Polypyrrole Nanostructures Self-Assembled in Magnetic Ionic Liquid as a Template

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ABSTRACT: Nanostructured conducting polypyrrole and poly(*N*-methylpyrrole) were successfully synthesized by simply adding monomers into a magnetic ionic liquid, bmim[$FeCl_4$]. In this process, self-organized conducting polymer nanostructures such as particles and tubes were formed without and with magnetic field. The shape of polypyrrole nanoparticles synthesized at room temperature was almost spherical with their size ranging around 60 nm with a relatively narrow size distribution. The conductivity of pelletized particles was 10^{1-2} S/cm. From the *N*-methylpyrrole monomer, more attractive nanostructured polymers were obtained. Tubes with nanoscaled inner holes and walls were synthesized using a self-assembly process for the first time. The self-assembled local structures in the solvent ionic liquid are likely to serve as templates of highly organized nanostructured polymers. External magnetic field seems to affect these local structures and hence the resultant polymer nanostructures. This research provides a new method to synthesize various nanosized conducting polymeric materials via simple self-assembly.

Introduction

π-Electron conjugated polymers have attracted considerable attention in the past few decades because of their electronic/physical properties and potential application in electronics devices.[1–4] In particular, polypyrrole (PPy), which consists of five-membered heterocyclic rings, has attracted much attention because of its good electrical conductivity, redox properties, and environmental stability. Nanostructured conducting polymers are known to play important roles in opto-electronic devices, ranging from organic transistors[1] and electronic flat-panel displays[2] to chemical sensors[3] and artificial actuators,[4] both as interconnecting and as active components. However, fabrication of nanostructured materials from conducting polymers has been a big challenge. These conducting polymers can be prepared through either chemical oxidation or electrochemical of the monomer or, in rare cases, photopolymerization or vapor-phase polymerization, both of which involve electron transfer. The prior term describes a solution process, and the latter involves depositing the polymer at an electrode.

In this paper, we report an entirely new approach to synthesize various nanosized conducting polymeric materials using a magnetic ionic liquid (MIL), Bmim[$FeCl_4$], as the solvent for pyrrole polymerization.

Bmim[$FeCl_4$] (1-butyl-3-methylimidazolium tetrachloroferrate: Figure 1) is a kind of ionic liquid (IL). ILs are organic salts composed of heterocyclic organic cations such as pyridinium, pyrrolidinium, imidazolium, and anions like PF_6^-, SbF_5^-, BF_4^-, Cl^-, Br^-, and so on. The possible choices of cation and anion that will result in the formation of ILs are numerous. The unique properties of these liquids include extremely low volatility, high thermal stability, wide temperature range of liquid phase, nonflammability, high chemical stability, high ionic conductivity, and so on.[5–10] A key feature of ILs is that their cations, substituents, and anions can be varied virtually at will to change their chemical and physical properties. The unique properties of these liquids, and the ability to tailor properties by judicious selection of cations, substituents, and anions, open the door to many processing options than have been available to us by using conventional organic solvents. Design of IL solvent has received increasing attention by many researchers in this respect.

MIL is basically a kind of IL. The only difference between IL and MIL is that the anion of MIL is $FeCl_4^-$. MILs have the unusual properties of ILs. Besides, they show a strong response to a magnetic field. Recently, we reported that an IL containing a magnetic anion, Bmim[$FeCl_4$], showed a strong response to a magnetic field.[11] It was prepared from 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and $FeCl_3$. Bmim[$FeCl_4$] is nearly paramagnetic, having a large magnetic susceptibility of 40.6×10^{-6} emu g^{-1}. We presumed 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 Bmim[$FeCl_4$]. We also hypothesized that specific self-assembled local structures possessing crystal-like ordering might be exist in imidazolium-based ionic liquid, and external magnetic field might affect the ordering process and local structures. The benefits of using ionic liquids for the electrochemical synthesis and cycling of conducting polymers has been demonstrated by a number of researchers.[12,13] ILs that are liquid at room temperature are ideal media for the synthesis and utilization of conducting polymers as they are nonflammable, have very low vapor pressure, and can be nontoxic and recyclable.[6,14] In this paper, we report on the nanostructured particles and tubes of conducting polymers using a magnetic ionic liquid (MIL), Bmim[$FeCl_4$], as the solvent. The mechanism governing the formation of these structures is discussed.

