A simple route for fabricating poly(*para*-phenylene vinylene) (PPV) particles by using ionic liquids and a solvent evaporation process

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Particles of a poly(*para*-phenylenevinylene) (PPV) precursor were prepared from an aqueous solution of the polymer by simple evaporation of water from the solution, which also contained an ionic liquid as a poor solvent (self-organized precipitation (SORP) method); PPV precursor nanoparticles were successfully converted to PPV nanoparticles after annealing at 240 °C under reduced pressure, this simple process constituting a novel route to nanoparticles of functional polymeric materials.

Nanoparticles of functional polymers are key materials in nanotechnology. Though there are several physical and chemical methods for preparing polymer particles, including mechanical milling and emulsion polymerization, these methods are elaborate and require expensive equipment. We have developed a simple fabrication method for making polymer nanoparticles by the evaporation of a suitable solvent from a polymer solution containing a poor solvent (a self-organized precipitation, or SORP method).[1] By using this method, nanoparticles of several kinds of polymer materials, including engineering plastics, biodegradable polymers and other hydrophobic polymers, have been prepared from their tetrahydrofuran (THF) solutions. Particles of polymer blends[2] and block copolymers[3] having unique nanostructures have also been prepared using the SORP method. After mixing with water as a poor solvent, THF was evaporated, causing the polymer molecules to precipitate as nanoparticles from the water. In this system, a volatile solvent with a boiling point lower than that of the poor solvent should be used as the good solvent.

Poly(*para*-phenylenevinylene) (PPV) is a well known electronically conductive polymer.[4] However, due to its low solubility and high glass transition temperature, it is difficult to fabricate PPV micro- and nanostructures.[5] Though PPV can be synthesized by thermal treatment of its water soluble precursor, poly(*para*-xylenetetrahydrothiophenium chloride),[6] there is no current method for fabricating nanoparticles of PPV precursors.

In this Communication, we describe a simple preparation of PPV nanoparticles using the SORP method. Ionic liquids, which are molten salts at room temperature, are unique solvents because of their low vapor pressure, excellent thermal stability, high proton conductivity, and so on.[7] Due to these unique properties, they are used as solvents for high temperature reactions, as proton carriers in lithium ion batteries and in other applications.[8] By using an ionic liquid as a poor solvent, PPV precursor nanoparticles could be obtained from an aqueous solution by using the SORP method, and PPV nanoparticles could be formed after annealing.

An aqueous solution of PPV precursor was purchased from Aldrich, USA and used as received. *N*,*N*-Diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium tetrafluoroborate $[\mathrm{DEMMEA}]^+[\mathrm{BF_4}^-]$ was purchased from Kanto Chemical Industry, Japan. 2 mL of $[\mathrm{DEMMEA}]^+[\mathrm{BF_4}^-]$ were slowly mixed into 1 mL of a 0.2 mg mL^{-1} aqueous solution of PPV precursor in a glass sample tube (Fig. 1). The water was evaporated under reduced pressure at 40 °C overnight. After evaporation, the sample was annealed at 240 °C for 8 h under reduced pressure.

The particle dispersion in $[\mathrm{DEMMEA}]^+[\mathrm{BF_4}^-]$ was diluted with water and the particle diameter determined by a dynamic light scattering (DLS) method (FDLS-3000, Ohtsuka Denshi,

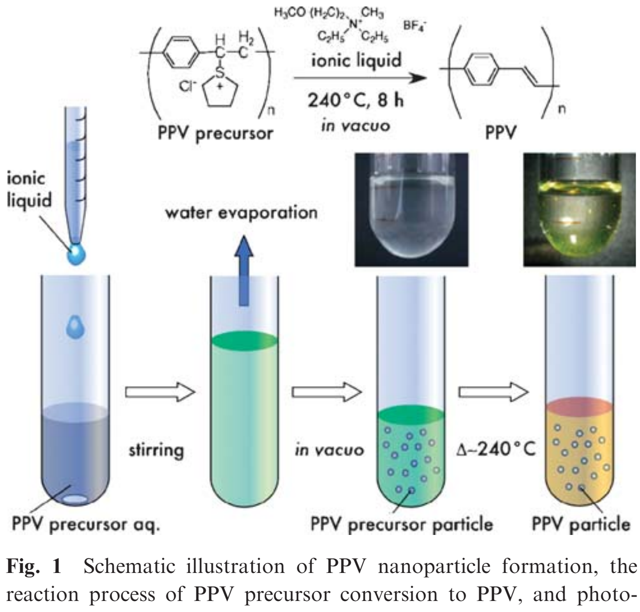

Fig. 1 Schematic illustration of PPV nanoparticle formation, the reaction process of PPV precursor conversion to PPV, and photographs of nanoparticle dispersion in the ionic liquid before and after thermal annealing.

