

Preparation and Characterization of Water Self-dispersible Poly(3-hexylthiophene) Particles

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The present paper describes the preparation and characterization of stable aqueous dispersions of poly (3-hexylthiophene) (P3HT) by a precipitation method. P3HT was first synthesized by oxidative polymerization of 3HT with iron(III) chloride as an oxidant. Number-average molecular weight (\bar{M}_n) of P3HT increased with an increase in 3HT concentration. Colloidal particles were prepared by adding a tetrahydrofuran (THF) solution of P3HT into a large amount of distilled water. TEM observations showed that the particle size increased with an increase in the concentration and \bar{M}_n of P3HT. The size of the particles was in the range of 50 to 600 nm. The spectral features of the aqueous dispersions were investigated by means of UV-vis spectroscopy. P3HT provided the π - π^* absorption band at 436 nm in THF. On the other hand, the dispersions brought about a bathochromic shift of the bands and a larger red shift was observed as the polymer concentration became higher, indicating that P3HT would take a well-stacked structure in the particles. Temperature dependence of UV-vis absorption spectra for P3HT aqueous dispersions was also studied in the temperature range of 0 to 80 °C, which revealed that P3HT in the dispersed state showed a thermochromism similar to that of P3HT in THF.

KEY WORDS: Polythiophene / π -Conjugated Polymer / Poly(3-hexylthiophene) / Colloidal Particle / Conducting Polymer / Precipitation Method / Thermochromism /

Poly(3-hexylthiophene) (P3HT) is a subject of extensive study because of its solubility, fusibility, and environmental stability.¹ P3HT also exhibits unique properties such as thermochromism and solvatochromism.²⁻⁶ This functional polymer is viewed as potentially useful materials in field-effect transistors, optical and electronic sensors, light-emitting devices, nonlinear optical materials, etc.⁷⁻⁹

Our attention has focused on colloidal dispersions of P3HT particles. Colloidal particles are of great importance due to their interesting physical properties as well as their potential technological applications.^{10,11} Several attempts have been made so far to produce P3HT particles. Yamamoto *et al.* employed a reprecipitation method to prepare colloidal dispersions of P3HT. Methanol, which is a poor solvent for P3HT, was added to the CHCl_3 solution of P3HT, resulting in the formation of P3HT particles.^{12,13} Takeuchi and Kobashi also investigated in detail the kinds of poor solvents and clarified the precipitation conditions for improved yields.¹⁴ Furthermore, it has been reported that the use of a nonionic surfactant, Tween 80, provided stable aqueous dispersions of P3HT.¹⁵

To our knowledge, few reports on water self-dispersible P3HT particles have been published.¹⁵ There is hence a lack of information about colloidal properties of P3HT water dispersions, such as particle size, particle morphology, optical property, etc. Development and characterization of such dispersions are of great significance from an environmental as well as industrial aspect. The purpose of the present study is to develop self-dispersible P3HT particles in aqueous media by a reprecipitation method. The particle size and the optical

property of the colloidal dispersions are discussed as a function of polymer concentration and molecular weight.

EXPERIMENTAL

Materials

3-Hexylthiophene (3HT, Aldrich Chemical Co.) and iron (III) chloride (FeCl_3 , Kanto Chemical Co.) were used as received. All other chemicals were of analytical grade unless specified otherwise.

Polymerization of 3HT

P3HT was synthesized by chemical oxidative polymerization of 3HT in chloroform with FeCl_3 as an oxidant.¹⁶ The polymerization was carried out under a N_2 atmosphere at room temperature for 12 h and then the reactants were poured into a mixture of concentrated hydrochloric acid and methanol (5/95, v/v). The black precipitates were collected on a Buchner funnel, purified by Soxhlet extraction with methanol, and finally dried under reduced pressure.

Preparation of Colloidal P3HT Particles

Colloidal P3HT particles were obtained by a reprecipitation method. A THF solution of P3HT was prepared at various concentrations ranging from 0.01 to 3.0 wt %. The polymer solution (1.0 mL) was then added into distilled water of 50 mL. The water was gently stirred in a vial at given temperature.

Characterization

The number-average molecular weight (\bar{M}_n) and the index

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of molecular weight distribution ($\overline{M}_w/\overline{M}_n$) were determined by size exclusion chromatography (SEC, Shodex GPC-101) equipped with high resolution columns (Shodex K-806M \times 2). Eluent solvent was HPLC grade chloroform with a flow rate of 1 mL/min. Polystyrene standards were used for calibration.

