

SYNTHESIS AND CHARACTERIZATION OF A NOVEL STYRYLTHIOPHENE MONOMER AND CORRESPONDING POLYURETHANE FOR NLO MATERIALS

Jiang-hong Wang*, Jian-feng Zhai, Jia-yun Zhou, Yu-xia Zhao and Yu-quan Shen
Institute of Photographic Chemistry, Academia Sinica, Beijing 100101, China

Abstract A novel monomer, (*trans*)-7-[4-*N,N*-(di- β -hydroxyethyl) amino-benzene]-ethenyl-3,5-dinitrothiophene (HBDT), was synthesized and characterized. The details of synthesizing the monomer and prepolymer, polyurethane with the monomer covalently incorporated are presented. The prepolymer and polyurethane exhibited good solubility in common organic solvents. Molecular nonlinear optical properties of the monomer (HBDT) substituted thiophene based stilbenes is presented.

Keywords Polyurethane, Thiophene, Hyperpolarizability

INTRODUCTION

It is well-known that the first and second-order molecular nonlinear hyperpolarizability (β , γ) increase with increasing donor and acceptor strengths and with increasing length of conjugation.^[1] Many donor-acceptor conjugated organic molecules reportedly fall into the following categories: substituted benzenes, biphenyls, stilbenes, azobenzenes and Schiff bases^[2, 3]. However, optical studies on compounds containing more than two benzenoid rings were rare. This could be attributed, in part, to the difficulty in the synthesis of extended conjugated compounds possessing more than two benzenoid rings as they are practically insoluble in most common organic solvents. Considering these limitations with benzenoid ring structures, there exists a need to explore and develop new organic chromophores with efficient nonlinearities, desired solubilities and high thermal and photochemical stabilities.

We employed five-membered thiophene as the conjugating moieties between donor and acceptor substituents. Since thiophene has a lower delocalization energy than that of benzene^[4], it can offer better effective conjugation than that of benzene in donor-acceptor compounds and its substitution in donor-acceptor compounds should be expected to result in enhanced charge-transfer properties and nonlinear responses than benzenoid rings. Here, we have synthesized (*trans*)-7-[4-*N,N*-(di- β -hydroxyethyl) amino benzene]-3,5-dinitro-ethenyl thiophene (HBDT) monomer and the monomer was further polymerized in 2 steps to form a polyurethane. $\beta\mu$ value of the monomer is dramatically enhanced by using thiophene as a conjugating moiety in (di- β -hydroxyethyl) amino-dinitro substituted stilbenes as shown in Table 1(f).

Electronic absorption spectra of all the push-pull compounds listed in Table 1 demonstrate an intense lowest energy charge-transfer absorption band in the visible region. The energy of this

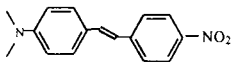
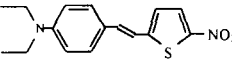
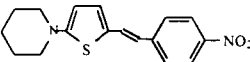
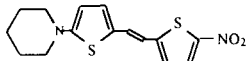
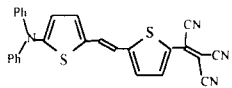
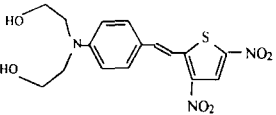
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** Corresponding author: Jian-hong Wang (王江洪), E-mail: shenyq@ipc.ac.cn

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lowest absorption band reflects the charge-transfer properties of these compounds, and is a function of the donor and acceptor strengths as well as the length and effectiveness of conjugation. Comparison of the electronic absorption spectra of 4-dimethylamino-4'-nitrostilbene (DANS) **a**, **c**, and **d** reveals that the replacement of any benzene ring with a thiophene ring causes a dramatic red shift of the charge-transfer band. This observation clearly indicates that the incorporation of thiophene moieties in push-pull compounds enhances their charge-transfer properties.

