JOURNAL OF MATERIALS SCIENCE **37** (2002) 4609–4614

In situ spectroelectrochemistry and colorimetry of poly(pyrrole-acrylamide)s

GÜRSEL SÖNMEZ, A. SEZAI SARAÇ*
Department of Chemistry, Istanbul Technical University, Polymer Science and Technology, 80626 Maslak, Istanbul, Turkey
E-mail: sarac@itu.edu.tr

Electropolymerization of pyrrole in the presence and absence of acrylamide was accomplished. Characterization of the soluble and insoluble products was carried out by using UV-visible and FTIR spectroscopy, cyclic voltammetry, colorimetry and four-point probe technique. Role of applied electrical conditions and effect of the presence of acrylamide on the formation of polymers in the solution and on electrode surface were investigated. Conductivity of polypyrrole and poly(pyrrole-acrylamide) free-standing films show a conductivity of 90 and 1.0 S/cm, respectively. Incorporation of the acrylamide to the resulting polymer was supported by electrochemistry, colorimetric and spectroscopic results. The presence of the acrylamide in the resulting polymer affects some of the properties of the polymer film (i.e., color, conductivity, electrochemistry, spectroelectrochemistry, etc.) that may bring some advantages for practical applications.

1. Introduction

The field of conducting polymers has attracted the interest of many academic and industrial researchers after the first report of electrical conductivity in a conjugated polymer (polyacetylene) in 1977 by Shirakawa *et al.* [1]. The electronic properties of conducting polymers have *focused the researchers* for various applications [2–4] including anti-static and anti-corrosion coatings, sensors, batteries, supercapacitors, light emitting diodes (LEDs) [5], electrochromic devices [6] and transparent electrode materials [7]. Polypyrrole is one of the most extensively studied conducting polymer due to the ease of synthesis, good redox properties, stability in the oxidized form, ability to give high electrical conductivies and useful electrical and optical properties [3, 8–11]. As a result of its good intrinsic properties, polypyrrole has proven promising for several applications including batteries, supercapacitors, electrochemical (bio)sensors, conductive textiles and fabrics, mechanical actuators, electromagnetic interference (EMI) shielding, anti-static coatings and drug delivery systems [12]. The intrinsic properties of polypyrrole are highly dependent on electropolymerization conditions. Many works have explored the effect of oxidation conditions such as solvent, electrolyte, additives, functional substituents and electrode potential on the properties of polymer [13–17]. One of the most important problems of polypyrrole and other conducting polymers is the difficulty *to dissolve them* in any solvent because of their delocalized π-electronic structures. Pyrrole has polymerized oxidatively in the presence of anionic polymers using different oxidizing agents to overcome the solubility problem of polypyrrole [18–20]. Observation and characterization of soluble intermediates during the polymerization of pyrrole is another route of research [21–24], which may help to understand the uncertain mechanism of pyrrole polymerization.

Conducting polymers can be prepared via chemical or electrochemical polymerization [25]. The second way is generally preferred because it provides a better control of film thickness and morphology, and cleaner polymers when compared to chemical oxidation. Electropolymerization involves many experimental variables such as solvent, monomer concentration, electrolyte type, temperature, electrode material and applied electrical conditions. As for the electrical conditions, the polymers are deposited under potentiostatic or galvanostatic conditions or by cyclic potential sweeps [26]. The applied electrical conditions introduce effect on both structure and properties of electrogenerated polypyrrole films and the rate of polymer production [27, 28]. In our previous studies, the effect of the presence of a comonomer during the polymerization of pyrrole was reported [23, 24, 29]. It was seen that the presence of the acrylamide with pyrrole stabilises the intermediate pyrrole species in the solution depending on the applied electrical conditions during the electropolymerization of pyrrole. The presence of acrylamide in the resulting polymer also affects some of the properties of the polymer (i.e., color, conductivity, electrochemistry, spectroelectrochemistry, etc.) that may bring some advantages

---

*Author to whom all correspondence should be addressed.

0022–2461 © *2002 Kluwer Academic Publishers*

for practical applications. Here, electrochemical and optical properties of polypyrroles and poly(pyrrole-acrylamide)s are reported comparatively.