The size and morphology of P3HT particles were observed by means of transmission electron microscopy (TEM) (JEOL EX-2000). Small amounts of the particle dispersions were infinitely diluted with distilled water. The diluted samples were applied on collodion-coated Cu grids to prepare TEM samples.

All UV-vis spectra were taken on the aqueous dispersions of P3HT with a Shimadzu UV-1600 spectrophotometer.

RESULTS AND DISCUSSION

Chemical Synthesis of P3HT

The synthesis of P3HT was carried out by chemical oxidation of 3HT with FeCl₃ as an oxidant. The oxidant was kept constant in a molar ratio 4:1 with respect to 3HT. The molecular weight and the distribution of P3HT were analyzed by means of SEC. Table I summarized the molecular characteristics of P3HT synthesized. The number-average molecular weight (\overline{M}_n) increased with an increase in 3HT concentrations in the feed. These results indicate that \overline{M}_n of P3HT can be controlled over a wide range of 0.4×10^4 to 7.0×10^4 by varying 3HT concentrations. In addition, polydispersities of all P3HT synthesized here were below 2.0, suggesting that P3HT with relatively narrow molecular weight distribution can be obtained by using chemical oxidation of 3HT with FeCl₃. Polymer samples are referred to as P3HT-Z, where Z $\times 10^4$ is the molecular weight of P3HT synthesized.

Particle Size and Morphology

P3HT has good solubility in CHCl₃ and THF, but it is insoluble in dimethylformamide, methanol, and water.¹² Addition of P3HT in good solvent into non-solvent, therefore, affords precipitation of P3HT chains from the solution, followed by aggregation of the precipitated chains. Stable (mature) colloidal dispersions could be obtained provided these aggregates have electrostatic or steric stability. This approach is called a reprecipitation method, which is a simple and useful technique for obtaining liquid dispersions of organic crystals and polymer.^{17,18}

In the present study, a reprecipitation method mentioned above was used to obtain self-dispersible P3HT colloidal

particles. Distilled water was also utilized as a disperse medium from an environmental point of view. P3HT water dispersions were prepared by adding a THF solution of P3HT into a large number of distilled water at varying polymer concentrations in THF. The stable and self-dispersible aqueous dispersions were obtained in the concentration range of 0.1 to 2.5 wt% and then these dispersions were stable at least for 6 months on standing. At higher concentrations above 2.5 wt%, however, macroscopic precipitates were formed on the water surface as soon as the polymer solution was added. The mechanism of colloidal stability for self-dispersible particles remains unclear, but electrophoretic mobility studies in an aqueous solution of 0.01 M KCl showed that P3HT particles have a negative charge and thus chloride ion adsorbed on the particles, which ion originate from FeCl₃ during polymerization, may contribute to the colloidal stability.

The particle size and morphology of P3HT particles were investigated as a function of polymer concentrations by means of TEM. Figure 1 describes the results of P3HT-6.8 particles. All particles were almost spherical, but the size distribution was relatively broad. Figure 2 summarizes the effect of polymer concentration and molecular weight on particle size. Increase in the average particle size was observed independent of \overline{M}_n as P3HT concentrations increased. The size increased somewhat steeply at the concentration of about 0.75 wt%. These results are probably due to an increase in the number of precipitated polymer chains as P3HT concentrations became higher. In addition, increased \overline{M}_n led to production of a larger particle size. Although several researchers reported the

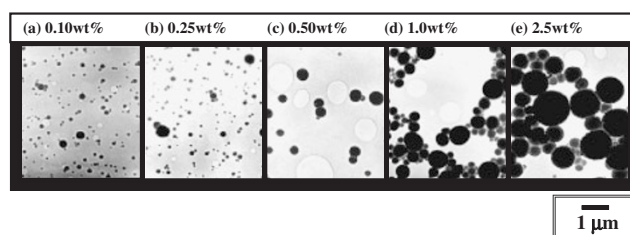


Figure 1. TEM images of P3HT-6.8 particles prepared at different P3HT concentrations.

