Electrochemical Synthesis of Polyaniline and Its Comparison with Chemically Synthesized Polyaniline

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ABSTRACT: The synthesis of polyaniline (PAni) powder was carried out from $0.15M$ of aniline and $1M$ of HCl in distilled water at room temperature in a single compartment electrochemical cell. The PAni was again synthesized chemically keeping the composition and temperature same as electrochemical process but adding equimolar amount of ammonium peroxydisulfate as an oxidizing agent. Then the PAni obtained from these two methods were characterized by the conductivity, solubility, X-ray, FTIR, TGA, UV, and SEM, and compared. Result shows that the electrochemically synthesized PAni (ECS-PAni) has somewhat lower conductivity, higher solubility, more benzenoid rings than quinoid rings, lower crystallinity, higher band energy, and higher particle size than that of chemically synthesized PAni (CS-PAni). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1900–1904, 2007

Key words: conducting polymer; electrochemistry; infrared spectroscopy; thermogravimetric analysis; X-ray

INTRODUCTION

The studies on the properties of intrinsically conducting polymers have been driven by both considerable curiosities as to the nature of these unusual materials and a wide variety of their possible applications.[1–3] Among the other conducting polymers such as polypyrrole, polythiophene, and polyacetylene, polyaniline (PAni) is the most promising polymers because of its good environmental stability, controllable electrical properties, and low cost of monomer.[4] Hence, the PAni has attracted much attention because of its novel properties and potential applications.[5]

The PAni can be synthesized from monomeric aniline either by oxidative polymerization[6,7] or by electropolymerization.[8,9] The electrochemical reaction is carried out either in one compartment or in two-compartment electrochemical cell in aqueous medium or in a suitable solvent.[10]

The literature dealing with the synthesis of PAni by different method is sufficient but the comparison between the chemical polymerization and the electropolymerization.

The present article deals with the synthesis of PAni both by the electrochemical and the chemical methods, comparison between them through the conductivity, solubility, X-ray, FTIR, TGA, UV, and SEM studies.

EXPERIMENTAL

Materials

The G.R. grade aniline (freshly distilled before use), ammonium peroxy disulfate (APS) (Merck, Mumbai, India), and hydrochloric acid (Ranbaxy, India) were used as received. A glass container of 30.0 cm height and 3.5 cm diameter was used as a single compartment electrochemical cell. A graphite rod of 0.7 cm diameter and 15.0 cm length was used as a working electrode, a stainless steel of 13.0 cm length, 2.0 cm width, and 0.03 cm thickness was used as a counter electrode, and a saturated calomel electrode (SCE) was used as a reference electrode. For the application of a constant electric potential, a DC power supply of model 3161 (HCL) was used.

Synthesis of PAni

Electrochemical synthesis (ECS-PAni)

The electropolymerization of aniline was carried out in a single compartment cell as mentioned earlier. Two hundred milliliters of distilled water, 3.1 mL of aniline ($\sim0.15M$), and 20 mL of concentrated HCl ($\sim1M$) were taken in the cell. If the monomer taken is very less, then the amount of product per batch is very low. If very high amount of monomer is taken, then productivity is decreased as high amount of product cannot accommodate on the surface of the electrode leading to the wastage of material. Hence, the quantity of aniline chosen is 3.1 mL. A potential difference of 0.7 V versus SCE across the electrodes was applied. The reaction was carried out for 2 h. The PAni formed

TABLE I
Difference in Properties of ECS-PAni and CS-PAni

Properties	ECS-PAni	CS-PAni
DC conductivity	1.7×10^{-4} S/cm	6.3×10^{-4} S/cm
Solubility of PAni per 100 g of DMF at room temperature	0.37 g	0.06 g
Quinoid to benzenoid ratio in PAni	0.8	1.1
Band energy for the third band (c)	2.06 eV	1.98 eV
Particle size from SEM	20–40 μm	0.1–1.0 μm

at the graphite electrode was collected and then washed with distilled water, filtered and dried in a vacuum oven at room temperature. The PAni thus obtained was treated with excess ammonia until basic to remove HCl and then redoped with PTSA (50 mol % of PTSA with respect to the repeat unit of PAni that is 1 g of PTSA per gram of PAni). Then the mass obtained was filtered, washed with distilled water, and finally dried in vacuum oven at room temperature.