2. Experimental

2.1. Materials

Pyrrole (Merck), acrylamide (Merck), sodiumperchlorate (Fluka), tetrabutylammonium perchlorate (TBAP) (Fluka) and lithium perchlorate (Fluka) were used as received without further purification. Acetonitrile (Riedel-de Haen) and propylene carbonate (Aldrich) were distilled over calcium hydride before use. For spectroelectrochemistry, indium tin oxide (ITO) coated glass slides were used.

2.2. Polymerization

Electrochemical polymerizations were performed with a Potentioscan Wenking POS 73 potentiostat and an EG&G (model 273) potentiostat/galvanostat in a three electrode setup employing platinum wires as working and counter electrodes, and a 0.01 M $Ag/AgNO_3$ reference (Ag/Ag^+) in a solution of 0.1 M TBAP-acetonitrile (ACN). Polymerization reactions were performed electrochemically at a constant potential or current vs. Ag/Ag^+ reference electrode in ACN solution containing 0.1 M TBAP and 0.01 M pyrrole with/without 0.5 M acrylamide. Free-standing films of polypyrrole (PPy) and poly(pyrrole-acrylamide) P(Py-AAm) were prepared at a constant current density of 0.2 mA/cm^2 using stainless steel electrodes in the same electrolyte system. For the colorimetric measurements 0.1 M $LiClO_4$/PC solution was used as electrolyte. The reference electrode was calibrated externally using a 5 mM solution of ferrocene (Fc/Fc^+) in the electrolyte ($E_{1/2}$ (Fc/Fc^+) = +0.075 V vs. Ag/Ag^+ in 0.1 M $LiClO_4$/PC). The potentials are reported versus Fc/Fc^+ as recommended by the IUPAC [30]. Polymer films for spectroelectrochemistry were prepared by galvanostatic deposition on ITO, which were grown at 0.2 mA/cm^2 in 0.1 M $LiClO_4$/PC containing 0.01 M pyrrole with/without 0.5 M acrylamide monomers.

2.3. Characterization

Cyclic voltammograms were recorded under nitrogen atmosphere using the same electrode setup explained before and EG&G (model 273) potentiostat/galvanostat. A UV-visible spectrometer (Shimadzu UV-160A) was used for spectroelectrochemistry. A three-electrode cell assembly was used where the working electrode was an ITO-coated glass, the counter was a platinum wire and a 0.01 M $Ag/AgNO_3$ reference electrode. The Potentioscan Wenking POS 73 potentiostat were used to alter applied potential. All reactions were monitored between 200 and 1100 nm. The IR spectra of the products were recorded with a Jasco 5300 FTIR by using KBr pellets. Conductivity of free-standing films were measured by using four point probe technique [31]. Constant current was applied between external probes using a Fluke-715 Volts/mA Calibrator while resulting voltage was measured between two central probes using a Brymen BM837RS Professional Multimeter.

Colorimetric measurements were obtained by use of a Minolta CS-100 chroma meter and CIE recommended normal/normal (0/0) illuminating/viewing geometry for transmittance measurements [32]. The same electrode setup in the spectroelectrochemistry measurements was also used for colorimetric measurements. The potential was controlled with the EG&G (model 273) potentiostat/galvanostat. The sample was illuminated from behind by a D50 (5000 K) light source in a light booth specially designed to exclude external light. The color coordinates are expressed in the CIE 1931 Yxy color space where the Y value is a measure of the luminance in Cd/m^2. The relative luminance, expressed in %, was calculated by dividing the Y value measured on the sample by the Y_0 value corresponding to the background. Note that the relative luminance is frequently reported instead of the luminance because it gives a more meaningful value [33].

3. Results and discussion

3.1. Polymer growth

Oxidative electropolymerization of mixture of the monomers 0.01 M pyrrole and 0.5 M acrylamide was carried out in acetonitrile (ACN) containing 0.1 M TBAP as electrolyte. Fig. 1 shows evolution of the potential during galvanostatic deposition at 0.5 mA/cm^2 and the current density during potentiostatic deposition at +1.020 V vs. Fc/Fc^+ on a Pt button from a solution of 0.01 M pyrrole and 0.5 M acrylamide in 0.1 M TBAP/ACN. It should be noted that both methods of deposition produced very homogeneous, extremely smooth and compact films. For the galvanostatic depositions, good P(Py-AAm) films were obtained starting from 0.2 mA/cm^2 in our conditions and after this current density the growth of polymer shows almost the same character. The potential change between 0.3 mA/cm^2 and 1.0 $mA/cm^2$is less than 0.1 V. The deposition at 0.5 mA/cm^2 is given as an example in Fig. 1a.

