Synthesis and Characterization of a Kind of Poly(3-butylthiophene methine) with Azo Side Groups

Ling-Jie Meng, Hong-Cai Wu, Chao Gao, Wen-Hui Yi

School of Electronics and Information Engineering, Xi'an Jiaotong University, Xi'an, 710049, China

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ABSTRACT: To enhance the third nonlinear optical properties of poly(thiophene methine), we synthesized a new kind of poly(3-butylthiophene methine) with azo side groups: poly[(3-butylthiophene-2,5-diyl)-*p*-(*N*,*N*-dimethylamino)azobenzylidenequinomethane] (PBTDMABQ). PBTDMABQ and its intermediate product were characterized with IR, ultraviolet–visible, and ^{1}H-NMR spectroscopy. The band gaps of PBTDMABQ were calculated to be 1.94 and 2.06 eV with two different models. The thermal stability, determined by thermogravimetric analysis, indicated that PBTDMABQ decomposed above 345°C. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1261–1265, 2005

Key words: conjugated polymers; Azo polymers; thin films

INTRODUCTION

Many scientists are interested in conjugated polymers because these polymers have a range of interesting electronic, optoelectronic, optical, and nonlinear optical properties that vary with their molecular architecture and the extent of π-electron delocalization. In 1986, Jenekhe[1] reported his discovery of a new type of conjugated polymer, poly(thiophene methine), which has a structure of alternating aromatic rings and quinoid structures. In recent years, our research group and Jenekhe's group have synthesized many kinds of poly(thiophene methine)s, poly(pyrrole methine)s, and their derivatives. By studying the conductibility, electroluminescence, and third-order nonlinear optical properties[2–7] of these polymers, we have found that poly(heterocyclic methine)s have rather large third-order nonlinear coefficients[5,6] and a fairly rapid nonlinear response time.[7]

To strengthen the third-order optical nonlinear character of poly(heterocyclic methine)s and obtain new third-order optical nonlinear materials, we intend to substitute azobenzene with aldehyde groups for aromatic aldehydes to polymerize with thiophene or pyrrole and to introduce azo dyes.[8,9] This should produce organic third-order optical nonlinear materials and a side branch to poly(heterocyclic methine). This article focuses on the synthesis method, structural characterization, and stability properties of a soluble poly(heterocyclic methine) with azo side groups. For infinitely long and ideal π-conjugated polymers, the third-order nonlinear polarizability ($\chi^{(3)}$), calculated by a packing model, is in inverse proportion to the hexad power of the band gap (E_g), so we measured and calculated E_g of this kind of poly(thiophene methine) with azo side groups and estimated its third-order nonlinear properties.

EXPERIMENTAL

Materials and characterization

3-Butylthiophene and 4-aldehyde-4′-dimethylamino azobenzene (ADMAA) were synthesized in our laboratory. Butylchlorbenzoquinone (BCBQ; analytical reagent), *p*-dioxane (analytical reagent), concentrated sulfuric acid (analytical reagent), methanol (analytical reagent), *n*-hexane (analytical reagent), and ammonia water (chemically pure) were used.

IR spectra of the polymers were taken from thin films cast onto KBr windows with a PerkinElmer 2000 (Wellesley, MA) Fourier transform infrared (FTIR) spectrometer. The ^{1}H-NMR spectra were obtained in chloroform ($CDCl_3$) with a PerkinElmer FX-90 instrument. The electronic absorption spectra of the polymer solutions were obtained at room temperature in the wavelength range of 190–1100 nm with a Hitachi U2001 (Santa Clara, CA) ultraviolet–visible (UV–vis) spectrophotometer. The thermogravimetric analysis (TGA) was performed with a TA 2000 thermal analyzer under a flowing nitrogen atmosphere. The transmissivity (T) of the poly[(3-butylthiophene-2,5-

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Correspondence to: L.-J. Meng (letianyao@hotmail.com).

