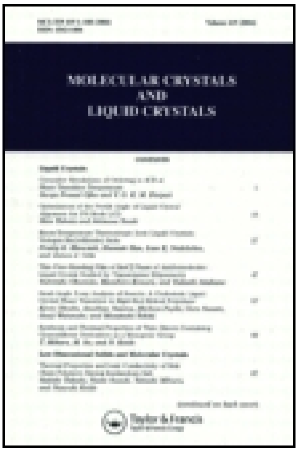
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 11:08
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electrochemically Fabricated Pyrrole Copolymer Thin Films and Their Electroactivity in Neutral Aqueous Solution

Rapiphun Janmanee [a] , Akira Baba [b] , Sukon Phanichphant [c] , Saengrawee Sriwichai [a] , Kazunari Shinbo [b] , Keizo Kato [b] & Futao Kaneko [b]

[a] Department of Chemistry, Faculty of Science , Chiang Mai University , Chiang Mai , Thailand

[b] Center for Transdisciplinary Research and Graduate School of Science and Technology , Niigata University , Niigata , Japan

[c] Materials Science Center, Faculty of Science , Chiang Mai University , Chiang Mai , Thailand

Published online: 11 Sep 2013.

To cite this article: Rapiphun Janmanee , Akira Baba , Sukon Phanichphant , Saengrawee Sriwichai , Kazunari Shinbo , Keizo Kato & Futao Kaneko (2013) Electrochemically Fabricated Pyrrole Copolymer Thin Films and Their Electroactivity in Neutral Aqueous Solution, Molecular Crystals and Liquid Crystals, 580:1, 29-34, DOI: 10.1080/15421406.2013.804775

To link to this article: http://dx.doi.org/10.1080/15421406.2013.804775

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,

Mol. Cryst. Liq. Cryst., Vol. 580: pp. 29–34, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.804775

Electrochemically Fabricated Pyrrole Copolymer Thin Films and Their Electroactivity in Neutral Aqueous Solution

RAPIPHUN JANMANEE,[1] AKIRA BABA,[2] SUKON PHANICHPHANT,[3,*] SAENGRAWEE SRIWICHAI,[1] KAZUNARI SHINBO,[2] KEIZO KATO[2] AND FUTAO KANEKO[2]

[1]Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand
[2]Center for Transdisciplinary Research and Graduate School of Science and Technology, Niigata University, Niigata, Japan
[3]Materials Science Center, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand

The functionalized pyrrole copolymers were fabricated by electropolymerization of pyrrole (Py) and functionalized pyrrole monomers, pyrrole-3-carboxylic acid (P3C) and 4-(3-pyrrole) butyric acid (PBA). The electrochemical behavior and doping/dedoping properties of the obtained copolymer thin films were investigated by cyclic voltammetry (CV) in neutral phosphate-buffered saline (PBS) solution. Moreover, the functionalized pyrrole copolymer films were characterized by UV-vis absorption spectroscopy and atomic force microscopy (AFM). The obtained copolymer thin films showed good stability and electroactivity in neutral PBS solution. The presented functionalized pyrrole copolymer thin films may possess potential applications to study in various systems of the biosensors.

