

Synthesis and Characterization of Small Band-gap Conjugated Polymers - Poly(pyrrolyl methines)

Wei YAN^{1*}, Chain Shu HSU², Yu WEI³

¹School of Environmental & Chemical Engineering, Jiaotong University, Xi'an 710049

²Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan

³English Department, Xi'an University of Science & Technology, Xi'an 710049

Abstract: A kind of small band-gap conjugated polymers-poly (pyrrolyl methines) and their precursors-(poly pyrrolyl methanes) have been synthesized by a simple method and characterized by ¹HNMR, FT-IR, TGA and UV-Vis. These polymers can be dissolved in high polar solvents such as DMSO, DMF or NMP. The results reveals that the band-gap of the synthesized conjugated polymers are in the range of 0.96~1.14 eV and they all belong to the small band-gap polymers. The conductivity of doped products with iodine is in the range of semiconductor.

Keywords : Small band-gap, conducting polymer, poly(pyrrolyl methine).

One of the original motivations of experimental work on small band-gap (E_g) conjugated polymers is the thought of control of the E_g value of a polymer by molecular design. This would allow the control of its optical, electronic and optoelectronic properties¹. Among a lot of theoretical and experimental small band-gap conjugated polymers, we focus on the poly(pyrrolyl methines) because their E_g values calculated by Bresas are very small, in the range of 0.75~1.10 eV². Here we report a simple stepwise method to synthesize poly(pyrrolyl methines). By this way, a kind of small band-gap conjugated polymers were synthesized and characterized successfully.

Experimental

The synthetic route of poly (pyrrolyl methines) is shown in **Scheme 1**. All reactions were carried out under nitrogen atmosphere. 3-Acetylpyrrole was synthesized by the method of literature³. All polymers were prepared and purified according to the literature⁴. Electronic absorption spectra of polymer solutions or thin films were obtained at room temperature in the wavelength range 190~1400 nm. The optical band-gap of the poly(pyrrolyl methines) was determined from the lowest energy band edge of the solid-state electronic spectra⁵. The conductivity of the polymer pellets was measured with a standard four-point technique in air at room temperature.

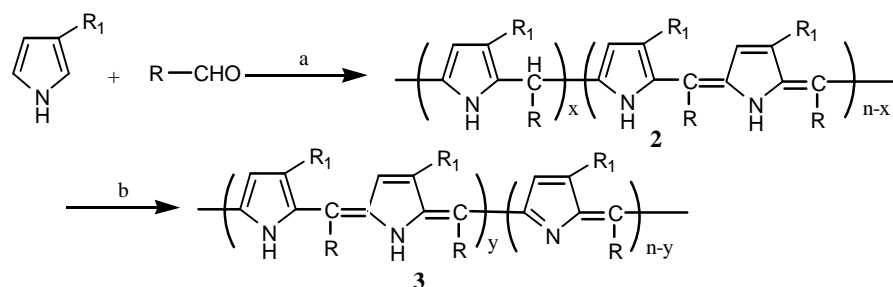
*E-mail: yanwei@mail.xjtu.edu.cn

Results and Discussion

FT-IR measurement on poly(pyrrolyl methines) showed the appearance of a strong absorption in the range of 1610~1640 cm^{-1} attributed to the conjugated C=C stretching vibration and aromatic C=C stretching vibration of phenylene. A distinct peak near 780 cm^{-1} was due to the $\text{C}_\beta\text{-H}$ out-of-plane vibration characteristic of the α -linkage in pyrrole rings. The ^1H NMR results also confirmed the structures of poly (pyrrolyl methines). Thermal gravimetric analysis of poly (pyrrolyl methines) showed that they belong to heat resistant polymers. The optical band-gaps of synthesized poly (pyrrolyl methines), were in the range of 0.96~1.14 eV. They were indeed small band-gap conjugated polymers with E_g values smaller than 1.5 eV. The measurement results were listed in **Table 1**.

The polymer PPDMOBE showed an insulating behavior before doping and its conductivity increased by five orders on p-doping. On the contrary, the experiment results indicated that PAPDMOBE, PAPD3HMBE and PAPD4HMBE were semiconductor even if they were in intrinsic state without any doping. This phenomenon might be caused by three reasons, longer conjugated structure, lower E_g value and donor-acceptor structure in the chains of these polymers. All these factors made electrons delocalize in larger area and increase their movability. But it must be pointed that the conductivity of intrinsic state of PPDFcE was higher than that of its H-doping and I_2 -doping state. The reason of this unusual phenomenon is under studying.

Scheme 1 Synthetic route of polymers



a) 1, 4-dioxane/ $\text{H}_2\text{SO}_4/\text{N}_2$

b) 2, 3-dicyano-5, 6-dichloro-quinone/THF/reflux

2:

R= p- PhOCH_3 , R_1 = H (PPDMOBA)
 R= ferrocenyl, R_1 = H (PPDFcA)
 R= p- PhOCH_3 , R_1 = COCH_3 (PAPDMOBA)
 R= 3-OH-4- $\text{Ph}(\text{OCH}_3)$, R_1 = COCH_3 (PAPD3HMBA)
 R= 4-OH-3- $\text{Ph}(\text{OCH}_3)$, R_1 = COCH_3 (PAPD4HMBA)

3:

R= p- PhOCH_3 , R_1 = H (PPDMOBE)
 R= ferrocenyl, R_1 = H (PPDFcE)
 R= p- PhOCH_3 , R_1 = COCH_3 (PAPDMOBE)
 R= 3-OH-4- $\text{Ph}(\text{OCH}_3)$, R_1 = COCH_3 (PAPD3HMBE)
 R= 4-OH-3- $\text{Ph}(\text{OCH}_3)$, R_1 = COCH_3 (PAPD4HMBE)

Table 1 Measurement results of poly(pyrrolyl methines)

Sample	Band-gap (eV)	TGA(°C)	Conductivity (S/cm)		
			Intrinsic state	H ⁺ -doped	I ₂ -doped
PPDMOBE	1.14	258.6	-----	3×10 ⁻⁷	4×10 ⁻⁶
PPDFcE	1.13	300.4	3.0×10 ⁻⁶	8.7×10 ⁻⁸	1.2×10 ⁻⁷
PAPDMOBE	1.08	290	1.8×10 ⁻⁷	4.7×10 ⁻⁵	1.0×10 ⁻⁴
PAPD3HMBE	0.96	262	5.2×10 ⁻⁷	7.1×10 ⁻⁵	2.2×10 ⁻⁵
PAPD4HMBE	0.99	307	2.3×10 ⁻⁶	3×10 ⁻⁵	5×10 ⁻⁴

Acknowledgment

This project was supported by the Foundation of the Organic Solid Laboratory, Institute of Chemistry, Chinese Academy of Science.

References

1. S.A. Jenekhe, *Nature*, 1986, 322, 345.
2. J.M. Toussiant, B. Themans, J.L. Bredas, *Synth. Met.*, 1989, 28, C205.
3. W. Yan, Z. C. Zhang, Z. X. Wei, L.L. Wang, *Chinese Chemical Reagents*, 2000, 22 (5), 264.
4. W. Yan, A. K. Li, C. S. Hsu, Z. C. Zhang, M. X. Wan, *Chinese. J. Poly. Sci.*, 2001, 19 (5), 499.
5. W. C. Chen, S. A. Jenekhe, *Macromolecules*, 1995; 28, 465.

Received 14 January, 2002