

# Raman Spectroscopic Studies on the Structural Changes of Electrosynthesized Polypyrrole Films During Heating and Cooling Processes

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**ABSTRACT:** Polypyrrole films were electrochemically synthesized by direct oxidative polymerization of pyrrole in acetonitrile containing  $\beta$ -naphthalene sulfonic acid or tetrabutylammonium tetrafluoroborate as a supporting electrolyte. We characterized the as-grown polypyrrole films by resonance Raman spectroscopy in the temperature region of  $-195$  to  $275^\circ\text{C}$ . During the heating process, the Raman bands related to the oxidized species decreased gradually, due mainly to the affect of oxygen and moisture in the air, and, finally, the neutral polymer chains decomposed into

disordered carbons. During the cooling process, polymer chains changed from disordered (coil-like) to ordered (rod-like) structures and caused the elongation of the conjugated chain length. This results in a red shift of the absorption of the electron spectra of the polymer and the enhancements of the Raman bands related to the oxidized species. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3390–3395, 2003

**Key words:** polypyrroles; Raman spectroscopy; structure

## INTRODUCTION

The instability of their physical properties is one of the important and, until now, unsolved problems of conducting polymers (CPs).<sup>1</sup> The thermal stability of CPs is usually studied by differential scanning calorimetry (DSC) or thermogravimetric analysis (TGA) techniques.<sup>2,3</sup> However, only a few articles have been concerned with the chain structure changes of CPs during heating and cooling processes.<sup>4</sup> Polypyrrole (PPy) is one of the most important conducting polymers due to its excellent long-term stability of the conductive state as compared, for example, with that of polythiophene and has wide use in microelectronic devices, batteries, gas sensors and actuators, etc.<sup>5–9</sup> Usually, thin films of PPy obtained by electrochemical synthesis and powders (named pyrrole black) can be produced by chemical oxidative polymerization.<sup>10–12</sup> The CP film prepared by electrochemical technology is usually used in the oxidized (doped) state without further treatment.<sup>13–16</sup> The motivation of this work was to study the polymer chain changes of as-grown electrosynthesized PPy film by heating and cooling treatments in air.

Raman spectroscopy has proved to be a useful method for studying the structural situations of CPs.<sup>17–19</sup> Raman spectra of PPy have been studied extensively and usually by using a surface-enhanced Raman scattering (SERS) technique.<sup>20–23</sup> SERS can identify a conducting polymer film whether in the doped (oxidized) or the dedoped (reduced) state. However, the SERS technique usually needs a roughened electrode surface, which does not represent the real condition of polymer synthesis. For example, we found that the thin PPy film ( $<200$  nm) deposited on a rough electrode surface was irregular and porous, while that deposited on a flat electrode surface was compact and smooth. In this work, a resonance Raman scattering technique was used and PPy films were peeled off from the electrode surfaces for Raman detection.