Experimental Section

The synthesis of Bmim[$FeCl_4$] has already been reported in the literature[15] and was dried and degassed before use. In the present

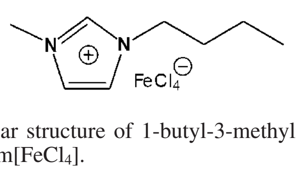

Figure 1. Molecular structure of 1-butyl-3-methylimidazolium tetrachloroferrate, Bmim[$FeCl_4$].

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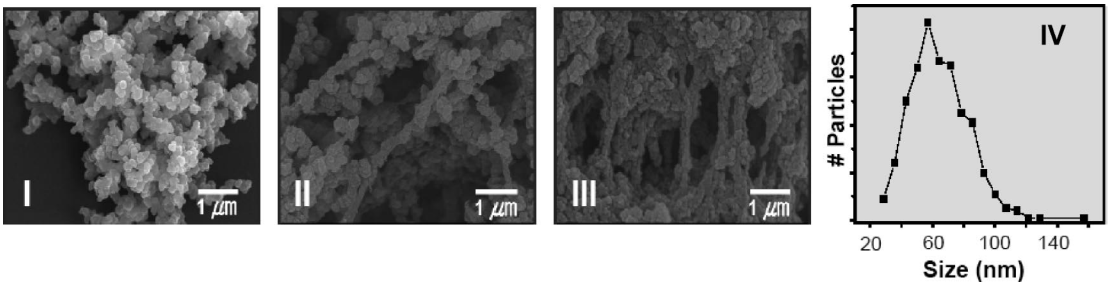

Figure 2. FE-SEM images of PPy nanoparticles obtained in MIL at 25 °C: (I) without magnetic field and (II and III) with magnetic fields. Magnetic field applied at (III) was higher than that at (II). PPy nanoparticles were favorably oriented with the direction of the applied field. (IV) shows the corresponding size distributions in particle as shown in (I).

study, we prepared Bmim[$FeCl_4$] by mixing crystal powder of 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) with anhydrous $FeCl_3$. Crystalline [Bmim]Cl was prepared according to the standard procedure followed by repeated recrystallization from dry acetonitrile. By mixing equimolar amounts of [Bmim]Cl (1.16 g) and $FeCl_3$ (1.07 g) in a drybox with N_2 atmosphere, a dark brown liquid was obtained as a result of an exothemic solid-state reaction. The synthesized Bmim[$FeCl_4$] is nearly paramagnetic, having a large magnetic susceptibility of 40.6×10^{-6} emu g^{-1}, and its structural and purity were identified from spectroscopic methods. The anhydrous iron(III) chloride (Aldrich GR, 99.9%) was used without further purification.

PPy nanostructures were fabricated by simply adding pyrrole monomer to Bmim[$FeCl_4$] as a magnetic ionic liquid solvent, with stirring. To 6 mL of Bmim[$FeCl_4$], 3 mL of pyrrole monomer was added. Pyrrole monomer (Aldrich, GR) was used after purification by vacuum evaporation. Polymerization took place very fast, and PPy was synthesized immediately. An immediate precipitate and darkening of solution occurred after 30 s. The solution was stirred for 3 h, and then the polymer was removed from the Bmim[$FeCl_4$] solution for filtering. The filtered PPy samples were dried for 3 h at 60 °C in a vacuum oven and further purified by methanol washing.

In this process PPy was synthesized by using MIL as a solvent. The Bmim[$FeCl_4$] 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.

