

Structural Analysis of Conductive Polypyrroles Synthesized in an Ionic Liquid

Eun-Ah Song, Woo-Gwang Jung, Dae-Woo Ihm,^{*} and Jin-Yeol Kim^{*}^{*}School of Advanced Materials Engineering, Kookmin University, Seoul 136-702, Korea. E-mail: jinyeol@kookmin.ac.kr^{*}Department of Semiconductor and Display Engineering, Hoseo University, Asan 336-795, Korea

Received December 2, 2008, Accepted April 3, 2009

Nano-structured conducting polypyrroles were synthesized in the ionic liquids (ILs) based on 1-alkyl-3-methyl-imidazolium family with tetrachloroferrate as an anion ($C_n\text{mim}[\text{FeCl}_4]$ with $n = 4, 8, \text{ and } 12$). The polypyrrole nanostructures synthesized in ILs were formed as spherical shapes. For ionic liquids with alkyl side chain length C_4 , $C_4\text{mim}[\text{FeCl}_4]$, the size of particles was ranged around 60-nm with a relatively narrow size distribution. As the length of alkyl chain increases, the particle sizes become larger and their distributions become wider. The self-assembled local structures in the solvent ionic liquids are likely to serve as templates of highly organized nano-structured polymers. The length of the alkyl chain in ionic liquids seems to affect these local structures.

Key Words: Magnetic ionic liquid, Polypyrrole, Nanoparticle

Introduction

Ionic liquids (ILs) are organic salts with low melting points, sometimes as low as $-96\text{ }^\circ\text{C}$,¹ whose unique properties have been leading to an increasing number of applications as solvents or reaction media. The ILs can be thermally stable up to temperatures in excess of $400\text{ }^\circ\text{C}$. Because of their unique properties, such as high polarity, negligible vapor pressure, high ionic conductivity, and thermal stability, ILs can be used in catalysis,² as inert solvents in electrochemistry,³ ideal media for polymer synthesis,⁴⁻⁵ and so on. Some of these properties were interpreted as the result of structural features of the liquid phase at the molecular level. ILs are organic salts composed of heterocyclic organic cations such as pyridinium, pyrrolidinium, imidazolium and anions like PF_6^- , SbF_6^- , BF_4^- , Cl^- , Br^- , and so on. A key feature of ILs is that their cations, substituent, and anions can be varied virtually at will to change their chemical and physical properties. Design of IL solvent has received increasing attention by many researchers in this respect. One of the most widely used and studied ionic liquid families is the one based on imidazolium salts, in particular 1-alkyl-3-methylimidazolium cation ($C_n\text{mim}$ [cation]). Imidazolium $[\text{FeCl}_4]$ is a kind of ionic liquids (ILs)

and have also been known as a magnetic ionic liquid (MIL). MIL has the unusual properties of ILs. Besides, they show strong response to magnetic field.⁶ Recently, we also reported that the FeCl_4^- moiety could play roles as a synthetic catalyst as well as a dopant, when polymerization of π -conjugated polymer was conducted in $\text{bmim}[\text{FeCl}_4]$.⁷ The benefits of using ionic liquids for the electrochemical synthesis and cycling of conducting polymers has been demonstrated by a number of authors in recent years.^{8,9}

In this paper, we report an entirely new approach to synthesize the conducting polypyrrole (PPy) using a ionic liquids (IL), imidazolium $[\text{FeCl}_4]$, as the solvent for pyrrole polymerization. Specifically, we studied the influences of varying the length of the alkyl side-chain in hetero-cyclic imidazolium salts. Three kinds of ILs such as 1-butyl-3-methyl-imidazolium tetrachloroferrate ($\text{bmim}[\text{FeCl}_4]$), 1-octyl-3-methylimidazolium tetrachloroferrate ($\text{omim}[\text{FeCl}_4]$), and 1-dodecyl-3-methylimidazolium tetrachloroferrate ($\text{dmim}[\text{FeCl}_4]$) (as shown in Fig. 1) were prepared with alkyl-chain lengths of C_4 , C_8 , and C_{12} and used for polymerization.