Keywords Conducting polymer; copolymer; electropolymerization; pyrrole

1. Introduction

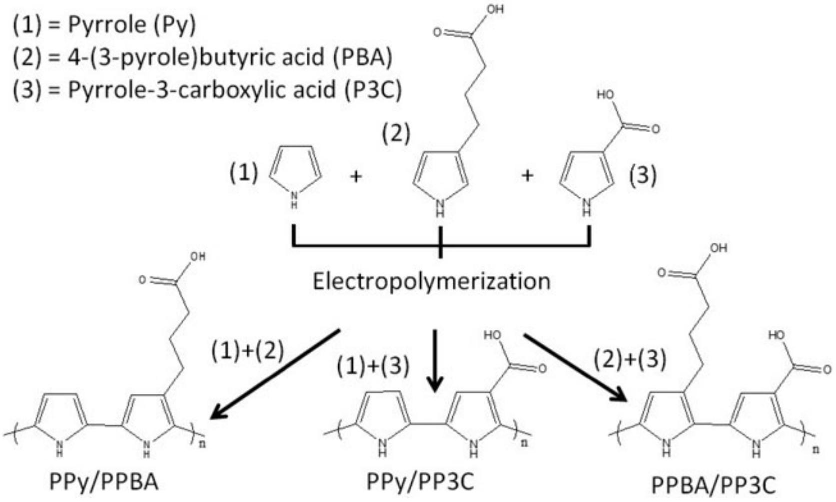
Conducting polymers (CPs) have received considerable attention because of their unique electrical optical, chemical and biochemical properties [1–3]. In recent years, CPs have potential applications in various fields such as fuel cells, electrochromic displays, field effect transistors (FETs) and biosensors [4–6]. The most widely investigated CPs includes polythiophene, polyaniline, poly(phenylene vinylene) and polypyrrole and their derivatives. CPs can be synthesized either chemically or electrochemically [1, 7]. Nowadays, electrochemical synthesis is a common alternative for making CPs, particularly because this synthetic procedure is relatively straightforward, ability of controlling thickness, shape and morphology of CPs [2, 3, 8]. Among these CPs, polypyrrole (PPy) and their derivatives are especially promising materials for commercial applications due to their good electrical

---

[*] Address correspondence to Sukon Phanichphant. Tel.: +66-81-882-7977; Fax: +66-53-892277. E-mail: sphanichphant@yahoo.com

conductivity, environmental stability to air and water, ease and high flexibility in preparation [1, 9]. In particular for biosensor application, PPy and their derivatives based biological sensor have been extensively investigated to detect the biomolecules for example glucose, hormones, antibodies and antigens [6, 9–11]. However, there are still few reports in terms of the electroactivity of pyrrole-based polymer films in neutral solution, although it is very important to construct effective biosensors based on conducting polymer mediators.

In this study, the fabrication and characterization of functionalized pyrrole copolymer thin films were reported. The pyrrole-3-carboxylic acid (P3C) and 4-(3-pyrrole) butyric acid (PBA) monomer as shown in Scheme 1, with various ratios in acidic aqueous solution were employed to fabricate functionalized polypyrrole copolymer films on indium tin oxide (ITO) coated glass slide by electropolymerization. Their electrochemical behavior and doping/dedoping properties were monitored by cyclic voltammetry (CV) in neutral PBS solution. Moreover, the UV-vis absorption spectroscopy and AFM were performed to characterize the copolymer films. In addition, the electroactivity of the obtained copolymer films in PBS solution were studied.



Scheme 1. Schematic representation of the electropolymerization of functionalized pyrrole copolymers.

2. Materials and Methods

2.1. Chemicals and Materials

The Py, P3C and PBA monomer and PBS (pH 7.4) were purchased from Sigma-Aldrich Co. All other chemicals were analytical grade with highest purity and used as received.

2.2. Electropolymerization of Functionalized Pyrrole Copolymers

The functionalized pyrrole copolymer, PPy/PPBA was electrochemically polymerized on ITO substrate. The precursor solutions containing α mM Py and β mM PBA with constant 10 mM monomer concentration in 0.5 M H_2SO_4 solution, the simple notation of α:β

Py/PBA, such as 9:1 Py/PBA 7:3 Py/PBA, 5:5 Py/PBA, etc., were used for fabricating the PPy/PPBA films. 0.5 M sulfuric acid was acted not only as electrolyte solution but also solvent in this study. It is assumed that the supplementary doping of the copolymer in sulfuric acid media could be introduced multiple charge carriers leading to an improvement of the electrical conduction along the polymer chain and ability to undergo easier diffusion of the dopants during the redox process. For the electrochemical system, platinum wire, Ag/AgCl and ITO were used as counter, reference and working electrodes, respectively. The electropolymerization was performed by CV in a range from 0 to 1.0 V at a scan rate of 20 mV/s. The same procedure was employed for the fabrication of PPy/PP3C and PPBA/PP3C copolymer films.

