Macromol. Symp. **2013**, 324, 55–61 DOI: 10.1002/masy.201200067

Design of New Reaction Fields for Spherical Polypyrrole Particle Synthesis

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Summary: Polypyrrole conducting polymers have been investigated widely for various applications because of their thermal and environmental stability and good electrical conductivity. Using chemical oxidative polymerization for the synthesis of polypyrrole particles, the reaction rate is very fast. In this study, we designed two new reaction fields for the synthesis of spherical polypyrrole nanoparticles. In the first system, oxidative polymerization of monomer droplets infused in a water/oil (W/O) emulsion reaction field was investigated. The second system employed dispersed monomer in an aqueous solution with a low concentration of oxidant in which polymerization was augmented by ultrasonic irradiation. Effective control of the reaction rate was important for enabling the synthesis of fine spherical polypyrrole particles.

Keywords: conducting polymers; emulsion; particle; polypyrroles; ultrasound

Introduction

Recently, many studies on the synthesis and characterization of conducting polymers, such as polyacetylene, polyaniline, and polythiophene have been reported. Polypyrrole (PPy) is one of the most studied conducting polymers because of its environmental stability and relative ease of synthesis. However, its poor processability is often a problem. Therefore, fine particles of this conducting polymer must be synthesized by chemical oxidative polymerization.

In general, PPy particles are obtained by chemical oxidative polymerization in various organic solvents and aqueous media in which an oxidative agent, such as ferric chloride, potassium persulfate, or ammonium persulfate is added.[1–4] However, the shape of the resulting PPy particles is not only spherical but also hexagonal, cubic, wire-like, and ribbon-like. It is imperative to control the size and shape of the synthesized particles because these features influence the properties of the particles, including their optical, physical, and chemical characteristics. In order to prepare monodispersed PPy nanoparticles, water soluble polymers such as polyvinylpyrrolidone are added as steric stabilizers, and the reaction is often run at a low temperature (~278 K).[5–7] However, water soluble polymer remains as an impurity in the synthesized PPy particle.

On the other hand, alternative reaction fields and methods have also been investigated. Yuasa *et al.* have reported that PPy nanoparticles are successfully synthesized in supercritical carbon dioxide as a solvent, and the density of carbon dioxide plays an important role in controlling the size of the synthesized particles.[8] Additionally, Cruz *et al.* have reported that nano and meso spherical iodine doped PPy particles are synthesized using plasma.[9]

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In this study, we explored two new reaction fields designed to synthesize spherical PPy nanoparticles. In particular, we focused on controlling the reaction rate. The first method uses monomer droplets in a W/O emulsion as the reaction field. Using this method, a W/O emulsion was initially prepared by combining an aqueous phase containing an oxidant and an organic phase incorporating a surfactant and stirring the resulting mixture. Subsequently, the Py monomer was dissolved in an organic solvent used as the continuous phase. In this polymerization method, diffusion of the monomer to a water droplet (the dispersed phase) was the rate-determining step, and thus, using this technique, we were able to control the reaction rate under room temperature conditions. The effects of the organic solvent used as the continuous phase and the volume fraction of the dispersed phase on the size and morphology of the synthesized PPy particles were investigated.

The second method employed water dispersed monomer polymerization assisted by ultrasound under a low oxidant concentration. Ultrasound is known to be useful for initiating reactions, enhancing reaction rates, and improving selectivity in many different chemical reactions. In particular, ultrasonic polymerization permits the use of lower surfactant concentrations, obviates the need for initiators, and can proceed at room temperature. Therefore, this technique is advantageous from the viewpoint of green sustainable chemistry.[10,11] Moreover, ultrasonic chemical effects and physical effects are dependent on frequency. Therefore, control of the reaction rate and morphology of the synthesized PPy particles was expected. Thus, using this method, frequency effects on the size and morphology of the synthesized PPy particles were investigated.

