

SYNTHESIS AND CHARACTERIZATION OF POLY(PYRROLYL METHINE)

Wei Yan,^{a*} An-kuo Li,^b Chain-shu Hsu^b and Zhi-cheng Zhang^a

^a College of Chemical Engineering, Xi'an Jiaotong University, Xi'an 710049, China

^b Department of Applied Chemistry, National Chiao Tung University, Hsinchu, China

Mei-xiang Wan

Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Abstract A novel small band-gap conjugated polymer — poly[(3-acetylpyrrole-2,5-diyl)(4-dimethylaminobenzylidene)(3-acetylpyrrolequinodimethane-2,5-diyl)] (PAPDMABE) — and its precursor were synthesized by a simple method and characterized by ¹H-NMR, FT-IR, TGA and UV-VIS. The polymer can be dissolved in strong polar solvents such as DMSO, DMF or NMP. The band-gap energy of PAPDMABE was found to be 0.95 eV. The conductivity of doped products with iodine falls in the range of a semiconductor.

Keywords Small band-gap, Conducting polymer, Poly(pyrrolyl methine)

INTRODUCTION

Conjugated polymers present interesting electronic, optoelectronic, optical, and nonlinear optical properties that vary with their molecular architecture and the extent of π -electron delocalization in the materials^[1, 2]. One of the original motivations of experimental work on small band-gap (E_g) conjugated polymers is the thought that control of the E_g value of a polymer by molecular design would allow the control of its optical, electronic and optoelectronic properties^[3]. Among a number of theoretical and experimental small band-gap conjugated polymers, poly(pyrrolyl methines) were chosen in the present work because their E_g values calculated by Bresas are very small, and fall in the range of 0.75–1.10 eV^[4]. Becker *et al.*^[5] have reported the preparation of poly(pyrrolyl methine) from the condensation reaction of 2-pyrrolecarboxaldehyde with POCl₃. But the resulting polymer was found to contain some impurities such as POCl₃ or HCl that could not be removed, and the molecular weight of the polymer was also small. So they can't get the expected band-gap energy.

Here we report a simple stepwise method to synthesize a novel small band-gap conjugated polymer — poly[(3-acetylpyrrole-2,5-diyl)(4-dimethylaminobenzylidene)(3-acetylpyrrolequinodimethane-2,5-diyl)] (PAPDMABE) and its precursor, poly[(3-acetylpyrrole-2,5-diyl)(4-dimethylaminobenzylidene)] (PAPDMABA), were synthesized and characterized successfully. PAPDMABA was prepared by the condensation reaction of 3-acetylpyrrole and 4-dimethylaminobenzaldehyde. The conjugated polymer PAPDMABE was synthesized by the oxidation of PAPDMABA with DDQ (2,3-dicyano-5,6-dichloro-1,4-benzoquinone). Their structure and characteristics were also studied.

EXPERIMENT

Materials

The synthetic route of PAPDMABE is shown in Fig. 1. All reactions were carried out under a nitrogen

* Corresponding author: Wei Yan (延卫), E-mail: yanwei@xjtu01.xjtu.edu.cn

Received October 12, 2000; Revised January 5, 2001; Accepted January 11, 2001

atmosphere. 3-Acetylpyrrole was synthesized by the method described in the literature^[6].