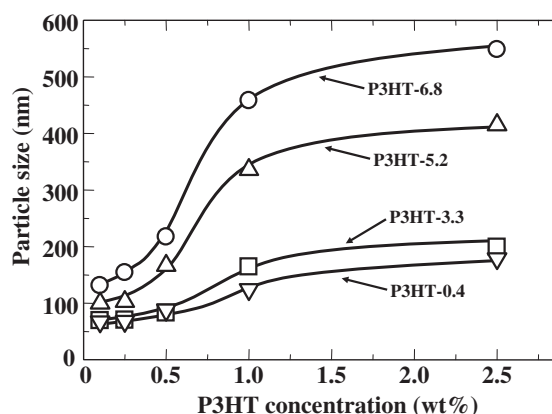


Figure 2. Effect of P3HT concentration and molecular weight on particle size.

Table I. Influence of polymerization conditions on molecular weights of P3HT

Code	[3HT] (mol/L)	3HT (g)	FeCl ₃ (g)	CHCl ₃ (g)	Temp. (°C)	Yield (%)	$\overline{M}_n \times 10^{-4a}$	$\overline{M}_w/\overline{M}_n^a$
P3HT-0.4	0.050	0.34	1.30	44.2	25	14.1	0.37	1.79
P3HT-3.3	0.068	0.46	1.74	44.2	25	13.7	3.32	1.73
P3HT-5.2	0.100	0.34	1.30	22.1	25	49.8	5.18	1.83
P3HT-6.8	0.200	0.68	2.60	22.1	25	68.1	6.83	1.95
P3HT-6.9	0.400	1.36	5.20	22.1	25	11.0	6.91	1.29

^aDetermined by SEC.

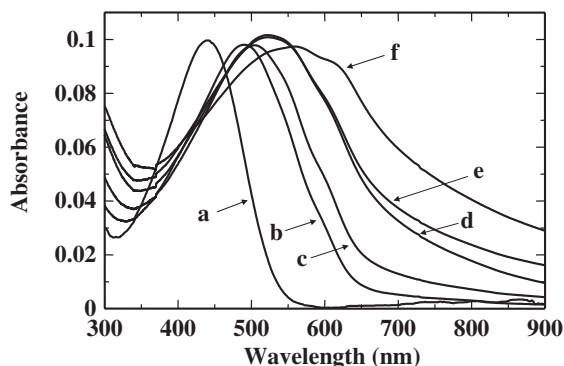


Figure 3. Optical absorption spectra of (a) P3HT THF solution, and colloidal P3HT-6.8 particles prepared at the concentration of (b) 0.10 wt %, (c) 0.25 wt %, (d) 0.50 wt %, (e) 1.0 wt %, and (f) 2.5 wt %.

preparation of P3HT colloidal dispersions in various solvents, the resulting average hydrodynamic size with dynamic light scattering was limited in the range below 100 nm.^{12–14} On the other hand, the present study demonstrated that the average size of P3HT particles can be controlled in the range of 50 to 600 nm by varying polymer concentrations and molecular weights.

Spectroscopic Properties

Figure 3 exhibits UV-vis spectra of the colloidal dispersions of P3HT-6.8 as a function of polymer concentrations. P3HT dissolved in THF provided the π - π^* absorption band at 436 nm. On the other hand, P3HT dispersions prepared at the concentration of 0.1 wt % had a similar spectral shape, but showed a red shift of the peak. Furthermore, a shoulder peak appeared around 600 nm, which can be assigned to vibronic structure with a 0-0 transition (π - π^* transition originated from π -electron orbital overlap between adjacent thiophene rings).^{2,19} Such a spectral profile is in agreement with that of P3HT colloidal dispersions in various solvents,^{12–15} indicating that π -stacking interaction caused by aggregation of polymer chains would take place in the particle. Figure 3 also shows that the increased polymer concentrations led to a larger red shift and a broader spectrum, suggesting that interchain interaction would be stronger as the concentration became higher. This is the first report on P3HT colloidal particles with different spectral profiles as far as we know.

Next we examined the effect of \overline{M}_n on optical properties. The results at the polymer concentration of 0.5 wt % are shown in Figure 4. Spectra were little affected by \overline{M}_n except for the lowest \overline{M}_n in the present study, whereas the particle size increased from 80 to 220 nm with an increase in \overline{M}_n . The fact that there was little difference in the spectra of the colloidal dispersions at different sizes suggests that an aggregation state of P3HT chains in particles would be mainly determined by not \overline{M}_n and size but polymer concentration at particle formation. In summary, an increase in the number of precipitated polymer chains at higher concentrations leads to stacking of polymer chains. The π -stacking in colloidal particles would cause an absorption band at longer wavelengths.