Table 1 Electronic absorption spectra and corresponding $\beta\mu$ value of the compounds a~f

Compound	$\lambda_{\max}$ (nm) in dioxane	$\beta\mu$ (10^{-48} esu) at 1907 nm	Ref.
a 	424	580	[5]
b 	478	600	[5]
c 	460	660	[5]
d 	516	1040	[5]
e 	665	10200	[6]
f 	530*	8443	—

* in methanol

EXPERIMENTAL

FTIR spectra were obtained using a BIO-RAD FTS-165 IR spectrometer, and UV-visible absorption spectra were measured on UV-1601PC Shimadzu spectrophotometer. MS, $^1\text{H-NMR}$ and elemental analysis were measured on Trio-2000, Varian Gemini 300 operating at 300 MHz, and Heraeus CHN-RAPID instruments, respectively. The solvents for polymerization, dioxane and THF, and the catalyst pyrrolidine were further purified by distillation over sodium. They were stored in a drybox before use. All reactions were monitored by TLC prior to work-up. Solvents were removed with a rotary evaporator. TLC was performed on silica plates 60 F₂₅₄ (Merck) and visualised with UV fluorescence (254 and 365 nm). 4,4'-Diisocyanato-3,3'-dimethoxydiphenyl was purchased from Pfaltz & Bauer and was purified by recrystallization from methanol prior to use. 2-methylthiophen was obtained from Aldrich Co..

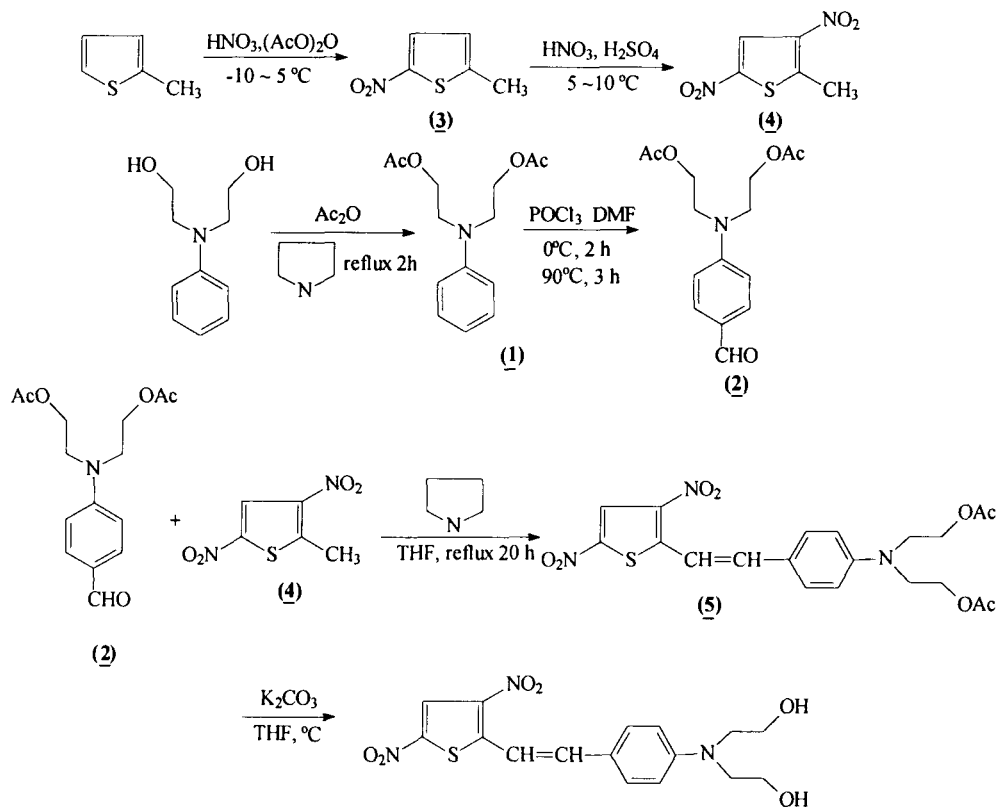
Synthesis of Monomers

HBDT was synthesized according to the reaction scheme illustrated in Fig. 1. Diacetyl-N-phenyldiethanolamine (**1**), 4-formyl-Diacetyl-N-phenyl diethanolamine (**2**), 2-methyl-5-nitrothiophene (**3**), and 2-methyl-3,5-dinitrothiophene (**4**) were synthesized according to the literature^[7, 8].

