

Enhanced Electrical Conductivity of Polyindole Prepared by Electrochemical Polymerization of Indole in Ionic Liquids

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ABSTRACT: The *in situ* electrical conductivity (resistance) of electrochemically prepared polyindole (PI) in ionic liquids was found to be strongly dependent on the nature of the solvents, size of ionic liquid counter ions and preparation technique. Accordingly, the conductivity can be enhanced by about one order of magnitude when using a 1-butyl-3-methylimidazolium tetrafluoroborate [BMIm] [BF₄⁻] or 1-butyl-3-methylimidazolium hexafluorophosphate [BMIm] [PF₆⁻] in comparison to acetonitrile (ACN). Moreover, the growth of polyindole in ionic liquid on gold electrode surface is faster than growth of polymer in acetonitrile. Additionally, a significant enhancement of the conductivity by using ionic liquids during the polymerization could be achieved. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40094.

KEYWORDS: electrochemistry; films; ionic liquids; synthesis and processing

Received 13 August 2013; accepted 20 October 2013

DOI: 10.1002/app.40094

INTRODUCTION

Among of conducting polymers, polyindole (PI) is a good candidate for applications in various domains like electronics, anode materials in battery, electrocatalysis, and pharmacology.¹ Another interest for the electrochemical polymerization of indole is due to its close structural similarities with pyrrole. Therefore, PI has received a significant share of attention in the past decade.^{2,3} Electro-synthesized PI films have the advantages of fairly good thermal stability,^{2,3} high-redox activity, and stability⁴ and an air stable electrical conductivity close to 0.1 S cm⁻¹ in the doped state.⁵ PI is traditionally performed in an electrolyte-molecular solvent system.⁶ The size and nature of the dopant counter-ions from the electrolyte-molecular solvent system, and the nature of the solvent itself, can have a marked influence on the properties of the resultant polymer film.^{6–8} PI films was mainly performed in ACN⁹ and CH₂Cl₂,³ using ClO₄⁻ or BF₄⁻ as the supporting electrolyte. Ionic liquids have a wide liquid range, good electrical stability with electrochemical windows and good thermal stability.¹⁰ Mattes et al. has suggested that π -conjugated polymers that are electrochemically cycled in ionic liquids have enhanced lifetimes without failure and fast cycle switching speeds.¹¹ It means that, they are recyclable and more environmentally benign than most conventional organic solvents. Recently, we found that high-quality polymer films of PI with good electrical properties can be electro-synthesized in LiClO₄⁻/ACN on gold electrode.⁷ In this communication, we use of three ionic liquid such as [BMIm]

[BF₄⁻], [BMIm] [PF₆⁻], and [EMIm] [NTf₂⁻] for the electrochemical polymerization of indole and compare this to the use of conventional solvent-electrolyte systems (LiClO₄/ACN). The *in situ* conductivity of polymer films in ionic liquids and LiClO₄/ACN were investigated.

EXPERIMENTAL

Reaction equipment and chemicals are described in an earlier paper.⁷ Films of PI were prepared from 0.1M solutions of indole in two ionic liquids, a solution of 0.1M [BMIm] [BF₄⁻] and [BMIm] [PF₆⁻] (Merck) or a solution of 0.1M LiClO₄/ACN. Our effort to polymerize of the indole in an ionic liquid of a solution of 0.1M [EMIm] [NTf₂⁻] (Merck) even by 1000 cycles was not successful. Acetonitrile (Merck), water content as determined by Karl Fischer method (<0.05%) was used as received and kept over molecular sieve.¹² The drying of ionic liquids requires heat and 48 h in vacuum. Cyclic voltammograms were performed using an Autolab model PGSTAT 30 potentiostat/galvanostat. The risk of over oxidation of the films was minimized by growing the films at the lowest possible potentials by thoroughly drying (control with IR spectrum) and degassing the ionic liquids before use to remove any traces of oxygen (soluble O₂). After vigorous mixing and nitrogen purging (10 min) electropolymerization was affected by scanning the electrode potential between -0.10 to 0.90, 1.33, and 1.40 V for LiClO₄/ACN, [BMIm] [BF₄⁻] and [BMIm] [PF₆⁻], respectively. For *in situ* resistivity measurements, a band-gap gold electrode

