http://dx.doi.org/10.5935/0103-5053.20140043

J. Braz. Chem. Soc., Vol. 25, No. 3, 597-601, 2014.
Printed in Brazil - ©2014 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Morphological and Electrochemical Characteristics of Electrosynthesized PPy/CD Composite

Rubênia S. Monte,[a] Lloyd R. V. Kotzebue,[a] Dalila L. Alexandre,[a] Roselayne F. Furtado,[b] Jorge A. C. Santos,[c] Joana D. P. Dantas[a] and Carlucio R. Alves*,[a]

[a]Department of Chemistry, State University of Ceara, Av. Paranjana, 1700, 60740-903 Fortaleza-CE, Brazil

[b]Embrapa Tropical Agroindustry, Rua Sara Mesquita, 2270, 60511-110 Fortaleza-CE, Brazil

[c]Atomic Force Microscopy Laboratory, University of Fortaleza, Av. Washington Soares, 1321, 60811-905 Fortaleza-CE, Brazil

Neste trabalho, a eletrodeposição do compósito polipirrol/cardanol (PPy/CD) foi realizada visando boa característica eletroquímica e melhoria de propriedade mecânica do filme. Compósitos de PPy/CD foram crescidos em superfície de ouro potenciodinamicamente e potenciostaticamente, em diferentes concentrações de Py e CD em meio de acetonitrila. A caracterização do compósito foi seguida com o uso de técnicas de espectroscopia de infravermelho, microscopia eletrônica de varredura, microscopia de força atômica e voltametria cíclica. O compósito apresentou a incorporação do CD no PPy com morfologia globular e também na forma de nódulos, com grãos de 1-2 nm. Os compósitos crescidos por voltametria cíclica e cronoamperometria apresentaram cargas anódicas de aproximadamente 2,9 e 5,7 mC, respectivamente.

This study was carried out to investigate the electrodeposition of polypyrrole/cardanol (PPy/CD) composite, targeting for good electrochemical characteristics and improved mechanical properties of the film. Composites of PPy/CD were grown on gold surface potenciodynamically and potenciostatically in different concentrations of CD and Py in acetonitrile. The characterization of the composite was followed using infrared spectroscopy, scanning electron microscopy, atomic force microscopy and cyclic voltammetry. The composite showed the incorporation of CD in PPy morphology globular and also in the form of nodules, with grains of 1-2 nm. The composites grown by cyclic voltammetry and chronoamperometry showed anodic charges of approximately 2.9 and 5.7 mC, respectively.

Keywords: Polypyrrole/cardanol, composite, conductor polymer, cardanol, CNSL

Introduction

Conducting polymers (CP) have aroused great technological and scientific interest because of the wide variety of applications, for example, in biosensors, organic solar cells, and electrochromic devices. One of the conducting polymers of interest is polypyrrole (PPy), which draws a lot of attention due to its great electric conductivity and its ease in synthesis by oxidizing the monomer in aqueous and non-aqueous solutions. Many researches, in order to improve the weak mechanical properties and low processability of the PPy film, have combined this polymer with other materials.[1-4] This can be achieved by copolymerization of the pyrrole, making blends of PPy with other polymers or composites of PPy with inorganic or organic materials.[5]

Conducting polymer composites (CPC) possesses flexibility, processability, light weight, ability to absorb mechanical shock and magnetic shielding property.[6-8] These materials consist of conductive filler contained in an insulating matrix which these can be obtained chemically or electrochemically. Studies on CPC involving PPy are being carried out and new applications already have been reported in the literature as an antistatic material and for drug delivery system.[9,10]

Cashew nut shell liquid (CNSL) is a toxic byproduct of processing cashew nuts which is obtained from the pericarp of the nut of *Anacardium occidentale* L.. This brown viscous liquid provides interesting phenolic compounds which are mainly anacardic acid, cardanol,

---

*e-mail: alvescr@pq.cnpq.br

cardol, polymeric materials and traces of 2-methyl cardol. By heating the natural CNSL, the anacardic acid will undergo decarboxylation transforming into cardanol. The natural CNSL after heat treatment is also called as technical CNSL.[11-14] The concentration of each compound of both CNSL can be seen on Table 1.

