Colloidal Dispersions of Surfactant-Stabilized Polypyrrole Particles

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We describe for the first time the preparation of colloidal dispersions of *surfactant*-stabilized polypyrrole particles in aqueous media using an anionic surfactant, sodium dodecylbenzenesulfonate. This novel colloidal form of polypyrrole has been characterized by various techniques including electron microscopy, photon correlation spectroscopy, FTIR spectroscopy, elemental microanalyses, and conductivity measurements.

Introduction

Polypyrrole is a relatively air-stable but unprocessable conducting polymer.[1] Since 1986 many groups have reported the preparation of stable dispersions of polypyrrole in both aqueous[2-8] and nonaqueous media.[9-11] With a few notable exceptions,[12,13] these colloids have been prepared via dispersion polymerization[14] utilizing a wide range of polymeric stabilizers. In most cases, the particles are uniform, spherical, and relatively monodisperse and the polypyrrole core diameter can be varied over the range 66–300 nm simply by selecting an appropriate polymeric stabilizer.[15]

There have been several papers concerning the electrochemical preparation of polypyrrole films or powders doped with surfactant-type anions.[16] In addition, Heeger's group has recently reported that surfactant dopant anions such as dodecylbenzenesulfonate can be utilized to render another conducting polymer, polyaniline, soluble in certain solvents even in the doped, conducting form.[17] In the present paper we describe, for the first time, the preparation of *colloidal dispersions* of polypyrrole using this "small-molecule" surfactant as a dispersion stabilizer.

Experimental Section

The polypyrrole colloid synthesis was carried out as follows: 10.0 g of sodium dodecylbenzenesulfonate (SDBS) and 7.85 g of $(NH_4)_2S_2O_8$ oxidant were codissolved in 200 mL of deionized water at 20 °C in a 250-mL glass bottle to give a turbid solution. Then pyrrole monomer (2.0 mL) was injected quickly via syringe and the reaction vessel sealed before being transferred to a roller mill (Unimix Model 840) for 4 h. The resulting black, viscous colloidal dispersion was centrifuged at 20 000 rpm for 75 min to produce a black sediment, which was then redispersed in deionized water simply by mechanical stirring. Finally, this redispersed colloid was filtered through a glass sinter under gravity in order to remove traces of nonredispersed material.

Discussion

A typical transmission electron micrograph of a dried, diluted SDBS-stabilized polypyrrole dispersion is shown in Figure 1. The particles are submicrometer-sized and have a nonspherical, irregular morphology quite unlike the uniform spherical particles obtained using polymeric stabilizers.[2-8,15] Similar nonspherical particle morphologies have been reported for polymer-stabilized polyaniline colloids by various groups[18-20] but as far as we are aware, have never before been reported for colloidal polypyrrole. We note that there have been several recent reports that polypyrrole "fibrils" or "tubules" can be prepared electrochemically or chemically using a microporous alumina membrane support.[21] Our dynamic light scattering studies on the SDBS-stabilized polypyrrole dispersions indicate particles of 200–500-nm intensity-average diameter, which is consistent with our electron microscopy studies.

We investigated the effect of the initial surfactant concentration on the colloidal stability of the polypyrrole particles and found that precipitation occurred at surfactant concentrations below approximately 3.0% w/v. Successful colloid formation was also very sensitive to the initial temperature of the reaction solution: on cooling to 10 °C, the oxidant/surfactant complex precipitated prior to the addition of pyrrole monomer, whereas raising the

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Figure 1. Transmission electron micrograph of a diluted, SDBS-stabilized polypyrrole colloid.

temperature to 25 °C resulted in a significant reduction of turbidity for the oxidant/surfactant solution, and only a macroscopic precipitate of polypyrrole was obtained.

The surfactant-stabilized colloid synthesis described above seems to be surprisingly sensitive to rather subtle changes in the reaction conditions. For example, the use of $FeCl_3$ as oxidant rather than $(NH_4)_2S_2O_8$ leads to the formation of an insoluble Fe–SDBS complex prior to the addition of the pyrrole monomer (cationic surfactants such as cetylpyridinium chloride also form insoluble complexes, even with $(NH_4)_2S_2O_8$). The less reactive 1:1 $FeCl_3$/5-sulfosalicylic acid oxidant favored by Kuhn et al.[22] for the polymerization of pyrrole does *not* form an insoluble complex with the surfactant, but neither does it lead to the formation of stable dispersions of polypyrrole particles. Remarkably, we find that simply changing the *cation* of the persulfate oxidant from NH_4^+ to Na^+ prevents *both* prepolymerization micelle formation *and* colloidal particle formation! We note that similar specific cation effects have recently been reported for aqueous solutions containing the sodium dodecyl sulfate surfactant.[23] Finally, the *order of addition* of the reagents can also be critical in determining the final physical state of the conducting polymer. Thus, we find that adding the $(NH_4)_2S_2O_8$ oxidant last to the reaction mixture leads to a fine polypyrrole precipitate, whereas adding the pyrrole monomer last (as described above) produces a stable dispersion of polypyrrole particles.