In order to apply magnetic field to the polymerization cell, two permanent neodymium iron boron magnets (Niroku Seisakusho Japan, Br; 13.3 kG, HC; 12.2 kOe, BHmax; 42 MGOe, dimension; 10 × 10 × 20 mm) were used. The glass cell (2 mm inner and 4 mm outer gap) containing Bmim[$FeCl_4$] was sandwiched by two fastened magnets in order to maintain the magnetic field directions of N−N or N−S across the cell. A near-infrared excited Raman microspectroscopic system is used for monitoring of polymerization process just after adding pyrrole monomer. The laser power at the sample point is 15 mW, and the exposure time for measurement is 10 s. The size and conductivity of conductive PPy nanostructures were measured using scanning electronic microscopy (SEM)(JSM-633F, Jeol) and the standard four-probe technique (Loresta-GP, Mitsubishi Chemical), respectively.

Results and Discussion

The self-assembly of molecules or small clusters, that is, the spontaneous association of atomic or molecular building blocks under conditions of equilibrium, is emerging as a successful chemical strategy to well-defined structures of nanometer dimensions, with potential applications in many areas of nanotechnology. Especially, the self-organizing, functional system is also the ultimate aim of bottom-up fabrication. This bottom-up approach of synthesis is a promising way to design novel nanoscale functional materials with atomic precision. By the above-mentioned experimental method, we synthesized PPy nanostructures by dissolving pyrrole monomer into the Bmim[$FeCl_4$] liquid containing no additional dopants or oxidants. Surprisingly, all polymers existed as particles and had similar spherical shapes. The well-defined polypyrrole particles was obtained without aggregation, and the size of particles synthesized at room temperature distributed around 50–100 nm, as shown in Figure 2. The size of the particle increased with increasing reaction temperature (until about 700 nm at 80 °C). Variation of other reaction conditions such as concentration and reaction time did not affect the generated polymer shapes. This time, Bmim[$FeCl_4$] 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 monodomains in ILs seems to play a key role in the enhancement of properties because the boundary in randomly oriented polydomains 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 MIL molecules with partially oriented anisotropic liquid domain being mixed in isotropic liquids. The boundary of this isotropic liquid domain is increased with increasing temperature. Accordingly, the size of the particle synthesized at high temperature becomes larger than that at low temperature. Gordon et al.[16] have already reported that Bmim[PF_6], as a kind of ionic liquid, displays liquid crystalline behavior at temperatures above their melting point. The polypyrrole synthesized in the ILs has been also reported by Pringle et al.,[17] and then ILs are used ideal media for the synthesis.

The effect of external magnetic field was then studied. The glass cell containing Bmim[$FeCl_4$] was sandwiched by two fastened magnets in order to maintain the magnetic field directions of N−N or N−S across the cell. Pyrrole was polymerized while the solution was kept still in the cell. Figure 2 shows SEM images of PPy nanostructures synthesized in Bmim[$FeCl_4$] at 25 °C with and without magnetic field. When polymerized without magnetic field (Figure 2, I), spherical PPy particles were formed as stated above. Interestingly, these nanoparticles were aggregated and aligned under magnetic field (N−N or N−S). The morphology of polymer products changed to a network structure or bridged form of particles (Figure 2, II and III), and they were oriented with the direction of the applied magnetic field. Thus, the external magnetic field seems to affect these local structures and hence the resultant polymer structure.

To compare the network formation behavior of PPy particles in MIL, methanol and nematic liquid crystal (4-*n*-pentyl-4′-biphenylcarbonitrile) were used as other solvents, as shown in Figure 3. In this case, a catalyst and dopant are additionally need for the polymerization and the realization of conductivity, respectively. In this work, $FeCl_3$ is used 3 wt % solution. Polypyrrole was actually synthesized in these liquids at the same conditions. As shown in Figure 3, the shape and size of Ppy particles synthesized in liquid crystal solvent were very similar to those synthesized in MIL. However, those synthesized in methanol show no regularity in their structure. The morphology