Experimental Part

Materials

All chemicals were used as acquired without further purification. Pyrrole (Py) monomer was purchased from Kanto Chemical Co. Aerosol OT (AOT) was purchased from Wako Pure Chemical Industries and used as a surfactant. Ammonium persulfate (APS) was purchased from Kanto Chemical Co. and used as an oxidant. The following organic solvents were purchased from Kanto Chemical Co.: *n*-hexane, *n*-heptane, *n*-octane, isooctane, *n*-decane, and *n*-dodecane. Ion exchanged water was used as a dispersed phase.

Polymerization Using a W/O Emulsion System

AOT was dissolved in an organic solvent, which was used as the continuous phase. The organic solvents were *n*-hexane, *n*-heptane, *n*-octane, isooctane, *n*-decane, *n*-dodecane, and a mixed solution of these solvents. The AOT concentration was 0.1 M. APS was dissolved in the aqueous phase, which was used as the dispersed phase. The APS concentration was 0.01 M. The APS solution was injected into the organic solvent containing AOT, and a W/O emulsion was prepared by mechanically stirring the mixture for 1 h at 298 K. The volume of the continuous phase was 25 mL, and the volume fraction of the dispersed phase varied between 12 and 35 vol%.

Py was then injected into the prepared emulsion with mechanical stirring at 500 rpm, and the polymerization reaction subsequently progressed for 24 h at 298 K. The amount of injected Py varied between 1.25 and 5.0 mmol, which maintained the ratio of monomer to oxidant at 74.

Polymerization Using an Ultrasonic System

Figure 1 shows the entire experimental apparatus. A stainless steel vibration plate attached to a PZT transducer (Honda Electronics Co., Ltd.) was installed at the center of the base of the water bath. The water bath was maintained at a constant temperature using a thermostat.

Pyrrole monomer was dispersed in water by stirring, and the APS solution was added, and the mixture was treated with

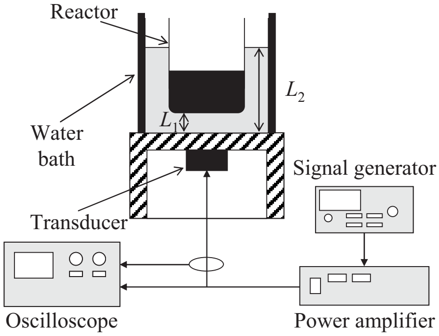

Figure 1.
Experimental setup.

ultrasonic irradiation. The total volume of the sample solution, volume fraction of Py, APS concentration, ultrasonic irradiation time, reaction temperature, and ultrasonic power were 30 mL, 10 vol%, 0.043 M, 1 h, 298 K, and 6.5 W, respectively. The ultrasonic frequency varied between 20 kHz and 1.6 MHz. An oxidative polymerization without ultrasonic irradiation was also performed for the comparison.

Analysis

After the polymerization was stopped, black PPy powder was isolated by a centrifugal separator, and the PPy particles were washed with ethanol and ion exchanged water to remove surfactant, oxidant, and monomer.

The morphology and size distribution of the PPy particles were determined by scanning electron microscopy (SEM, S-5000, Hitachi). The particle size distribution was also determined by a dynamic light scattering method (DLS). The molecular weight of PPy was determined by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOFMS, Voyager DE, Applied Biosystems).

For the polymerization using the ultrasonic system, the ultrasonic power in the reactor was measured by calorimetry.[12]

Results and Discussions

Effects of the Organic Solvent in the W/O Emulsion System

Figure 2 shows the effects of using different organic solvents on the SEM micrographs of the PPy particles. The amount of Py was 5.0 mmol, and the volume fraction of the dispersed phase was 21.3 vol%. The PPy particle size decreased as the carbon

