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Synthesis and characterization of an active styrlthiophene monomer and its polyurethane with second-order optical nonlinearity

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A novel monomer, (*trans*)-7-[4-*N*,*N*-(di-β-hydroxyethyl) amino-benzene]-ethenyl-3,5-dinitrothiophene (HBDT), and the corresponding prepolymer, polyurethane were synthesized and characterized. The details of synthesis of the monomer and its further polymerization were presented. The prepolymer and polyurethane exhibited good thermal stability and good solubility in common organic solvents. The d_{33} coefficient of the poled films was determined to be 40.3 pm/V. © *2000 Kluwer Academic Publishers*

1. Introduction

Heterocyclic polymers, including polyimides, are typically high-T_g polymers due to their rigid backbone, strong interactions between the polymer chains, and high degree of crystallinity or cross-linking [1]. Because of their excellent thermal stability, they are good candidates for use as second-order nonlinear optical materials [2–7].

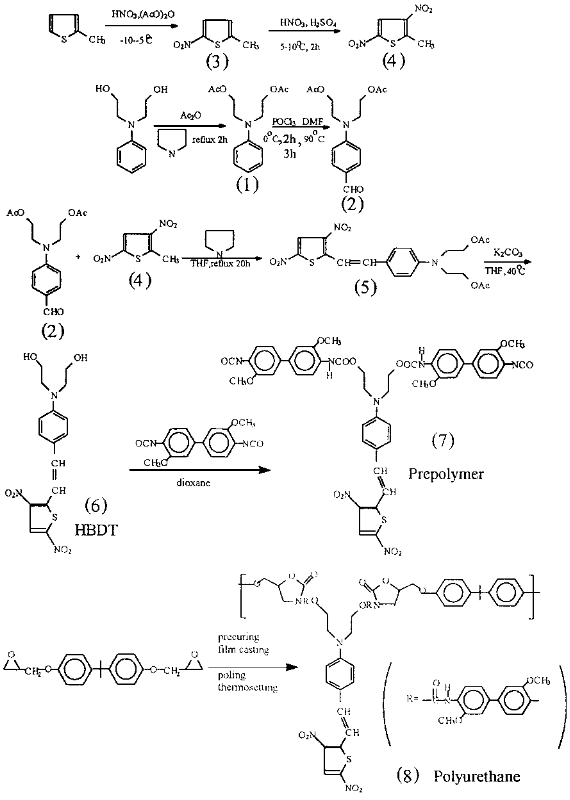
One problem associated with high-T_g polymers is solubility. For example, many polyimides are not soluble and polyamic acids have limited solubility in common organic solvents and polar solvents such as 1-methyl prolidinone (NMP), N,N-dimethylacetamide (DMAc), DMSO must be used. To obtain processible heterocyclic polymers for second order nonlinearity, one should use oligomers that are soluble in common organic solvents and can be processed into thin films. These oligomers should contain end-capped functional groups that can be thermally cured into heterocyclic polymers. The conditions of the thermal curing and poling process should be carefully controlled, because the chain growth and/or cross-linking deriving from curing not only increases T_g but also increases the fraction of as-yet-unreacted functional groups that become fixed in the network and spatially isolated. In this communication, we describe an approach employing a chromophore with nonlinear optical (NLO) properties containing prepolymer to synthesize a thermally stable polyurethane and show that the polymer can be efficiently poled. The NLO properties are also presented.

2. Experimental

2.1. Synthesis of monomer and polymers

The synthetic scheme of the monomer 6 (HBDT), prepolymer 7 and polyurethane 8 are shown in Scheme 1.