PPy is a kind of conducting polymers having π -conjugated bond system and has attracted much attention in the last few decades because of their good electronic/physical properties and potential application in electronics devices.¹⁰⁻¹³ PPy polymers have been synthesized either through chemical oxidation or electro-chemical of the monomer or, in rare cases, photo-polymerization or vapor-phase polymerization, both of which involve electron transfer.

Experimental

$\text{Bmim}[\text{FeCl}_4]$, $\text{omim}[\text{FeCl}_4]$, and $\text{dmim}[\text{FeCl}_4]$ were prepared according to the literature procedure,¹⁴ dried and degassed before use. Their structure and purity were identified from the spectroscopic methods. The anhydrous trichloroferrate (Aldrich GR, 99.9%) was used without further purification. PPy nanostructures were synthesized by simply adding pyrrole monomer to imidazolium $[\text{FeCl}_4]$ as the ionic liquid solvent, with stirring. To 6 mL of imidazolium $[\text{FeCl}_4]$, 1.5 mL of pyrrole

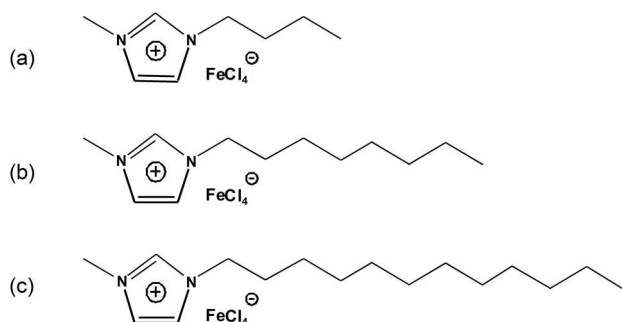


Figure 1. Molecular structures of ionic liquid based on imidazolium salts; (a) $\text{bmim}[\text{FeCl}_4]$, 1-butyl-3-methylimidazolium tetrachloroferrate, (b) $\text{omim}[\text{FeCl}_4]$, 1-octyl-3-methylimidazolium tetrachloroferrate, (c) $\text{dmim}[\text{FeCl}_4]$, 1-dodecyl-3-methylimidazolium tetrachloroferrate.

monomer is added. Pyrrole monomer (Aldrich GR, 99.9%) was used after purification by the evaporation method. Polymerization took place very fast and PPy was synthesized immediately. An immediate precipitate and darkening of solution occurred after 30 seconds. The solution was stirred for 12 hours, and then the polymer products were removed from the imidazolium $[\text{FeCl}_4]$ solution for filtering. The filtered PPy samples were dried for 3 hours at 60 °C in vacuum oven and further purified by methanol washing. In this process, PPy was synthesized by using IL as a solvent. The imidazolium $[\text{FeCl}_4]$ liquid acts as a catalyst and dopant as well as a solvent. It is worth noting that no additional dopants or oxidants were used in the synthesis. The size and conductivity of conductive PPy nano-structures were measured using scanning electronic microscopy (SEM: JSM-633F, Jeol) and the standard four-probe technique (Loresta-GP, Mitsubishi Chemical), respectively.

Results and Discussion

Recently a number of research investigations have been carried out on the polymerization and characteristics of nano-scale PPy for various applications.¹⁰⁻¹³ To prepare the nanostructures such as fibrils and tubules of the desired materials, the pores in nanoporous membranes were used as templates. This "template-synthesis" approach has been used to prepare nano-tubules, nano-fibrils, nano-wires of PPy.^{15,16} For example, PPy nano-tubules and nano-fibrils were chemically synthesized with oxidizing agent using the pores of nano-porous membrane as templates.¹⁵ PPy nano-wires were electrochemically synthesized using a carbon electrode modified by electro-grafting reaction with polyethylacrylate as a template.¹⁶

