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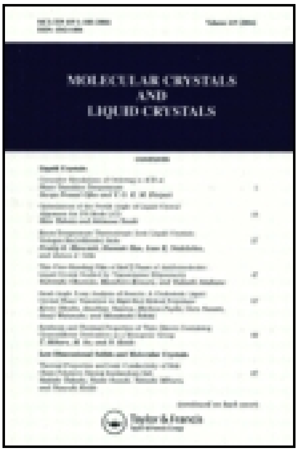

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Preparation of Polyaniline Nanoparticles by Polymer Surfactants

Deokgeun Kim [a], Jin-Yeol Kim [a], Eung-Ryul Kim [a] & Daewon Sohn [a]

[a] Dept. of Chemistry, Hanyang Univ., 17 Haengdang Dong, Sungdong Gu, Seoul, 133-791, Korea

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Preparation of Polyaniline Nanoparticles by Polymer Surfactants

DEOKGEUN KIM, JIN-YEOL KIM, EUNG-RYUL KIM and DAEWON SOHN*

Dept. of Chemistry, Hanyang Univ., 17 Haengdang Dong, Sungdong Gu, Seoul, 133-791, Korea

We have synthesized polyaniline (PANI) particles in amphiphilic copolymer micelles. These associative copolymers, hydrophobically end-capped polyurethane resins (HEURs), aggregate in “flower-type” micelles at low concentration and used as a nanoreactor. The prepared PANI particles are “donut-like” shape, and have the typical peaks of UV-vis and FT-IR in emeraldine base (EB) form.

Keywords: Polyaniline; Associative polymer micelle; HEUR; Nanoparticle

INTRODUCTION

Polyaniline (PANI) has attracted considerable attention among many other types of conducting polymers because of its easy polymerization process, environmental stability, and relatively high conductivity. Recently, oxidative polymerization of aniline has been studied to improve its electrical conductivity and processability.[1,2] PANI has been synthesized in emulsion[2], micelle[3], and reverse microemulsion as polymerization medium. In this work, we prepared PANI particles in micelle formed by associating ethylene oxide-urethane copolymers. This amphiphilic copolymer has been known to form aggregates as other block copolymer

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surfactants. Many works have been performed to reveal the shape and inner structure of micelle.[4] The aim of present work is to characterize the properties of PANI nanoparticles prepared in amphiphilic copolymer micelles which consist of hydrophobic core surrounded by a corona of long polyethylene oxide (PEO) chains that form loop.

We measure dynamic light scattering (DLS) of micellar solution before and after polymerization to see the change of micelle size. To investigate the oxidation state and the structure of obtained PANI particles, UV-vis and FT-IR spectra were taken. In TEM images, we observed "donut-like" shape of PANI particles in HEUR micelles.

EXPERIMENTAL

Synthesis of HEUR: Scheme 1 shows the schematic diagram of HEUR synthesis and the structure of HEUR, which were used in this study.

$$HO\text{-}(CH_2\,CH_2O)_n\text{-}H + 2\,C_{18}H_{37}\text{-}N{=}C{=}O \xrightarrow[\text{Toulene}]{\text{Dibutyltin dilaurate}}$$

$$C_{18}H_{37}\text{-}NH\text{-}CO\text{-}(CH_2\,CH_2O)_n\text{-}CO\text{-}NH\text{-}\,C_{18}H_{37}$$

HEUR 2000; n≅45 **HEUR 4000; n ≅ 90**

SCHEME 1. The schematic diagram of HEUR synthesis and the structure of HEUR 2000 and HEUR 4000.

Preparation of PANI: After HEUR micelle was formed, we took DLS measurements to determine the size of micelle, and then hexane (as organic phase) and aniline monomers were added. After 4hours mechanical stirring, we measure the size of HEUR micelle again. The polymerization was performed at 5℃ with the mechanical stirring at 600~700rpm for 12hours and APS (ammonium persulfate) was added as oxidant.