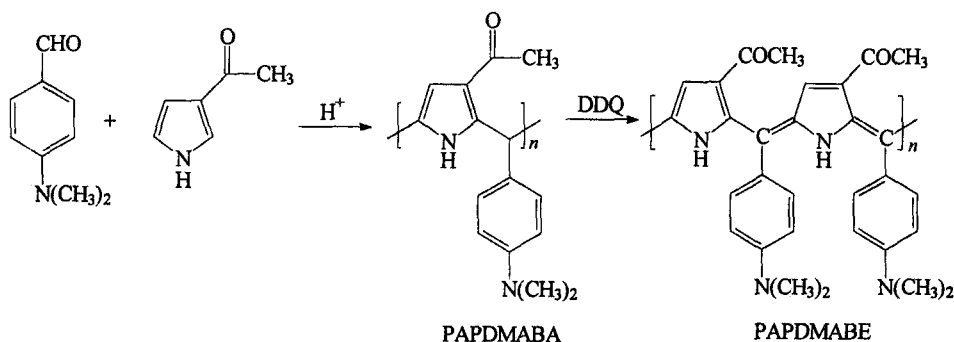


Fig. 1 Synthetic scheme for PAPDMABA and PAPDMABE

Poly[(3-acetylpyrrole-2,5-diyl)(4-dimethylaminobenzylidene)] (PAPDMABA)

3-Acetylpyrrole (1.35 g, 12 mmol), *p*-dimethylamino benzaldehyde (2.22 g, 15 mmol), 50 mL 1,2-dioxane and 6 mL hydrochloric acid (12 mol/L) were mixed and reacted at 65°C for 24 h. After completion of the reaction, the red reaction solution was poured into 500 mL hexane with stirring. A dark red/black product was recovered. For further purification, the product was reprecipitated from THF/hexane twice. Then the polymer obtained was stirred with 40 mL aqueous ammonia solution for 2 h, filtered, washed with water to neutral and dried in a vacuum oven at 40°C for 24 h. The yield was 90%. Elemental anal: (C₁₅H₁₆N₂O)_n, calcd (%): C 74.97, H 6.71, N 11.65; found (%): C 75.00, H 6.78, N 11.39. ¹H-NMR (δ): 1.7–2.5 (COCH₃), 2.6–3.1 (N(CH₃)₂), 5.1–5.3 (C(R)H), 5.9–8.0 (phenylene and pyrrole ring). *M_w* = 17850.

Poly[(3-acetylpyrrole-2,5-diyl)(4-dimethylaminobenzylidene)(3-acetylpyrrolequinodimethane-2,5-diyl)] (PAPDMABE)

1.5 mmol PAPDMABA, 0.5 mmole DDQ and 60 mL anhydrous *p*-dioxane were mixed and reacted at 50°C for 4 h. Then the reaction solution was poured into 500 mL methanol with stirring and the precipitate was recovered, extracted with hot methanol and dried in a vacuum oven at 70°C for 24 h. ¹H-NMR (δ): 2.1–2.3 (COCH₃), 2.8–3.0 (N(CH₃)₂), 5.9–8.0 (phenylene and pyrrole ring).

Characterization

The infrared spectra of polymers were recorded using a Nicolet Model 550 FT-IR spectrometer. The ¹H-NMR spectra were obtained with a Bruker-300 MHz instrument. Elemental analyses were done by using a Heraeus CHN—O Rapid instrument. The electronic absorption spectra of polymer solutions or thin films were obtained within the wavelength range 185–3200 nm with a Perkin-Elmer Lambda 9 UV-VIS-near-IR spectrophotometer. Thermal degradation of the samples was examined by using a Seiko SSC5200 system with TGA thermogravimetric analyzer. About 10 mg sample was analyzed from 30 to 650°C with a heating rate of 10 K/min under a flowing nitrogen atmosphere. The average molecular weight of the polymer was determined by GPC (Shimatsu R-7A data module; LC-10AS pump). The separation columns were connected in series. The flow rate for THF was 1 mL/min at 35°C using polystyrene as standard. The conductivity of polymer pellets was measured with a standard four-point technique in air at room temperature by using a Keithley Model 220 current source and a Model 617 electrometer as the voltmeter. Iodine doping of the polymer powders were performed as follows. The polymers powders were placed into a jar containing iodine vapor and sealed under 100°C for 4 h, then placed in a vacuum oven at 50°C for 2 h to remove any excess iodine from the sample.

