5314 *Macromolecules* **2002,** *35,* 5314−5316

Notes

Size Control of Polyaniline Nanoparticle by Polymer Surfactant

Deokgeun Kim, Jinwoo Choi, Jin-Yeol Kim, Yang-Kyoo Han, and Daewon Sohn*

Department of Chemistry, Hanyang University,
17 Haengdang Dong, Sungdong Ku, Seoul 133-791, Korea

Received January 31, 2002
Revised Manuscript Received April 16, 2002

Among several electrically conducting conjugated polymers, polyaniline (PANI) has been widely studied for electronic and photonic applications. Solution characteristics of PANI determine the polymer morphology in the solid state. Thus, many researchers have studied the oxidative polymerization of aniline in the presence of micelles,[1] a steric stabilizer,[2−4] colloidal silica particles,[5−7] or reverse microemulsion[8] as a polymerization medium to increase thermal stability and processability. However, the products of these methods are limited in their ability to control the size of the nanoparticle, which depends on the concentration and kinds of surfactant molecules. Size control of nanoparticles is very tedious using conventional surfactants.

In this study, we introduce the amphiphilic polymer molecules, hydrophobically end-capped poly(ethylene oxide)s (HEURs), which make the different size of micelle by changing the length of the hydrophilic middle block. The HEUR polymer forms "flower type" micelles at low concentrations, and when the concentration exceeds the critical aggregation concentration (cac), each micelle is bridged in an aqueous solution.[9] This associative polymer has a microdomain of spherical shape at the micelle core, which is composed of hydrophobic end groups. As a result, the micellar system is composed of two phases: a hydrophobic center as the dispersed phase and aqueous medium as the continuous phase. The micellar shells, poly(ethylene oxide), can be regarded as an interfacial region. In the presence of the hydrophobic micellar core and hydrophilic interface, the polymerization reaction was mainly performed at the oil−water interface because of the orientation of reactants.[10] Figure 1 shows the schematic representation of the HEUR flowerlike micelle and orientation of the aniline monomer.

Since the polymerization reaction proceeds in the micellar solution, the size of the micelle controls the size and the structure of the PANI particles. We have focused on the effect of the surfactant structure on the crystallinity, conductivity, and the morphology of the PANI nanoparticle.

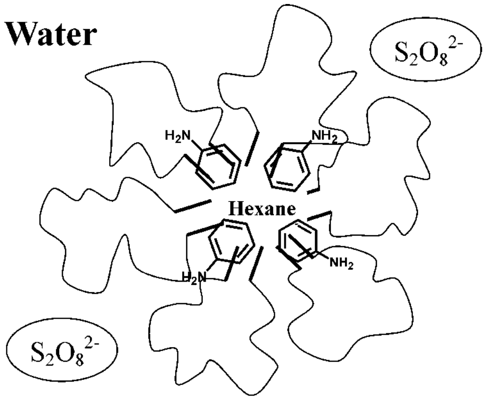

Figure 1. Schematic representation of HEUR flowerlike micelle and the orientation of aniline monomer: ∼, PEO chain; −, alkyl chain.

To make HEUR polymer, poly(ethylene glycol) (M_w = 1000, 2000, 4000, or 35 000), which has hydroxyl groups on both ends, was mixed with toluene and distilled for over 2 h at 110 °C to remove the trace of water. The mixture was cooled to 80 °C, and octadecyl isocyanate and dibutyl tin dilaurate were added. Then it was stirred for 24 h at 80 °C, and butanol was added to react with excess octadecyl isocyanate. After stirring for 24 h in toluene, the mixture was cooled to room temperature, and toluene was removed using a vacuum evaporator. The product was recrystallized twice from THF and hexane to remove alkyl urethane. To remove other impurities, the HEUR polymer was dissolved in ethyl acetate and filtered with a 0.4 μm pore sized membrane filter. The filtered solution was stored overnight at 0 °C, and precipitating polymer was collected.