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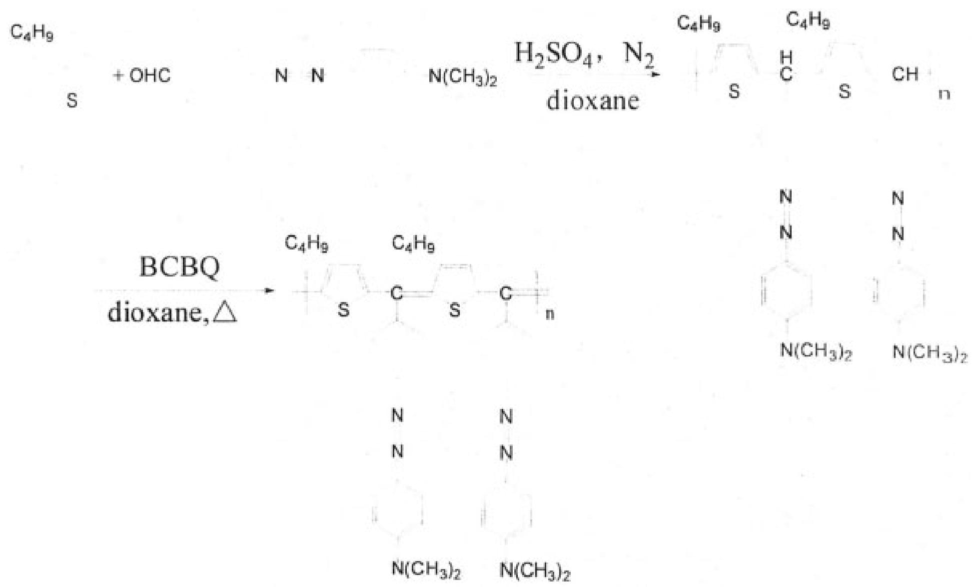

Figure 1 Synthetic route for PBTDMABQ.

diyl)-*p*-(*N*,*N*-dimethylamino)azobenzylidenequinomethane] (PBTDMABQ) films was determined with a Chinese 721 spectrophotometer.

Synthesis

PBTDMABQ was synthesized according to the scheme shown in Figure 1; the synthesis procedures are described next.

Poly[(3-butylthiophene-2,5-diyl)-*p*-(*n*,*n*-dimethylamino)azobenzylidene] (PBTDMAB)

The polymerization mixture consisted of 3-butylthiophene (1.65 g, 11 mmol), ADMAA (2.53 g, 10 mmol), 30 mL of *p*-dioxane, and 3 mL (54 mmol) of 96% sulfuric acid. The reaction temperature was kept at 85°C for 24 h. First, a dark red reaction solution was poured into 400 mL of a stirring saturated NaCl solution. Then, a dark solid was collected and soaked in ammonia water (2 mol/L) for 6 h. After that, the product was washed with deionized water until it was neutral, and it was dried in a vacuum oven at 70°C for 24 h. The yield was 73%.

^{1}H-NMR [δ, ppm, tetramethylsilane (TMS) reference]: 0.85 (3H, CH_2CH_3*), 1.3 (2H, CH_2CH_2 CH_2*CH_3), 1.6 (2H, CH_2*CH_2CH_3), 3.1 [6H, N(CH_3*)$_2$] 3.6 (2H, CH_2*CH_2 CH_2CH_3), 4.2 [1H, C(R)H], 6.8 (1H, thiophene ring), 7.25 (4H, phenylene), 7.95 (4H, phenylene), 8.0 (1H, aromatic thiophene ring).

PBTDMABQ

The reaction mixture consisted of 0.5 g of PBTDMAB, 0.25 g of BCBQ, and 40 mL of anhydrous dioxane. The reaction temperature was kept at 80°C for 8 h. A dark brown polymer was recovered in 100 mL of stirring methanol, dissolved in dioxane, recovered in *n*-hexane, and finally dried in a vacuum oven at 70°C for 24 h. The yield was 68%.

^{1}H-NMR (δ, ppm, TMS reference): 0.9 (3H, CH_2CH_3*), 1.3 (2H, CH_2CH_2 CH_2*CH_3), 1.6 (2H, CH_2CH_2*CH_2CH_3), 3.12 [6H, N(CH_3*)$_2$], 3.55 (2H, CH_2*CH_2 CH_2CH_3), 6.8 (1H, thiophene ring), 7.3 (4H, phenylene), 8.0 (4H, phenylene), 8.05 (1H, aromatic thiophene ring).