Scheme 1



Syntheses scheme of monomer 6 (HBDT), prepolymer 7 and polyurethane 8

2.1.1. *Diacetyl-N-phenyldiethanolamine (1) [8]*

A solution of N-phenyl-diethanolamine (25.0 g, 0.138 mol), acetic anhydride (31.0 g, 0.31 mol), and pyridine (25.0 g, 0.356 mol) was refluxed for approximately two hours under a nitrogen atmosphere. The resulting solution was cooled and vacuum distilled (160 °C/130 Pa) to yield a diacetate (34.3 g, 93.7%) as a pale golden colored oil. IR (liquid film, cm^{-1}): 3451, 2962, 2896, 1738, 1599, 1507, 1380, 1229, 1036, 750, 696.

2.1.2. 4-formyl-diacetyl-N-phenyldiethanolamine (2) [8]

Phosphorus oxychloride (22.0 g, 0.144 mol) was added dropwise at 0 °C to 1×10^{-4} m^3 of N,N′-dimethylformamide (DMF), and the resulting solution was stirred at 0 °C for two hours. A solution of diacetate (34.3 g, 0.129 mol) in 1×10^{-4} m^3 DMF was added slowly, and the reaction mixture was heated to 90 °C for three hours. After cooling, the solution was poured onto 2×10^{-3} m^3 of ice water containing 60 g of sodium carbonate. The mixture was stirred for 24 hours and the resulting solid was collected by vacuum filtration to give a total of 31.1 g of (2), (82% yield from diacetate) as a pale brown solid, and used without further purification. The characterization result were as follow: melting point (mp) 39 °C. IR (KBr pellet, cm^{-1}): 2991, 2819, 2746, 1737, 1723, 1675, 1598, 1561, 1525, 1409, 1227, 1173, 1116, 1044, 979, 903, 820, 710, 597. ^{1}H NMR (CD_3OD) δ: 2.14(s, $-CH_3$, 6H), 3.7560 (t, $-CH_2O-$, $J = 6.03$, $J = 6.00$, 4H), 4.2825 (t, $-CH_2N-$, $J = 5.85$, $J = 5.97$, 4H), 6.9286 ~ 7.7552(dd, $J = 8.87$, $J = 9.09$, 4H), 9.65(s, 1H).

2.1.3. 2-methyl-5-nitrothiophene (3) [9]

A nitrating mixture was first made by adding 12 g fume nitric acid ($d = 1.51$), drop by drop to 24 g acetic anhydride, cooled to −10 to −5 °C and this was then added slowly with continuous agitation to 15 g of 2-methylthiophene diluted with 30 g acetic anhydride and cooled to −10 °C. In spite of the low temperature, a considerable amount of colouring occured. The nitration mixture was poured on to ice and the solution was neutralized with solid Na_2CO_3, and taken up in ether. The ether solution was dried with $MgSO_4$ and the ether evaporated. The residue was distilled in steam, again extracted with ether and distilled in a vacuum, the fraction boiling at 104 °C/2 KPa, the weight of distillate (3) was 7 g (82% yield). IR (liquid film, cm^{-1}): 3105, 3083, 3061, 3027, 2919, 2851, 2364, 1946, 1715, 1601, 1450, 1357, 1220, 1159, 1134, 1069, 968, 812.

2.1.4. 2-methyl-3,5-dinitrothiophen (4) [9]

2-methyl-5-nitrothiophen 2 g was introduced a small portion at a time into a mixture of 8 g fume nitric acid ($d = 1.51$), and 8 g concentrated sulphuric acid, kept at a temperature of 5–10 °C by cooling in iced water. The nitration mixture was again stirred for 30 minutes and poured onto ice, and the crystalline mass, 2 g of (4) was separated as a crystal from ethanol. The yield was 76% and the m.p. of the glittering leaf-like product was 99–100 °C . Elemental analysis for $C_5H_4N_2O_4S$, Calc. (%): C, 31.92; H, 2.14; N, 14.89; S, 17.04. Found (%): C, 31.61; H, 2.12; N, 14.23; S, 16.52. IR (KBr pellet, cm^{-1}): 3442, 3111, 1555, 1511, 1329, 1103, 1040, 889, 818, 731, 675. ^{1}H NMR ($(CD_3)_2CO$)δ : 2.8978 (s, $-CH_3$, 3H), 8.3916 (s, 1H). MS (%): 188(M^+, 36.44), 173(M^+-15, 4.36), 171(75.35), 95(83.10), 69(85.92), 51(67.61), 44(100).