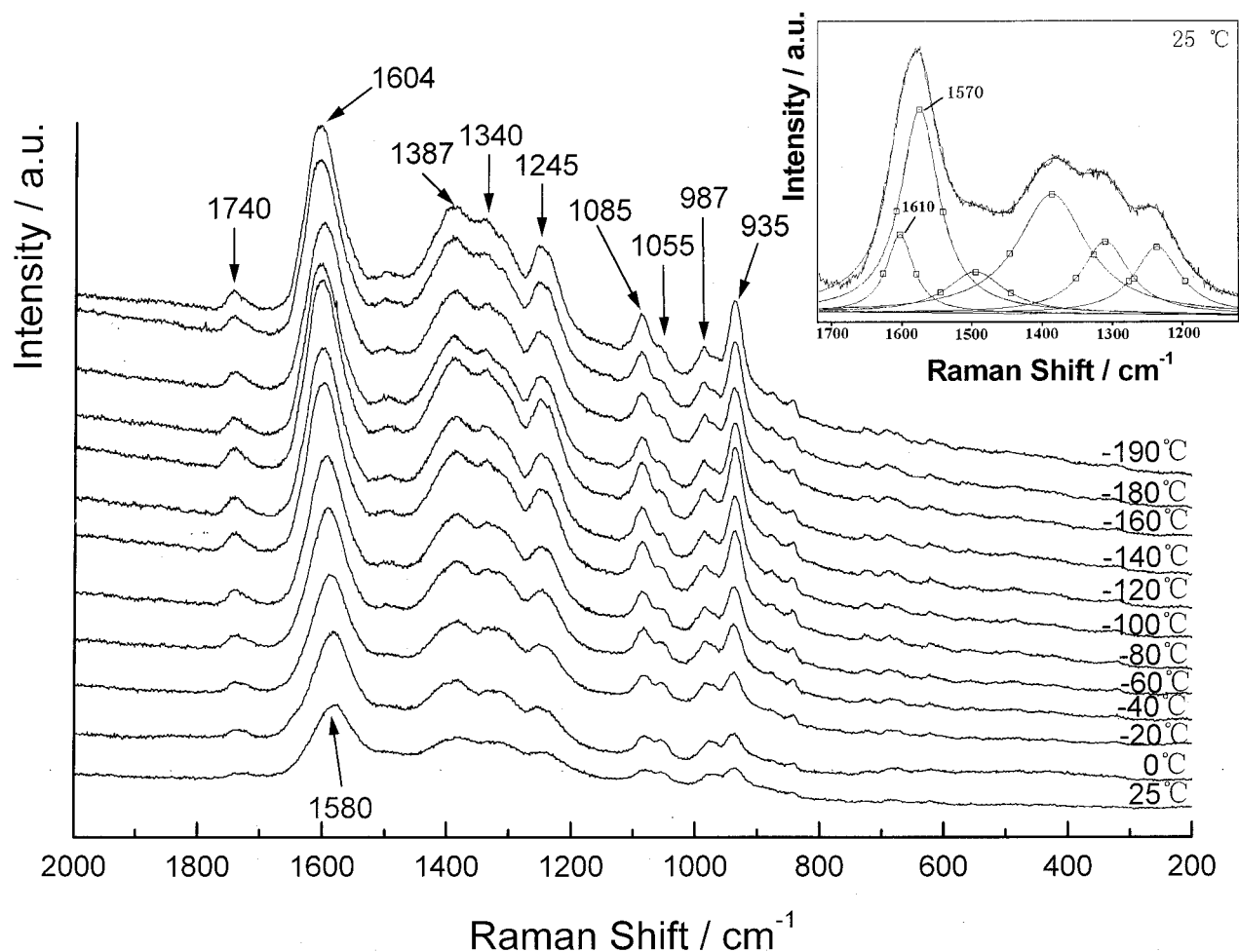
## EXPERIMENTAL

### Chemicals

Pyrrole (98%) was purchased from the Chinese Army Medical Institute (Beijing, China) and used after distillation.  $\beta$ -Naphthalene sulfonic acid ( $\beta$ -NSA) was a product of the Beijing Yucai Fine Chemical Factory (Beijing, China) and used after recrystallization from a 2M HCl aqueous solution. Tetrabutylammonium tetrafluoroborate (Acros, 98%, TBATB, Geel, Belgium) was dried at  $60^\circ\text{C}$  for 24 h before use. Commercial

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**Figure 1** Raman spectra of a  $\beta$ -NSA-doped PPy sample at different temperatures recorded during cooling process. Inset: Decomposition of the bands in the region of  $1100\text{--}1700\text{ cm}^{-1}$  into components of Lorentzian profiles from the Raman spectrum recorded at  $25^\circ\text{C}$ .

HPLC-grade acetonitrile with a purity higher than 99.9% (Tianjing Shiyou Biological and Medical Technological Co., Tianjing, China) was used as received.

#### Electrochemical polymerization of pyrrole

Electrochemical syntheses of PPy films were performed in a one-compartment cell using a Model 283 potentiostat–galvanostat (EG&G Princeton Applied Research) under computer control. The working and counterelectrodes were two shiny flat platinum sheets with a surface area of  $0.5\text{ cm}^2$  each. The reference electrode is an Ag|AgCl wire that was immersed directly in the solution. PPy deposition was carried out at a constant applied potential or at a constant current density in a deoxygenated acetonitrile solution containing 0.1M pyrrole, 0.1M supporting salt, and 1% water (by weight). The temperature of the electrolysis cell was controlled to be  $0^\circ\text{C}$  by an ice bath.