The micellar solution was prepared by adding HEUR polymer into 100 mL of distilled water. We have controlled the concentration of solution about cac, which was determined by static fluorescence.[11] After the micelles were formed, 0.02 M hexane (as organic phase) and 0.02 M aniline were added. Ammonium persulfate (APS) was dissolved in 20 mL of distilled water and added dropwise into 100 mL mixtures as the same molar ratio to aniline for 1 h. The polymerization was performed at 5 °C with mechanical stirring at 600−700 rpm in a jacketed three-neck round-bottomed flask connected to a thermostat-controlled circulating chiller unit for 12 h. An excess amount of acetone was added to precipitate PANI powder and to stop the reaction. The obtained PANI was then filtered in a paper filter and washed several times with methanol, acetone, and pure water to remove the nonreacted chemicals and HEUR. Then the PANI particles were dried in a vacuum oven for other experiments. UV−vis spectra showed an exciton absorption peak of quinoid at about 640 nm and a maximum $\pi \rightarrow \pi^*$ aborption peak of benzoid rings at 330 nm, and FT-IR spectra had five characteristic vibrational peaks at 1590, 1500, 1310, 1160, and 830 cm^{-1}. It indicated that the prepared PANI particles had emeraldine base form.[12,13]

To show the changes of micelle size after addition of hexane and aniline, we measured dynamic light scat-

---

* Corresponding author: e-mail dsohn@ihanyang.ac.kr.

10.1021/ma020162a CCC: $22.00

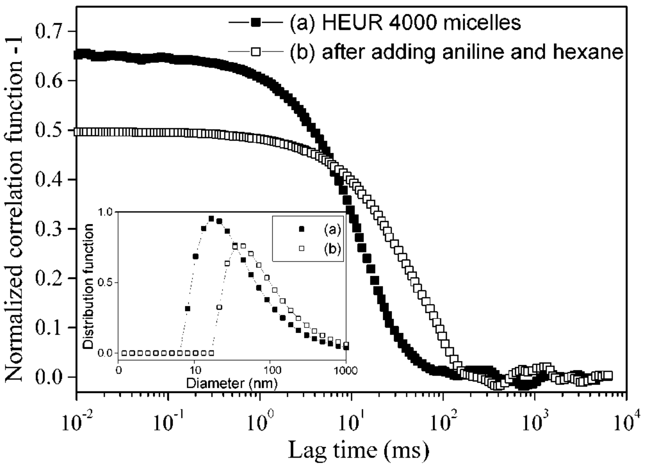

Figure 2. Autocorrelation functions of HEUR 4000 micelles before (a) and after (b) addition of hexane and aniline. The inset shows size distributions of micelles obtained from DLS. For clarity, data for HEUR 1000, 2000, and 35 000 micelles are omitted.

tering (DLS, ALV-5000) using a UNIPHASE He–Ne laser operating at 632.8 nm. Figure 2 presents the normalized autocorrelation functions of HEUR 4000 micelles before and after addition of hexane and aniline. The HEUR concentration was 1.3×10^{-6} M, and the measured angle was 30°.

HEUR micelles have a broad distribution of hydrodynamic radius (R_h) during the process of particle preparation, and the effects of aniline and hexane make it difficult to interpret the correlation functions. But, we can clearly see the distribution functions shift to the longer relaxation time region after addition of hexane and aniline, which means that the size of HEUR micelles increased by hexane and aniline. Hexane will be absorbed to the micelle core and support the HEUR micelle structure forming organic microdomain. Aniline monomers prefer to exist around the PEO chain through hydrogen bonding.

The morphology of PANI nanoparticles could be revealed by transmission electron microscopy (TEM). For TEM examination, a drop of the diluted dispersion was placed on a carbon-coated copper grid and dried in ambient conditions. Figure 3 shows TEM images of PANI made from various HEUR micelles. We added the same amount of aniline to each micellar solution to see the effect of PEO chain length on the structure of PANI in Figure 3a–d. In Figure 3a, PANI (black spots) has aggregated all around the micelles because of the relatively short PEO chain. Figure 3b shows, however, that PANI has regular “ringlike” shape and size of 20–25 nm. When the molecular weight of PEO chain increased, the HEUR micelle forms a 3-dimensional shell structure, which is due to the empty space inside of the hydrophobic chains and high-density PEO block. The TEM image is the collapsed 2-dimensional ringlike structure. The micelles prepared by HEUR 2000 would sustain their structures effectively outside of the organic microdomain composed of an alkyl chain. In the case of HEUR 4000 and 35 000 micelles, PEO chain lengths are relatively long compared to the amount of added aniline, and the thickness of PANI (black band) around the micelles is thin. To verify the growing site of PANI in the micellar structure, we added 0.5 wt % aniline to the HEUR 2000 and 4000 micellar solution and observed a manifest ring shape structure as shown in Figure 3e,f.