Table 1. Composition of technical cashew nut shell liquid (CNSL)[13]

Phenolic compounds	Technical CNSL / %
Anacardic acid	1.0-1.7
Cardanol	67.8-94.6
Cardol	3.8-18.8
2-Methyl cardol	1.2-4.1
Minority components	3.0-4.0
Polymeric materials	0.3-21.6

Cardanol (CD) is a mixture of 3-alkyl-phenols differing in degree of unsaturation in the side chain: 3-(pentadecyl)-phenol, 3-(8Z-pentadecenyl)-phenol, 3-(8Z, 11Z-pentadecadienyl)-phenol, and 3-(8Z, 11Z, 14-pentadecatrienyl)-phenol (Figure 1). These compounds show to be very promising as renewable building blocks for a variety of applications for bio-based polymers, novolac resins, surfactants, fire retardants, nanowires, nanotubes, antibacterial coatings, porphyrins, fullerene conjugates, composites and many others.[15-22]

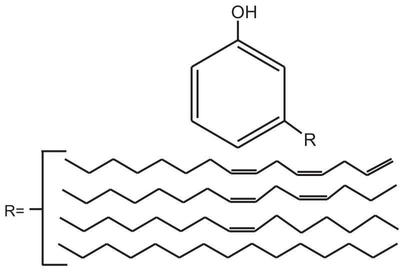

Figure 1. Structural representation of cardanol components.

To our best knowledge, we have shown for the first time polypyrrole/cardanol composites (PPy/CD) synthesized by electrochemical methods on gold surface in acetonitrile medium. Studies were performed on morphology, topography, and charge transfer reaction of the electropolymerized novel composites.

Experimental

Materials and reagents

The chemical reagents used for growth and electrochemical characterization were of analytical grade. The pyrrole (Aldrich Chemicals) was previously purified by distillation (59 °C, 50 mmHg) in nitrogen atmosphere and was stored at low temperature in absence of light. The acetonitrile was used as aprotic medium, (Merck, HPLC-grade). The lithium perchlorate (Janssen, 99%) was heated to 80 °C for 2 h before use. The cardanol was concentrated by chromatographic column (Merck, silicagel 60, 70-230 mesh), with hexane (Merck, HPLC-grade) as eluent.

Equipments and electrodes

Electrochemical cell (Methroms) consisted of three electrodes. A gold disc working electrode (Ø = 1.77 mm^2), a gold helical wire counter electrode (area of 30 mm^2) and potential *vs.* Ag/AgCl, 3 mol L^{-1} reference electrode. The working electrode was polished with alumina powder of 0.3 µm, sonicated, cleaned electrochemically using a solution of H_2SO_4 (0.5 mol L^{-1}) and then washed with Milli-Q water (18.2 MΩ cm) after each procedure.

The morphological characterization was carried by scanning electron microscopy (SEM) using a Zeiss 940 A. Investigations of the surface topography were performed by atomic force microscope (AFM) with an Agilent 5500 AFM/SPM microscope. Fourier transform infrared (FT-IR) of the films was recorded on a Varian 660-IR spectrometer.

Electrosynthesis and characterization of PPy/CD film

The conducting PPy/CD composites were synthesized by electrochemical techniques of cyclic voltammetry and chronoamperometry using the potentiostat/galvanostat Autolab® PGSTAT-12 controlled by GPES software. Films were synthesized: (*i*) potentiodynamically with ten cycles (from –0.5 to 1.0 V), and a scan rate of 50 mV s^{-1}, and (*ii*) potentiostatically with fixed potential of 0.8 V for 600 s. In order to obtain a film with good electrochemical properties, different concentrations of Py and CD were evaluated. Py and CD concentrations ranged from 0.1 to 0.5 mol L^{-1} and 0.01 to 0.1 mol L^{-1}, respectively; in acetonitrile medium containing lithium perchlorate (0.1 mol L^{-1}) as supporting electrolyte. After the synthesis, the films were washed with acetonitrile to remove possible residue.

After synthesizing the films, electrochemical studies were carried to analyze its ability to store charge at a scan rate of 50 mV s^{-1}. Both studies were evaluated by cyclic voltammetry using only the supporting electrolyte in acetonitrile medium in a potential range from –0.3 to 0.7 V. The PPy/CD composites grown by cyclic voltammetry and chronoamperometric methods were characterized and compared by SEM, AFM and FT-IR.