Chemical synthesis of PAni (CS-PAni)

In the chemical synthesis, same composition as in the electrochemical synthesis was maintained but instead of applying constant voltage, an equimolar (with respect to aniline) amount of oxidizing agent namely ammonium peroxydisulfate (APS) was added. Hundred and ninety milliliters of distilled water, 3.1 mL of aniline (~0.15M), and 20 mL of concentrated HCl (~1M) were taken in a beaker and stirred. APS (7.6 g) is dissolved in 10 mL of distilled water and then added to the above solution slowly, stirred for 2 h by means of a mechanical stirrer at room temperature. A deep green particle was obtained, which was filtered, washed with distilled water, and dried in a vacuum oven at room temperature. The PAni thus obtained was treated with excess ammonia until basic to remove HCl and then redoped with PTSA (50 mol % of PTSA with respect to the repeat unit of PAni that is 1 g of PTSA per gram of PAni). Then the mass obtained was filtered, washed with distilled water, and finally dried in vacuum oven at room temperature.

Characterization

For the analysis of DC conductivity of the synthesized PAni, the sample was prepared in the pellet form with Perkin–Elmer hydraulic press using 15 ton pressure. The DC conductivity was measured with the Milli-Ohm Meter, GOM 802, GW Instek, Taiwan.

The XRD analysis was carried out using X Pert PRO, PANalytical instrument, USA with Cu detector using 1.54 Å wavelength of the X-ray.

The FTIR spectra were taken from FTIR spectrometer, spectrum RX 1, USA. The sample was prepared in the pellet form by mixing the PAni powder with KBr by the ratio 1:10 and pressing it in the Perkin–Elmer hydraulic press using 15 ton pressure.

The thermogravimetric analysis was carried out using TGA, Q50, TA Instruments, USA. The experiment was carried out under the N_2 atmosphere from 30 to 800°C at a heating rate of 20°C/min.

The UV analysis was carried out using UV–visible Spectrophotometer, UV-1601, Shimadzu, Japan. Testing was carried out taking only the soluble portion of PAni in DMF. Solution of 0.05% was prepared for each sample.

The particle size was determined from the photograph of SEM, JSM 5800, JEOL, Japan.

RESULTS AND DISCUSSION

Depending on the oxidation state and protonation level, PAni can either be conducting or insulating in nature. The protonated or doped EB form is significantly conducting, the LEB and PNB are insulating in nature, and rest are in between.[7,11,12]

The conduction mechanism is explained by the polaron/bipolaron formation[7,13,14] and the hopping mechanism[7,15,16] or hole theory of conduction. The increase in the crystallinity is expected to increase the conductivity both for the intrachain mobility of electron and hole, and interchain mobility of the same. Again with the decrease in the d-spacing, the probability of interchain hopping is increased and hence the conductivity is increased. It is generally observed that the increase in the degree of doping (up to 50%) of PAni causes increase in the conductivity via the formation of polaron, but at very high doping levels (>50%) the conductivity is again found to decrease due to the formation of bipolaron.[16]
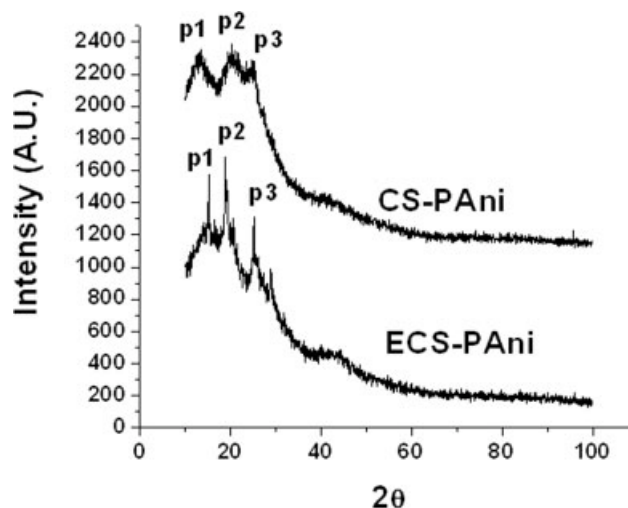
Figure 1 X-ray diffractogram of ECS-PAni and CS-PAni.