#### Characterization techniques

Raman spectra were recorded using an RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC., England) employing a 633 laser beam and a CCD detector with a  $4\text{-cm}^{-1}$  resolution. As-grown PPy films were washed repeatedly with methanol and diethyl ether to remove the electrolyte and the monomer and then dried at room temperature. Finally, they were peeled off from the electrode surface into free-standing states with a knife before Raman characterizations. The spectra were recorded using a  $50\times$  objective and accumulated for 30 s. The power was always kept very low ( $\sim 0.5\text{ mW}$ ) to avoid destroying the samples. A cell set made by Linkam Scientific Instruments Ltd. controlled the temperature of the sample. The sample was cooled by liquid nitrogen. Some complex Raman peaks were divided into component Lorentzian peaks with proper background subtraction using an “automatic fitting” program provided by the Raman spectrometer. A DSC 821e calo-

**TABLE I**  
**Intensity Ratios of the 1610- and 1570-cm<sup>-1</sup> Bands ( $I_{1610}/I_{1570}$ ) in Terms of Temperature Based on Figure 1**

Temperature (°C)	$I_{1610}/I_{1570}$
25	0.38
0	0.40
-20	0.42
-40	0.50
-60	0.62
-80	0.65
-100	0.68
-120	0.78
-140	0.78
-160	0.92
-180	1.30
-190	1.96

rimeter of Mettler Toledo was used to carry out differential scanning calorimetry tests. The temperature-increase rate was controlled to be 10°C/min.

## RESULTS AND DISCUSSION

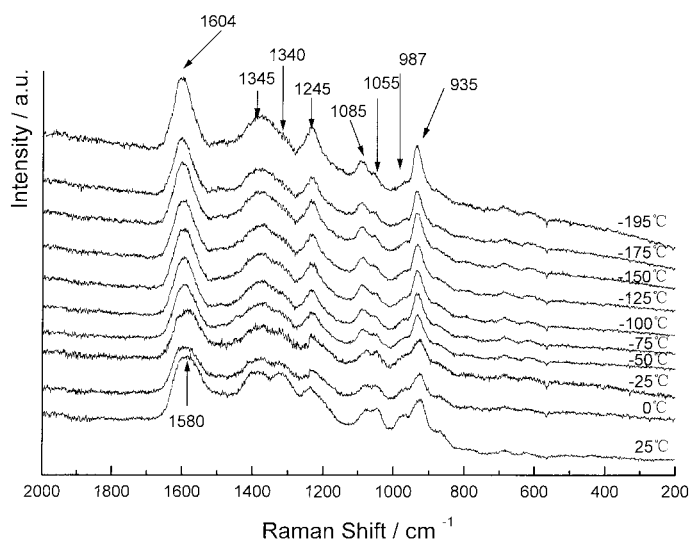
### Raman spectra recorded during cooling process

Figure 1 shows 633-nm excited Raman spectra of an as-grown PPy film recorded in the temperature scale of 25 to -190°C. The polymer was deposited at 1.2 V (versus Ag|AgCl) from an acetonitrile solution of 0.1M Py + 0.1M  $\beta$ -NSA + 1 % H<sub>2</sub>O (by weight). A weak "fluorescence" background and high signal-to-noise ratio are found in these spectra. As can be seen from this figure, there is a weak C=O band about 1730 cm<sup>-1</sup> in all the spectra, indicating that the polymer is slightly overoxidized. It is also clear from this figure that the overall features of the spectra are changed with the temperature. The most important peak shown in Figure 1 is the one about 1600 cm<sup>-1</sup>, which