RESULTS AND DISCUSSION

IR spectra

Figure 2 shows the FTIR spectra of the precursor PBTDMAB and its dehydrogenated derivative PBTDMABQ. The C—H stretching vibration of CH_3— and —CH_2— is around 2800–3000 cm^{-1}.The absorption band at 1700 cm^{-1} is due to the stretching vibration of the aldehyde group. The absorption band at 1608 cm^{-1} can be assigned to the $C{=}C$ ring stretching vibration band of the phenyl ring. The stretching vibration bands, due to the aromatic thiophene ring and $N{=}N$, can be observed at 1526 and 1450 cm^{-1}, respectively. The vibration bands at 600–880 cm^{-1} come from the C_β—H vibration bands of the phenyl or thiophene ring.

The absorption bands at 1700 cm^{-1} disappear for PBTDMAB and PBTDMABQ, and this shows that ADMAA reacted completely. However, the band at 1650 cm^{-1}, in the spectrum of PBTDMABQ, which can be assigned to the $C{=}C$ stretching vibration band of the quinoid thiophene, is stronger than that of PBTDMAB.

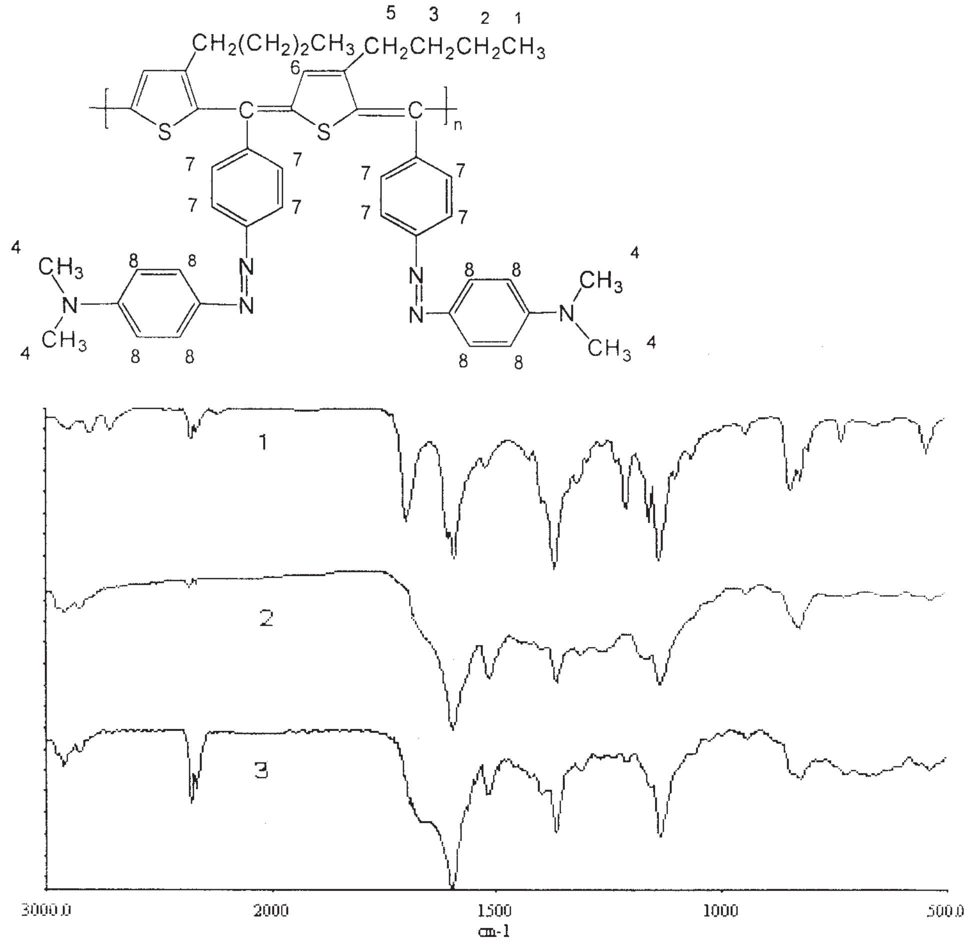

Figure 2 FTIR spectra of (1) ADMAA, (2) PBTDMAB, and (3) PBTDMABQ.

The FTIR spectroscopy results suggest that PBTDMAB was successfully dehydrogenated into PBTDMABQ by BCBQ, and PBTDMAB was partially dehydrogenated in the first step of the reaction. Therefore, the appropriate structure of PBTDMAB can be described as shown in Figure 2.