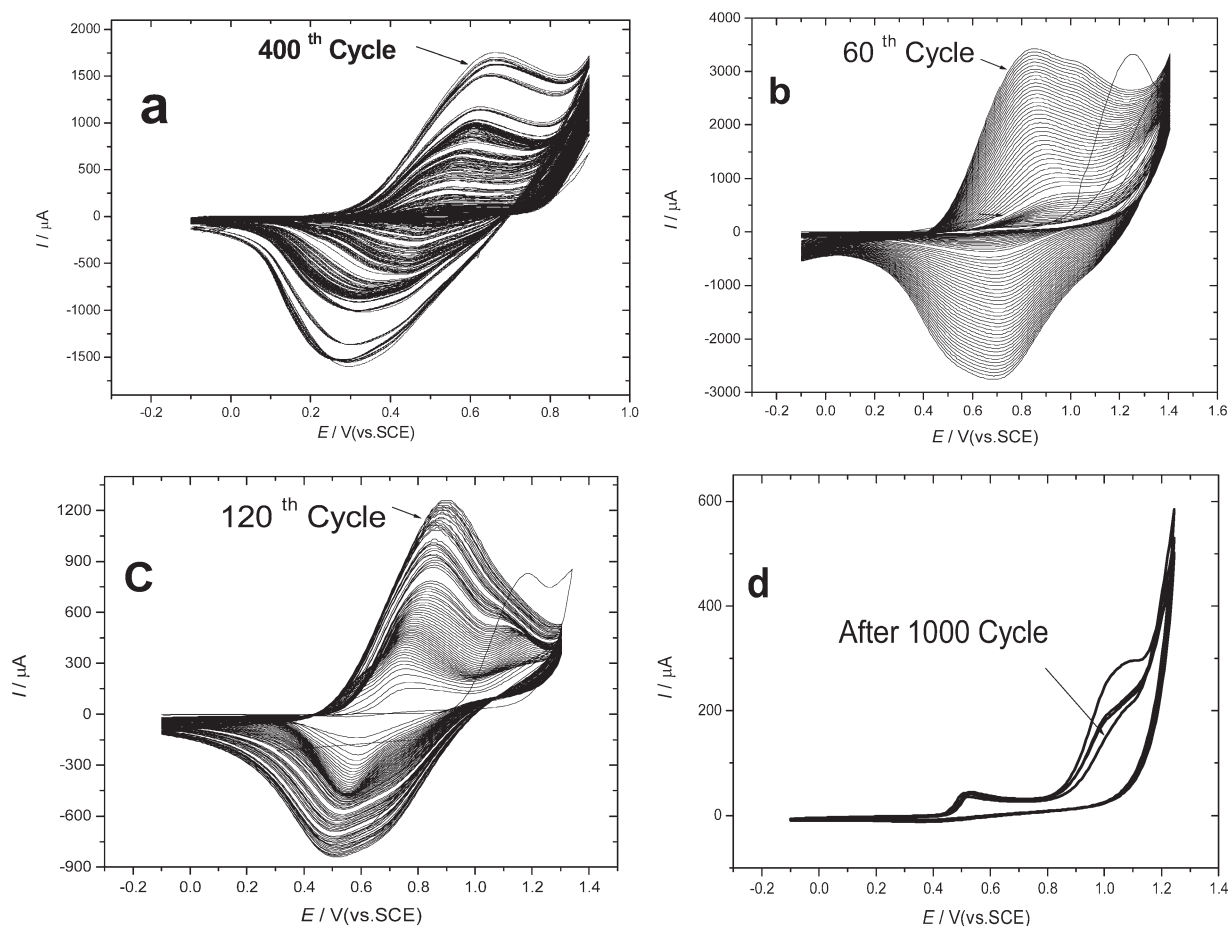


Figure 1. CVs during formation of PIn in (a) ACN/containing 0.1M LiClO₄, (b) [BMIm] [BF₄⁻], (c) [BMIm] [PF₆⁻] and (d) [EMIm] [NTf₂⁻] on gold electrode, scan rate was 50 mV s⁻¹, respectively.