RESULTS AND DISCUSSION

Spectral Analysis

FT-IR spectrum of PAPDMABA (Fig. 2) shows the appearance of a strong absorption at 1610 cm^{-1} which is attributed to the stretching vibration of conjugated $\text{C}=\text{C}$ and the stretching vibration of aromatic $\text{C}=\text{C}$ in phenylene. The spectrum of PAPDMABE also has the same strong absorption band at 1613 cm^{-1} , but its relative absorption intensity increases noticeably, indicating that the content of conjugated $\text{C}=\text{C}$ chain in the polymer chain is increased. A distinct peak near 780 cm^{-1} is due to the out-of-plane vibration of $\text{C}_\beta\text{-H}$ characteristic of the α -linkage in pyrrole rings. The strong peak at 1645 cm^{-1} is assigned to the $\text{C}=\text{O}$ stretching vibration. The $^1\text{H-NMR}$ spectrum of PAPDMABA is shown in Fig. 3.

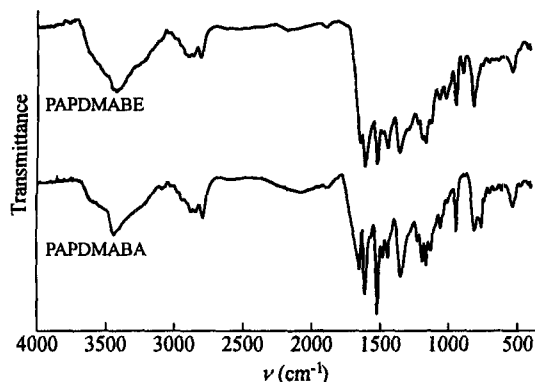


Fig. 2 The FT-IR spectra of PAPDMABA and PAPDMABE

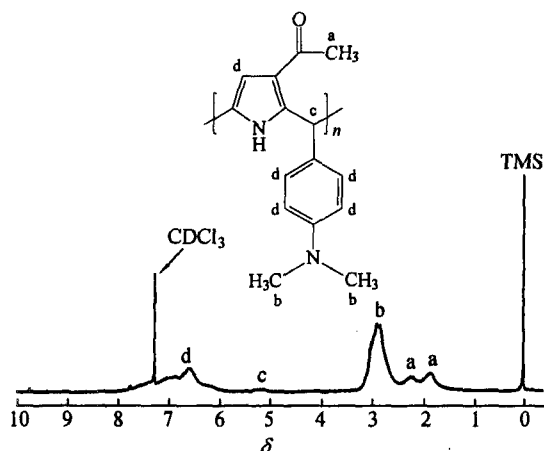


Fig. 3 The $^1\text{H-NMR}$ spectrum of PAPDMABA

Figure 4 shows the UV-VIS absorption spectra of PAPDMABA and PAPDMABE in DMSO. The visible absorption band arises from $\pi\text{-}\pi^*$ transition of the long conjugated structure in the polymer. For PAPDMABA, it has a broad absorption band from 432 nm to 535 nm, indicates the polymer partly dehydrogenates to form longer conjugated structure. For PAPDMABE, this visible absorption band made a red-shifted of 50 nm and the corresponding absorption intensity also increased noticeably. This result means that the extent of conjugation of polymer chains has increased substantially. This result is in consistent with the $^1\text{H-NMR}$ analysis data.