2.1.5. (Trans)-7-[4-N,N-di-(β-diacetoxyethyl) amino benzene] ethenyl 3,5-dinitrothiophene (5)

Distilled pyrrolidine (2 drops) and 2-methyl-3,5-dinitrothiophene (4) (0.94 g, 5 mmol) were added to a solution of 4-formyl-diacetyl-N-phenyldiethanolamine (2.2 g, 7.5 mmol) (2) in 40×10^{-6} m^3 of dry THF. The mixture was refluxed for 20 h. THF was then evaporated and the residue was recrystallized from methanol ($3 \times 20 \times 10^{-6}$ m^3) to yield shining black crystals (5) (1.3 g, 56%). m.p. 169–170 °C. Elemental analysis for $C_{20}H_{21}N_3O_8S$, Calc. (%): C, 51.83; H. 4.57; N, 9.07; S, 6.92. Found (%): C, 51.69; H. 4.44; N, 8.79; S, 6.81. IR (KBr, cm^{-1}): 2975, 2928, 2848($-CH_2-$, CH_3), 1738($-CO-$), 1584, 1382 (thiophene ring), 1538, 1318($-NO_2$), and 1271 ($-C-O-$ $C-$). ^{1}H NMR (DMSO-d_6, δ): 1.9785 (s, $-CH_3$, 6H), 3.6984(t, $-CH_2O-$, 4H), 4.1834 (t, $-CH_2N-$, 4H), 6.8722–7.6183(dd, $-C_6H_4-$, $J = 8.58$, $J = 9.06$, 4H), 7.6801–7.8692(dd, $-CH{=}CH-$, $J = 16.02$, $J = 15.90$, 2H) and 8.4524(s, 1H). MS (%): 463(M^+, 4.62), 87(100) and 43(85.90).

2.1.6. (Trans)-7-[4-N,N-di-(β-hydroxyethyl) amino benzene] ethenyl 3,5-dinitrothiophene(monomer 6, HBDT)

A mixture of compound (5) (1.0 g, 2.15 mmol) in THF (40×10^{-6} m^3), potassium carbonate (4 g, 28 mmol) and a little tetrabutylammonium bromide in water (10^{-4} m^3) was warmed to 40 °C for 24 h with stirring. The reaction mixture was concentrated and extracted with chloromethane (3×10^{-4} m^3), the organic layers was washed with water ($2 \times 0.5 \times 10^{-4}$ m^3), dried (sodium sulphate), and evaporation of the solvent affords a syrup which was purified via flash column chromatography (silica gel, ethyl acetate/hexane, 90/10) affording HBDT (0.36 g, 22%) as a blue-black crystals, m.p. 218 °C. Elemental analysis for $C_{16}H_{17}N_3O_6S$, Calc. (%): C, 50.65; H. 4.52; N, 11.08; S, 8.43. Found (%): C, 50.57; H. 4.45; N, 10.80; S, 8.35. IR (KBr, cm^{-1}): 3384, 3110, 2927, 1737, 1612, 1537, 1522, 1382, 1315, 1267, 1182, 1046, 820, and 725. ^{1}H NMR (DMSO-d_6, δ): 3.5334 (t, $-CH_2O-$, 4H), 3.5409 (t, $-CH_2N-$, 4H), 6.7834–7.5585(dd, $-C_6H_4-$, $J = 9.81$, $J = 9.91$, 4H), 7.7291~7.7959(dd, $-CH{=}CH-$, 2H) and 8.4567(s, 1H) as shown in Fig. 1. MS (%): 379(M^+, 17.92) and 348(M^+-31, 100). UV-vis (CH_3OH, λ_{max}): 200, 276 and 530 nm.