The current was also monitored during the polymer deposition on the electrode surface as a function of time. It should be noted that polymer films were observed starting from 0.95 V vs. Fc/Fc^+ in our conditions and the growth of the polymer at constant potential doesn't show very different character after this potential. A deposition at 1.020 V vs. Fc/Fc^+ is given in Fig. 1b where

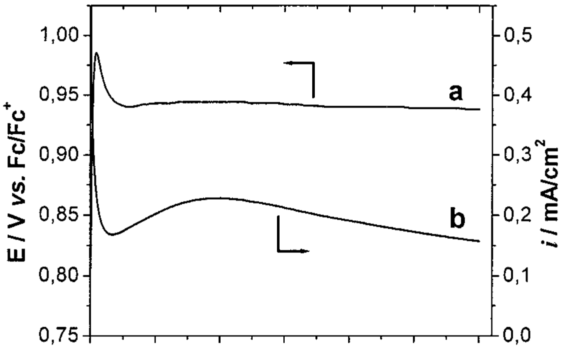

Figure 1 Evolution of the (a) potential during galvanostatic deposition (at 0.5 mA/cm^2) and (b) current density during potentiostatic deposition (at +1.020 V vs. Fc/Fc^+) on a Pt button (area = 0.02 cm^2) from a solution of 0.01 M pyrrole and 0.5 M acrylamide in 0.1 M TBAP/ACN.

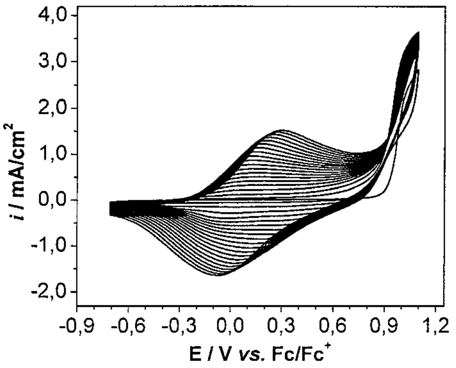

Figure 2 Electrodeposition of P(Py-AAm) copolymer by potential scanning from a solution of 0.01 M pyrrole and 0.5 M acrylamide in 0.1 M TBAP/ACN at 50 mV/s on a Pt button (area = 0.02 cm^2).

the oxidation of monomer can be seen. At higher potentials, the nucleation, which is represented by an increase in the current and then this increase is limited by mass transport [34] illustrated by a peak and a subsequent decrease. The decrease of the current suggests an increase of the diffusion layer since the growth rate is now diffusion limited.

Electropolymerization of the mixture of monomers, 0.01 M pyrrole and 0.5 M acrylamide, was also performed using multiple scan cyclic voltammetry in acetonitrile (ACN) containing 0.1 M TBAP as electrolyte (Fig. 2). The cyclic voltammogram shows the fast and regular growth of the polymer at Pt working electrode. The irreversible oxidation of the monomer appears at the potential starting from 0.85 V vs. Fc/Fc$^+$ and then followed by a nucleation loop which can be seen clearly on the first cycle. On subsequent cycles, monomer oxidation happens at a slightly lower potentials and current density increases as a result of the modification of the electrode surface after the first cycle. A redox system grows up rapidly at about 0.0 V vs. Fc/Fc$^+$ with a slower electrodeposition rate than PPy that might be explained by the incorparation of a non-conjugated monomer in the polymer thus decreasing the conductivity and character of the resulting polymer. In addition, the peak separation between anodic and cathodic peak potentials (ΔE_p) during the polymer growth increases as the number of cycles increases in the presence of acrylamide.