(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**) (0.94g, 5 mmol) were added to a solution of 4-formyl-diacetyl-N-phenyldiethanolamine (2.2 g, 7.5 mmol) (**2**) in 40 mL of dry THF. The mixture was refluxed for 20 h. THF was then evaporated and the residue was

recrystallized from methanol to produce shining black crystals (**5**) (1.3g, 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 ($-C-O-C-$). ^1H -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 m (*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).



HBDT

Fig. 1 Synthesis of monomer

(Trans)-7-[4-N,N-di-(β-Hydroxyethyl) Amino Benzene] Ethenyl 3,5-Dinitrothiophene(Monomer (HBDT))

A mixture of compound (**5**) (1.0g, 2.15 mmol) in THF (40 mL), potassium carbonate (4 g, 28 mmol) and a little tetrabutylammonium bromide in water (100 mL) was warmed to 40°C for 20 h with stirring. The reaction mixture was concentrated and extracted with chloromethane (3×100 mL) and the organic layers were washed with water (3×150 mL) and dried (sodium sulphate). Evaporation of the solvent produces a syrup which was purified via flash column chromatography (silica gel, ethyl acetate/hexane, 90/10) yielding HBDT (0.36g, 22%) as 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, 50.61; 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. ^1H -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). MS (%): 379 (M^+ , 17.92) and 348 ($M^+ - 31$, 100). UV-vis (CH₃OH, λ_{max}): 200, 276 and 530 nm. The UV-visible spectrum of HBDT in methanol is shown in Fig. 2.

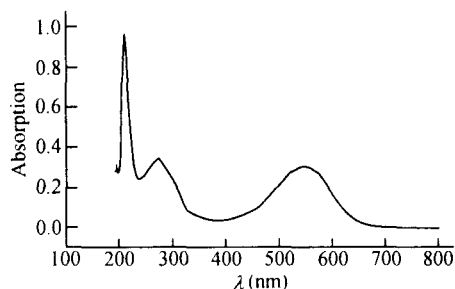


Fig. 2 UV-visible spectrum of HBDT in methanol

Synthesis of the Polymer

The preparation of polyurethane containing HBDT monomer is shown in Fig. 3. HBDT prepolymer: HBDT (0.3790g, 1.000 mmol) and 4,4'-diisocyanato-3,3'-dimethoxydiphenyl (**6**) (0.6222g, 2.100 mmol) were added to dioxane (10.0 mL). The resulting mixture was heated and refluxed for 2 h under nitrogen atmosphere. The solution was cooled to room temperature and then filtered. The solvent was removed by vacuum evaporation, and a purple blue solid prepolymer (0.8694g, 89.5%) was obtained. The prepolymer was stored in a drybox.