Results and Discussion

Obtaining of cardanol

CNSL was obtained by Cione Industry (Fortaleza, Brazil), from processes of cashew nuts production. The cardanol was seperated by column chromatography with silicagel and hexane, according to the methodology proposed by Pillai *et al.*.[23]

Electrosynthesis of PPy/CD film

Potentiodynamic and potentiostatic electrodepositions of composites varying the Py and CD concentrations were performed. The growth and the conductivity of the films were previously analysed and therefore of Py (0.5 mol L^{-1}) and of CD (0.1 mol L^{-1}) was chosen for this work (Figure 2).

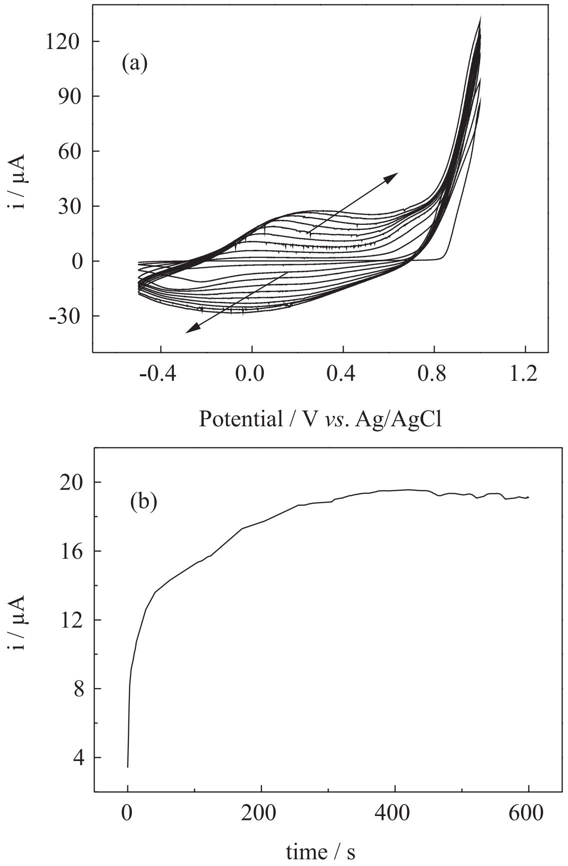

Figure 2. PPy/CD grown on gold surface with concentrations of [Py] = 0.5 mol L^{-1} and [CD] = 0.1 mol L^{-1} in acetonitrile medium in the presence of [$LiClO_4$] = 0.1 mol L^{-1}. Cyclic voltammetry curves with (a) v = 50 mV s^{-1}, and chronoamperommetric curve (b) at E_p = 0.8 V.

In Figure 2a is observed the increase of current due the formation of the composite with oxidation of the monomer, a nucleation loop was observed till the switchable potential, incorporating the cardanol in the composite.[24] It was verified on each cycle the oxidation potential was shifted to more positive direction which is the overpotential due the deposition of new layers of the composite.

The potentiostatic response (Figure 2b) to the applied potential indicated the presence of hydroxyl groups being incorporated in the PPy chain. According to Otero *et al.*,[25] the incorporation of the termination groups showed overoxidation reducing the electropolymerization. The chronoamperometric measurement points out the time that the whole gold surface was covered by the composite (about 600 s) leading to a new electron transfer of the monomer and the composite interface.

The composite grown potenciostatically and potenciodynamically can be detached from the gold surface after being washed with acetonitrile and dried at room temperature.

Morphological, spectral, topographic, and electrochemical studies

In general, PPy possesses a globular morphology in nature[26] and this is affected by the electrochemical methods used for the growth the film. Images of the PPy/CD conducting composite growth by cyclic voltammetry and chronoamperometric methods in acetonitrile and lithium perchlorate medium are shown in Figure 3.

The film grown potentiodynamically (Figure 3a) showed a rough surface and globular morphology which is similar to the morphology of PPy in nature. The composite grown potentiostatically (Figure 3b) showed beside the globular morphology also a form of nodules. The morphology of the PPy/CD composite containing perchlorate ions suggests three-dimensional or isotropic growth.[26]

The SEM images showed a granular surface, and when the PPy/CD composites were observed by AFM, a granular structure is visible on the surface. These granules or nodules are aligned to form a long ordered structure. The diameter of these nodules is very similar and the corrugation is 1.0-2.0 nm approximately. Figure 4 shows AFM images of the PPy/CD composites obtained by cyclic voltammetry and by applying constant potential. Films obtained by constant potential are more compact and the granules are bigger.