UV–vis spectra

Figure 3 shows the solution UV–vis optical absorption spectra of PBTDMAB and PBTDMABQ in CCl_3. The polymer solutions were all brown. There are two major absorption bands in the spectra. The bands around 280 nm can be assigned to the $\pi \rightarrow \pi^*$ transition of the phenyl and thiophene rings. The band in the visible region of 380–550 nm can be assigned to the $\pi \rightarrow \pi^*$ E_g transition. In comparison with the absorption peak of PBTDMAB, that of PBTDMABQ moves 15 nm in the direction of red. In addition, Figure 3 shows that, after the dehydrogenation reaction, the extinction coefficient of the visible absorption band, at a maximum absorbance wavelength of 470 nm, increased progressively.

Thermal stability

The thermal stability of PBTDMABQ was investigated with TGA. Figure 4 shows the TGA curves of PBTDMABQ obtained in a nitrogen atmosphere at a heating rate of 20°C/min. PBTDMABQ was thermally stable, with an onset-of-decomposition temperature greater than 345°C.

Measurement and calculation of E_g of PBTDMABQ[10]

The Bouguer–Lamber formula, with which the absorption coefficient (α) can be calculated, is as follows:

$$\alpha = \frac{1}{d} \ln \frac{(1 - r_1)(1 - r_2)}{T} \tag{1}$$

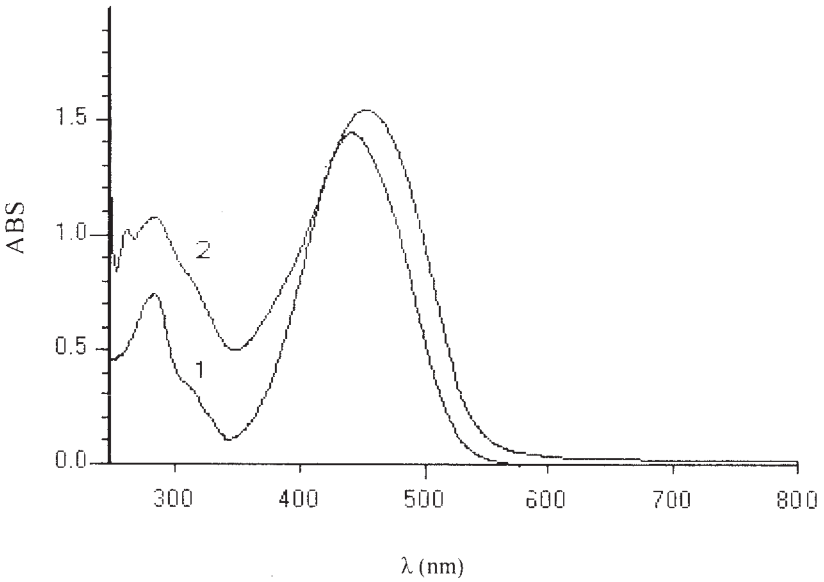

Figure 3 UV–vis absorption spectra of (1) PBTDMAB and (2) PBTDMABQ.

where d is the thickness of the films and r_1 and r_2 are the indices of the air–film and film–substrate reflections, respectively. d was approximately 100 nm, and r_1 and r_2 were neglected when α was calculated.

The relationship between E_g of the films and the energy of incident photons ($h\nu$) is as follows:

$$(\alpha h\nu)\propto(h\nu - E_g)^r \tag{2}$$

The $(\alpha h\nu)^\gamma$–$h\nu$ curves, constructed by eq. (2), are called Tauc (τ) curves. E_g was obtained from the intercept of the linear part of the curve on the $h\nu$ axis. Three models are usually used to compute E_g ($r = 0.5$,