(electrodes made by AZAR electrode) was used as working electrodes.^{13–16} The instrument for conductivity measurement was made by Sama Research Center. The two strips of the band-gap electrode are spaced apart only around 0.08–0.10 mm; this gap can easily be bridged by deposition of conducting polymers. The length of the gap (between the electrodes) is around 3–4 mm. The polymer films are deposited electrochemically on the electrode strips as desired, even very thin films usually form good bridges over the gap between the electrodes. Before each polymer deposition, the electrode was polished with fine emery paper (1000 grit) and alumina (1 μm) to remove the previously deposited material, washed with water, and cleaned ultrasonically.¹⁷ Infrared spectra of dedoped samples were recorded on a Perkin Elmer FT-IRGX spectrometer using the KBr pellet technique. Films were scraped of the electrode, milled with KBr, and pressed into pellets.

RESULTS AND DISCUSSIONS

Figure 1 shows the growth cycles of PIn synthesized on a gold electrode recorded during the electropolymerization of indole in LiClO₄/ACN compared with those recorded during film growth in an ionic liquids.

Initial CVs of indole monomer in a LiClO₄/ACN⁷ and ionic liquid solvents ([BMIm] [BF₄⁻], [BMIm] [PF₆⁻] and [EMIm]

[NTf₂⁻]) shows a steep current increase around 0.66, 0.76, 0.91, and 0.83 V in the positive going scans and in the negative going scans trace crossing occurs at 0.58, 0.71, 0.91, and 0.83 V, respectively. PIn films grows on the electrode surface during the electropolymerization process and oxidation peaks are observed around 0.60, 0.87, and 0.90 V in LiClO₄/CAN, [BMIm] [BF₄⁻] and [BMIm] [PF₆⁻] during further oxidative polymerization, respectively. As the cycling continues, a steady-state voltamograms are reached after 400, 60, and 120 cycles for [LiClO₄/ACN], [BMIm] [BF₄⁻], and [BMIm] [PF₆⁻], respectively. A PIn film in an [EMIm] [NTf₂⁻] not grows on the electrode surface during the electropolymerization process even by 1000 cycles [Figure 1(d)]. The CVs recorded during film growth are sensitive to the nature of the electrolyte, solvent viscosity, concentration, etc. The film growth in LiClO₄/ACN and [BMIm] [BF₄⁻] results in a steady and significant increase in current and capacitance with increasing cycles. This is not so apparent during film growth in the [BMIm] [PF₆⁻] ionic liquid and even less so in the [EMIm] [NTf₂⁻]. This may initially suggest that the films produced are either less electrochemically active or thinner, but this is contradicted by analysis the films in blank solutions. Growth of the films in [BMIm] [BF₄⁻] or [BMIm] [PF₆⁻] ionic liquids are more comparable to that of ACN solvents, suggesting faster growth of rougher and less dense films.

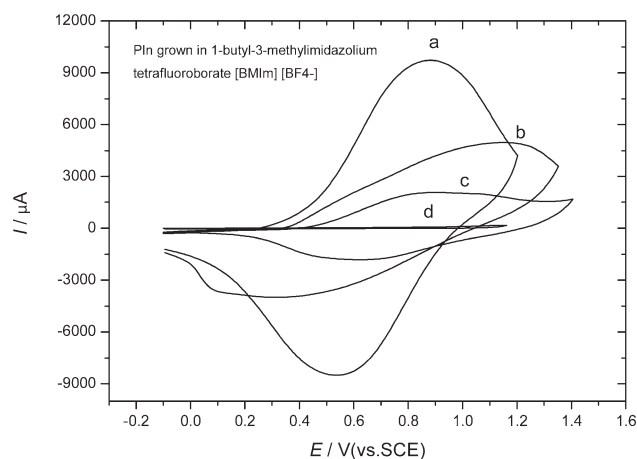


Figure 2. CVs of a gold electrode coated with PIn grown in 1-butyl-3-methylimidazolium tetrafluoroborate [BMIm] [BF₄⁻] in a blank solution containing: (a) ACN/0.1M LiClO₄⁻ (b) [BMIm] [BF₄⁻], (c) [BMIm] [PF₆⁻], and (d) [EMIm] [NTf₂⁻], scan rate 150 mV s⁻¹.