Infrared spectra (Figure 5) showed the presence of PPy and CD for the composites grown potentiostatically and potentiodynamically. The spectrum of the film grown by cyclic voltammetry is seen in Figure 5a. According to Jing *et al.*,[27] the hydroxyl group of the cardanol is indicated by the band absorption at around 3345 cm^{-1}, which was different of the observed band absorption at 3565 cm^{-1}. This high

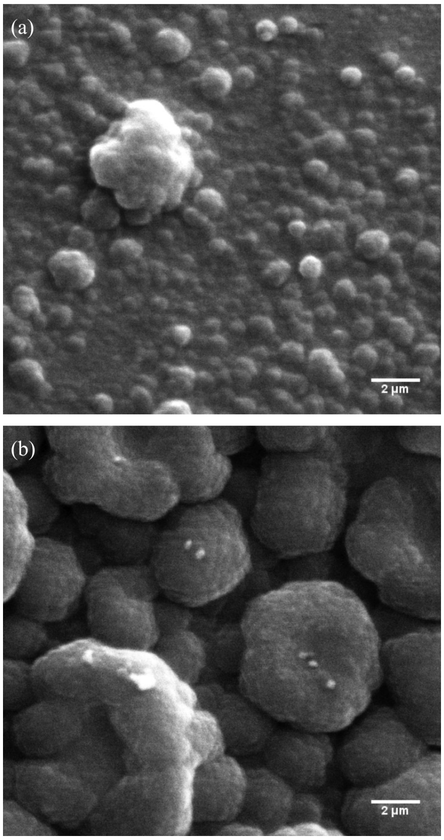

Figure 3. SEM micrographs of PPy/CD films growth on Au with [Py] = 0.5 mol L^{-1} and [CD] = 0.1 mol L^{-1} in acetonitrile medium in the presence of [$LiClO_4$] = 0.1 mol L^{-1}. Cyclic voltammetry with (a) v = 50 mV s^{-1}, and chronoamperommetry (b) at E_p = 0.8 V. SEM operated at 15 kV, and at 5000× magnification.

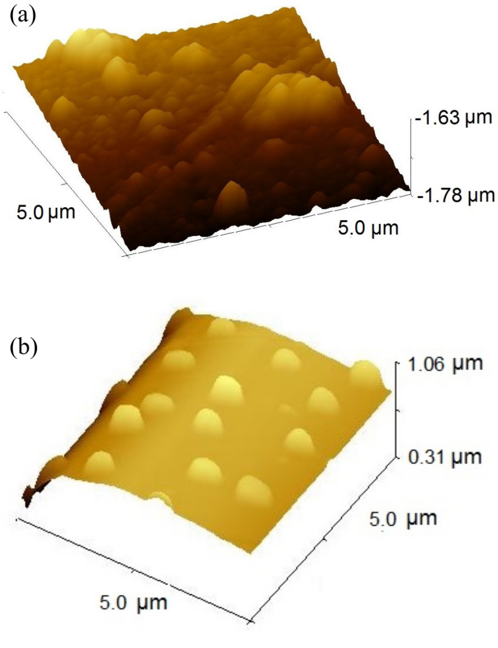

Figure 4. AFM topography of PPy/CD films prepared on Au with [Py] = 0.5 mol L^{-1} and [CD] = 0.1 mol L^{-1} in acetonitrile medium in the presence of [$LiClO_4$.] = 0.1 mol L^{-1}. Voltammetry cyclic with (a) v = 50 mV s^{-1}, and chronoamperommetry (b) at E_p = 0.8 V.

wavenumbers indicated the presence of "free" OH group, meaning that there is a low absorption of the hydrogen bonds. Broad band absorption at 3306 cm^{-1} indicated the N-H stretching of the PPy and the C-H stretching of both aromatic regions. The presence of the C-H stretching of the alkyl chain of the phenolic compound was indicated at frequencies at 3003-2850 cm^{-1}. In the literature, PPy has three weak bands at frequencies around 1610, 1490, and 1410 cm^{-1}, caused by the C=C stretching of the aromatic ring, but these bands are not so clear due the overlapping of the strong peaks, 1546 and 1453 cm^{-1}, caused by the C=C stretching of the cardanol. Another absorption of the PPy is the absorption at the frequency around 1032 cm^{-1} due the N-H bending.[28]

The composite grown potentiostatically (Figure 5b) showed characteristic bands for pyrrole and cardanol. In the spectrum, a small broad band absorption at 3279 cm^{-1} was observed, which is typical due to the absorption of hydrogen bonds. Strong absorptions peaks at 2919 and 2850 cm^{-1} were observed with almost the same intensity as the potentiodynamic composites (Figure 4a). CD and PPy have the same absorption range on aromatic region and the hydroxyl/amine region, making it difficult to identify the Py of the composite.

