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Synthesis and characterization of a novel nonlinear optical polyurethane polymer

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Abstract

A cross-linked polyurethane with a novel nonlinear optical (NLO) chromophore [2-(4′-*N*,*N*-dihydroxyethylphenylazo)-3,5-dinitrothiophene] covalently incorporated for second-order optical nonlinearity was developed. High optical-quality films can be obtained from the prepared polymer. Resonance-enhanced second-harmonic coefficient (d_{33}) of 66 pm V^{-1} at 1.064 μm fundamental wavelength of the poled films was obtained. Test on temporal stability shows that when the films were kept in an oven at 100°C for 1000 h in air, 75% of the NLO signal still remained. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Nonlinear optical chromophore; Thiophene; Thermosetting; Polyurethane

1. Introduction

In the past decade, the research on organic nonlinear optical (NLO) materials has been developed quickly for their many merits such as easy molecular designing, larger electro-optic (E-O) coefficient, ultrafast response, excellent properties in processing, etc. At present, devices based on E-O polymers have begun to enter the market. However, several important properties such as E-O coefficient, dipole orientation stability and optical loss are still needed to be further investigated and improved. In order to achieve these objectives, many research groups have made a great deal of effort on optimizing the optical nonlinearity, stabilizing the dipole orientation, and decreasing the optical loss [1–13]. It has been shown that the dipole orientation in the polymer matrix can be frozen, and the temporal stability of the second-order NLO activity of the polymer can therefore be enhanced through attaching one or both ends of the aligned chromophores to polymer chains by thermal cross-linked schemes [5–8] and using a rigid polymer matrix with high glass transition temperature [9–13].

For a common donor–acceptor conjugated molecule, it is well known that its first- and second-order molecular nonlinear hyperpolarizabilities increase with increasing lengths of conjugation and increasing strengths of electron donor or electron acceptor. However, most extended conjugated compounds possessing more than two benzenoid rings are practically insoluble in most common organic solvents. It is quite difficult to synthesize and process them. Considering these limitations with benzenoid ring structures, we employed thiophene ring as the conjugating moieties between donor and acceptor substituents. Since the thiophene ring has a lower delocalization energy than that of benzene, its substitution in donor–acceptor compounds should be expected to result in an enhanced charge transfer properties and nonlinear responses than benzenoid rings.

In this paper, we designed and synthesized a new bifunctionalized NLO chromophore 5-dinitrothiophene (DHDT) containing a thiophene ring and two nitro groups, which can be directly incorporated into polymer

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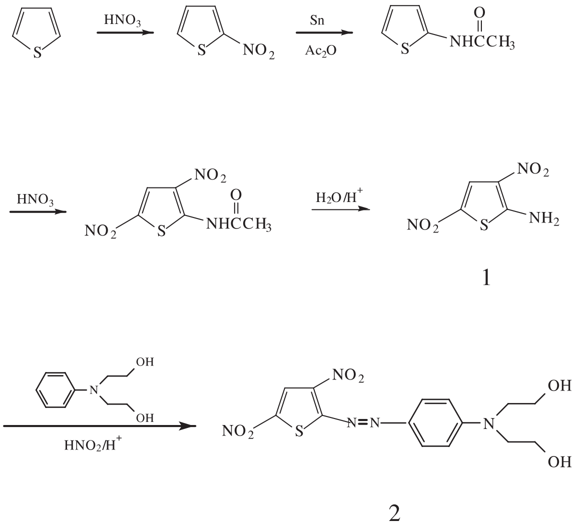
backbones. Through cross-linking reaction, the NLO monomers were covalently incorporated into the polyurethane backbone, so it was possible to gain higher dipole orientation stability. The prepolymer exhibited good solubility in common organic solvents and can be easily cast into optical-quality films. Resonance-enhanced second-harmonic coefficient of 66 pm V^{-1} at a 1.064 μm fundamental wavelength was obtained after cross-linking of the prepolymer. The SHG signal exhibited no decay at room temperature for a long time, and stability at 100°C was also observed.