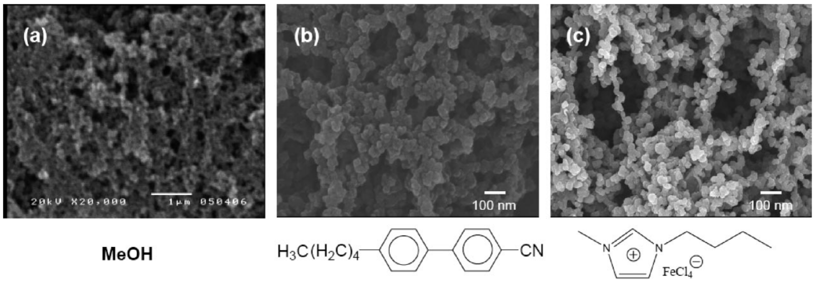

Figure 3. Morphological structures of PPy synthesized in (a) methanol, (b) nematic liquid crystal, and (c) Bmim[FeCl$_4$] without magnetic field at 25 °C.

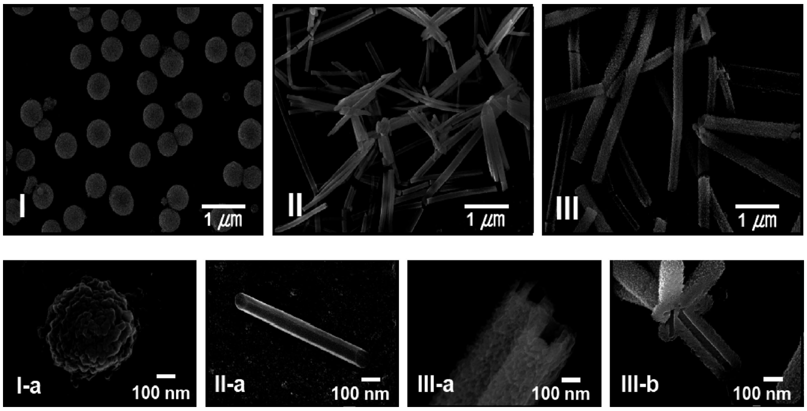

Figure 4. SEM images of poly(*N*-methylpyrrole) nanostructures formed in MIL without (I) and with magnetic fields (II and III): (I) bead, (II) rod, and (III) tube shapes. Corresponding enlarged images are given in (I-a), (II-a), (III-a), and (III-b), respectively. (III-a) and (III-b) clearly show the shape of hollow nanotube and wall constructed by building up the spherical particle (I). (III-a) and (III-b) show formation of double-layered nanotube with nearly uniform diameter.

of polymer synthesized in MIL solutions is very similar to that prepared in liquid crystal but differs from that prepared in methanol solvents. In light of this, it also seems reasonable to speculate that the behavior of MIL molecular could be similar to that of liquid crystal.

Conductivity can also be varied by the fabrication method. In this study, 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. 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, etc. In this means, we can consider that PPy polymer fabricated in MIL solvents have more attractive well-defined nanostructures, highly organized molecule, and/or high doping ratio with $FeCl_3$ for high conductivity. Pringle et al.[17] have actually synthesized polypyrrole in the ILs, 1-methyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)amide, with gold chloride, Fe tosylate, silver nitrate, and $Fe(ClO_4)_3$ as a dopant. And then the sizes of polypyrrole particles were about 100−500 nm in diameter, and the conductivity of those only was about 1–3 mS/cm.

From *N*-methylpyrrole monomer, more attractive nanostructured polymers were obtained. Figure 3 shows the SEM images of the poly(*N*-methylpyrrole) nanostructures formed by the polymerization of *N*-methylpyrrole in Bmim[FeCl$_4$]. From the polymerization without applying magnetic field, spherical nanoparticles (Figure 4, I) were mainly obtained as in the case of PPy (Figure 2). However, the morphology of poly(*N*-methylpyrrole) formed under magnetic field were quite different from that of PPy. Under magnetic field, highly organized shapes such as rods and tubes were observed (Figure 4, II and III). It seems that the methyl group of *N*-methylpyrrole exerted a more pronounced influence upon the formation of characteristic nanostructures. On the basis of these observations, the mechanism of nanostructure formation in MIL is speculated as follows. When the monomer is fed into MIL, the macroscopically orientated polymer particles are formed by self-assembling, and their structures were dramatically built up from spherical particles to sophisticatedly assembled shapes, such as rods and tubes with nanoscaled holes and walls (Figure 4, III) under a magnetic field. The self-assembled local structures in the solvent ionic liquid are likely to serve as templates of highly organized nanostructured polymers. External magnetic field seems to affect these local structures and hence the resultant polymer nanostructures. These results indicate a new synthetic route to produce novel conducting polymer with nanotubular structures via simple self-assembly.