In this paper, the ionic liquids used were 1-alkyl-3-methyl-imidazolium tetrachloroferrate, which we found to be a good liquid template for the electrochemical polymerization of pyrrole.⁷ Here, ILs having alkyl-chain lengths of C_4 , C_8 , and C_{12} are used for polymerization. Specifically, we show that PPy nano-particle synthesized in ILs is influenced by the length of alkyl side-chain in ILs. By the above-mentioned experimental method, we synthesized PPy nanostructures by dissolving pyrrole monomer in the imidazolium $[\text{FeCl}_4]$ liquid containing no additional dopants or oxidants. All polymers existed as particles and had similar spherical shapes. The well-defined PPy particles were obtained without aggregation and the size distribution of particles synthesized at room temperature are shown in Fig. 2. SEM image of PPy nanoparticles synthesized in bmim $[\text{FeCl}_4]$ having alkyl-chain length of carbon number four is shown in Fig. 2. (I). A size of the particles is distributed at around 40-80 nm as shown in Fig. 2. (II-a). However, that obtained by using omim $[\text{FeCl}_4]$ having alkyl-chain length of carbon number eight was about 70 to 130 nm (Fig. 2. (II-b)) and that of dmim $[\text{FeCl}_4]$ having carbon number twelve was about 120 to 200 nm (Fig. 2. (II-c)), respectively. From these observations, we can see that particle size increased with increasing alkyl-chain length in ILs and their distributions become wider. Variation of other reaction conditions such as concentration and reaction time,

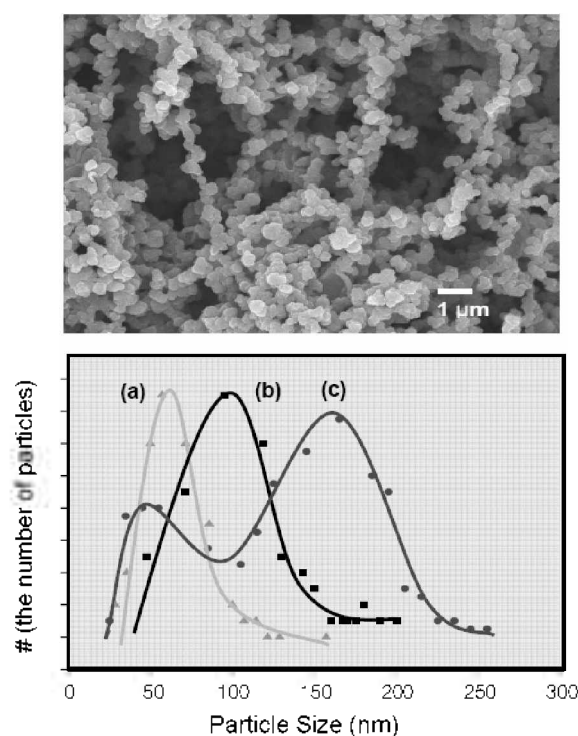


Figure 2. FE-SEM image of PPy nanoparticles synthesized in IL (I) and the distributions of PPy particles (II) synthesized in (a) bmim $[\text{FeCl}_4]$, (b) omim $[\text{FeCl}_4]$, and (c) dmim $[\text{FeCl}_4]$ solutions, respectively.

did not affect the generated polymer shapes. This time, IL solutions seem to act as a template of liquid phase. Here, the ILs are isotropic organic liquids composed entirely of ions, but they are also expected to serve as anisotropic conductors due to their self-organized structures. The macroscopic orientation of self-organized mono-domains in ILs seems to play a key role in the enhancement of properties because the boundary in randomly oriented poly-domains highly disturbs anisotropic transportation of charges and ions. Thus, the structure and properties of PPy can be explained by proposing the structure formation of these IL molecules with partially oriented anisotropic liquid domain being mixed in isotropic liquids. The boundary of this isotropic liquid domain is increased with increasing alkyl-chain length. Accordingly, the size of the particle synthesized in ILs having long chain-lengths of carbon becomes larger than that in ILs having short chain-length.