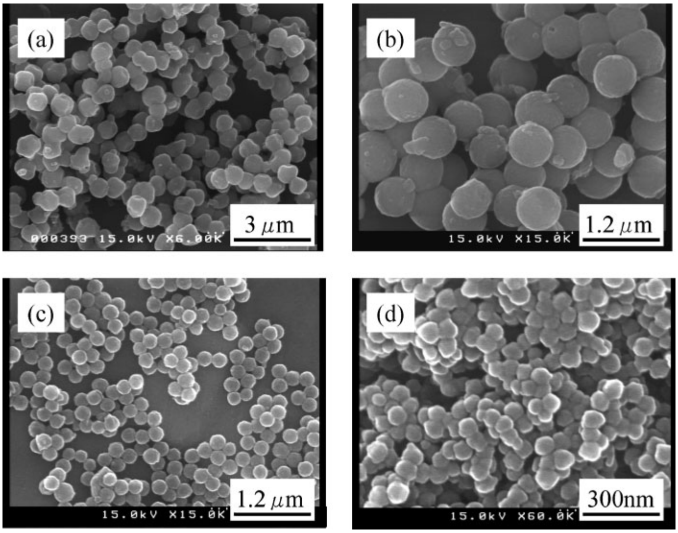

Figure 2.
SEM micrographs of PPy particles using various organic solvents: (a) *n*-hexane, (b) *n*-heptane, (c) *n*-octane, and (d) *n*-decane.

number of the alkane used as the organic solvent increased. Py monomer, which is dissolved in the organic solvent, moves into the micro water droplet, and the polymerization reaction is thereby initiated. The mass transfer rate of the Py monomer in the organic phase is expected to decrease with increasing solvent viscosity, which is controlled by increasing the carbon number of the alkane. Thus, Figure 3 shows the influence of the viscosity of the organic solvent on the average diameter of the PPy particles and the relative standard deviation (RSD). The size of the PPy particle decreased with increasing viscosity of the continuous phase. On the other hand, RSD was not dependent on the viscosity, and the value remained constant at approximately 0.1. Therefore, it is clear that fine monodispersed PPy particles were accessible using the W/O emulsion system. The degree of polymerization analyzed by MALDI-TOFMS was approximately 10.

When APS was used as the oxidant, an induction period preceding pyrrole oxidation was not observed,[13] and the monomer that reached the aqueous phase was anticipated to react rapidly. Thus, the rate-determining step in this polymerization reaction is expected to be the diffusion of the Py monomer in the continuous phase, and the process for the formation of the PPy particles is influenced by the rate of diffusion of Py monomer. Figure 4 shows the relationship between the diffusion coefficient of the Py monomer in the different organic solvents and the average PPy particle diameter. Here, the diffusion coefficient of the Py monomer in an organic solution was estimated using the Wilke–Cheng equation (Equation (1)).[14] Here, D_{AB}, φ, M_B, T, μ_B, and V_A represent the diffusion coefficient, association factor of the solvent, molecular weight of the solvent, temperature, viscosity of the solvent, and molar volume of the solute, respectively. There is a strong correlation between the diffusion coefficient of the Py monomer in the continuous phase and the average PPy particle diameter, and the empirical formula is shown in Equation (2). Here, d_{Ave} represents the average diameter of the synthesized PPy particles.

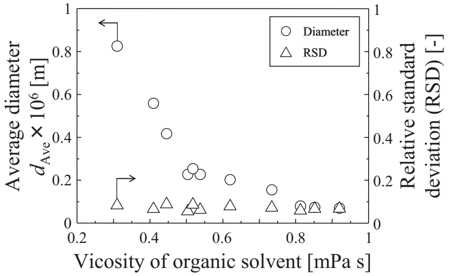

Figure 3.
Influence of the viscosity of the organic solvent on the average diameter of the PPy particle and the relative standard deviation.