2.2. Synthesis of the polymer

The HBDT prepolymer was prepared following the literature method with some modifications. HBDT

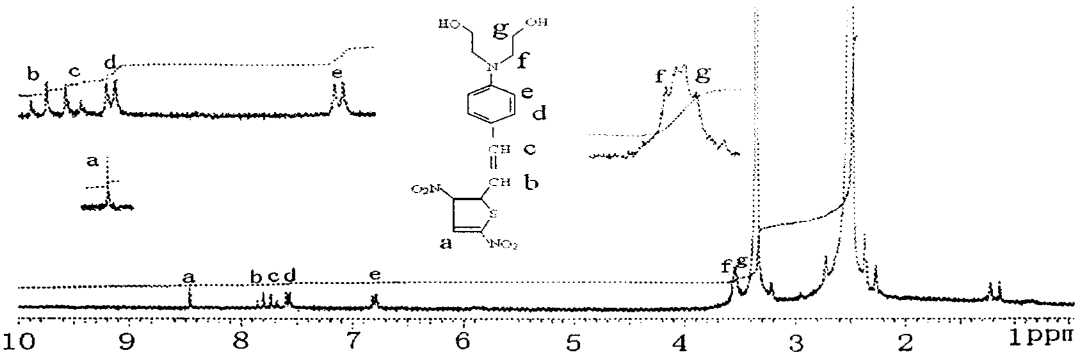


Figure 1 ^{1}H-NMR spectrum of HBDT (DMSO-d_6, 300 MHz).

(6, 0.3790 g, 1.000 mmol) and 4,4′-diisocyanato-3,3′-dimethoxydiphenyl (0.6222 g, 2.100 mmol) were added to dioxane (10^{-5} m^3). The equivalent amount of 4,4′-diisocyanato-3,3′-dimethoxydiphenyl was added to facilitate the formation of the prepolymer. The resulting mixture was refluxed for 2 h under nitrogen atmosphere. The solution was cooled to room temperature and then filtered through a 0.2 μm Teflon filter. The solvent was removed by vacuum evaporation, and a purple blue solid prepolymer (0.8694 g, 89.5%) was obtained. The prepolymer was stored in a drybox.

Bisphenol A diglycidyl ether (BADGE, 4, 1.7020 g, 5.000 mmol) was dissolved in 5×10^{-5} m^3 of dioxane to form a 0.100 mM solution. The HBDT prepolymer (0.0971 g, 0.1 mmol) was dissolved in BADGE/dioxane solution (10^{-6} m^3, 0.1 mmol of BADGE). The mixture was precured at 85 °C for 1 h. The resulting solution was filtered and spin-coated onto normal glass slides. The thickness of blue film was measured by alpha-step 250 TENCOR instruments, and found to very from 0.75 to 1.50 μm, depending on the precuring time and the spin rate. The films were dried for 12 h in a vacuum at 100 °C. The ultraviolet spectra of the polyurethane film containing HBDT is shown in Fig. 4. Maximum absorption peak is located at 465 nm.

2.3. The corona poling of the polyurethane containing monomer HBDT

After the films were dried, they were poled and cured at elevated temperatures using a corona-discharge setup, with a tip-to-plane distance of 15 mm. The poled polymer films were cooled to room temperature in the presence of the electric field to freeze in the poling-induced order. The poling voltages and temperatures, which affect both the poling efficiency and polymerization, were so selected that poling efficiency and polymerization were optimized while the film quality was preserved (Fig. 2). To precure the prepolymer, the films were heated to 110 °C for 5 min and then cooled to 100 °C and maintained at that temperature for 5 min, then a corona voltage of 6 kV was applied for 10 min, and 10.7 kV was applied for 25 min at 100 °C. The precuring step was necessary because the high voltage can damage the prepolymer films.