The electrochemical response of the films when cycled in a LiClO₄/ACN is dramatically different with cycled in [BMIm] [BF₄⁻] or [BMIm] [PF₆⁻]. It is clear from the CVs in blank solutions of LiClO₄/ACN that the use of ionic liquids as the growth solvent for the electropolymerization of indole results in films that are significantly more electrochemically active than those prepared in the LiClO₄/ACN solvent system under comparable conditions (Figure 2).

The peak current of the anodic wave of the PIn films grown in [BMIm] [BF₄⁻] is more than two times that of the film grown in LiClO₄/ACN. The improved electrochemical performance of polymer films grown in [BMIm] [BF₄⁻] or [BMIm] [PF₆⁻] were further confirmed by comparison with PIn films grown from a LiClO₄/ACN solvent system. The electrochemical response of the PIn films produced from [BMIm] [BF₄⁻] or [BMIm] [PF₆⁻] ionic liquid solutions with PIn in ACN may be rationalized when taking in to account the electrosynthesis process or electrochemical cycling of PIn in an ionic liquid. When the [BMIm] [BF₄⁻] or [BMIm] [PF₆⁻] ionic liquids are used as the growth solvent, the films produced are so dense that, when they are cycled in ionic liquids, only the redox behavior of the outer PIn layers are measured. However, when these films are placed in ACN, swelling of the PIn film occurs, allowing movement of dopant ions and the redox of the entire polymer layers.⁸ The results clearly demonstrate that the growth rates of PIn film in the [BMIm] [BF₄⁻] are faster than PIn growth in [BMIm] [PF₆⁻] or [EMIm] [NTf₂⁻] solvents. This is strongly dependant on the nature of the ionic liquid and size of dopant ions. The size of [NTf₂⁻] and [PF₆⁻] dopant ion are larger than [BF₄⁻] and consequently, the immigration of big dopant ions toward the PIn will be slowly. In trying to understand the role that the ionic liquid plays in producing such electrochemically active polymer films, *in situ* conductivity measurements has been performed. For *in situ* resistivity measurements PIn were deposited potentiodynamically in ionic liquid at 50 mV s⁻¹, on a gold band gap electrode. The schematic presentation of double band gap electrode was given previously.¹⁶ Figure 3

shows the resistivity behavior of PIn in ACN system and ionic liquids solvent systems ([BMIm] [BF₄⁻] and [BMIm] [PF₆⁻]). PIn films prepared potentiodynamically on double bond gold electrode by cycling the potential in [BMIm] [BF₄⁻] and [BMIm] [PF₆⁻] solutions and measured in ACN/containing 0.1M LiClO₄ [Figure 3(a,c)], [BMIm] [BF₄⁻] [Figure 3(b)], and [BMIm] [PF₆⁻] [Figure 3(d)], respectively.