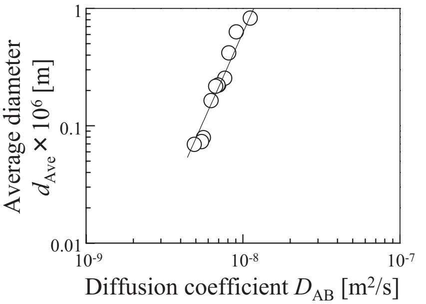

Figure 4.
Relationship between the diffusion coefficient of Py in different organic solvents and the average PPy particle diameter.

$$D_{AB} = \frac{7.4 \times 10^8 (\phi M_B)^{1/2} T}{\mu_B V_A^{0.6}} \tag{1}$$

$$d_{Ave} = 7.0 \times 10^{20} D_{AB}^{3.38} \tag{2}$$

Effects of the Volume Fraction of the Dispersed Phase in the W/O Emulsion System

Figure 5 shows the effects of the volume fraction of the dispersed phase on SEM micrographs of the PPy particles. The organic solvent was *n*-octane, and the amount of injected Py varied between 1.25 and 5.0 mmol, keeping the ratio of monomer to oxidant constant. The size of the PPy particle decreased as the volume fraction of the dispersed phase increased.

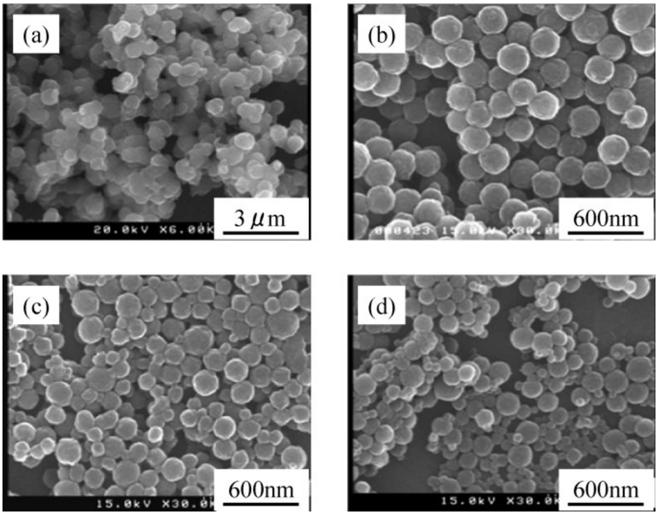

Figure 5.
SEM micrographs of PPy particles for various dispersed phase volume fractions: (a) 11.9 vol%, (b) 21.3 vol%, (c) 30.0 vol%, and (d) 35.1 vol%.

Furthermore, the viscosity of the emulsion was observed to increase with an increase in the volume fraction of the dispersed phase. Therefore, an inverse relationship between the size of the synthesized PPy particle and the viscosity of the emulsion was anticipated.

Effects of the Frequency of Ultrasonic Irradiation

Figure 6 shows SEM micrographs of the spherical PPy particles synthesized using chemical oxidative polymerization assisted by ultrasound at various frequencies. The degree of polymerization analyzed by MALDI-TOFMS was in the range of 30 to 60.

Figure 7 shows the effects of the ultrasonic frequency on polymer yield and the average PPy particle diameter. The average diameter of PPy particles synthesized without ultrasonic irradiation at 24 h was 190 nm, which was smaller than that of the particles synthesized with ultrasonic irradiation. However, the size was not influenced by the frequency. The Py monomer dissolves in water, and under the conditions of this study, half of the added monomer dissolved in the aqueous phase. Therefore, it was found that the monomer underwent polymerization not as monomer droplets but as dissolved monomer, and no effects on the particle size were observed by varying the frequency. With respect to yield, in the absence of ultrasonic irradiation, the quantity of polymer produced after 1 h and 24 h was 0.098 g and 0.14 g, respectively. The polymer yield with ultrasonic irradiation after 1 h was larger than 0.1 g, and thus, adding ultrasonic irradiation for a comparable period of time improved the yield. Therefore, ultrasound is considered to improve the polymerization reaction, and the enhancement (in terms of yield) was influenced by frequency.