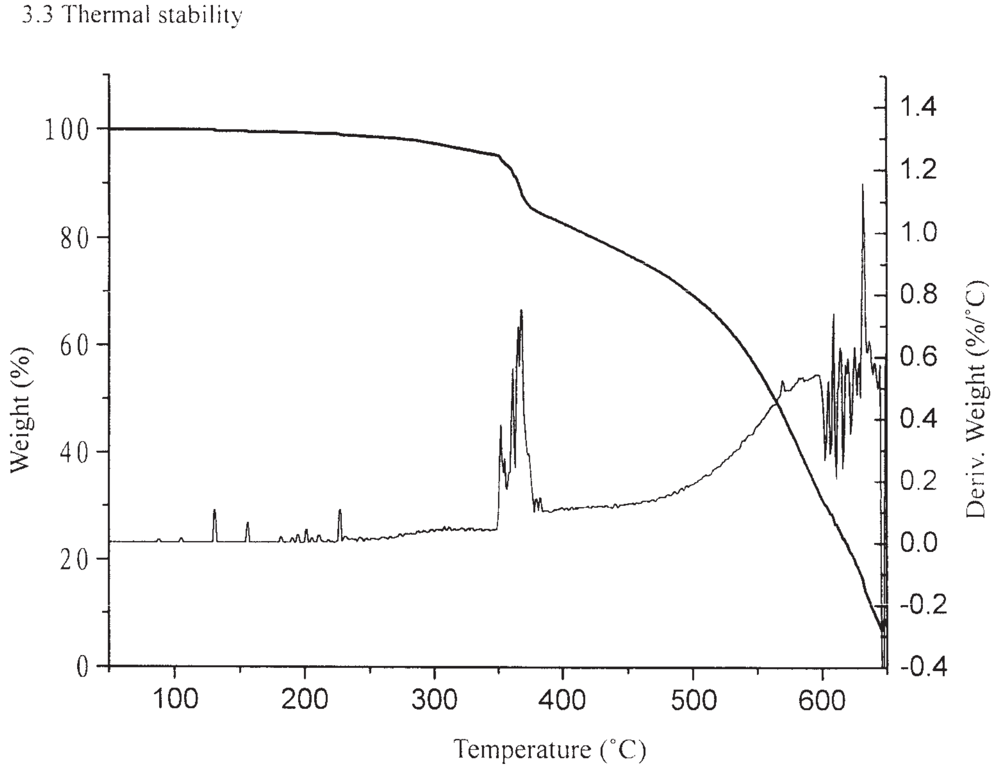

Figure 4 TGA curves of PBTDMABQ.

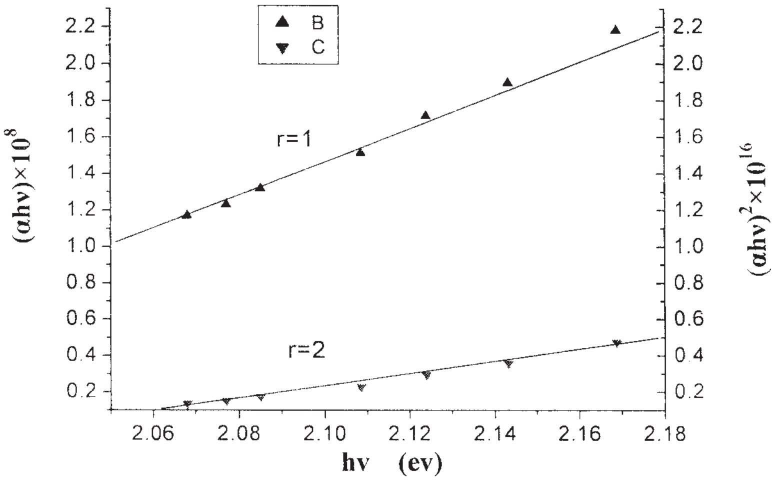

Figure 5 Optical band gaps of the PBTDMABQ films.

$r = 1$, and $r = 2$), where r is a constant depending on the kind of optical transition that prevails. In this study, two values, $r = 1$ and $r = 2$, were adopted for the calculation of the films' E_g values. The calculated results, which were treated with a linear fit, are shown in Figure 5. The E_g values were 1.94 and 2.06 eV, respectively. According to these data, we believe that PBTDMABQ has a large $\chi^{(3)}$ value.

CONCLUSIONS

A new kind of soluble poly(butylthiophene methine) with azo side groups (PBTDMABQ) was synthesized. PBTDMABQ and its intermediate product were characterized with IR, UV–vis, and ^{1}H-NMR spectroscopy. The enlarged absorption peak at 1650 cm^{-1} in the IR spectrum and the bigger absorption peaks at 250–550 nm in the UV–vis spectrum, along with the disappearance of the peak at 4.2 ppm in the ^{1}H-NMR spectrum, implied that a quinoid structure was really formed in PBTDMABQ. The thermal stability was studied with TGA, which indicated that PBTDMABQ decomposed above 345°C. E_g of PBTDMABQ was calculated to be 1.94 or 2.06 eV with two different models. In summary, PBTDMABQ is a very promising polymer as a third-order nonlinear material.

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