RESULTS AND DISCUSSION

The associative polymer has broader concentration region around the critical aggregate concentration (CAC) than that of low molecular weight diblock surfactants, and its aggregates are of the "flower-type" because of the long PEO chains and rigid hydrophobic ends.[4]

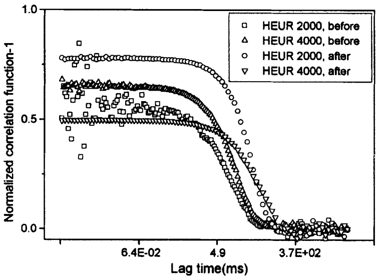

FIGURE 1. Correlation functions of swelling behavior of HEUR micelles in different PEO chain length before and after the addition of hexane and aniline, measured at 30° scattering angle.

In Figure 1, the normalized correlation functions shift to the longer relaxation time, which means the micelles are enlarged, as the PEO chain length of HEUR copolymer increased and addition of hexane/aniline to the micellar solution. That means hydrodynamic radius of HEUR micelle depends on the PEO chain length and enlarges as the hydrophobic core adsorbs hexane and aniline. Figure 2 shows the TEM images of HEUR micelles containing PANI particles prepared inside of HEUR 2000 and HEUR 4000.

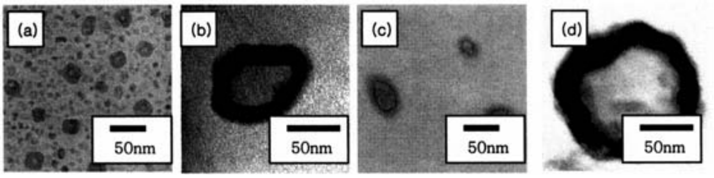

FIGURE 2. Transmission electron micrographs of PANI particles prepared inside of HEUR micelle; (a) HEUR 2000 (×30k), (b) HEUR 2000 (×100k), (c) HEUR 4000 (×30k), and (d) HEUR 4000 (×100k)

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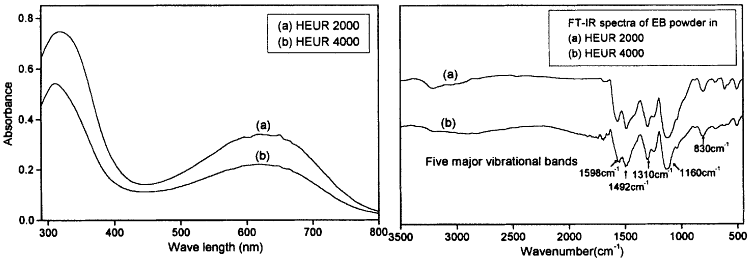
In the case of Figure 2(a) and (c), 0.3 wt% of aniline and hexane were added to the micellar solution. When we increased the amount of hexane and aniline to 0.5 wt%, we observed the PANI band more clearly in Figure 2(b) and (d). The polymerization process seems to be occurred at the hexane/water interface and to form "donut-type" PANI particles.

To examine the characteristics of PANI made from HEUR micellar solution, we measure UV-vis and FT-IR spectra. In Figure 3(a), the PANI/1-methyl-2-pyrrolidone (NMP) solution has characteristic peaks of emeraldine base (EB) form;[5] that is, the first absorption band arises from $\pi \rightarrow \pi^*$ transition of benzoid rings at 330nm and the second band is due to the exciton absorption peak of quinoid at about 640nm.

In Figure 3(b), the FT-IR spectrum of PANI powder has five vibrational peaks and three absorption peaks (1590, 1310, 1160cm^{-1}) which are related to the quinoid ring, N = Benzoid unit = N stretching peak at 1500cm^{-1}, and the aromatic absorption C – H bending peak at 830cm^{-1}.



(a) (b)

FIGURE 3. (a) UV-vis absorption spectra of PANI/NMP solution, (b) FT-IR spectra of PANI powder made from different HEUR micelle.

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