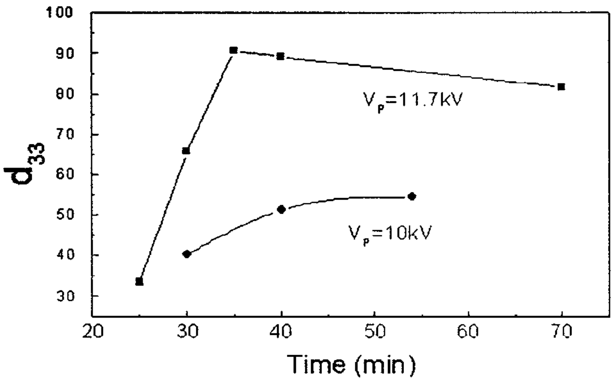


Figure 2 Relationship of d_{33} and poling time for polyurethane film containing HBDT.

3. Results and discussion

3.1. Synthesis and characterization of the chromophore monomer

(Trans)-7-[4-*N*,*N*-di-(β-diacetoxyethyl) amino benzene] ethenyl 3,5-dinitrothiophene (5) was synthesized by the condensation of an aromatic aldehyde (2) with 2-methyl-3,5-dinitrothiophen (4), which is the product of two-stage nitration of 2-methylthiophen. Owing to the methyl group of the compound (4) is sufficiently activated by the vicinal nitro groups to enable the methyl group facile condensation with the aldehydes, thus, compound (5) were obtained in 56% yield. After agitation for 20 hr at 40 °C, compound (5) was hydrolysed with a potassium carbonate solution in the catalyst, tetrabutylammonium bromide. The crude HBDT was extracted with dichloromethane and purified by column chromatography to obtain pure HBDT in 22% yield as a blue-black crystals. The coupling constant (15.90–16.02 Hz) for the olefinic protons in ^{1}H-NMR(DMSO-d_6, 300 MHz) spectrum of HBDT (cf. Fig. 1) indicated that this compound is in the trans configuration.

3.2. Synthesis and characterization of the polymers

The isocyanate group in the prepolymer reacts with the epoxy group to form an oxazolidone ring upon heating [10]. The 4,4′-Diisocyanato-3,3′-dimethoxydiphenyl chain segment is more flexible than tolylene 2,4-diisocyanate in the polymer. The HBDT can form a

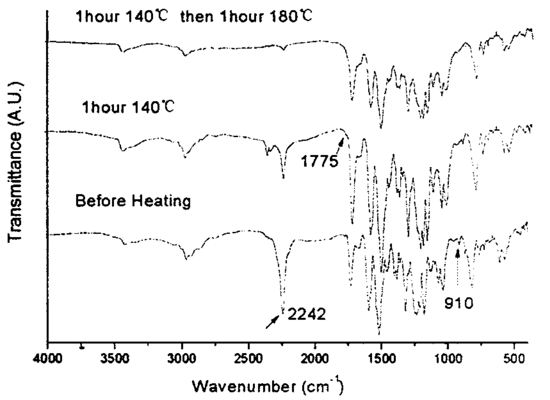


Figure 3 FTIR spectra of the polyurethane at different polymerization stages. The arrows at 2242, 1775, and 910 cm^{-1} indicate the disappearing isocyanate group, the emerging oxazolidone, and the disappearing epoxy, respectively.