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Japan). The shape of the particles were observed using a field emission-type scanning electron microscope (FE-SEM, S-5200, Hitachi, Japan). A water dispersion of the particles was cast on a mica substrate, and osmium was sputtered onto the sample for FE-SEM observation. The prepared particles were characterized by Fourier transform infrared (FT-IR) spectroscopy (FT-200, Jasco, Japan), fluorescence spectroscopy (RF-5300PC, Shimadzu, Japan) and fluorescence microscopy (BX-51, Olympus, Japan).

After evaporation of the water from the mixed solution, it became opaque due to light scattering from the precipitated particles in $[\mathrm{DEMMEA}]^+[\mathrm{BF}_4{}^-]$ (Fig. 1). The dispersion subsequently turned yellow after annealing at 240 °C. This color change denoted an increase in π-conjugation of the PPV main chain and the reduction of the sulfonium moieties. The side products (mainly tetrahydrothiophene, bp 119 °C) were evaporated and removed from the system under vacuum during thermal annealing.[9]

Fig. 2(a) shows an FE-SEM image of a particle formed after annealing. Spherical particles were successfully formed, with a hydrodynamic diameter of 340.3 ± 70.7 nm, as determined by DLS measurements. After thermal annealing, the particles were insoluble in water, chloroform and other organic solvents. Fig. 2(b) shows the FT-IR spectra of the PPV precursor (grey line) and of the particles after annealing (black line). The absorptions at 2923 (Fig. 2(b)-a) and 2857 (Fig. 2(b)-b) cm^{-1} in the PPV precursor were attributed to the asymmetric ($\nu_{\mathrm{as}}\mathrm{CH}_2$) and symmetric ($\nu_{\mathrm{s}}\mathrm{CH}_2$) C–H stretching vibrations, respectively.[10] These peaks disappeared in the spectrum of the annealed nanoparticles, and a new peak emerged at 3020 cm^{-1} (Fig. 2(b)-e), attributed to alkene C–H stretching (=C–H). Moreover, aromatic C=C in-plane stretching vibrations at 1514 (Fig. 2(b)-c) and 1431 (Fig. 2(b)-d) cm^{-1} were still present after annealing (Fig. 2(b)-f,g). Also, strong peaks emerged at 957 (Fig. 2(b)-h) and 831 (Fig. 2(b)-i) cm^{-1}, which were attributed to the out-of-plane bending of *trans*-vinylene and *para*-phenylene C–H groups. These results strongly suggested that the nanoparticles indeed consisted of PPV.

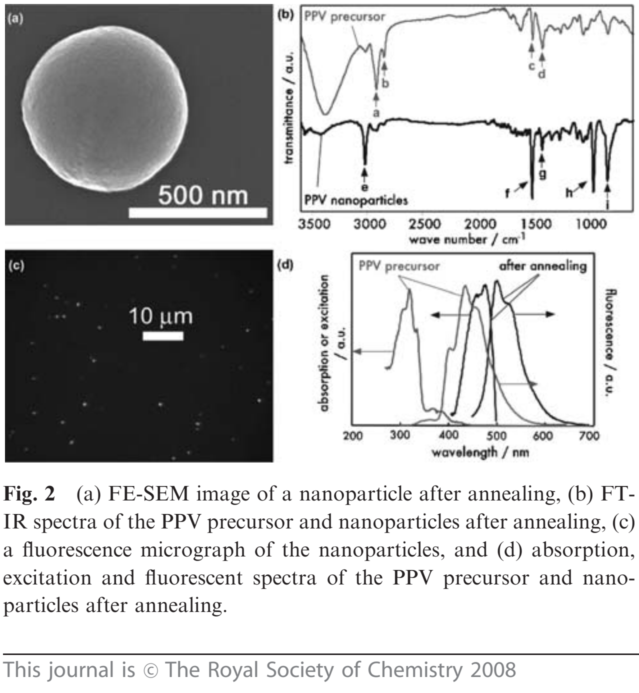

Fig. 2 (a) FE-SEM image of a nanoparticle after annealing, (b) FT-IR spectra of the PPV precursor and nanoparticles after annealing, (c) a fluorescence micrograph of the nanoparticles, and (d) absorption, excitation and fluorescent spectra of the PPV precursor and nanoparticles after annealing.