Padua *et al.*¹⁷ has reported the nanometer-scale structuring in 1-alkyl-3-methylimidazolium hexafluorophosphate using molecular simulation method. They observed, for ionic liquids with alkyl side chains longer than or equal to C_4 , aggregation of the alkyl chains in nonpolar domains. These domains permeate a three-dimensional network of ionic channels formed by anions and by the imidazolium rings of the cations. As the length of the alkyl chain increases, the nonpolar domains become larger and more connected and cause swelling of the ionic network. Watanabe *et al.*¹⁸ have studied the dependence of viscosity and diffusion on the alkyl-chain length in ILs, with carbon number 1-8. They observed that the viscosity increases and that both the self-diffusion

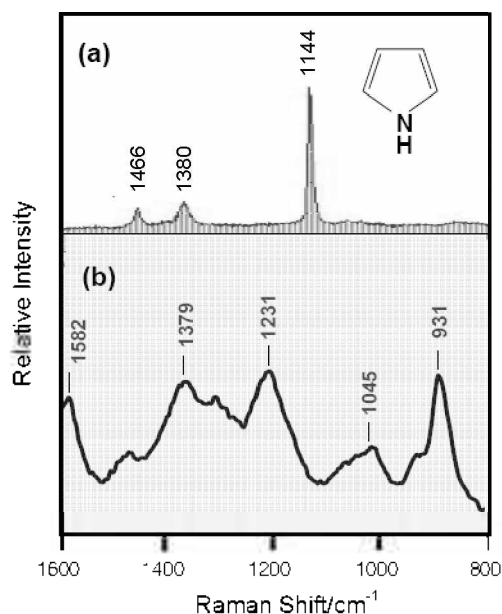


Figure 3. Raman spectra of (a) pyrrole monomer and (b) polypyrrole nanostructure self-assembled in bmim [FeCl₄] ionic liquid solvent.

coefficient and the degree of ion dissociation decrease with increasing chain length. Pringle *et al.*¹⁹ also reported the use of ionic liquids for the chemical synthesis of polypyrrole using a variety of oxidants, which demonstrated that ILs are ideal media for the synthesis and application of conducting polymers.

The conductivity of these polymers, dried and pressed into pellets, was measured using a four-probe measurement. The conductivity of pelletized polypyrrole particles was 10^1 – 10^2 S/cm and these *I*–*V* characteristics display exponential increase until they saturate at the highest full-scale current of 100 nA with ohmic behavior. The conductivity values of 10^1 – 10^2 S/cm observed from the present study is much higher than that of polypyrrole synthesized in the ionic liquid, 1-methyl-3-ethyl-imidazolium bis(trifluoromethanesulfonyl)amide, with gold chloride, Fe-tosylate, silver nitrate, and Fe(ClO₄)₃ as a dopant, as reported by Pringle *et al.*¹⁹ They reported the conductivity values of about 1–10 S/cm and the sizes of polypyrrole particles were about 100–500 nm in diameter. In general, the conductivity of polymers are related with the synthetic methods, molecule size and/or structure, degree of crystallinity or arrangement on molecule, kind of dopants and doping rate, and so on. This apparent higher conductivity can be attributed to the well-defined nanostructures, highly organized molecule, and/or high doping ratio with FeCl₃.