2.3. Characterization

UV-vis spectra of the obtained copolymers film deposited on the ITO-glass electrode were recorded using Jasco V-650 spectrophotometer. In addition, the obtained copolymer films with applied constant potentials at −0.2, 0, 0.3 and 0.6 V in PBS solution to study the electroactivity property were monitored by UV-vis measurement. Moreover, AFM was employed to characterize the topology of the functionalized pyrrole copolymer films, the measurements were conducted with tapping mode at ambient temperature.

3. Results and Discussion

3.1. Electropolymerization of Functionalized Pyrrole Copolymers

Figure 1 shows electrochemical property during the electropolymerizaition of PPy/PPBA, PPy/PP3C and PPBA/PP3C copolymers. As shown in the CV trace of PPy/PPBA, PPy/PP3C and PPBA/PP3C copolymers, the current in the anodic scan increased at about 0.3, 0.6 and 0.5 V respectively, indicating the beginning of the formation of functionalized pyrrole copolymers on ITO electrodes. The current slightly decreased at about 0.15, 0.3 and 0.4 V respectively in the cathodic scan, which indicated the dedoping process of the deposited copolymer films. The current of electropolymerized PPy/PPBA copolymer exhibited higher current than that of other copolymers due to the large amount of deposited film on the electrode. These results indicate that the PPy/PPBA has lower oxidation potential which facilitates the electropolymerization of the copolymer film as compared to other combinations [12]. Based on these results, PPy/PPBA copolymer films were employed to represent the properties of functionalized pyrrole copolymer films.

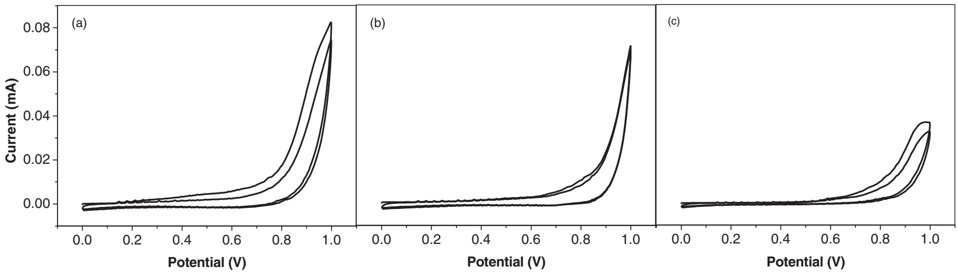


Figure 1. CV trace of the electropolymerizaition of (a) PPy/PPBA, (b) PPy/PP3C and (c) PPBA/PP3C copolymers.

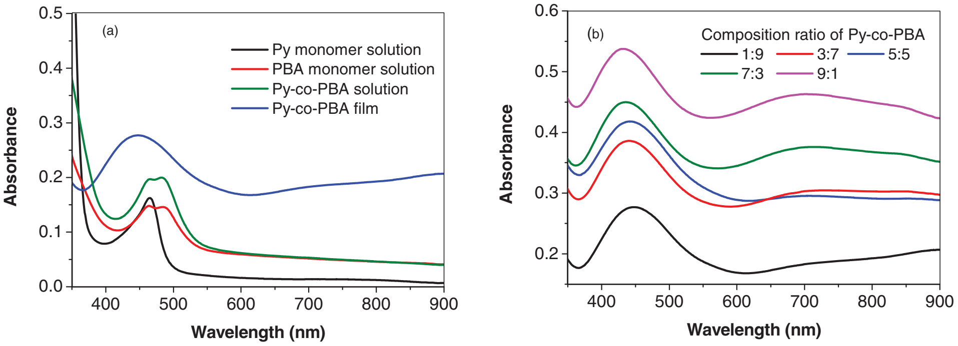


Figure 2. UV-vis spectra of (a) Py monomer, PBA monomer, Py/PBA monomer solution, and PPy/PPBA copolymer film and (b) PPy/PPBA copolymer film at different concentration ratios.