TABLE II
The *d*-Spacing and the Percent Crystallinity of ECS-PAni and CS-PAni

Sample	$2\theta^a$ (p1)	d^b (Å)	PC (%)	2θ (p2)	d (Å)	PC^c (%)	2θ (p3)	d (Å)	PC (%)	TC^d (%)
ECS-PAni	15.2	5.8	18.0	18.9	4.7	6.4	25.2	3.5	6.4	30.8
CS-PAni	13.4	6.6	33.7	20.3	4.4	19.1	24.8	3.6	8.0	60.8

^{a} 2θ is the angle of the peak.
^{b} *d* is *d*-spacing of the corresponding peak.
^{c} PC is the percent crystallinity of corresponding peak.
^{d} TC is the total percent crystallinity.

Unless and until molecules attain a certain definite size, the conductivity of the system does not increase significantly. This is mainly because long-range delocalization of electron cloud due to the formation of conjugated double bond does not occur until the molecule attains a definite size. However, at a very high molecular weight, again some kind of imperfection like distortion in chain symmetry may develop, which in turn adversely affects the delocalized system.[6] Hence, the conductivity of PAni mainly depends on the (i) oxidation state or molecular structure and arrangement, (ii) degree of doping, (iii) degree of crystallinity, (iv) the *d*-spacing, and (v) molecular weight or molecular chain length.

To find out the effect of different synthesis procedure on the conductivity of the PAni, the polymer structure or oxidation state was determined from the IR analysis, degree of doping was fixed at 50% during synthesis. The degree of crystallinity and the *d*-spacing were determined from the XRD analysis, the band energy of polaron/bipolaron transition was determined from the UV analysis, but the molecular weight could not be determined due to poor solubility of PAni in most of the solvent. In fact for highly polar and crystalline material like PAni, which is also thermoset in nature, the estimation of molecular weight by conventional methods is impossible.

The DC conductivity of the ECS-PAni (1.7×10^{-4} S/cm) is somewhat higher than that of the CS-PAni (6.3×10^{-4} S/cm) as shown in Table I. The conductivity of the CS-PAni is about 3.5 times higher than that of the ECS-PAni.

The solubility of the ECS-PAni is 0.37 g/100 g of dimethyl formamide (DMF) at room temperature and that of the CS-PAni is 0.06 g/100 g of DMF (Table I). The solubility of the ECS-PAni is almost six times higher than that of the CS-PAni.

The percentage of crystallinity and the *d*-spacing was calculated[17–20] from the XRD curve (Fig. 1) as shown in Table II. There are three crystalline peaks named as p1, p2, and p3. The degree of crystallinity and the *d*-spacing corresponding to each peak were determined. The total degree of crystallinity of the ECS-PAni is almost half that of the CS-PAni. This may be due to the difference in the method of preparation. In the electrochemical process, the aniline, which is used as monomer, is attracted by the anode (graphite) and releases an electron to form cation radical. This cation radical successively form the polymer.[21] There may be less chance of orientation due to the attraction by the anode and hence the degree of crystallinity may be less for the ECS-PAni. In the chemical process though the polymerization mechanism is same,[22] here
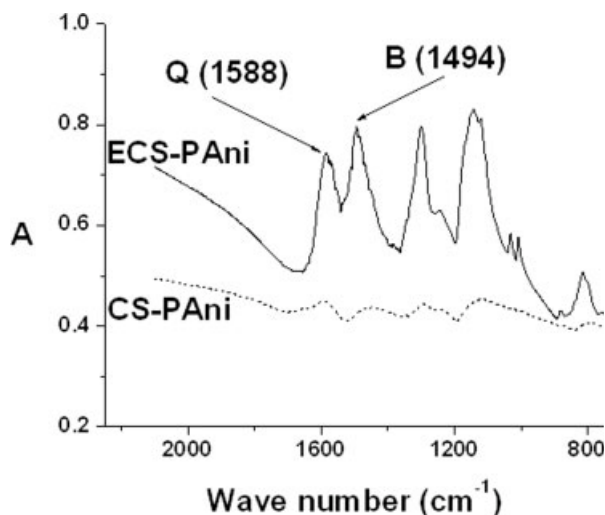
Figure 2 FTIR spectra of ECS-PAni and CS-PAni.
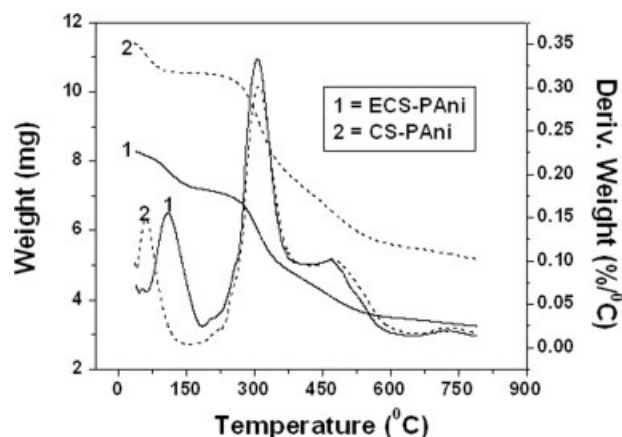
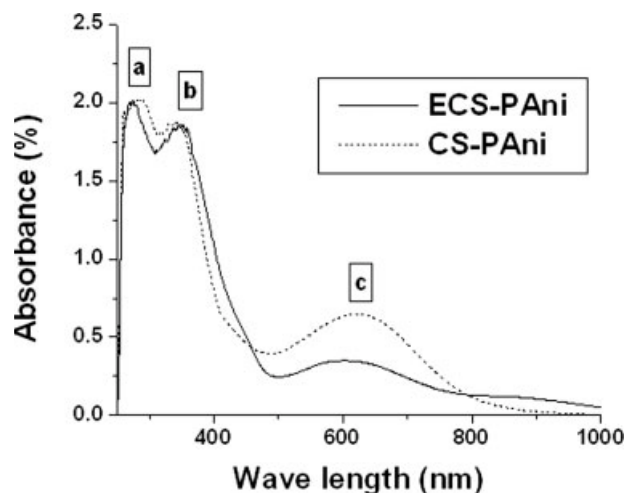**Figure 3** TGA curve of ECS-PAni and CS-PAni.