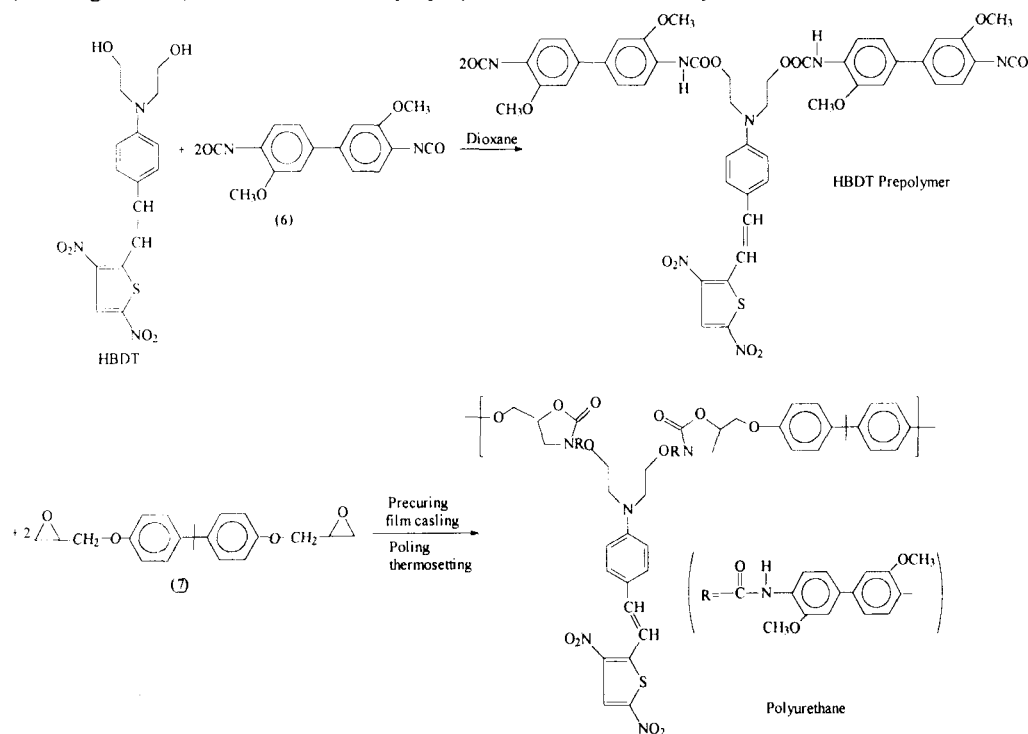


Fig. 3 Synthesis of HBDT prepolymer and polyurethane

The Formation of the Polyurethane Containing HBDT and Corona Poling

Bisphenol A diglycidyl ether (BADGE, (**7**), 1.7020 g, 5.000 mmol) was dissolved in 50.00 mL of dioxane to form a 0.100 mM solution. The HBDT prepolymer (0.0971g, 0.1 mmol) was dissolved in BADGE/dioxane solution (1.00 mL, 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 was found to vary from 0.75 to 1.0 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 are shown in

Fig. 4. The maximum absorption peak is located at 470 nm.

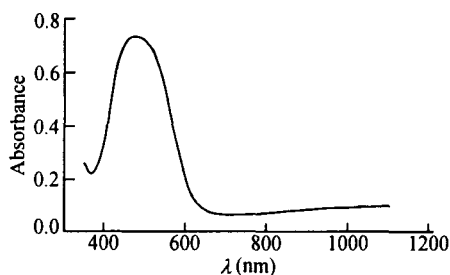


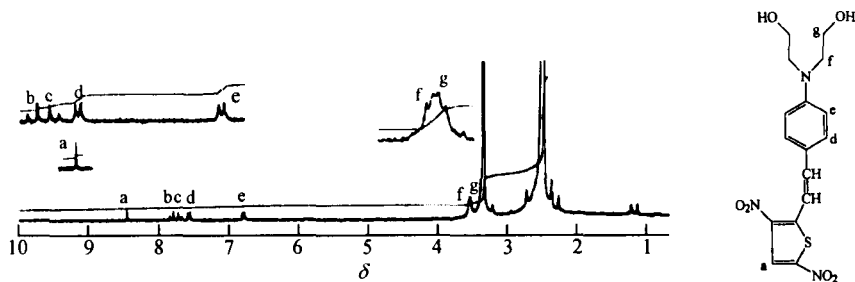
Fig. 4 UV-visible spectrum of the polyurethane film containing HBDT

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 1.0 cm. The poled polymer films were cooled to room temperature in the presence of the electric field to freeze in the poling-induced order. To pre-cure the prepolymer, the films were heated to 140°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 0.5 h, and 9 kV was applied for 0.5 h at 100°C. The molecular second order nonlinear hyperpolarizabilities (β) of the poling films will then be measured.

RESULTS AND DISCUSSION

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-dinitrothiophene (**4**), which is the product of two-stage nitration of 2-methylthiophene. Due to the fact that 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, compound (**5**) was obtained in 56% yield. After agitation for 20 h 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 crystal.

Fig. 5 ^1H -NMR spectrum of HBDT(DMSO- d_6 , 300MHz)

The coupling constant (15.90–16.02 Hz) for the olefinic protons in ^1H -NMR (DMSO- d_6 , 300 MHz) spectrum of HBDT (cf. Fig. 5) indicated that this compound is in the *trans* configuration.