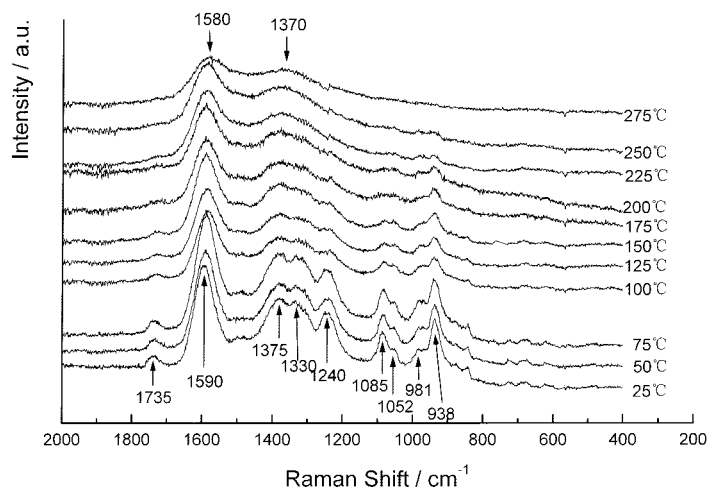
represents the backbone stretching mode of C=C bonds. This band can be divided into two Lorentzian peaks. One is at about 1610 cm<sup>-1</sup> and one is at about 1570 cm<sup>-1</sup>, as shown in the insert of Figure 1. They are attributed to the C=C bond stretching of the oxidized and the reduced species, respectively.<sup>20-28</sup>

According to Figure 1, the intensity ratio of these two bands,  $I_{1610}/I_{1570}$ , increased from 0.38 to 1.96 as the temperature decreased from 25 to -190°C (Table I). As a result, the position of the maximum of these two overlapped bands was shifted from 1580 to 1604 cm<sup>-1</sup>. The double peaks at about 1050 and 1080 cm<sup>-1</sup> are assigned to C-H in-plane deformation.<sup>22</sup> The other double peaks at about 1320 and 1380 cm<sup>-1</sup> are attributed to the ring-stretching mode of PPy.<sup>21,22</sup> However, the 1080 and 1380 cm<sup>-1</sup>, belonging to the C-H in-plane and the ring stretching, respectively, are assigned to the oxidized PPy as reported previously.<sup>21,22</sup> With decreasing temperature, the 1080-cm<sup>-1</sup> band is strengthened in comparison to the 1050-cm<sup>-1</sup> band. Furthermore, the 1380-cm<sup>-1</sup> band also increases while the 1320-cm<sup>-1</sup> band decreases with decrease of the temperature. The bands about 940 and 990 cm<sup>-1</sup> are assigned to the ring deformation associated with dication (bipolaron) and radical cation (polaron), respectively.<sup>24,27,28</sup> In the spectrum recorded at 25°C, the strength of the 940-cm<sup>-1</sup> band is comparable to that of the 990-cm<sup>-1</sup> band. However, in the spectrum recorded at -190°C, the 940-cm<sup>-1</sup> band is much stronger than is the 990-cm<sup>-1</sup> band. The spectral results indicated that the Raman bands related to the oxidized species were enhanced by the temperature decrease.

Similar spectral phenomena were also observed from BF<sub>4</sub><sup>-</sup>-doped PPy films as shown in Figure 2. The PPy sample was synthesized at 1.2 V (versus Ag|AgCl) from an acetonitrile solution containing 0.1M Py, 0.1M TBATF, and 1% H<sub>2</sub>O (by weight). During the cooling



**Figure 2** Raman spectra of BF<sub>4</sub><sup>-</sup>-doped PPy at different temperatures recorded during the cooling process.