2. Experimental

N,*N*-dihydroxyethyl aniline was purchased from Aldrich Chemical Co. and used as received. 4,4′-Diisocyanato-3,3′-dimethoxy-diphenyl was recrystallized three times from toluene before use. Dioxane was purified by refluxing in hydrochloric acid for 6–12 h, then distilled from sodium, stored in the dark and protected with nitrogen gas.

FTIR spectra were taken with a Bio-Rad FTS165 spectrometer. UV–VIS spectra were obtained with a UV–2001 spectrometer. MS spectra were recorded with a Trio-2000 spectrometer. ^{1}H-NMR spectra were obtained with a Varian Gemini-300 spectrometer. Elemental analysis was carried out with Heraeus CHN-RAPID instruments. The thickness of the films was measured with a model L116B step meter.

DHDT was synthesized in five steps, as shown in Scheme 1. 2-Methylthiophene, 2-acetylaminothiophene and 2-acetylamino-3,5-dinitrothiophene were synthesized according to the methods in the literature [14]. The numbering of the compounds is shown in Scheme 1.



Scheme 1. Synthesis of the monomer.

2.1. Compound 1

2-Acetylamino-3,5-dinitrothiophene (3.0 g, 13 mmol) and 50% sulphuric acid (30 ml) were added in a flask. The mixture was refluxed for 4 h at 100°C, then it was cooled and poured into 300 ml of ice water under vigorous stirring. A yellow precipitate was obtained. The product was filtered, washed with water, dried, and further purified by silica column chromatography using ethyl acetate and petroleum ether (v:$v = 1$:3) as eluent, yielding 1.3 g of compound 1 (53%). m.p.: 179–180°C. IR (KBr, cm^{-1}): 3418.39, 3353.99, 3273.64, 3185.38, 3112.03, 1614.85, 1550.52, 1529.9, 1487.84, 1405.17, 1353.05, 1249.52, 1050.71; ^{1}H-NMR(δ_H, DMSO-d_6, ppm) 8.1 (s, 1 H), 8.7 (s, 2H). Anal. calcd for $C_4H_3N_3O_4S$: C, 25.40%; H, 1.59%; N, 22.22%; S, 16.93%. Found: C, 25.86%; H, 1.61%; N, 21.71%; S, 16.81%.

2.2. Compound 2 (DHDT)

Sodium nitrite (0.482 g, 7 mmol) was added in portions into 5.7 ml of sulphuric acid and the mixture was warmed up to 60°C till the solid was dissolved completely. The mixture was then cooled to 5°C and another mixture of propionic acid (3.2 ml) and acetic acid (19 ml) was added slowly; the temperature rose up to 15°C and was then maintained at this temperature for 30 min. After the solution was cooled to 0°C, compound 1 (1.32 g, 7 mmol) was added over 30 min. The resulting solution was added to a solution of *N*,*N*-dihydroxyethyl aniline (1.27 g, 7 mmol) in 41 ml of water containing 1.9 ml of concentrated hydrochloric acid. The mixture was stirred for 50 min at 0°C, and the blue precipitate was filtered off. The product was washed with water and dried, further purified by silica column chromatography using ethyl acetate as eluent, yielding 0.98 g of compound 2 (37%). m.p.: 209–210°C. UV–VIS(λ_{max}, DMCO) 641 nm. IR (KBr, cm^{-1}): 3398.74, 3241.02, 2919.11, 1602.33, 1544.25, 1386.25, 1293.48, 1255.66, 1134.45. MS: 381(M^+); ^{1}H-NMR(δ_H, DMSO-d_6, ppm) 0.85(s, 2H, 2OH), 3.90(t, 8H, 4CH_2), 7.1–7.9(m, 4H, C_6H_4) 8.38(s, 1H, C_4HS). Anal. calcd for $C_{14}H_{15}N_5O_6S$: C, 44.09%; H, 3.94%; N, 18.37%; S, 8.40%. Found: C, 44.35%; H, 4.07%; N, 18.07%; S, 8.52%.