In order to trace the polymerization of pyrrole in Bmim[FeCl$_4$], we monitored Raman spectral change of the liquid before and after adding pyrrole monomer. The 780 and 1064 nm near-infrared excitation was used for avoiding strong fluorescence from polypyrrole. The results are shown in Figure 5. Asterisked marks of Raman spectrum (a) are bands of Bmim[FeCl$_4$] magnetic ionic liquid, and spectrum (b) is that of only pyrrole monomer. Spectrum (c) was measured after 30 s from adding pyrrole monomer in Bmim[FeCl$_4$] liquid cell. The characteristic bands of pyrrole monomer (b) are not found in the Raman spectrum (c), and it indicates that all monomers are already polymerized after 30 s. New peaks at 1593, 1378, 1231, 1086, and 938 cm^{-1} in (d) are assigned to polypyrrole, ring CC, CN stretch, symmetrical C−H in-plane bend, and ring deformation, respectively.[18]

In conclusion, we present a new polymerization method to fabricate nanostructured conducting polymers. The synthesis can be accomplished by just adding monomer to a magnetic ionic liquid bmim[FeCl$_4$]. For polypyrrole and poly(*N*-methylpyrrole), we obtained various nanostructures, such as nanoparticles,

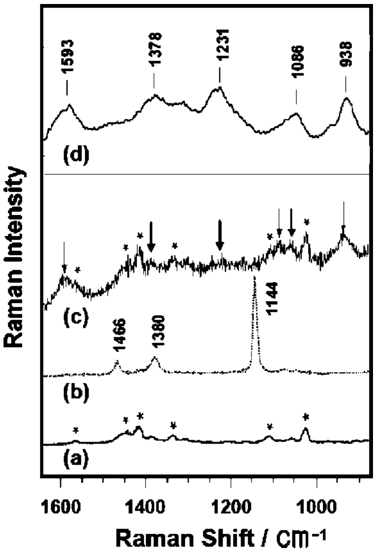

Figure 5. Raman spectra of (a) Bmim[$FeCl_4$] magnetic ionic liquid solvent only, (b) pyrrole monomer, (c) magnetic ionic liquid solvent added pyrrole monomer (after 30 s from adding pyrrole), and (d) measured at solid state of polypyrrole nanostructure self-assembied in Bmim[$FeCl_4$] magnetic ionic liquid solvent, respectively. The 780 and 1064 nm near-infrared lasers were used for Raman spectrum a, b, c, and d, respectively. Asterisked marks in the Raman spectrum (a and c) are characteristic bands of Bmim[$FeCl_4$] magnetic ionic liquid. Arrowed marks in spectrum c are new bands arising from newly synthesized polypyrrole molecular in Bmim[$FeCl_4$].

nanorods, and nanotubes. These polymer morphologies are differently assembled according to the monomer structure and the reaction conditions with and without magnetic field. Magnetic 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, and the strength and direction of magnetic field. Another merit of the use of magnetic 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.

Finally, the present results give a somewhat support for our working hypothesis[19] that self-assembled local structures exist in imidazolium-based ionic liquid including bmim[$FeCl_4$] although an evident experimental proof does not have enough. It was also shown that external magnetic field can affect these local structures. This research also provides a new method to synthesize complicated nanotubular structures by using magnetic ionic liquids via simple self-assembly in a very efficient and economic manner.

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