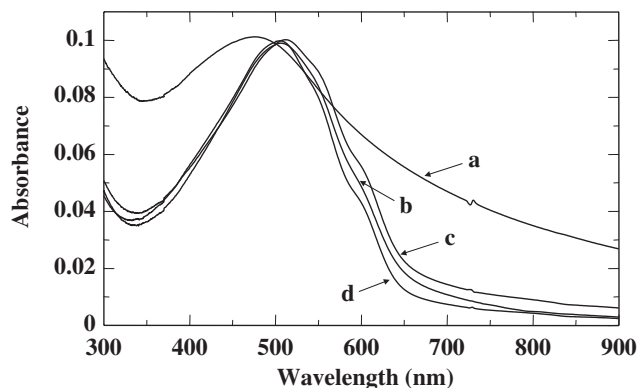


Figure 4. Optical absorption spectra of colloidal particles of (a) P3HT-0.4, (b) P3HT-3.3, (c) P3HT-5.2, and (d) P3HT-6.8. The particles were prepared at the concentration of 0.50 wt %.

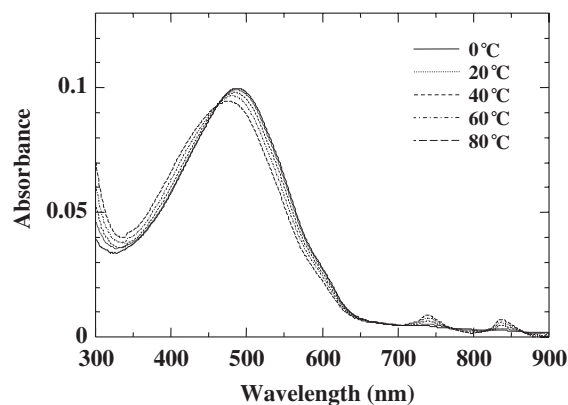


Figure 5. Temperature dependence of UV-vis absorption spectra of P3HT-6.8 colloidal particles prepared at the concentration of 0.25 wt %.

Thermochromism

Figure 5 shows temperature dependence of UV-vis absorption spectra of P3HT in the water dispersion state. The spectra were recorded at 20 °C intervals between 0 and 80 °C. P3HT-6.8 particles prepared at the concentration of 0.25 wt % were used in this experiment. At 0 °C an absorption maximum around 487 nm was observed. Upon heating, the absorption peak shifted to a shorter wavelength and also the absorbance of the peak slightly decreased. In addition, two new peaks appeared near 740 and 840 nm and the intensity of these peaks increased with an increase in temperature. These bands have not been assigned yet. An internal particle structure should be investigated as a function of temperature to assign them. This thermochromic behavior was reversible. Figure 6 summarizes an absorption maximum of P3HT colloidal dispersions in water and P3HT solution in THF as a function of temperature. Two samples with different molecular states exhibited similar behavior, indicating that a transition from ordered phase to quasi-ordered phase in particles would take place upon heating.^{6,20}

CONCLUSIONS

Preparation and characterization of water self-dispersible

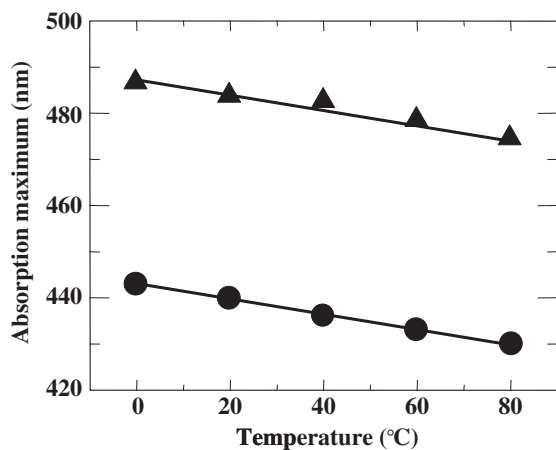


Figure 6. Temperature dependence of absorption maximum for P3HT colloidal dispersions in water (▲) and P3HT solution in THF (●).

P3HT particles with a precipitation method leads to the following conclusions:

1. Stable aqueous dispersions of P3HT can be obtained by adding a THF solution of P3HT into a large amount of distilled water. The particle size can be controlled in the range of 50 to 600 nm by varying polymer concentrations and molecular weights.
2. Increased polymer concentrations at particle preparation leads to a larger red shift of the corresponding colloidal dispersions, suggesting that interchain interaction would be stronger as the concentration became higher.
3. P3HT in the dispersed state shows a thermochromic transition from ordered phase to quasi-ordered phase upon heating.

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