**Figure 3** Raman spectra of a doped PPy at different temperatures recorded during the heating process.

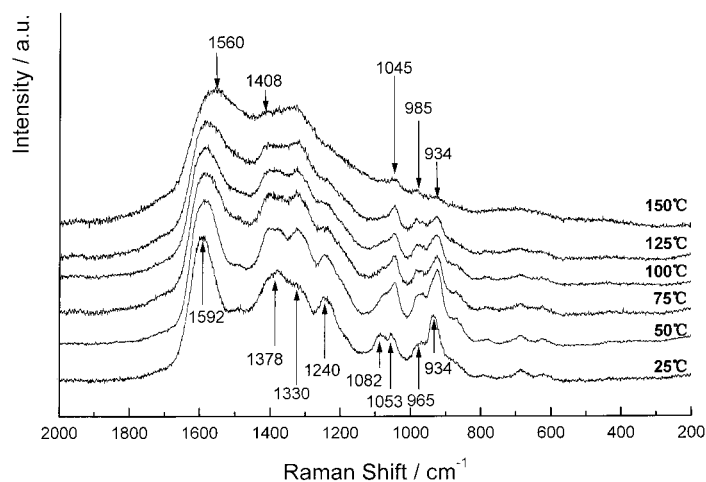
process, the Raman bands related to the oxidized species increased with decrease of the temperature. Furthermore, the peak of the C=C symmetrical stretching band shifted from 1580 to 1604  $\text{cm}^{-1}$ , indicating that the 1610- $\text{cm}^{-1}$  band was enhanced. The spectral changes described above are possibly due to that the polymer chain is changed from a disordered (coil-like) conformational state to an ordered (rodlike) conformation state by lowering the temperature.<sup>4</sup> This elongated the conjugation length of the polymer chain and caused a red shift of the optical absorption of PPy.

The optical variations caused by conformational transitions were also observed in several another conducting polymers.<sup>29–33</sup> Optical absorption changes led to the enhancements of the Raman bands related to the oxidized species caused by a resonance effect.<sup>18</sup> Furthermore, although it cannot be recovered immediately after a cooling-heating cycle, the Raman spectrum recorded at 25°C can be recovered extensively after the sample was kept at room temperature for over 2 h. This result also supports that the spectral

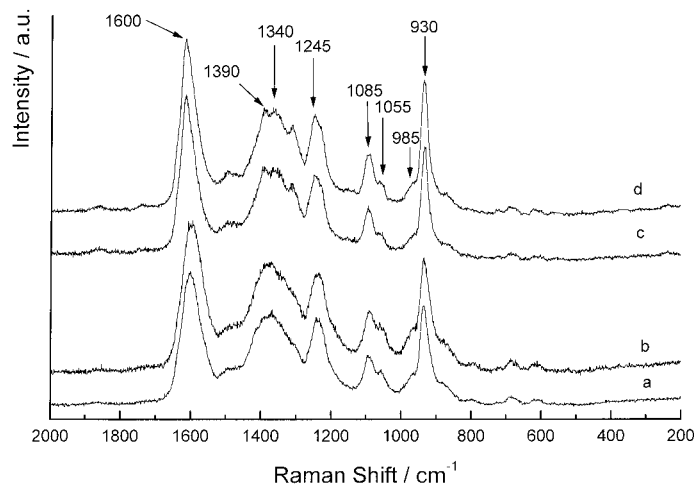
changes are caused by conformational changes of the polymer chains.

#### Raman spectra recorded during heating process

The Raman spectra of the PPy film doped with  $\beta$ -NSA and recorded during the heating process are illustrated in Figure 3. The spectrum of as-grown PPy film at room temperature shows strong Raman bands related to the oxidized and neutral species. This spectrum is relatively stable if the temperature is lower than 50°C. Above this temperature, the Raman bands related to the oxidized and neutral species decrease with increase of the temperature. The decreasing rate of the Raman bands related to the oxidized species is faster than that of the neutral species. Finally, the PPy sample was decomposed and showed a spectrum with features similar to that of a carbonaceous material about 250°C. Two broad bands were found about 1600 and 1400  $\text{cm}^{-1}$ , respectively.<sup>34</sup>



**Figure 4** Raman spectra of  $\text{BF}_4^-$ -doped PPy at different temperatures recorded during the heating process.



**Figure 5** Raman spectra of (a,b)  $\text{BF}_4^-$ -doped and (c,d)  $\beta$ -NSA-doped PPy films; (a,c) were recorded for the as-grown films and (b,d) were recorded for the same films after heating under a vacuum at  $100^\circ\text{C}$  for 30 min.

