu)	Film thickness[d] (μm)	n
4	422	8.43×10^{-9}	0.19	2.62×10^{-10}	0.52	1.55

[a] Polymer film after poling.

[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes [20].

[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 [19].

temperature was raised gradually to 125°C, 6.5 kV of corona voltage was applied and this temperature was maintained for 30 min. The UV-Vis absorption spectra of the polymer before and after poling were recorded. After electric poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectrum of polymer **4** 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 **4** was equal to 0.19. SHG measurements were performed at a fundamental wavelength of 1560 nm using a mode locked Nd-YAG laser. NLO properties of polymer **4** 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 **4**. 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 Pascal fitting program according to the literature procedure [21]. The measured values of d_{33} and d_{31} for polymer **4** were 8.43×10^{-9} and 2.62×10^{-9} 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.

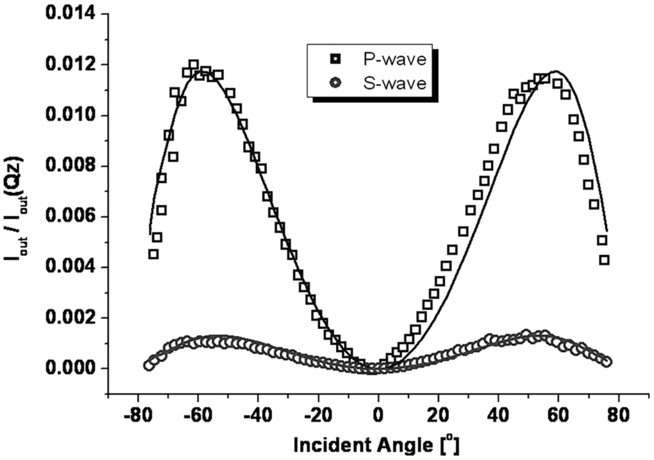


Figure 2. Angular dependence of SHG signal for a poled film of polymer **4**.

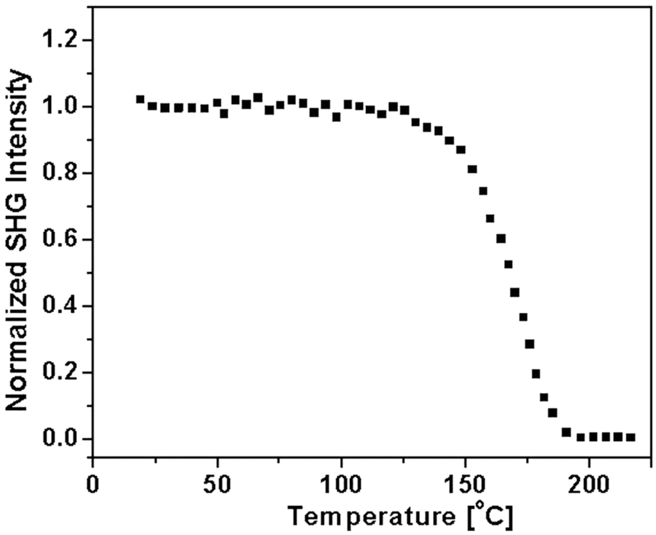


Figure 3. Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 4.5°C/min.

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 **4**. 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 4.5°C/min from 25°C to 220°C. The polymer film exhibited a greater thermal stability even at 12°C higher than T_g, and there was no SHG decay below 130°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 [21,22]. The enhanced thermal stability of SHG of polymer **4** is due to the stabilization of dipole 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.

Conclusions

We synthesized novel Y-type polyurethane **4** with pendant NLO chromophores, which are parts of the polymer main chains. This mid-type NLO polyurethane is soluble in common organic solvents. The resulting polymer **4** showed a thermal stability up to 250°C from TGA thermograms with T_g value near 118°C. The SHG coefficient (d_{33}) of corona-poled polymer film was 8.43×10^{-9} esu. The striking feature of this polymer is that it exhibits SHG stability even at 12°C higher than T_g, and no SHG decay was observed below 130°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 backbone, and partly by hydrogen bonds between the neighboring urethane linkages.

Acknowledgements

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