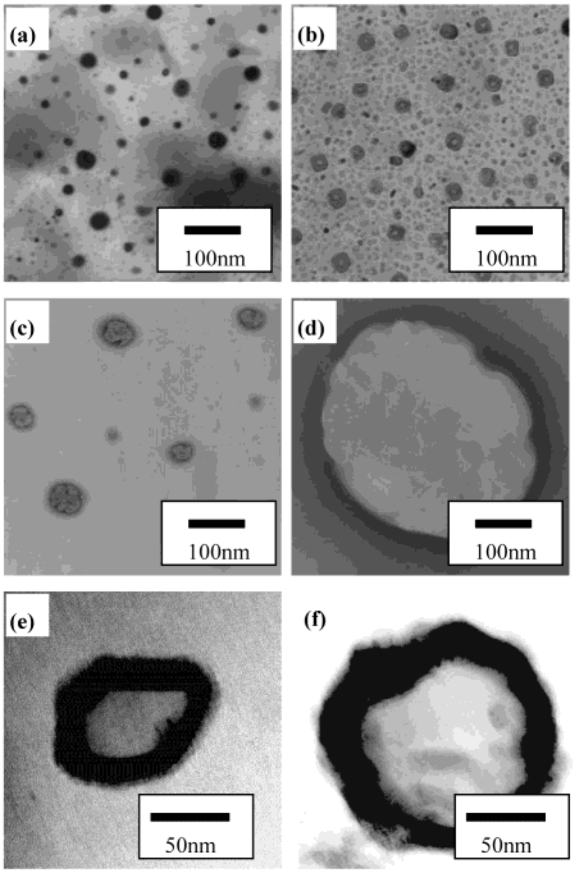

Figure 3. TEM (HITACHI H-600) images of PANI prepared in various HEUR micelles: (a) HEUR 1000, (b) HEUR 2000, (c) HEUR 4000, and (d) HEUR 35 000. PANI prepared by adding 0.5 wt % aniline to (e) HEUR 2000 and (f) HEUR 4000 micelles.

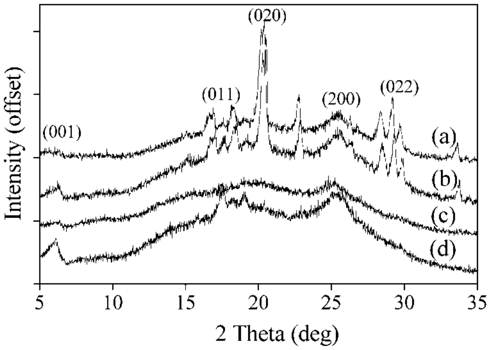

Figure 4. XRD patterns of PANI powder prepared in different HEUR micellar solutions: (a) HEUR 1000, (b) HEUR 2000, (c) HEUR 4000, and (d) HEUR 35 000.

As the amount of aniline increased, the polymerization, which takes place on the interface of the hydrophilic and hydrophobic HEUR domains, proceeds in more condensed conditions, and the hydrophobic organic domains are enlarged.

X-ray diffraction (XRD) patterns were taken by a Shimadzu XRD-6000 to compare the crystallinity and the structure of PANI powder which was prepared by washing and drying the previous PANI solutions. The X-ray source was Ni-filtered Cu Kα radiation, and the wavelength was 1.54 Å. Characteristics about the XRD peaks based on the theoretical calculations and experimental studies are found elsewhere.[14,15]

In Figure 4, the PANI powders prepared in HEUR 4000 and 35 000 have the typical patterns in the previous work. In contrast, the PANI particles made from HEUR 1000 and 2000 micellar solutions show the presence of high crystallinity and condensed structure as shown in Figure 4a,b. The reason is that the PANI nanoparticles prepared in HEUR 1000 and 2000 micelles have small sizes, and the polymerization of aniline in micelles could proceed in denser and more compact structure. Because the aggregation and stacking of the PANI chains depend on the hydrogen bonding between the imine and amine nitrogen sites, the crystallinity and the structure of PANI nanoparticles are affected by the oxidation state of the polymer, the size of the HEUR micelles, and the amount of aniline.