3.2. Characterization of Functionalized Pyrrole Copolymer Films by UV-vis and AFM

UV-vis absorption spectra of Py, PBA, 5:5 Py/PBA monomer solution and 5:5 PPy/PPBA copolymer film are shown in Fig. 2(a). The absorption peak at around 480 nm are obtained in the UV-vis spectra of 5:5 Py and PBA monomer solution. The peak of PPy/PPBA copolymer film on ITO are obtained at around 450 nm. The presensce of a absorption peak for the copolymer spectra, which is absent in the monomer absorption peak, indicates the monomers are transformed to polymer and extended degree of conjugation in the polymer chain. Especially, the broad absorption peak seen at higher than 600 nm corresponds to polaron/biporalon band due to the doping of the conjugated polymer chain. Fig. 2(b) shows UV-vis absorpation spectra at several ratio of Py:PBA for the electropolymerization. The results show that the absorption intensity increases with increasing the ratio of Py, indicating that the presence of Py facilitates the electropolymerization and deposition of the film.

The topology of PPy/PPBA copolymer film was characterized by AFM in order to investigate the roughness of the film. The roughness of the obtained copolymer films over an area of two-dimensional views of 2 × 2 μm^2 AFM image are shown in Table 1. The obtained results indicated that the topology of PPy/PPBA copolymer films increased with increasing PBA ratio.

3.3. Potentiostatic Measurement

UV-vis spectra of the 5:5 PPy/PPBA copolymer film deposited on an ITO glass substrate at constant applied potentials of −0.2, 0.0, 0.3 and 0.6 V are shown in Fig. 3(a). The absorbance in visible region of the copolymer film increased with increasing the potentials, which indicates that the PPy/PPBA copolymer can be electroactive in neutral PBS solution due to the topological changes of the copolymer films, because the film might swell due to the doping effect by the applying the potentials [9]. The electroactivity property of PPy/PPBA copolymer film was compared with PPy and poly (4-(3-pyrrole) butyric acid)

Table 1. The surface roughness of PPy/PPBA copolymer film

$\alpha:\beta$ PPy/PPBA	9:1	7:3	5:5	3:7	1:9
Surface roughness (nm)	3.425	3.963	4.082	4.315	4.652

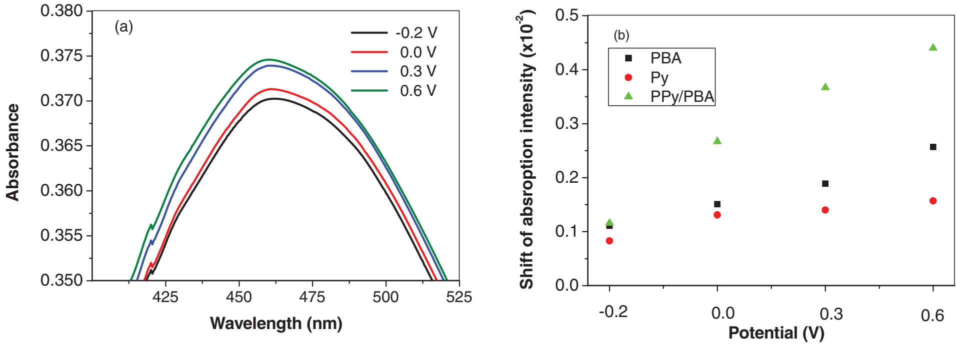


Figure 3. UV-vis spectra of (a) 5:5 PPy/PPBA copolymer thin film and (b) the comparison of the shift of absorption intensity with PPy, PPBA and PPy/PPBA thin film on ITO substrate at different constant applied potentials.

(PPBA) at different constant applied potentials as shown in Fig. 3(b). It was found that the absorption intensity of PPy/PPBA copolymer shifted changed much more steeply with the applied potential among than the homopolymers. The reason for this shifting is that the PPy/PPBA copolymer thin film produced higher π-π^* transition formation due to the doping of the polymer among applied potential than that of PPy and PPBA thin films, indicating that the increase of the absorption intensity much more than the homopolymers. Moreover, the increase of PPBA content in the copolymer could be obtained higher absorption intensity with the potential as shown in Fig. 4 but this behavior was less effective than that of the applied potential.

These results indicated that the functionalized pyrrole copolymer films showed good electroactivity in neutral solution and their electroactivity property could be enhanced with the electrochemically controlled potential, which may possess potential applications to study in various systems of the biosensors.