On the basis of these latter two observations, we believe that prepolymerization complexation between the $(NH_4)_2S_2O_8$ oxidant and the surfactant is a *prerequisite* for the formation of a stable colloidal dispersion of polypyrrole particles. There is considerable literature evidence to

suggest that the turbidity observed on mixing these two components is due to the formation of rodlike micelles.[24,25] Presumably the pyrrole is polymerized *within* these micelle structures, leading to the formation of the irregular polypyrrole particles shown in Figure 1.

In the absence of any surfactant a macroscopic precipitate of polypyrrole is obtained. Our elemental microanalyses indicate that such "bulk powder" polypyrrole contains SO_4^{2-} (rather than HSO_4^-) dopant anions and has a fractional dopant level of 0.28, in good agreement with the literature.[1] Our FTIR spectroscopy studies on the dried colloid (KBr disk) confirm the presence of the surfactant anions (additional bands at 1401 and 1009 cm^{-1}) as well as the formation of doped polypyrrole. In our colloid syntheses described above there is clearly the possibility of the surfactant molecules being *absorbed* into the polypyrrole particles as additional dopant anions as well as being *adsorbed* at the particle surface as a steric stabilizer. The reduced nitrogen content (10.6%) of the dried colloid relative to that of the polypyrrole bulk powder (16.4%) indicates that the polypyrrole particles comprise approximately 35 wt % SDBS surfactant. If we assume that this surfactant is the *only* dopant anion species for the polypyrrole component, we calculate an apparent doping level of 0.03 from our S:N element ratio. The observed dopant level of our polypyrrole bulk powder (see above) suggests that this value is much too low, and therefore we conclude that the dodecylbenzenesulfonate anion cannot be the major dopant species. On the other hand, if we assume that the polypyrrole component in the colloid is doped exclusively with SO_4^{2-} anions (i.e., like the polypyrrole bulk powder) and that the SDBS is present primarily as a surface-adsorbed stabilizer, then we calculate a more realistic dopant level of 0.33 for the polypyrrole and a SO_4^{2-}:SDBS mole ratio of 1.25:1.

Our preliminary X-ray photoelectron spectroscopy studies on the SDBS-stabilized polypyrrole colloid[26] have confirmed (i) the presence of both the SO_4^{2-} and the SDBS species; (ii) the presence of sodium, which suggests that at least some of the surfactant is present in the form of its sodium salt as well as the dodecylbenzenesulfonate anion; and (iii) that the polypyrrole component of the colloid is indeed heavily doped, which is consistent with the assumptions made in our above-mentioned microanalytical calculations.

Conductivities of compressed pellets or cast films fabricated from these colloids are approximately 0.01 S cm^{-1} as measured by four-point probe techniques. We have obtained higher conductivities ($>$1 S cm^{-1}) when using sodium dodecyl sulfate (SDS) as a surfactant stabilizer under similar synthesis conditions. However, these SDS-stabilized polypyrrole dispersions seem to be more susceptible to aggregation, and in our hands these latter syntheses are not always reproducible.

The long-term colloidal stability of these surfactant-stabilized dispersions appears to depend on the dispersion concentration. For example, we have several samples of both SDBS- and SDS-stabilized polypyrrole dispersions which have shown no discernible particle aggregation (apart from gravitational sedimentation) for at least six months at a solid concentration of 1–2% w/w. However, in our photon correlation spectroscopy experiments de-

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scribed above, we found that the SDBS/polypyrrole particles were stable to initial dilution but flocculated if diluted further. Presumably, this aggregation is due to desorption of the surfactant stabilizer from the particles.

Our preliminary experiments suggest that polyaniline colloids cannot be prepared using the analogous $(NH_4)_2$-S_2O_8/1.2 M HCl/surfactant system. It is unclear at present if this observation is related to differences in pH and/or ionic strength between the respective reaction mixtures. However, we have very recently prepared surfactant-stabilized polyaniline colloids using dodecylbenzenesulfonic acid, i.e., with the *surfactant* providing the required solution acidity rather than HCl. These results will be published elsewhere in the near future.[27]

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