When the applied potential is increased the resistivity of PIn [Figure 3(a)] prepared in [BMIm] [BF₄⁻] and measured in ACN/ClO₄⁻ decreases sharply by 2.5 orders of magnitude from 0.10 V to 0.30 V and remains nearly constant up to 0.70 V and then increases up to 0.90 V by 0.75 orders of magnitude. When the applied potential is reversed, the resistivity increases slowly up to 0.30 V and remains constant up to -0.10 V. Maximum conductivity is observed in the potential range between 0.40 V and 0.70 V. In the case of PIn prepared in [BMIm] [BF₄⁻] and measured in [BMIm] [BF₄⁻] ionic liquid [Figure 3(b)], the resistivity decreases sharply by 1.7 orders of magnitude from 0.10 to 0.20 V and remains nearly constant up to 0.70 V and then increases up to 0.90 V by 0.25 orders of magnitude. When the applied potential is reversed, the resistivity increases slowly up to 0.20 V and remains constant up to -0.10 V. The conductivity of PIn in ACN is higher than PIn in [BMIm] [BF₄⁻] ionic liquid by 0.8 orders of magnitude. The PIn films grown in ionic liquids are predicted to contain more dopant ions than those grown in ACN/ClO₄⁻, movement of these ions within the PIn appears to require some solvent swelling-the improved electrochemical response of the films grown from the [BMIm] [BF₄⁻] ionic liquids is only observed during cycling in ACN/ClO₄⁻ and not to such a large extent during cycling in the ionic liquids themselves.⁸ The same result observed for PIn prepare in [BMIm] [BF₆⁻] and in ACN solvent systems. The conductivity of PIn in ACN/ClO₄⁻ is higher than PIn in [BMIm] [BF₆⁻] ionic liquid by 0.4 orders of magnitude [Figure 3(c,d)]. However, the conductivity of PIn prepared in [BMIm] [BF₄⁻] ionic liquid and measured in ACN/ClO₄⁻ is more than polymer prepared in [BMIm] [BF₆⁻] ionic liquid and measured in ACN/ClO₄⁻. The relation between viscosity and conductivity of ionic liquids ([BMIm] [BF₄⁻], [BMIm] [PF₆⁻] and [EMIm] [NTf₂⁻]), acetonitrile and PIn is very important. With respect to the available reports of viscosity data for selected ionic liquids and acetonitrile,^{18,19} there is a competition between dopant anion size and solvent viscosity on conductivities of PIn films. If we consider only to the solvent viscosity factors, the best route for formation and growth of PIn in acetonitrile and [EMIm] [NTf₂⁻] is expected. However, in comparing with acetonitrile and without viscosity attentions, the route of polymer formation with suitable thickness is very slow for [BMIm] [BF₄⁻] and [BMIm] [PF₆⁻] and no evidence for [EMIm] [NTf₂⁻]. Thus, it seems that, the effect of anion dopant size (doping process) on route of conducting polymer formation in comparing with solvent viscosity is dominated. In acetonitrile solvent and with increasing the size of dopant anions, the doping process will be a slower process and it is expected that for [EMIm] [NTf₂⁻] with larger dopant anion. In the case of [BMIm] [BF₄⁻] and [BMIm] [PF₆⁻], the size of dopant anions is nearly equal and therefore, the formation of conducting polymer film will be slow due to solvent viscosity