3.2. Polymer characterization

The polymers were deposited by galvanostatically on the Pt electrode from the mixture of monomers (0.01 M pyrrole and 0.5 M acrylamide) and electrolyte (0.1 M TBAP/ACN). Then 1.0 μm thick polymer films were characterized by cyclic voltammetry in monomer free 0.1 M TBAP/ACN electrolyte solution. The influence of the scan rate was investigated for P(Py-AAm) film as shown in Fig. 3. The peak currents in the cyclic voltammogram appeared to increase linearly with the increase of scan rate suggesting that an electroactive layer is deposited on the electrode and that the oxidation and reduction processes are not limited by diffusion. The half wave potential ($E_{1/2}$) of the polymer is about 0.0 V vs. Fc/Fc$^+$. There is also very large capacitive current in the anodic region of the redox potential. This effect may come from the larger surface area of the electrode when the film is oxidized and conducting [35].

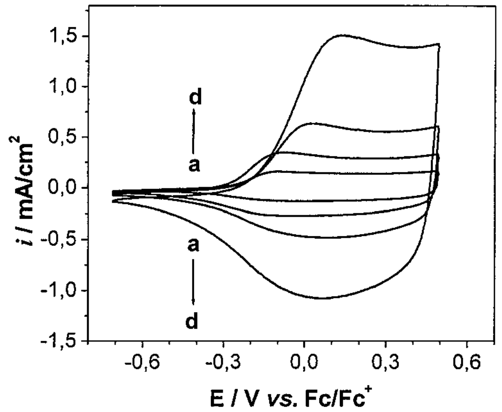

Figure 3 Cyclic voltammogram of thin P(Py-AAm) films in monomer free solution of 0.1 M TBAP/ACN at a scan rate of (a) 5 mV/s, (b) 10 mV/s, (c) 20 mV/s, (d) 50 mV/s.

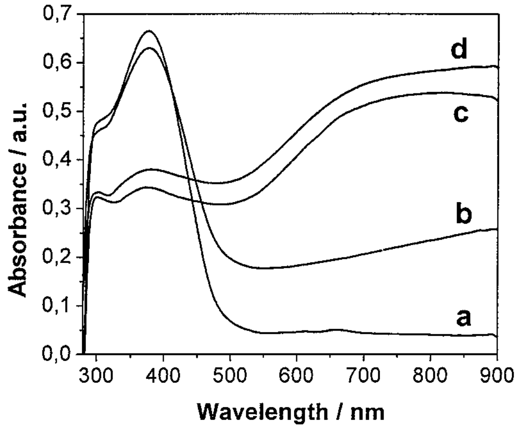

Figure 4 Spectroelectrochemistry of PPy and P(Py-AAm) in 0.1 M TBAP/ACN at different oxidation states: (a) neutral PPy, (b) neutral P(Py-AAm), (c) oxidized PPy and (d) oxidized P(Py-AAm).

3.3. Spectroelectrochemistry

PPy and P(Py-AAm) films have been deposited on ITO coated glass substrates galvanostatically at a constant current density of 0.2 mA/cm^2 from a mixture of 0.01 M pyrrole and 0.5 M acrylamide monomers in 0.1 M TBAP/ACN solution. The spectroelectrochemistry of this 0.4 μm thick PPy and P(Py-AAm) films is presented in Fig. 4. The π-π^* transition of both polymers gave a maximum of absorbance (λ_{max}) at 377 nm (3.29 eV) which correspond to a band gap (measured from the edge of the π-π^* absorption band) of 2.58 eV and 2.38 eV for PPy and P(Py-AAm) respectively. This small change in the band gap may stem from the incorporation of the AAm in the resulting polymer. It should also be noted that in the case of P(Py-AAm), the polymer can not be reduced completely as much as PPy which also supports the incorporation of AAm to the polymer. Moreover, the high absorption at lower energies in the oxidized state of both polymers makes them useful for some applications in the near IR region. At this point, acrylamide brings an advantage since as it incorporate into the structure, polymer become more

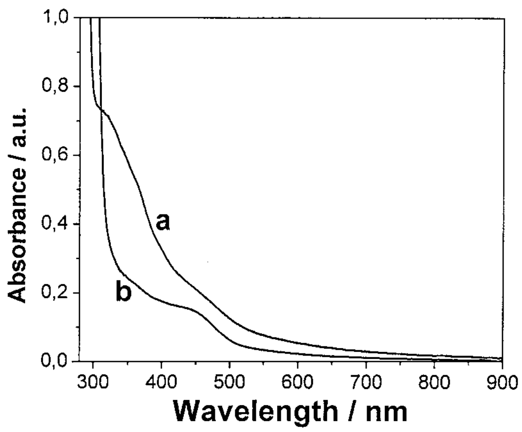

Figure 5 UV-visible spectrum of the electrolyte solution of (a) PPy and (b) P(Py-AAm) after electrolysis.