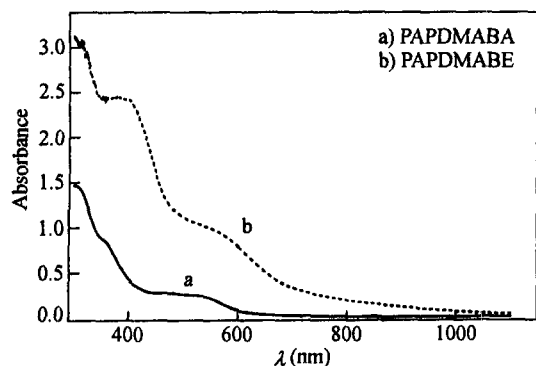


Fig. 4 Optical absorption spectra of PAPDMABA and PAPDMABE in DMSO

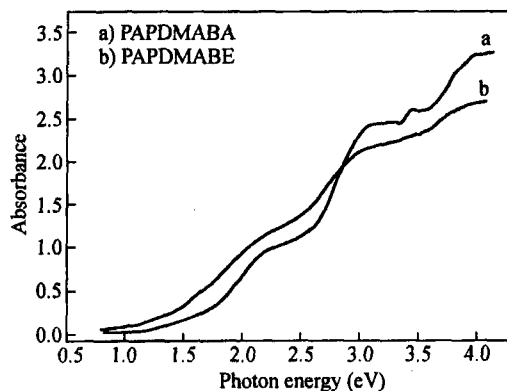


Fig. 5 Optical absorption spectra of thin films of PAPDMABA and PAPDMABE on quartz

Figure 5 shows the optical absorption spectra of the present neutral PAPDMABA and PAPDMABE films coated on quartz. The optical band-gap of the PAPDMABA and PAPDMABE, which is determined from the lowest energy band edge of the solid-state electronic spectra^[7] is 1.12 and 0.95 eV, respectively. They are indeed small band-gap conjugated polymers with E_g values smaller than 1.5 eV.

Thermal Analysis

The result of thermal gravimetric analysis of PAPDMABA (Fig. 6) shows its decomposition temperature to be 304 °C, while PAPDMABE begins to decompose at 217 °C due to the decomposition of carbonyl group connecting with quinoid 2,5-pyrrolylene rings.

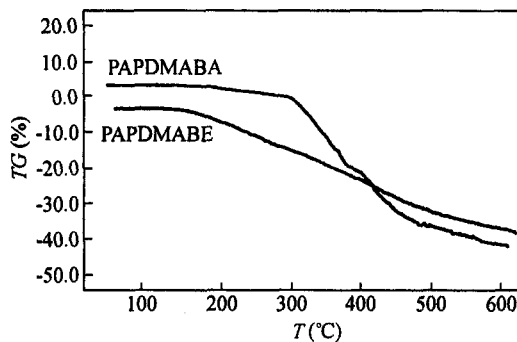


Fig. 6 The TGA spectra of PAPDMABA and PAPDMABE

Conductivity Measurement

The conductivity of PAPDMABA and PAPDMABE were measured with four-probe conductivity measurement and the results are shown in Table 1.

Table 1. Conductivity of PAPDMABA and PAPDMABE ($S \cdot cm^{-1}$)			
Sample	Intrinsic state	H ⁺ -doped	I ₂ -doped
PAPDMABA	$< 10^{-9}$	1.8×10^{-6}	2×10^{-5}
PAPDMABE	1.1×10^{-6}	2.3×10^{-4}	8×10^{-4}

The polymer PAPDMABA shows an insulating behavior before doping and its conductivity increases by five orders on *p*-doping. In contrast, the experimental results indicate that PAPDMABE is a semiconductor even in its intrinsic state without any doping. This phenomenon may be caused by three reasons, longer conjugated structure, lower E_g value and donor-acceptor structure in the chain of PAPDMABE.

REFERENCES

- 1 Kiess, H.G., ed. "Conjugated Conducting Polymers", Springer Series in Solid State Science; Springer-Verlag, Berlin, Heidelberg, 1992, Vol. 102
- 2 Roncali, J., Chem. Rev., 1992, 92: 711
- 3 Jenekhe, S.A., Nature, 1986, 322: 345
- 4 Toussiant, J.M., Themans, B. and Bredas, J.L., Synth. Met., 1989, 28: C205
- 5 Bredas, J.L. and Chance, R.R., "Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics", Kluwer Academic Publishers, Dordrecht, Holland, 1990, p.133
- 6 Yan, W., Zhang, Z.C., Wei, Z.X. and Wang L.L., Chemical Reagents (Chinese), 2000, 22(5): 264
- 7 Chen, W.C. and Jenekhe, S.A., Macromolecules, 1995, 28: 465