Figure 8 shows the relationship between the sonochemical efficiency and polymer yield. When the frequency is 22.8 kHz, the polymer yield is high in spite of low sonochemical efficiency. It is found that not only chemical but also physical effects influence activation of the polymerization reaction. On the other hand, the effects of frequency on particle diameter and sonochemical efficiency show a similar trend in that the minimum diameter and maximum sonochemical efficiency appear at the same frequency. The monomer droplet size was expected to be influenced by the frequency, thereby regulating the total surface area of

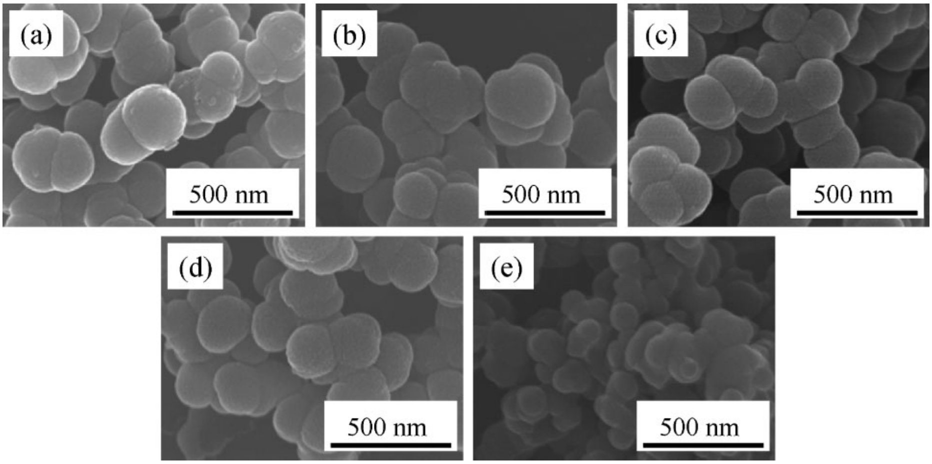

Figure 6.
SEM micrographs of PPy particles formed using ultrasonic irradiation at various frequencies: (a) 22.8 kHz, (b) 490 kHz, (c) 940 kHz, and (d) 1.6 MHz and (e) in the absence of ultrasonic irradiation and with a longer reaction time (24 h).

the monomer. It is also expected that the rate of generation of OH radicals was influenced by the frequency.[15] Therefore, the particle nucleation and growth rate were influenced by the frequency, and the particle size was determined by these factors. The development of a detailed mechanism of the PPy particle formation by analyzing monomer droplet size distribution and the rate of radical generation is the subject of ongoing studies.

Conclusion

The synthesis of monodispersed spherical PPy particles was accomplished at room temperature by chemical oxidative polymerization using water droplets in a W/O emulsion reaction field. In this polymerization system, the diffusion of the Py monomer in the continuous phase to a water droplet was the rate-determining step, and the particle size of the synthesized PPy was influenced by the diffusion coefficient of the monomer in the organic solvent. Spherical PPy particles were also synthesized by chemical oxidative polymerization assisted by ultrasound, and the yield of polymer was larger with ultrasound than without after the same reaction time. It is concluded that controlling the reaction rate is an important factor in the synthesis of fine spherical PPy particles.

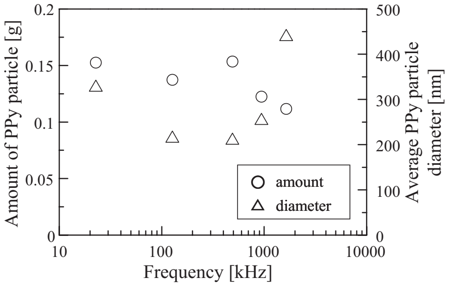

Figure 7.
Effect of ultrasonic frequency on polymer yield and the average particle diameter of PPy.

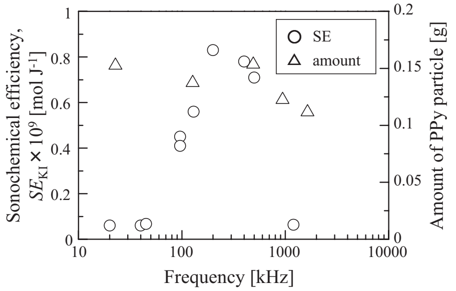

Figure 8.
Relationship between sonochemical efficiency[15] and polymer yield.

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