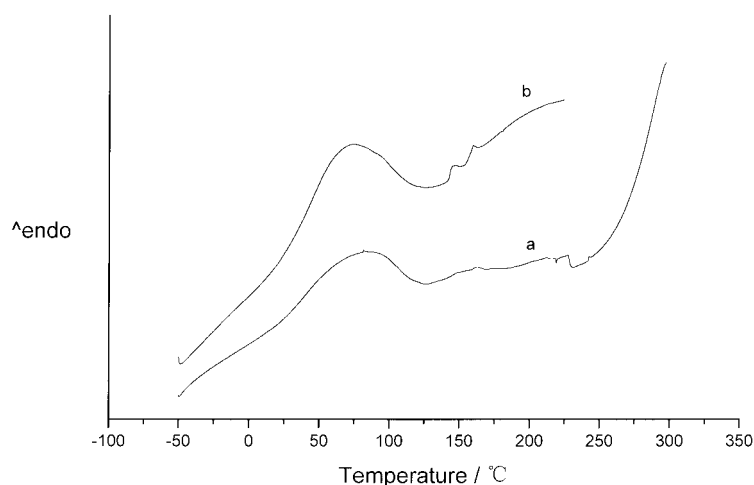
The Raman spectra of the PPy film doped with  $\text{BF}_4^-$  were also changed with increase of the temperature (Fig. 4). During the heating process, the Raman bands related to the oxidized species decreased with the temperature, while the bands related to the neutral species did not change even when the temperature was as high as  $150^\circ\text{C}$ . This result indicated that the neutral species were much more stable than were the oxide species. In comparison of Figures 3 and 4, it can be found that the thermal stability of  $\text{BF}_4^-$ -doped PPy is worse than that of the  $\beta$ -NSA-doped PPy sample. The former showed a spectrum of carbonaceous material at  $150^\circ\text{C}$ , while that of the latter appeared about  $250^\circ\text{C}$ .

The Raman spectra changes during the heating process resulted from the reactions of PPy and oxygen and moisture in the air. Experimental results demonstrated that the PPy sample has the same Raman spectra before and after heat treatment under a vacuum at  $100^\circ\text{C}$  for 0.5 h, as shown in Figure 5. It is well known

that the conductivity of doped CPs, including PPy, decreases gradually as samples are stored in air due mainly to the attack of oxygen and moisture.<sup>22</sup> Increase of the temperature can accelerate the reaction processes and the structural changes of PPy can be detected by Raman spectroscopy in a relatively short time as described above.

#### DSC studies

Figure 6 demonstrates the DSC traces of (a)  $\beta$ -NSA- and (b)  $\text{BF}_4^-$ -doped PPy films. It is clear from this figure that these two PPy samples have glass transitions in the temperature scales of  $0$ – $50^\circ\text{C}$ .  $\beta$ -NSA-doped PPy showed a decomposition temperature about  $260^\circ\text{C}$  and that of the  $\text{BF}_4^-$ -doped PPy sample was found about  $150^\circ\text{C}$ . These results are in good agreement with the Raman spectral observations described above. Glass transition causes the conformational transition of PPy and decomposition results in



**Figure 6** DSC curves of (a)  $\beta$ -NSA- and (b)  $\text{BF}_4^-$ -doped PPy films.

the formation of carbon. However, the Raman results demonstrated that there are dramatic structural changes that resulted from the reactions between polymer chains and oxygen (or moisture) in air before polymer decomposition.

### CONCLUSIONS

Resonance Raman spectroscopy is a useful technique to study the structural changes of electrosynthesized PPy film during the processes of cooling and heating in air. Cooling the PPy sample causes the conformational transition of the polymer chain and results in the enhancement of the Raman bands related to the oxidized species. Heating the PPy sample leads to the destruction of the oxidized species of the polymer, and, finally, the polymer decomposed into a carbonaceous material. The thermal stability of the  $\beta$ -NSA-doped PPy sample was better than that of  $\text{BF}_4^-$ -doped PPy.