In HBDT a rod-like thirteen π -electrons delocalization system containing a thiophene ring (π_5^6) will have large nonlinear effects; and the thiophenes heterocycle, which contains sulfur atoms rich in electrons can also enhance the solubility of the monomer, which is normally insoluble in common organic solvents. In fact, HBDT readily dissolved in common solvents like methanol, acetone, dichloromethane. In HBDT chromophore, donor (di-(β -hydroxyethyl) amino) and

acceptor (two nitro groups) can boost π -electrons delocalization on the side chain, which will improve molecular optical nonlinearity. On the other hand, the di-(β -hydroxyethylamino) group of HBDT can react with isocyanate group to form a linear chain prepolymer or a polyurethane, while the other compounds listed in Table 1 do not do so. So far, we still do not find the prepolymer or the polyurethane of HBDT discussed in literature.

Synthesis and Characterization of The Polymers

The isocyanate group in the prepolymer reacts with the epoxy group to form oxazolidone ring upon heating^[9]. 4,4'-Diisocyanato-3,3'-dimethoxydiphenyl chain segment is more flexible than tolylene 2,4-diisocyanate in the polymer. Therefore, an extra 10% of 4,4'-diisocyanato-3,3'-dimethoxydiphenyl was added to facilitate the formation of the prepolymers and to react with any moisture present. The remaining 4,4'-diisocyanato-3,3'-dimethoxydiphenyl can be removed by filtration because it does not dissolve in the solvent at room temperature.

The HBDT can form a linear chain prepolymer with the isocyanate group and further form a polyurethane. This is demonstrated by the FT-IR spectra as shown in Fig. 6.

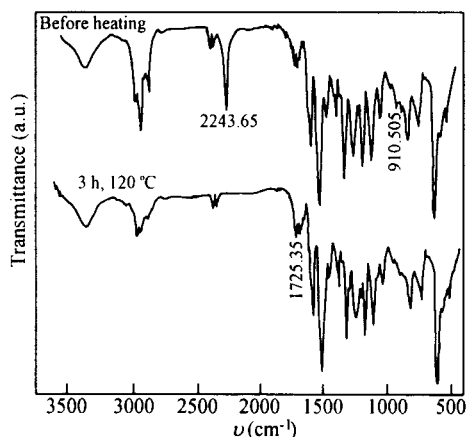


Fig. 6 FTIR spectra of the polyurethane at different polymerization stages
The absorption peaks at 2243, 1725, and 910 cm^{-1} signify the disappearing isocyanate group, the emerging oxazolidone, and the disappearing epoxy, respectively

Before the prepolymer with an equal amount of BADGE (7) was heated, the peak at 2243 cm^{-1} associated with isocyanate and the peak at 910 cm^{-1} associated with epoxy group appeared. After the polymer was heated at 120 $^{\circ}\text{C}$ for 3 h, the peak at 2243 cm^{-1} almost completely disappeared and the peak at 1725 cm^{-1} associated with polyurethane was enhanced, indicating that the polymerization was nearly complete. Aside from the changes in those three peaks, there is no other change in the FT-IR spectra. This demonstrates that the HBDT chromophores do not degrade during the thermal curing process.

NLO Properties

Electric field induced second harmonic generation (EFISH) measurements was performed to determine the molecular nonlinear optical properties of HBDT. In order to minimize possible resonance enhancement, which would exaggerate the measured nonlinear responses, the measurement was performed at a fundamental wavelength of 1.907 μm . At this wavelength, the second harmonic generated at a wavelength of 0.954 μm would be quite distant from the lowest energy electronic transition of the HBDT molecule. 1,4-Dioxane was employed as a solvent for the EFISH measurement, the result of which is presented in Table 1 (f). The $\beta\mu$ value of the monomer HBDT was found to be 8.443×10^{-45} esu.

CONCLUSION

(*trans*)-7-[4-*N*, *N*-di-(β -hydroxyethyl) amino benzene] ethenyl 3,5-dinitrothiophene(HBDT) and its corresponding polyurethane were synthesized. The above results demonstrate that HBDT monomer exhibits good optical nonlinearity.

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