Figure 4 UV spectra of ECS-PAni and CS-PAni.

the aniline cation radical is formed by the APS. Hence, the cation radicals are more free and can easily orient during the progress of the polymerization. This may be the reason for the higher degree of crystallinity for the CS-PAni. The lower the crystallinity, higher is the amorphous zone. Hence, solvent can easily enter between chains leading to the increase in the solubility. This may be the reason for the higher solubility of the ECS-PAni. The higher crystallinity in the CS-PAni indicates that the chains are more ordered where chances for both the intrachain and interchain hopping are more, that means the carrier charge mobility is higher leading to the higher conductivity for the CS-PAni. The d-spacing corresponding to the peak p1 is less important because the interchain distance is too high (the d-spacing value is too high) and hence chance for the interchain hopping is less. The d-spacing corresponding to the peaks p2 and p3 are more important. The d-spacing of the CS-PAni corresponding to p2 is much lower compared to that of the ECS-PAni, which may contribute more toward the conduc-

tivity by interchain hopping. The d-spacing of ECS-PAni corresponding to p3 is marginally lower than that of CS-PAni.

The FTIR spectra of the ECS-PAni and CS-PAni are shown in Figure 2. The bands at 1588 and 1494 cm^{-1} are assignable to the ring stretching vibration of quinoid (Q) and benzenoid (B), respectively,[23–26] while bands at 1294 and 1136 cm^{-1} are due to the stretching vibration of C—N—C and B—NH^+=Q, respectively. From the ratio of area of peaks corresponding to the1588 and 1494 cm^{-1}, the ratio of quinoid to benzenoid structure present in a PAni, which means the oxidation level of that PAni, can be estimated. In the ECS-PAni, Q/B is 0.8 (Table I), which means benzenoid rings are more in number than quinoid ones and in the CS-PAni Q/B is 1.1 (Table I), which means quinoid rings are more than benzenoid ones. Hence, there may be higher chance for the increased concentration of conducting EB structure in the CS-PAni compared to that in ECS-PAni. This may also be the reason for its higher conductivity in CS-PAni. The effectiveness of chemical oxidation by APS during chemical synthesis may be more than that of oxidation process in electrochemical synthesis. The continuous discharging of aniline and deposition of polyaniline on the electrode may lead to the reduction in the effectiveness of the electrode for further discharging and deposition.

The TGA curve of the ECS-PAni and CS-PAni is depicted in Figure 3. In the TGA graph, the first weight loss may be due to the loss of moisture, the second weight may be due to the loss of dopant (HCl), and the third weight loss may be due to the loss of the polymer.[27–30] The DTG peaks for both the ECS-PAni and CS-PAni are almost same (470–475°C), which means the thermal stability of the ECS-PAni and the CS-PAni are almost the same.