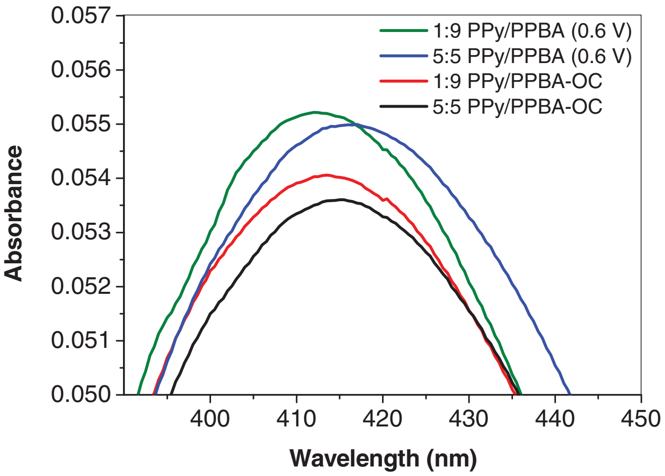


Figure 4. UV-vis spectra of PPy/PPBA copolymer film at different concentration ratios with and without applied potential.

4. Conclusions

The functionalized pyrrole copolymer thin films were successfully prepared by electropolymerization. The AFM images of the topology of PPy/PPBA copolymer showed that the roughness increased with increasing PBA proportion. Moreover, it was found that the obtained copolymer thin film of PPy/PPBA showed obvious change of UV-vis spectra with applied constant potentials in neutral PBS solution. These results indicate that the topology and electroactivity of the fabricated copolymer can be controlled by applying electrochemical potentials. Therefore, it can be concluded that an electrochemically fabricated functionalized pyrrole copolymer is a promising candidate as smart materials for the biosensors application in the future.

Acknowledgments

The authors gratefully acknowledge the Office of Higher Education Commission, Ministry of Education under the program Strategic Scholarships for Frontier Research Network; Department of Chemistry, Faculty of Science, Chiang Mai University and Graduate School Chiang Mai University; the National Research University Project under Thailand's Office of the Higher Education Commission, Thailand and the "Global Circus" Program of Niigata University supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan for financial support.

References

[1] Vidal, J. C., Ruiz, E. G., & Castillo, J. R. (2003). *Microchim. Acta*, *143*, 93.
[2] Peng, H., Zhang, L., Soeller, C., & Travas-Sejdic, J. (2009). *Biomaterials*, *30*, 2132.
[3] Guimard, N. K., Gomez, N., & Schmidt, C. E. (2007). *Prog. Polym. Sci.*, *32*, 876.
[4] Damos, F. S., Luz, R. C. S., & Kubota, L. T. (2006). *Electrochim. Acta*, *51*, 1304.
[5] Adhikari, B., & Majumdar, S. (2004). *Prog. Polym. Sci.*, *29*, 699.
[6] Baba, A., Mannen, T., Ohdaira, Y., Shinbo, K., Kato, K., Kaneko, F., Fukuda, N., & Ushijima, H. (2010). *Langmuir*, *26*, 18476.
[7] Dong, H., Cao, X., Li, C. M., & Hu, W. (2008). *Biosens. Bioelectron.*, *23*, 1055.
[8] Ravichandran, R., Sundarrajan, S., Venugopla, V. R., Mukherjee, S., & Ramakrishna, S. (2010). *J. R. Soc. Interface*, *10*, 1098.
[9] Janmanee, R., Baba, A., Phanichphant, S., Sriwichai, S., Shinbo, K., Kato, K., & Kaneko, F. (2011). *Jpn. J. Appl. Phys.*, *50*, 01BK02-1.
[10] Sriwichai, S., Baba, A., Phanichphant, S., Shinbo, K., Kato, K., & Kaneko, F. (2010). *Sens. Actuators B*, *147*, 322.
[11] Janmanee, R., Baba, A., Phanichphant, S., Sriwichai, S., Shinbo, K., Kato, K., & Kaneko, F. (2012). *ACS Appl. Mater. Inter.*, *4*, 4270.
[12] Peng, H., Soeller, C., Vigar, N., Kilmartin, P. A., Cannell, M. B., Bowmaker, G. A., Cooney, R. P., & Travas-Sejdic, J. (2005). *Biosens. Bioelectron.*, *20*, 1821.