flexible [29]. UV-visible spectrum of the electrolyte solutions of PPy and P(Py-AAm) after electrolysis was also followed (Fig. 5). Since the presence of AAm stabilizes the intermediate species present in the solution and gives a solubility to the PPy [23, 24], the ratio between the absorptions at 335 nm and 430 nm decreases.

3.4. Colorimetry

Color of polymer is one of the most important property for the use in display applications and needs to be defined precisely. In order to further study the changes in coloration of PPy and P(Py-AAm) upon doping for potential display applications, *in situ* colorimetric analysis of the polymers PPy and P(Py-Aam) were studied and the results are expressed in the CIE 1931 Yxy and CIE 1976 L*a*b* color spaces as recommended by the "Commission Internationale de l'Eclairage" (CIE) [36]. The color of PPy changes from a brown-green to very dark green-blue upon oxidation. The presence of AAm in the polymer affects the color and makes it slightly darker. This slight change in the color of the P(Py-AAm) may stem from the carbonyl groups present in the acrylamide. The color track of both polymers PPy and P(Py-AAm) in the CIE 1931 Xxy color space is shown in Fig. 6A. It should also be noted that the scale of xy coordinates and the distance between each potential step is enlarged when AAm is incorporated to the polymer and almost the same color is obtained at the potentials, 0.8 V for PPy and 0.3 V for P(Py-AAm). Moreover the color of the P(Py-AAm) is more saturated at high positive potentials (i.e., +1.0 V).

The luminance, which is a coordinate in the Yxy color space, represents the brightness of a color. It is also very informative since with only one value, it provides information about the perceived transparency of a sample over the entire visible range of light. Instead of Y, it is usually more convenient to express the luminance as %Y that corresponds to the luminance of the sample divided by the luminance of the light source. It should be pointed out that %Y is different from %T because it takes into account the light sensitivity of the human eye, which is not constant over the entire visible range [32, 37]. The relative luminance (%Y) of PPy and P(Py-AAm) is presented in Fig. 6B. In PPy, relative luminance decreases upon oxidation from 27% in the reduced state to 7% in the completely oxidized state. On the other hand, relative luminance of P(Py-AAm) shows a slightly different character and decreases upon oxidation from 26% in the doped state to 4% in the oxidized state. It should also be noted that the decrease of the relative luminance in the case of P(Py-AAm) is more regular than PPy during oxidation that is a little sharper in the case of PPy especially between the potentials −0.2 V and +0.7 V vs. Fc/Fc$^+$. The decrease of the relative luminance in both polymers is not surprising since the absorbance of the π-π^* transition located at 377 nm is not completely depleted at the expense of lower energy transitions (see Fig. 4).

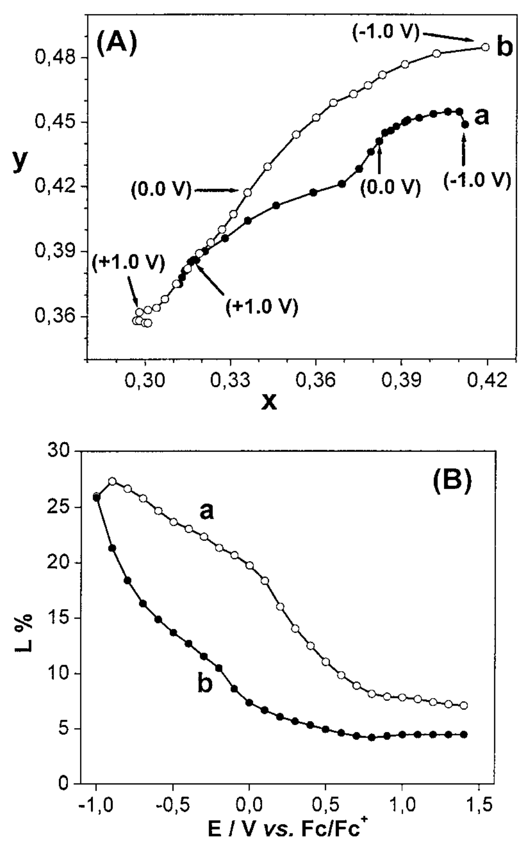

Figure 6 (A) Colorimetry (x-y diagram) of (a) PPy and (b) P(Py-AAm), (B) Relative luminance of (a) PPy and (b) P(Py-AAm) as calculated from the Yxy coordinates as a function of the potential applied vs. Fc/Fc$^+$.