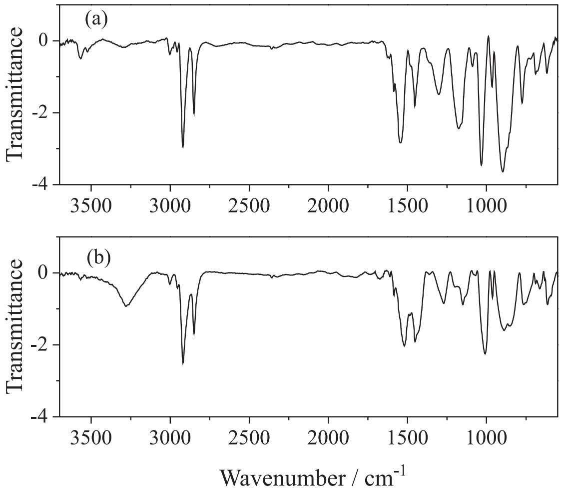

Figure 5. FTIR spectra of PPy/CD films prepared on Au with [Py] = 0.5 mol L^{-1} and [CD] = 0.1 mol L^{-1} in acetonitrile medium in the presence of [$LiClO_4$.] = 0.1 mol L^{-1}. Cyclic voltammetry with (a) v = 50 mV s^{-1}, and chronoamperommetry (b) at E_p = 0.8 V.

In Figure 6, oxidation-reduction properties of composites are presented. The observed anodic charge of voltammetric grown composite was around 2.9 mC and, the obtained value of cronoamperometric grown composite was around 5.7 mC.

The charge difference may be due to the existence of conglomerates of CD on the films, hindering the

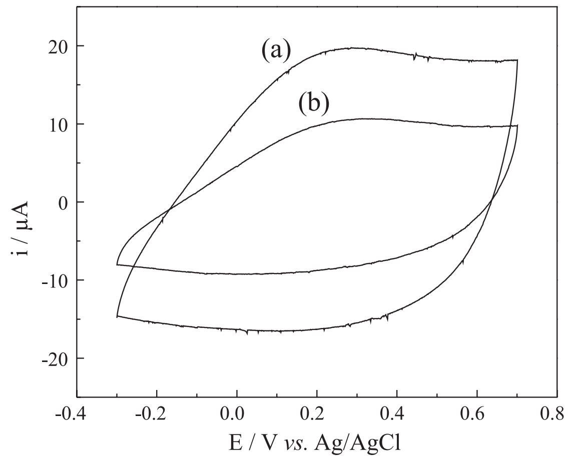

Figure 6. Cyclic voltammograms of PPy/CD composite in acetonitrile medium with [LiClO$_4$.] = 0.1 mol L^{-1}, v = 20 mVs^{-1}. PPy/CD films prepared on Au with [Py] = 0.5 mol L^{-1} and [CD] = 0.1 mol L^{-1} in acetonitrile medium in the presence of [LiClO$_4$.] = 0.1 mol L^{-1}, by chronoamperommetry (a) at E$_p$ = 0.8 V and cyclic voltammetry (b) with v = 50 mV s^{-1}.

conductivity. This behavior of the films may be presented according to the reaction equation:

$$[(PPy)(CD)]_s + n(Li^+)_{aq.} + n(e^-) \Leftrightarrow [PPy(Li)_nCD]_{(s)} \qquad (1)$$

Conclusions

In this work, we showed a methodology for PPy/CD composite grown by cyclic voltammetry and chronoamperometry, whose formation was evident from the chemical analysis and electrochemical evaluation. The film possesses good electrochemical properties. Moreover, the composite grown potentiostatically showed a better charge storage of the lithium ion than the potentiodynamic grown composite.

Acknowledgments

The authors would like to thank the Brazilian agencies: CNPq, FUNCAP and CAPES for their financial support.