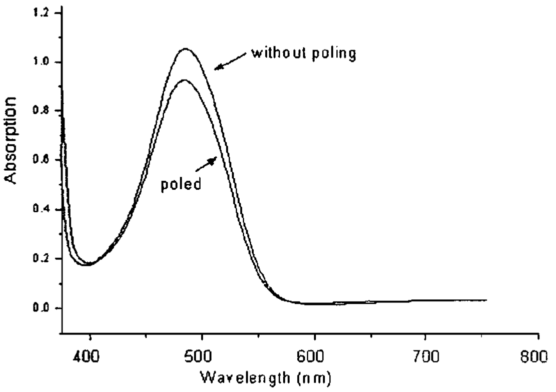


Figure 4 The UV-vis absorption spectra of the polyurethane, with and without poling.

linear chain prepolymer with the isocyanate group and further form a polyurethane. This is demonstrated by the FT-IR spectra of the prepolymer with BADGE heated at different temperatures for different periods time as shown in Fig. 3. When the prepolymer with a stoichiometrically equal amount of BADGE was heated at 140 °C for 1 h, the peak at 2242 cm^{-1} associated with isocyanate and the peak at 910 cm^{-1} associated with the epoxy group decreased, while the peak at 1775 cm^{-1} associated with polyurethane appeared. After the polymer was further heated at 180 °C for 1 h, the peak at 2242 cm^{-1} and 910 cm^{-1} almost completely disappeared, indicating the polymerization was nearly complete. Besides changes in those three peaks, no other change was observed in the FT-IR spectra. This demonstrates that the HBDT chromophores do not degrade during the thermal curing process. No isocyanurate function, whose characteristic absorption is at 1710 cm^{-1} (isocyanurate carbonyls), was observed in the spectra after the polymer was heated. This observation clearly indicates that the side reaction, trimerization of isocyanate to form isocyanurate, did not occur.

The UV-vis absorption spectra of the polyurethane, with and without poling, are shown in Fig. 4. The spectra were obtained with films treated with the same heating profile described above and with or without the electric field applied. Using these procedures, the bleaching at ∼480 nm caused by high temperatures is eliminated from the data and the absorbance change solely resulted from the applied voltage. The absorption maxima with poling and without poling are 460 and 465 nm, respectively. The spectra exhibited a blue shift upon poling. The absorption peak is due to the intramolecular charge transfer band of the NLO chromophores. Alignment of chromophore dipoles along the poling field direction, which is the incident light direction as well, will cause the peak absorbance to decrease. If one assumes that the molecular electronic transition moment is parallel to the permanent ground-state dipole moment, one can obtain the order parameter Φ by measuring the absorbance of an unpoled system A_0 and of a poled sample with light polarized perpendicular to the poling direction $A_\perp$: $\Phi = 1 - (A_\perp / A_0)$ [11]. From the absorbance change, the ordering parameter was determined to be 0.134. the second-order NLO properties of the poled films were characterized by second harmonic generation (SGH) at 1064 nm fundamental wavelength, with a Y-cut quartz crystal ($d_{11} = 0.5$ pm/V) as the reference. A SGH d_{33} coefficient of 40.3 pm/V (film thickness 1.10 μm) was obtained. This moderate value may be accounted for by the relatively low loading density of 70% of the NLO chromophore incorporated in the polymer and the relatively low β value of the NLO chromophore. $\beta\mu$ value of 3.54×10^{-54} m^4 V^{-1} of the monomer (HBDT) was measured by solvatochromism.

From our experience, the materials have long-term stability (i.e., 70% of the NLO signal remains after 300 h) at a temperature approximately 80 °C where the NLO activity starts to decrease. Another polyurethane is produced by cross-linking prepolymer 7 with triethanolamine. A SGH d_{33} coefficient of 16.5 pm/V (film thickness 0.174 μm) was obtained. Because of its relatively high nonlinearity and excellent processibility, the thermosetting polyurethane is still being used for device fabrication years after its introduction. However, poor thermal stability is a serious problem with this material. The polyurethane described here possesses the same processibility and higher stability. The rigidity of the heterocyclic ring is responsible for the improvement in thermal stability of the polyurethane.

In conclusion, we have prepared a new polyurethane with NLO chromophores covalently incorporated. The materal exhibited excellent processibility, good thermal stability, and a moderate SHG signal. The synthesis scheme is desirable because it is easy to execute and can be extended to prepare other polymers with better NLO properties.

Acknowledgement

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