### References

1. Fedorko, P.; Skakalova, V. *Synth Met* 1998, 94, 279.
2. Lu, Y. Q.; Shi, G. Q.; Liang, Y. Q. *J Appl Polym Sci* 1998, 70, 2169.
3. Li, C.; Chen, F. E.; Shi, G. Q.; Xu, J. K.; Xu, Z. J. *J Appl Polym Sci* 2002, 83, 2462.
4. Fedorko, P.; Skakalova, V.; Vegh, D.; Hulman, M. *Synth Met* 1999, 101, 308.
5. *Advances in Synthetic Metals*; Bernier, P.; Lefrant, S.; Bidan, G., Eds.; Elsevier: New York, 1999.
6. Otagawa, T.; Madou, M.; Wing, S.; Alexander, J. R.; Kusanagi, S.; Fujioka, T.; Yasuda, A. *Sens Actuators B* 1990, 1, 319.
7. Stanke, D.; Hallensleben, M. L.; Toppare, L. *Synth Met* 1993, 55-57, 1108.
8. Liang, W. B.; Martin, C. R. *Chem Mater* 1991, 3, 390.
9. Lee, J. Y.; Kim, D. Y.; Kim, C. Y. *Synth Met* 1995, 74, 103.
10. Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. *J Chem Soc Chem Commun* 1979, 635.
11. Armes, S. P. *Synth Met* 1987, 20, 365.
12. Li, H. H.; Shi, G. Q.; Ye, W.; Li, C.; Liang, Y. Q. *J Appl Polym Sci* 1997, 64, 2149.
13. *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986.
14. Waltman, R. J.; Bargon, J.; Diaz, A. F. *J Phys Chem* 1983, 87, 1459.
15. Lere-Porte, J. P.; Sauvajol, J. L.; Hasoon, S.; Chenouni, D.; Galtier, M.; Pertrissans, J. *Mol Cryst Liq Cryst* 1988, 161, 223.
16. Sakamoto, A.; Fukukawa, Y.; Tasumi, M. *J Phys Chem* 1992, 96, 3870.
17. Bazzaoui, E. A.; Marsault, J. P.; Aeiach, S.; Lacaze, P. C. *Synth Met* 1994, 66, 217.
18. Bazzaoui, E. A.; Levi, G.; Aeiach, S.; Aubard, J.; Marsault, J. P.; Lacaze, P. C. *J Phys Chem* 1995, 99, 6628.
19. Bazzaoui, E. A.; Levi, G.; Aeiach, S.; Lacaze, P. C. *Synth Met* 1996, 83, 159.
20. Holze, R. *Synth Met* 1991, 40, 379.
21. Liu, Y. C.; Hwang, B. J.; Jian, W. J.; Santhanam, R. *Thin Solid Films* 2000, 374, 85.
22. Liu, Y. C.; Hwang, B. J. *Synth Met* 2000, 113, 203.
23. Zarbin, A. J. G.; De Paoli, M. A.; Alves, O. L. *Synth Met* 1999, 99, 227.
24. Furukawa, Y.; Tazawa, S.; Fujii, Y.; Harada, I. *Synth Met* 1998, 24, 329.
25. Jenden, C. M.; Davidson, R. G.; Turner, T. G. *Polymer* 1993, 34, 1649.
26. Zhong, C. J.; Tian, Z. C.; Tian, Z. W. *J Phys Chem* 1990, 94, 2171.
27. Duchet, J.; Legras, R.; Demoustier-Champagne, S. *Synth Met* 1998, 98, 113.
28. Gongcalves, A. B.; Mangrich, A. S.; Zarbin, A. J. G. *Synth Met* 2000, 114, 119.
29. Patel, G. N.; Chance, R. R.; Witt, J. D. *J Chem Phys* 1979, 70, 4387.
30. Yoshino, K.; Park, D. H.; Park, B. K.; Onada, M.; Sugimoto, R.-I. *Jpn J Appl Phys* 1988, 27, L 1612.
31. Chen, S.-A.; Ni, J.-M. *Macromol Chem Rapid Commun* 1992, 13, 31.
32. Chen, S.-A.; Ni, J.-M. *Synth Met* 1993, 55, 576.
33. Chen, S.-A.; Ni, J.-M. *Macromolecules* 1992, 25, 6081.
34. Shi, G. Q.; Chen, F. E.; Wu, S. X.; Zhu, Y. F.; Hong, X. Y.; Hou, W. H.; Ming, L. *J Appl Polym Sci* 2001, 81, 116.