These differences in the color track and the relative luminance of the polymer film when acrylamide is incorporated may bring some advantages to PPy in applications.

3.5. FTIR spectrum

FTIR spectra of the oxidized PPy and P(Py-AAm) free standing films are shown in Fig. 7. The conjugated double bonds of pyrrole ring absorb around 1100 cm^{-1} as splitted into three peaks (1030, 1120 and 1160 cm^{-1}) and 1550 cm^{-1} [38, 39]. Since ClO_4^- also absorbs at 1100 cm^{-1}, the presence of a strong absorption band at this wavenumber in both PPy and P(Py-AAm) shows that these polymers are doped with this anion. Moreover, the sharp peak around 1650 cm^{-1} corresponding to C=O in the polyacrylamide appears clearly in the copolymer which is not present in the PPy (Fig. 7A).

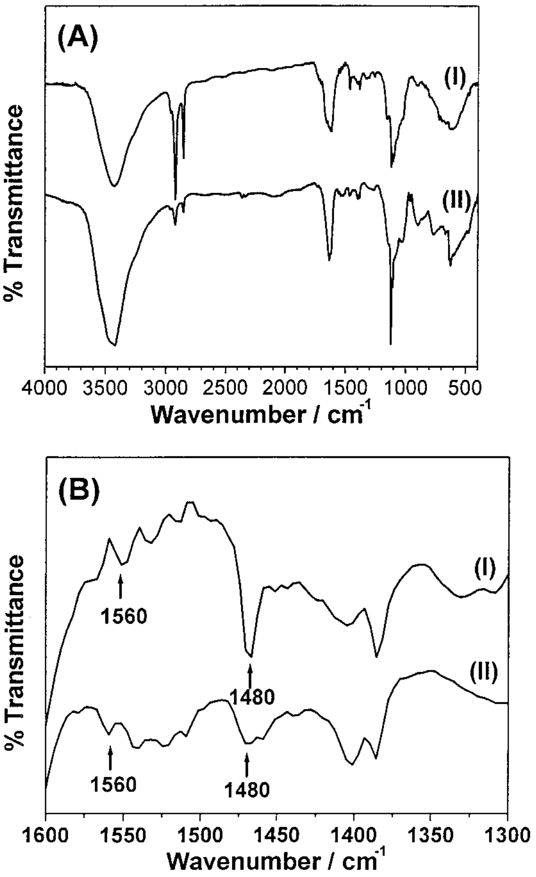

Figure 7 FTIR spectrum of (I) PPy and (II) P(Py-AAm) free-standing films: (A) full spectrum, (B) inset spectrum.

The electronic properties of conductive polymers are strongly dependent on conjugation length. Defects interrupt conjugation including sp^3 carbons, carbonyl groups, crosslinks, etc. [40]. We have used the method based on the theoretical work by Tian and Zerbi [41, 42] to explore conjugation lengths and interruption of the conjugation by AAm in our polymers PPy and P(Py-AAm) free standing films. Tian and Zerbi have used a parameter called the effective conjugation coordinate to calculate IR spectra for PPy. This theory successfully predicts the number and position of the main infrared bands of PPy and shows that the IR spectrum is strongly influenced by the conjugation length. In particular, Zerbi's calculations predict that as the conjugation length is increased, the intensity of the antisymmetric ring-stretching mode at 1560 cm^{-1} will decrease relative to the intensity of the symmetric mode at 1480 cm^{-1}. As a result, the ratio of the intensities of the 1560 cm^{-1} and 1480 cm^{-1} bands in an experimental IR spectrum can be used to obtain a relative measure of the conjugation length [40].