2.3. Prepolymer

Compound 2 (0.098 g, 0.257 mmol), 4,4′-diisocyanato-3,3′-dimethoxy-diphenyl (0.152 g, 0.514 mmol) and 2.5 ml dioxane were added into a two-necked flask. To accelerate the reaction, 0.02 ml of triethylamine was added as a catalyst. The resulting mixture was refluxed for 2 h under nitrogen atmosphere. Then, the solution of prepolymer was obtained. The solution was cooled and 0.025 g of triethanolamine (cross-linking agent) dissolved in 2 ml of dioxane was added. The mixture was continued to react for 1 h at 90°C, so that the prepolymer can be partly cross-linked.

2.4. Preparation of thin solid films

After being cooled, the above-obtained solution was filtered through a 2 μm Teflon filter and then spin-cast onto glass substrates. The polymer film was dried under vacuum for two days. The thickness of the film, which varied from 0.1–1 μm, can be controlled by adjusting the concentration of the solution and the spin-coating speed.

2.5. Cross-linking while poling

The above-obtained film was slowly heated to 160°C, while corona poling with d.c. electric field. The poling conditions were as follows: The film was heated from 20°C to 80°C during a period of 30 min, at an electric field of 4.6 $\mathrm{kV\,cm^{-1}}$; from 80°C to 120°C, 30 min, 5.6 $\mathrm{kV\,cm^{-1}}$; from 120°C to 160°C, 30 min, 6.3 $\mathrm{kV\,cm^{-1}}$; at 160°C for 30 min, 6.3 $\mathrm{kV\,cm^{-1}}$; was then cooled down to room temperature in the presence of the 6.3 $\mathrm{kV\,cm^{-1}}$ electric field to lock the poling-induced order. The poling current was 1–5 μA.

2.6. NLO measurement

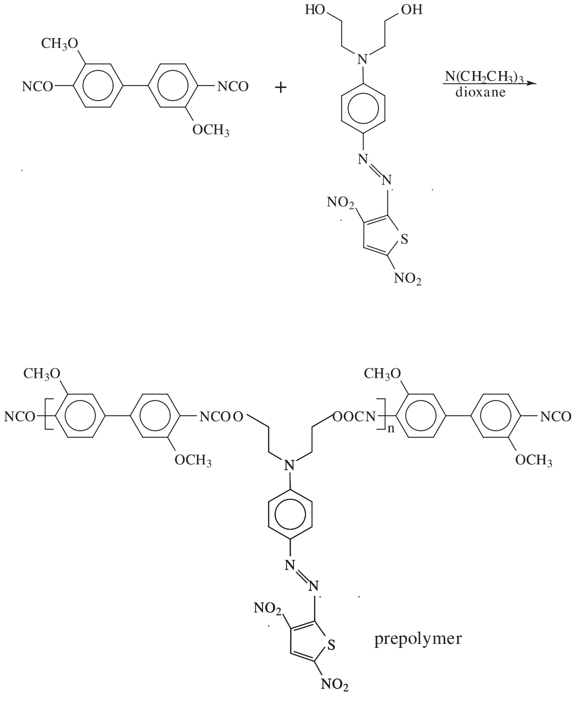
The SHG signal of the poled polymeric films was measured by using a Q-switched Nd:YAG laser (a pulse width of 8 ns and a repetition rate of 10 Hz) as a fundamental light source (1064 nm). The polymer sample was held at a 45–60° angle to the incident laser beam. A photomultiplier tube (PMT) was used to detect the SHG signal, which was amplified and averaged in a boxcar integrator.