We measured the conductivity of each PANI powder using a four-point system connected to a Keithly voltmeter−constant current source system based on the van der Pauw theorem.[16] The electrical conductivities of PANI powder pellets made from HEUR 1000, 2000, 4000, and 35 000 micellar solutions showed 0.078 ± 0.002, 0.128 ± 0.004, 0.013 ± 0.0002, and 0.118 ± 0.002 S/cm, respectively. PANI from HEUR 2000 has the highest value of conductivity. This fact proves that when pure PANI stacks orderly in regular "ringlike" shape as shown in Figure 3b, the conducting phase can have efficient distribution. The prepared PANI nanoparticles were emeraldine base (EB) form, which was proved by FT-IR and UV−vis spectra.

In summary, polyaniline (PANI) particles were prepared in a micellar solution composed of various molecular weights of hydrophobically end-capped poly(ethylene oxide)s (HEURs). Not only the "ringlike" shape of PANI particles but also the crystallinity and the conductivity strongly depend on the size of micelle, which could be controlled by changing the length of poly(ethylene oxide) middle block and the amount of aniline. Polymerization of aniline occurs at the micelle−water interface and around hydrophilic PEO chain loop in an aqueous system, and PEO chain can act as a steric stabilizer. The particles start to polymerize at the oil−water interface separated by the polymer surfactant, and the "ringlike" shape and structure were confirmed by transmission electron microscopy (TEM) images and X-ray diffractometer (XRD). The conductivity of pure PANIs strongly depends on the regular distribution of conducting phase and the structure of PANI prepared in HEUR micelles.

Acknowledgment. This work was supported by Korea Research Foundation Grant KRF-2001-015-DP0248.

References and Notes

(1) Sapurina, I.; Stejskal, J.; Tuzar, Z. *Colloids Surf. A* **2001**, *180*, 193.
(2) Chattopadhyay, D.; Mandal B. M. *Langmuir* **1996**, *12*, 1585.
(3) Armes, S. P.; Aldissi, M. *J. Chem. Soc., Chem. Commun.* **1989**, 88.
(4) Armes, S. P.; Aldissi, M.; Agnew, S. F.; Gottesfeld, S. *Langmuir* **1990**, *6*, 1745.
(5) Stejskal, J.; Kratochvil, P.; Armes, S. P.; Lascelles, S. F.; Riede, A.; Helmstedt, M.; Prokes, J.; Krivka, I. *Macromolecules* **1996**, *29*, 6814.
(6) Maeda, S.; Armes, S. P. *Synth. Met.* **1995**, *73*, 151.
(7) Chattopadhyay, D.; Banerjee, S.; Chakravorty, D.; Mandal B. M. *Langmuir* **1998**, *14*, 1544.
(8) (a) Kinlen, P. J.; Liu, J.; Ding, C.; Graham, R.; Remsen, E. E. *Macromolecules* **1998**, *31*, 1735. (b) Kinlen, P. J.; Frushour, B. G.; Ding, Y.; Menon, V. *Synth. Met.* **1999**, *101*, 758.
(9) Semenov, A. N.; Joanny, J. F.; Khokhlov, A. R. *Macromolecules* **1995**, *28*, 1066.
(10) Kim, B. J.; Oh, S. G.; Han, M. G.; Im, S. S. *Langmuir* **2000**, *16*, 5841.
(11) Paeng, K.; Kim, B.; Kim E.; Sohn, D. *Bull. Korean Chem. Soc.* **2000**, *21*, 623.
(12) Lee, Y. M.; Kim, J. H.; Kang, J. S.; Ha, S. Y. *Macromolecules* **2000**, *33*, 7431.
(13) Zheng, W.; Angelopouos, M.; Epstein, A. J.; MacDiarmid, A. G. *Macromolecules* **1997**, *30*, 2953.
(14) Stejskal, J.; Riede, A.; Hlavata, D.; Prokes, J.; Helmstedt, M.; Holler, P. *Synth. Met.* **1998**, *96*, 55.
(15) Luzny, W.; Banka, E. *Macromolecules* **2000**, *33*, 425.
(16) Yoshimura, S.; Yasujima, H. *Kobunshi* **1988**, *37*, 886.

MA020162A