The ratio between the absorption bands at 1560 cm^{-1} and 1480 cm^{-1} is calculated from the FTIR spectrum of PPy and P(Py-AAm) films prepared on stainless steel electrodes by galvanostatic deposition with a current density of 0.2 mA/cm^{2}from the same electrolyte system described before. This ratio is found to be higher in the case of P(Py-AAm) films showing the decrease of the conductivity because of the interruption of the conjugation by incorparation of the non-conjugated AAm to the structure (Fig. 7B). This result is supported by the conductivity of the polymer films measured by four point probe conductivity that the PPy and P(Py-AAm) free-standing films show a conductivity of 90 and 1 S/cm, respectively.

4. Conclusion

Electropolymerization of pyrrole in the presence and absence of acrylamide was achieved. The role of applied electrical conditions and effect of the presence of acrylamide on the formation of the polymers in solution and on electrode surface were investigated. Polymer films deposited by galvanostatically, potentiostatically and potentiodynamically have shown good electrochemical and optical properties. Characterization of the polymer films have shown that the resulting poly(pyrrole-acrylamide)s were electroactive as much as polypyrroles even they lost 90 times of their conductivity. Incorporation of the acrylamide to the resulting polymer was supported by electrochemistry, colorimetry, conductivity and spectroscopic results. The presence of the acrylamide in the resulting polymer affects some of the properties of the polymer film (i.e., color, conductivity, electrochemistry, spectroelectrochemistry, etc.) that may bring some advantages for practical applications. For example, mechanical properties of the polypyrrole are very poor and the incorporation of the acrylamide to the structure with better mechanical properties may enhance the mechanical properties of polypyrrole. The solubility is also a problem for polypyrrole, so that the presence an anionic structure, such as acrylamide, improves the solubility [23, 24]. The differences in the color track and the relative luminance of the polymer film when acrylamide is incorporated to the structure and the high absorption at the lower energies in the oxidized state of the polymer is also important for practical applications.

Acknowledgements

The authors would like to thank Prof. John R. Reynolds and his group at University of Florida for helpful discussions and technical assistance to perform the colorimetric measurements.

References

1. H. SHIRAKAWA, E. J. LOUIS, A. G. MACDIARMID, C. K. CHIANG and A. J. HEEGER, *J. Chem. Soc., Chem. Commun.* (1977) 578.
2. H. S. NALWA, in "Handbook of Organic Conductive Molecules and Polymers" (John Wiley & Sons, New York, 1997).
3. T. A. SKOTHEIM, R. L. ELSENBAUMER and J. R. REYNOLDS, in "Handbook of Conducting Polymers" 2nd ed. (Marcel Dekker, New York, 1998).
4. J. L. REDDINGER and J. R. REYNOLDS, *Adv. in Polym. Sci.* edited by G. Wegner (Springer-Verlag, Berlin, 1999) p. 57.
5. R. H. FRIEND, R. W. GYMER, A. B. HOLMES, J. H. BURROUGHES, R. N. MARKS, C. TALIANI, D. C. BRADLEY, D. A. DOS SANTOS, J. L. BRÉDAS, M. LÖGDLUND, and W. R. SALANECK, *Nature* **397** (1999) 121.
6. I. D. BROTHERSON, D. S. K. MUDIGONDA, J. M. OSBORN, J. BELK, J. CHEN, D. C. LOVEDAY, J. L. BOEHME, J. P. FERRARIS and D. L. MEEKER, *Electrochim. Acta* **44** (1999) 2993.