3. Results and discussion

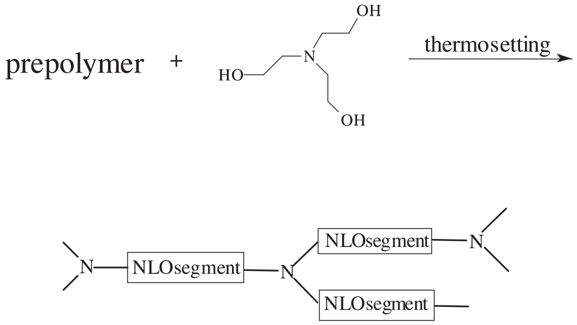
Monomer DHDT was prepared by the diazonium coupling reaction of 2-amino-3,5-dinitrothiophene with *N*,*N*-dihydroxyethyl aniline and further purified by silica column chromatography. During the monomer's synthesis, the key step was the synthesis of 2-amino-3,5-dinitrothiophene. Because 2-amino thiophene was a compound sensitive and unstable to light and heat, it could be oxidized quickly when exposed to air [15], which increased the difficulties of the synthesis and purification of its derivatives. In our selected synthesis routine, by introducing two strong electron acceptors (nitro), the amino's stability was increased significantly so that the stable and pure hydrolysis product, 2-amino-3,5-dinitrothiophene, could be obtained.

The monomer DHDT has two active hydroxyl groups, which can be incorporated into many polymers. Considering the anchoring of the chromophores into a three-dimensional network could significantly enhance the temporal stability of dipole alignment, we selected the cross-linked polyurethane system as the polymer backbone. So far, we still do not find any report on cross-linked polymer containing DHDT in the literature. The formation of the prepolymer is shown in Scheme 2, wherein 4,4′-diisocyanato-3,3′-dimethoxy-diphenyl was chosen because it was not very sensitive to the moisture compared to other common diisocyanates and the biphenyl units can increase the rigidity of the polymer chain. Because isocyanato is a group sensitive to moisture and any other group containing active hydrogen, all agents and glassware used in the synthesis of prepolymer need to be purified or dried before polymerization. Otherwise, the polymer film's quality could be affected greatly.

To carry out further cross-linking, triethanolamine was used as cross-linking agent (Scheme 3). A stoichiometric amount of the prepolymer and triethanolamine was mixed to form a clear solution which was pre-cross-linked for 1 h at 90°C and then cast into thin films. After



Scheme 2. Synthesis of the prepolymer.



Scheme 3. Formation of the cross-linked network.

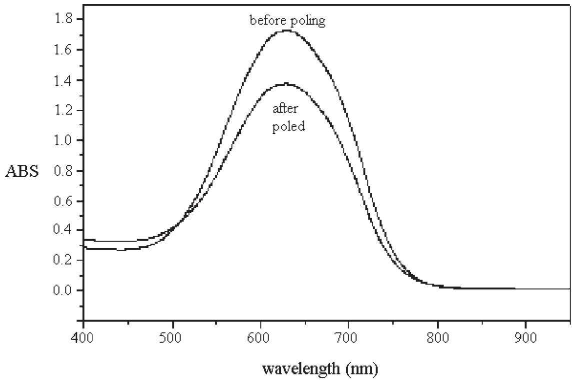


Fig. 2. UV-near-IR spectra of the polymer before and after poling.

the film was heated above 160°C for about 30 min, an extremely stable, tough and chemically inert film with a high optical quality can be obtained. It is worth noting that during the processing, the pre-cross-linking for 1 h at 90°C is beneficial to the film quality. One possible reason is that the prepolymer's sensitivity to moisture decreases after it is partly cross-linked. The thermally cured polymer was insoluble in common organic solvent, such as chloroform, dioxane, *N*,*N*-dimethylformamide, and *N*-methyl-2-pyrrolidine. However, the prepolymer before thermal curing was soluble or partially soluble in these solvents. The results indicated that the prepolymer was completely cross-linked with triethanolamine. As shown in Fig. 1, FTIR spectra provided further evidence. After the prepolymer film was heated at 80°C for 1 h, the absorption of the isocyanate group at 2241 cm^{-1} was reduced, and the absorption of the ester group at 1742 cm^{-1} was increased compared with the pristine film; after continuing to be heated at 120°C for 1 h, the absorption of isocyanate group was continually reduced and the absorption of ester group become stronger; following heating at 160°C for 5 min, the 2241 cm^{-1} peak disappeared completely, while the other absorption bands remain unchanged. These data give a clear indication of how the cross-linking progressed.