The UV spectra of PAni shows three characteristic absorption bands, 250–280, 340–370, and 550–650 nm (Fig. 4). The first absorption (a) is due to the excitation
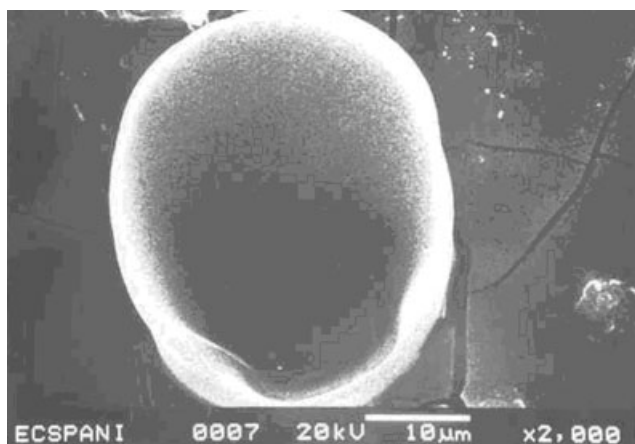

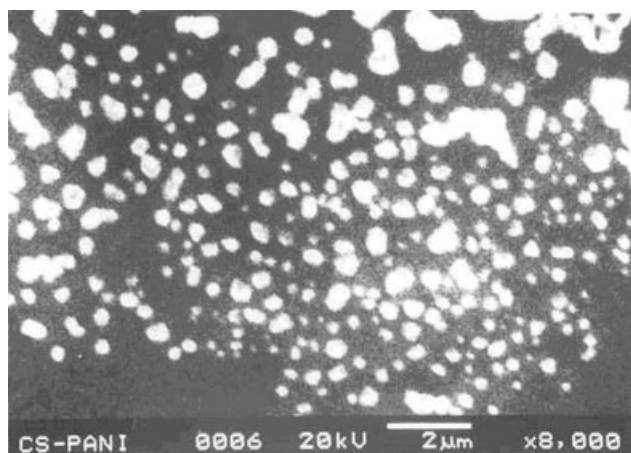**Figure 5** SEM photograph of ECS-PAni.

Figure 6 SEM photograph of CS-PAni.

of the nitrogen in the benzenoid segments ($\pi - \pi^*$ transition), while the second (b) and the third (c) ones are ascribed to polaron/bipolaron transition that occurs in doped PAni.[31,32] The band energy of the ECS-PAni and the CS-PAni for the second band (b) is almost the same. The band energy of the ECS-PAni for the third band (c) is 2.06 eV and that of the CS-PAni is 1.98 eV (Table I). The lower band energy of the CS-PAni indicates easier polaron/bipolaron transition occurring in it, leading to the higher conductivity.

The particle size was determined from the SEM photograph. The morphology and the structural pattern of PAni depend on the method of synthesis.[1,33,34] From the SEM photographs, it is clear that the particles of both ECS-PAni (Fig. 5) and CS-PAni (Fig. 6) are almost spherical in nature. The size of the ECS-PAni is 20–40 μm, whereas the size of the CS-PAni is 0.1–1.0 μm (Table I). The size of the ECS-PAni is 20–400 times bigger than that of the CS-PAni. The formation of bigger size particles during electrochemical process compared to that during chemical process may be due to the higher tendency of coalescence of smaller particles into bigger one. This tendency may be due to deposition of PAni layer after layer on the same electrode surface till the screening effect of multiple layers (each layer reduces the discharging efficiency of cathode) significantly reduces the efficacy of cation radical discharge on the screened electrode surface.[21]

CONCLUSIONS

The PAni obtained from the electropolymerization (ECS-PAni) has somewhat lower conductivity, higher solubility, lower crystallinity, higher band energy, structure with higher benzenoid rings and higher size than that of the chemically synthesized PAni (CS-PAni). This is due to the difference in synthesis method and hence difference in the efficiency of oxidation or polymerization and different ways of arrangement of polymer chains.

The PAni obtained from both the electrochemical and chemical polymerization has almost similar thermal stability.