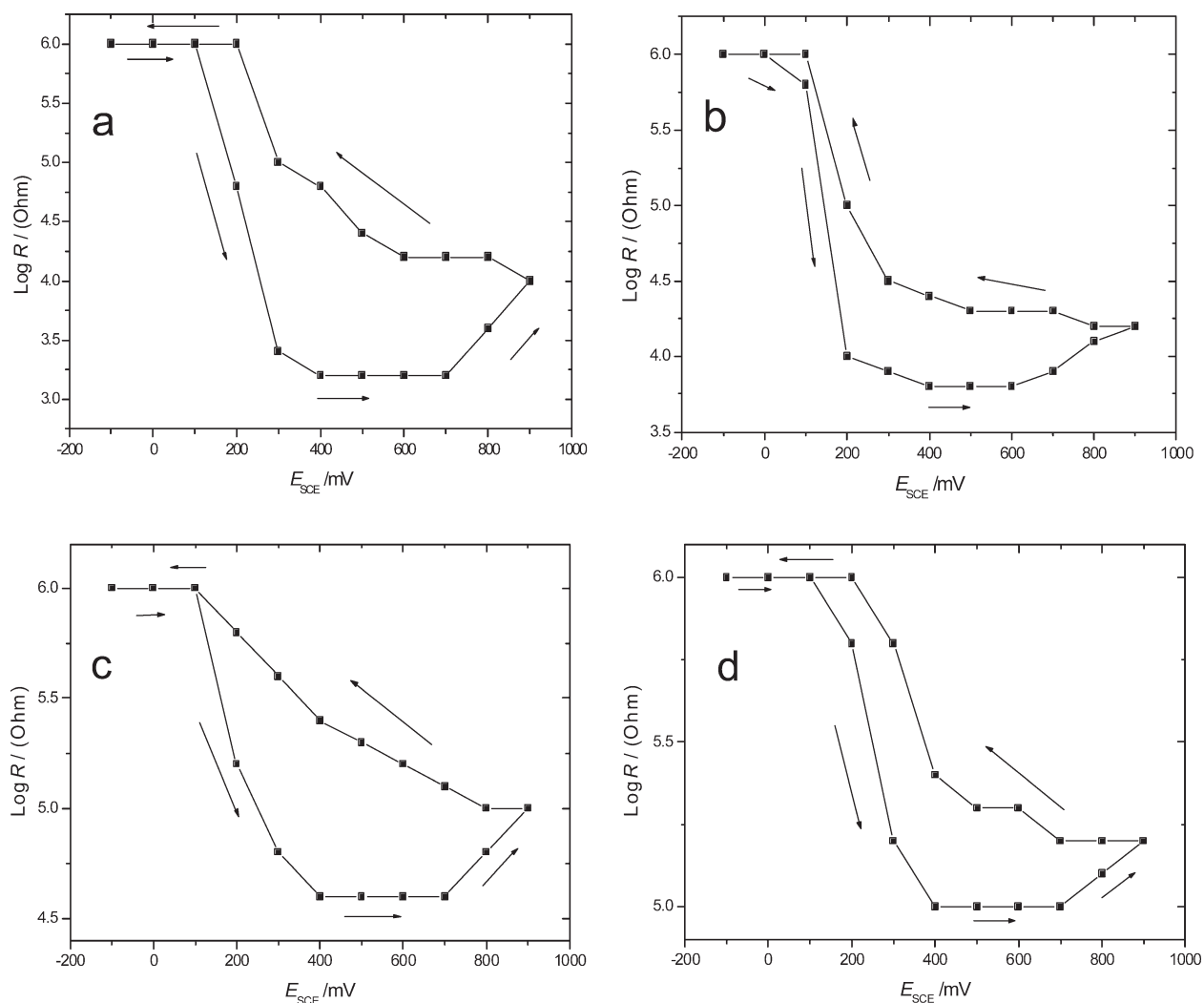


Figure 3. Plots of resistivity (conductivity) versus electrode potential data for PIn films prepared potentiodynamically on double bond gold electrode by cycling the potential in [BMIm] [BF₄⁻] and [BMIm] [PF₆⁻] solutions and measured in (a), (c) ACN/containing 0.1M LiClO₄, (b) [BMIm] [BF₄⁻], and (d) [BMIm] [PF₆⁻], respectively.

effect. Meanwhile, the conductivity of polymer films in these solvent decreased due to the low speed of movement of ions. It is interesting to note that, a significant enhancement of the conductivity in wet condition or using *in situ* technique by using ionic liquids during the polymerization could be achieved. The incorporation of ions in the structures of PIn was studied by FTIR technique in the ranges of 500–4000 cm⁻¹ (not show here). The transmission spectra of PIn indicate that the absorption bands for NH₂ group of indole monomer have been remained. It can be concluded that polymerization don't take place in the NH position of monomer (indole). Also the observation of an intense band at 1057 cm⁻¹ indicates that there are BF₄⁻ anions in the structure of PIn.²⁰

CONCLUSIONS

Polyindole has been synthesized by electrochemically method by using LiClO₄/ACN and three ionic liquids on gold electrode. The result demonstrates that the growth rate of PIn film in the [BMIm] [BF₄⁻] is faster than polymer growth in [BMIm]

[PF₆⁻] or [EMIm] [NTf₂⁻] solvents. The ionic liquids produced films with significantly enhanced electrochemical activity than films grown in ACN/ClO₄⁻ systems with the more viscous and less conductive ionic liquid. The conductivity of polyindole prepared in ionic liquids compared with polymer prepared in acetonitrile significantly increased in conventional solvent system. Moreover, this is probably due to doping of anion or cation from solution.

ACKNOWLEDGMENTS

This work was sponsored by the Bu-Ali Sina University and gratefully appreciated.

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