7. L. GROENENDAAL, F. JONAS, D. FREITAG, H. PIELARTZIK and J. R. REYNOLDS, *Adv. Mater.* **12** (2000) 481.
8. D. L. WISE, G. E. WINEK, D. J. TRANTOLO, T. M. COOPER and J. D. GRESSER, in "Electrical and Optical Polymer Systems" (Marcel Dekker, New York, 1998) p. 17.
9. J. RODRIGUEZ, H. J. GRANDE and T. F. OTERO, in "Handbook of Organic Conductive Molecules and Polymers" edited by H. S. Nalwa (John Wiley & Sons, New York, 1997).
10. J. SIMONET and J. R. BERTHELOT, *Progress in Solid State Chemistry* **21** (1991) 1.
11. A. F. DIAZ and J. BARGON, in "Handbook of Conducting Polymers," edited by T. A. Skotheim (Dekker, New York, 1986) Vol. I, p. 81.
12. B. SCROSATI, in "Applications of Electroactive Polymers" (Chapman & Hall, London, 1993).
13. A. F. DIAZ, J. CROWLEY, J. BARGON, G. P. GARDINI and J. B. TORRENCE, *J. Electroanal. Chem.* **121** (1981) 355.
14. A. F. DIAZ, A. MARTINEZ and K. K. KANAZAWA, *ibid.* **130** (1981) 181.
15. L. F. WARREN and P. J. ANDERSON, *J. Electrochem. Soc.* **134** (1987) 101.
16. F. T. A. VORK and L. J. J. JANSSEN, *Electrochim. Acta* **33** (1988) 1513.
17. A. J. DOWNARD and D. J. PLETCHER, *J. Electroanal. Chem.* **206** (1986) 139.
18. R. B. BJORKLUND and B. LIEDBERG, *J. Chem. Soc. Chem. Commun.* (1986) 1293.
19. A. S. SARAÇ, G. SÖNMEZ, B. USTAMEHMETOĞLU and M. I. MUSTAFAEV, *J. Polym. Sci. Part A: Polym. Chem.* **35** (1996) 1255.
20. B. USTAMEHMETOĞLU, S. BAYÜLKEN, S. ÖZKARA, G. SÖNMEZ and A. S. SARAÇ, *ibid.* **37** (1999) 1115.
21. G. ZOTTI, S. CATTARIN and N. COMISSO, *J. Electroanal. Chem.* **235** (1987) 259.
22. D. E. RAYMOND and D. J. HARRISON, *ibid.* **355** (1993) 115.
23. G. SÖNMEZ, PhD Thesis 2002.
24. A. S. SARAÇ and G. SÖNMEZ, *Polym. Int.*, in press.
25. J. HEINZE, in "Topics in Current Chemistry" Vol. 152 (Springer-Verlag, Berlin, 1990) p. 2.
26. K. DOBLHOFER and K. RAJESHWAR, in "Handbook of Conducting Polymers," 2nd ed., edited by T. A. Skotheim, R. L. Elsenbaumer and J. R. Reynolds (Marcel Dekker, New York, 1998) p. 531.
27. M. ZHOU and J. HEINZE, *Electrochim. Acta* **44** (1999) 1733.
28. T. F. OTERO and E. DELARETTA, *Synth. Met.* **26** (1988) 79.
29. A. S. SARAÇ, G. SÖNMEZ and B. USTAMEHMETOGLU, *ibid.* **98** (1999) 177.
30. G. GRITZNER and G. KUTA, *J. Pure Appl. Chem.* **56** (1984) 461.
31. L. H. MASSEL and R. GIANG (Ed.), in "Handbook of Thin Film Technology" (New York, McGraw Hill, 1983).
32. K. NASSAU, in "Color for Science, Art and Technology" (Elsevier, Amsterdam, 1998).
33. R. D. OVERHEIM and D. L. WAGNER, in "Light and Color" (Wiley, New York, 1982) p. 77
34. J. M. PERNAUT, R. C. D. PERES, V. F. JULIANO and M. A. DE PAOLI, *J. Electroanal. Chem.* **274** (1989) 225.
35. A. F. DIAZ, J. I. CASTILLO, J. A. LOGON and W.-Y. LEE, *ibid.* **129** (1981) 115.
36. CIE, Colorimetry (Official Recommendations of the International Commission on Illumination, CIE Publi. No: 15 Paris, 1971).
37. B. C. THOMPSON, P. SCHOTTLAND, G. SONMEZ and J. R. REYNOLDS, *Synth. Met.* **119** (2001) 333.
38. R. C. LORD and F. A. MILLER, *J. Chem. Phys.* **10** (1942) 328.
39. R. A. JONES, *Aust. J. Chem.* **19** (1966) 289.
40. J. T. LEI, Z. CAI and C. R. MARTIN, *Synth. Met.* **46** (1992) 53.
41. B. TIAN and G. ZERBİ, *J. Chem. Phys.* **92** (1990) 3892.
42. *Idem.*, *ibid.* **92** (1990) 3886.

Received 26 October 2001
and accepted 18 July 2002