References

1. Choi, S. J.; Park, S. M. J Electrochem Soc 2002, 149, E26.
2. Cho, M. S.; Park, S. Y.; Hwng, J. Y.; Choi, H. J. Mater Sci Eng 2004, C24, 15.
3. Saroop, M.; Ghosh, A. K.; Mathur, G. N. Int J Plast Technol 2003, 7, 41.
4. Park, S. Y.; Cho, M. S.; Choi, H. J. Curr Appl Phys 2004, 4, 581.
5. Longa, Y.; Chena, Z.; Wanga, N.; Lib, J.; Wanb, M. Phys B: Condens Matter 2004, 344, 82.
6. McDiarmid, A. G. Synth Met 1997, 84, 27.
7. Bhadra, S.; Singha, N. K.; Khastgir, D. Synth Met 2006, 156, 1148.
8. Ozyılmaz, A. T.; Tuken, T.; Yazıcı, B.; Erbil, M. Prog Org Coat 2005, 52, 92.
9. Tuken, T.; Ozyılmaz, A. T.; Yazıcı, B.; Erbil, M. Appl Surf Sci 2004, 236, 292.
10. Marie, E.; Rothe, R.; Antonietti, M.; Landfester, K. Macromolecules 2003, 36, 3967.
11. Pron, A.; Rannou, P. Prog Polym Sci 2002, 27, 135.
12. Silva, J. E. P.; Torresi, S. I. C.; Torresi, R. M. Corros Sci 2005, 47, 811.
13. Stafstrom, S.; Bredas, J. L.; Epstein, A. J.; Woo, H. S.; Tanner, D. B.; Huang, W. S.; MacDiarmid, A. G. Phys Rev Lett 1987, 59, 1464.
14. Zuo, F.; Angelopoulos, M.; MacDiarmid, A. G.; Epstein, A. J. Phys Rev B: Condens Matter 1989, 39, 3570.
15. Wolter, A.; Rannou, P.; Travers, J. P.; Gilles, B.; Djurado, D. Phys Rev B: Condens Matter 1998, 58, 7637.
16. Luthra, V.; Singh, R.; Gupta, S. K.; Mansingh, A. Curr Appl Phys 2003, 3, 219.
17. Han, D.; Chu, Y.; Yang, L.; Liu, Y.; Lv, Z. Colloids Surf A 2005, 259, 179.
18. Paul, R. K.; Vijayanathan, V.; Pillai, C. K. S. Synth Met 1999, 104, 189.
19. Murugesan, R.; Subramanian, E. Mater Chem Phys 2003, 80, 731.
20. Cai, L. T.; Yao, S. B.; Zhou, S. M. J Electroanal Chem 1997, 421, 45.
21. Iroh, J. O.; Zhu, Y.; Shah, K.; Levine, K.; Rajagopalan, R.; Uyar, T.; Donley, M.; Mantz, R.; Johnson, J.; Voevodin, N. N.; Balbyshev, V. N.; Khramov, A. N. Prog Org Coat 2003, 47, 365.
22. Ahmed, S. M. Polym Degrad Stab 2004, 85, 605.
23. Sung, J. H.; Kim, S. J; Lee, K. H. J Power Sources 2004, 126, 258.
24. Nakayama, M.; Saeki, S.; Ogura, K. T. Jpn Soc Anal Chem 1999, 15, 259.
25. Cho, M. S.; Lee, J. H.; Choi, H. J.; Ahn, K. H.; Lee, S. J.; Jeon, D. J Mater Sci 2004, 39, 1377.
26. Mathew, R.; Mattes, B. R.; Espe, M. P. Synth Met 2002, 131, 141.
27. Rao, P. S.; Subrahmanya, S.; Sathyanarayana, D. N. Synth Met 2002, 128, 311.
28. Campos, T. L. A.; Kersting, D. F.; Ferreira, C. A. Surf Coat Technol 1999, 122, 3.
29. Han, M. G.; Lee, Y. J.; Byun, S. W.; Im, S. S. Synth Met 2001, 124, 337.
30. Zeng, X. R.; Ko, T. M. Polymer 1998, 39, 1187.
31. Svelko, N. K.; Reynaud, S.; Francois, J. Synth Met 2005, 150, 107.
32. Pillai, Z. S.; Kamat, P. V. Res Chem Intermed 2005, 31, 103.
33. Venancio, E. C.; Wang, P. C.; MacDiarmid, A. G. Synth Met 2006, 156, 357.
34. Rao, P. S.; Subrahmanya, S.; Sathyanarayana, D. N. Synth Met 2003, 139, 397.