In order to trace the polymerization of pyrrole in bmim [FeCl₄], we monitored Raman spectral change of the liquid before and after adding pyrrole monomer. The 1064-nm near-infrared excitation was used for avoiding strong fluorescence from polypyrrole. The results are shown in Fig. 3. The characteristic bands of pyrrole monomer (a) are not found in polymer spectrum (b), and it indicates that all monomers are already polymerized. From PPy nanoparticles, some new peaks at 1582, 1379, 1231, 1045, and 931 cm⁻¹ are measured,

respectively. These peaks are assigned to polypyrrole, symmetrical C=C and C-C stretching, C-N stretching, symmetrical C-H in-plane bend, and ring deformation due to a bipolaron, respectively.²⁰

In conclusion, PPy nanoparticles have been synthesized using ILs as solvents and their morphologies were investigated by SEM. Especially, the synthesis can be accomplished by just adding monomer to a ionic liquid bmim [FeCl₄]. As the length of alkyl chain increases, the PPy particle sizes become larger and their distributions become wider. It seems that the self-assembled local structures in the solvent ionic liquids are likely to serve as templates of highly organized nano-structured polymers and the length of the alkyl chain in ionic liquids affects these local structures. Thus, it can be expected that the ionic liquids are promising new solvents for π -electron conjugated polymer fabrication. They are controllable by a lot of factors such as temperature, concentration, structure including the alkyl chain length of the cation. Another merit of the use of ionic liquids is their potential as recycling solvents. It was found that the morphology of the tubes could be adjusted by varying the polymerization conditions such as the molar ratio of anion and cation.

Acknowledgments. This work was financially supported in part by the ERC program of MEST/KOSEF (R11-2005-048-0000-0) and the Research Program 2007 of Kookmin University in Korea.

References

- Seddon, K. R.; Stark, A.; Torres, M. *Pure Appl. Chem.* **2000**, *72*, 2275.
- Sheldon, R. *Chem. Commun.* **2001**, *23*, 2399.
- Fuller, J. R.; Carkin, T. J. *Electrochem. Soc.* **1997**, *144*, 3881.
- Zhao, Y. L.; Zhang, J. M. J.; Jiang, C. F.; Chen, F. Xi. *J. Polym. Sci. Part A* **2002**, *40*, 3360.
- Kubisa, P. *Pro. Polym. Sci.* **2004**, *29*, 3.
- Hayashi, S.; Hamaguchi, H. *Chem. Lett.* **2004**, *33*, 1590.
- Kim, J. Y.; Kim, J. T.; Song, E. A.; Min, Y. K.; Hamaguchi, H. *Macromolecules* **2008**, *41*, 2886.
- Wasserscheid, P. *Ionic liquid in Syntheses*; Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 2003.
- Davis, Jr.; Fox, J. H. P. A. *Chem. Commun.* **2003**, *11*, 1209.
- Yao, Z.; Postma, H. W. C.; Balents, L.; Dekker, C. *Nature* **1999**, *402*, 273.
- Normile, D. *Science* **1999**, *286*, 2056.
- Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *287*, 622.
- Baughman, R. H.; Cui, C.; Zakhidov, A. A.; Iqbal, Z.; Barisci, J. N.; Spinks, G. M.; Wallace, G. G.; Mazzoldi, A.; De Rossi, D.; Rinzler, A. G.; Jaschinski, O.; Roth, S.; Kertesz, M. *Science* **1999**, *284*, 1340.
- Sitze, M. S.; Schreiter, E. R.; Patterson, E. V.; Freeman, R. G. *Inorg. Chem.* **2001**, *40*, 2298.
- Menon, V. P.; Lei, J.; Martin, C. R. *Chem. Mater.* **1996**, *8*, 2382.
- Jerome, C.; Jerome, R. *Angew. Chem. Int. Ed.* **1998**, *37*, 2488.
- José, N.; Lopes, C.; Margarida, F.; Costa Gomes, C.; Agilio, A. H.; Padua, A. H. *J. Phys. Chem. B* **2006**, *110*(34), 3330.
- Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, A.; Watanabe, B. H. *J. Phys. Chem. B* **2005**, *109*, 6103.
- Pringle, J. M.; Ngamna, O.; Chen, J.; Wallace, G. G.; Forsyth, M.; MacFarlane, D. R. *Synth. Met.* **2006**, *156*, 979.
- Furukawa, Y.; Tazawa, S.; Fujii, Y.; Harada, I. *Synth. Met.* **1988**, *24*, 329.