Fig. 2 gives the UV-near-IR spectra of the polymer with and without poling. As the result of the alignment of the chromophore dipoles along the poling field direction, we can see the absorption maximum of the chromophore at 629 nm shifted to 625 nm and the peak intensity decreased. The ordering parameter of the poled films can be calculated from it [16]. This was found to be 0.21. In order to prove that the decrease of the peak absorption is not induced by the decomposition of the chromophores, the polymer film without poling was heated at 160°C for 30 min and less than 1% decrease of the peak intensity in its UV–VIS spectrum was observed. That means that the decrease in the peak intensity after poling is the result of dipole orientation, as the vector of

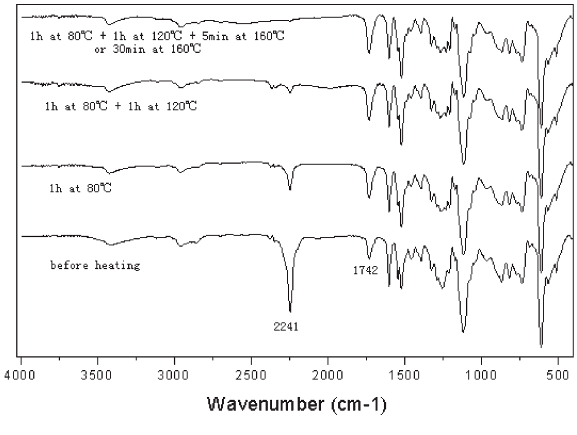


Fig. 1. Fourier transform infrared spectra of the cross-linked polymer at different cross-linking stages.

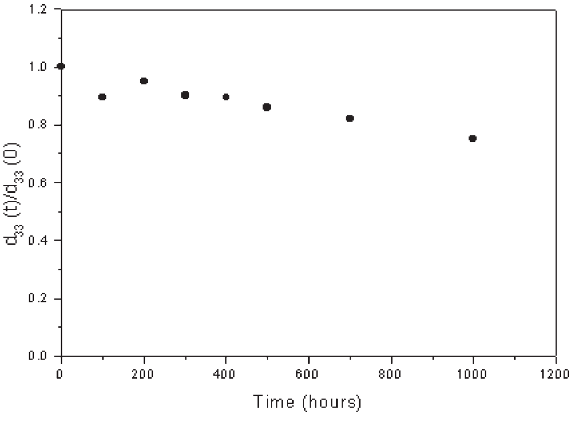


Fig. 3. Temporal behavior of the second-order NLO coefficient, $d_{33}(t)/d_{33}(0)$, at 100°C in air.

the molecular dipole is moved to the position perpendicular to the vector of the electric field of the light beam.

Second harmonic generation measurements were performed by using a Nd:YAG laser. A resonance-enhanced d_{33} coefficient of 66 pm V^{-1} at a fundamental wavelength of 1064 nm was obtained. As we expected, the cured polymers indeed exhibit large and stable optical nonlinearity. No obvious decay in the d_{33} value was detected at room temperature for over two months. For practical applications, E-O polymer devices need to meet reliability standards which require the device to be stably operated for thousands of hours at 80–125°C. Fig. 3 shows the temporal behaviour of the second-order NLO coefficient, $d_{33}(t)/d_{33}(0)$, at 100°C, as *d* function of the time. Long-term stability was observed even when the films were kept in an oven at 100°C for 1000 h, and 75% of the signal still remained.

4. Conclusion

A new NLO chromophore was synthesized and covalently incorporated into a polyurethane network. Through efficient poling and cross-linking, a large resonance-enhanced second-harmonic coefficient (d_{33}) of 66 pm V^{-1} at a 1.064 μm fundamental wavelength from the poled film was obtained and a high temporal stability of the polar order was also observed when the films were kept in an oven at 100°C.

Acknowledgements

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