Fig. 2(c) shows a fluorescence image of the PPV particles. A clear green emission was observed from each particle fixed on a mica substrate. The absorption and fluorescence spectra of the PPV precursor are shown in Fig. 2(d) (grey line). The absorption peak was at 321 nm, and excitation at 320 nm gave a fluorescence peak at 436 nm. On the other hand, the fluorescence peak after annealing was red-shifted, and the peak and shoulder (500 and 524 nm, respectively) observed upon excitation at 400 nm were identical to the reported fluorescence spectra of PPV films.[11] These peak and shoulder features indicated that well-packed PPV chains were formed in the particles.[12] It is important to note that no precursor peaks were observed in the UV-vis or fluorescence spectra after thermal annealing. These results indicate that quantitative conversion of the PPV precursor to PPV was successfully achieved.

We have demonstrated the preparation of PPV particles from a PPV precursor solution by using the SORP method, with an ionic liquid as a poor solvent. PPV nanoparticles were successfully formed after annealing under reduced pressure in an ionic liquid. These PPV nanoparticles may find applications as electroluminescent (EL) materials. In addition to the preparation of PPV nanoparticles, this method may also be extended to other intractable functional polymers (*e.g.*, polyimide).

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Notes and references

1 H. Yabu, T. Higuchi, K. Ijiro and M. Shimomura, *Chaos*, 2005, **15**, 047505.
2 A. Tajima, T. Higuchi, H. Yabu and M. Shimomura, *Colloids Surf., A*, 2008, **313–314**, 332; T. Higuchi, A. Tajima, H. Yabu and M. Shimomura, *Soft Matter*, 2008, **4**, 1302.
3 H. Yabu, T. Higuchi and M. Shimomura, *Adv. Mater.*, 2005, **17**, 2062; T. Higuchi, H. Yabu and M. Shimomura, *J. Nanosci. Nanotechnol.*, 2007, **7**, 856; T. Higuchi, H. Yabu, S. Onoue, T. Kunitake and M. Shimomura, *Colloids Surf., A*, 2008, **313–314**, 87.
4 J. H. Burroughes and A. B. Holmes, *Nature*, 1990, **347**, 539; S. Son, A. Dodahakaour, A. J. Lovinger and M. E. Galvin, *Science*, 1995, **269**, 376.
5 R. A. Wessling and R. G. Zimmerman, *US Pat.*, 3,401,152, 1968I. Murase, T. Ohnishi, T. Noguchi, M. Hirooka and S. Murakami, *Polym. Commun.*, 1984, **25**, 327; J. B. Schlenoff and L. J. Wang, *Macromolecules*, 1991, **24**, 6653; M. Fahlman, M. Lögdlund, S. Stafström, W. R. Salaneck, R. H. Friend, P. L. Burn, A. B. Holmes, K. Kaeriyama, Y. Sonoda, O. Lohst, F. Meyers and J. L. Brédas, *Macromolecules*, 1995, **28**, 1959.
6 C. Seoul, J. I. Kang, S. I. Mah and C. H. Lee, *Synth. Met.*, 1999, **99**, 35.
7 T. Welton, *Chem. Rev.*, 1999, **99**, 2071; C. Guerrero-Sanchez, R. Hoogenboom and U. S. Schubert, *Chem. Commun.*, 2006, 3797.
8 A. B. McEwen, H. L. Ngo, K. LeCompte and J. L. Goldman, *J. Electrochem. Soc.*, 1999, **146**, 1687.
9 A. B. Holmes, D. D. C. Bradley, A. R. Brown, P. L. Burn, J. H. Burroughes, R. H. Friend, N. C. Greenham, R. W. Gymer, D. A. Halliday, R. W. Jackson, A. Kraft, J. H. F. Martens, K. Pichler and I. D. W. Samuel, *Synth. Met.*, 1993, **57**, 4031.
10 V. H. Tran, V. Massardier, T. P. Nguyen and J. Davenas, *Polymer*, 1996, **37**, 2061.
11 J. D. Hong, D. Kim, K. Cha and J. Jin, *Synth. Met.*, 1997, **84**, 815.
12 M. Woodruff, *Synth. Met.*, 1996, **80**, 257.