References

1. Pringlea, J. M.; Efthimiadisb, J.; Howletta, P. C.; Efthimiadisb, J.; MacFarlanea, D. R.; Chaplinc, A. B.; Hallc, S. B.; Officerc, D. L.; Wallaced, G. G.; Forsythb, M.; *Polymer* **2004**, *45*, 1447.
2. Selampinar, F.; Akbulut, U.; Toppareb, L.; *Synth. Met.* **1997**, *84*, 185l.
3. Kassim, A.; Mahmud, H. N.; Yee, L. M.; Hanipah, N.; *Pac. J. Sci. Technol.* **2006,** *7*, 103.
4. Dejeu, J.; Taouil, A. E.; Rougeota, R.; Lakard, S. S.; Lallemand, F.; Lakard, B.; *Synth. Met.* **2010***, 160,* 2540.
5. Eisazadeh, H.; *World J. Chem.* **2007**, *2*, 67.
6. Genetti, W. B.; Yuan, W. L.; Grady, B. P.; O'Rear, E. A.; Lai, C. L.; Glatzhofer, D. T.; *J. Mat. Sci.* **1998**, *33*, 3085.
7. Zou, J.; Yu, Z.; Pan, Y.; Fang, X.; Ou, Y.; *J. Polym. Sci. Pol. Phys.* **2002**, *40*, 954.
8. Merle, G.; Grillet, A. C.; Allemandb, J.; Lesueur, D.; *Polym. Test.* **1999**, *18*, 217.
9. Takano, T.; Mikazuki, A.; Kobayashi, T.; *Polym. Eng. Sci.* **2013**, *53*, 1.
10. Ramanavicius, A.; Ramanaviciene, A.; Malinauskas, A.; *Electrochim. Acta* **2006**, *51*, 6025.
11. Kimb, Y. H.; An, E. S.; Park, S. Y.; Songa, B. K.; *J. Mol. Catal. B: Enzym.* **2007**, *45*, 39.
12. Smith Jr., R. L.; Malaluan, R. M.; Setianto, W. B.; Inomata, H.; Arai, K.; *Bioresource Technol.* **2003**, *1*, 88.
13. Mazzetto, S. E.; Lomonaco, D.; Mele, G.; *Quim. Nova* **2009,** *32*, 732.
14. Mele, G.; Vasapollo, G.; *Mini-Rev. Org. Chem.* **2008**, *5*, 243.
15. Balachandran, V. S.; Jadhav, S. R.; Vemula, P. K.; John, G.; *Chem. Soc. Rev.* **2013**, *42*, 427.
16. Yuliana, M.; Tran-Thi, N. Y.; Yi-Hsu, J.; *Ind. Crops Prod.* **2012**, *35*, 230.
17. Avelar, G. J.; Godoy, K.; Magalhães, G. C.; *J. Braz. Chem. Soc.* **2000**, *11*, 22.
18. Rao, B. S.; Palanisamy, A.; *Eur. Polym. J.* **2013**, *49*, 2365.
19. Yadav, R.; Srivastava, D.; *Eur. Polym. J.* **2009**, *45*, 946.
20. Devi, A.; Srivastava, D.; *Mater. Sci. Eng. A* **2007**, *458*, 336.
21. Maffezzolia, A.; Calò, E.; Zurloa, S.; Melea, G.; Tarziab, A.; Stifanib, C.; *Compos. Sci. Technol.* **2004**, *64*, 839.
22. Greco, A.; Brunetti, D.; Renna, G.; Mele, G.; Maffezzoli, A.; *Polym. Degrad. Stab.* **2010**, *95*, 2169.
23. Pillai, C. S. K.; Prasad, V. S.; Sudha, J. D.; Bera, S. C.; Menon, A. R. R.; *J. Appl. Polym. Sci.* **1990**, *41*, 2487.
24. Zhou, M.; Heinze, J.; *Electrochim. Acta* **1999**, *44*, 1733.
25. Otero, T. F.; Herrasti, P.; Ocón, P.; Alves, C. R.; *Electrochim. Acta* **1998**, *43*, 1089.
26. Kaplin, D. A.; Qutubuddin, S.; *Polymer* **1995**, *36*, 1275.
27. Jing, S.; Li, T.; Li, X.; Xu, Q.; Hu, J.; Li, R.; *J. Appl. Polym. Sci.* **2014**, *131*, DOI: 10.1002/app.39942.
28. Cheung, K. M.; Bloor, D.; Stevens, G. C.; *Polymer* **1988**, *29*, 1709.

Submitted on: November 6, 2013
Published online: February 18, 2014