Preparation of Polypyrrole Nanoparticles in Mixed Surfactants System

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ABSTRACT: Polypyrrole nanoparticles were prepared by emulsion polymerization, and the surface charge of PPy nanoparticles was controlled by the mixed surfactant system of dodecylbenzene sulfonic acid and isooctylphenyl ether. The shape and size of nanoparticles prepared could be controlled by changing concentration of surfactant. In addition, it was confirmed that the nanoparticles with good conductivity could be obtained by this preparation method. Consequently, well dispersed PPy nanoparticles with 60–100 nm in diameter with cubic shape were obtained and whose conductivity was 56.53 S/cm. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1324–1329, 2008

Key words: polypyrrole; surfactant; nanoparticles; dodecylbenzene sulfonic acid; iso-octylphenyl ether

INTRODUCTION

Conducting polymers have been utilized in the field of transparent EMI shielding, antistatic coating, display devices and electrodes, sensing, information processing, and actuation, polymer battery fabrication, and super capacitors.[1,2] However, because of their inherent insoluble and intractable properties, modifications of conducting polymers are required to overcome these drawbacks. Alteration to alkyl chain substituted moiety monomers, blending with other polymers and preparing colloidal particles are the typical methods for modifications of intrinsic properties. Among these methods, formation of colloidal dispersions is the most attractive method, because it not only causes less significant loss in inherent properties of conducting polymers, such as electrical conductivity, but also can be prepared with simple solution polymerization processing. In addition, conducting polymer nanoparticles have the advantages in improved electrical, optical, opto-electrical properties due to well known nano effect. Conducting polymer nanoparticles can be prepared either by emulsion method[3–5] (macro, mini, and microemulsion depending on surfactant amount and cosurfactant) or by steric stabilizer utilization method,[6–8] which uses bulky steric stabilizer to prevent aggregation caused by charge interaction. Both of these techniques are suitable for large scale production of nanoparticles using relatively simple and inexpensive apparatus.

Because of quantum confinement effects and differences between bulk and surface properties in nanoparticles, both the size and shape have a profound influence on the properties of nanoparticles such as physical, optical, and chemical characteristics. Therefore, it is very important to control the size and shape of the nanoparticles when it is prepared. The shape of the nanoparticles prepared by emulsion method can be varied from sphere to hexagonal, cubic, and lamellar structure. Microemulsion with a mixed surfactant/cosurfactant system has been known as a better method to control the size and shape of the nanoparticles over single surfactant microemulsion method. Because the kinetic process, mechanism, and particle growth in a mixed surfactant/cosurfactant system are quite complicated, this method directly influences the particle size and surface functionality. It is also known that the size of the nanoparticle depends on the chain length of surfactant, the concentration of surfactant, and the polymerization temperature.[9] As the polymerization temperature increases, the size of the nanoparticle also increases as a result of the increased mobility of surfactant chains, and the size of the nanoparticles decreased with decreasing surfactant chain length. As concentration of the surfactant increases, the size of the nanoparticle decreases and approaches an asymptotic value.

Polypyrrole (PPy) is one of the most attractive conducting polymers among various conducting polymers because of its high conductivity and environment stability.[10–12] The preparation of PPy nanoparticles by emulsion polymerization is one of the attractive alternatives to obtain transparent conducting film. Some research groups have been investigated the preparation of PPy nanoparticles by using various surfactants. Stejskal and coworkers[10,13] studied the physical characteristics of PPy such as thermal stability and conductivity prepared with anionic surfactant: dodecylbenzenesulfonic acid (DBSA) and sodium dodecyl sulfate (SDS); cationic surfactant: Tetradecyltrimethylammonium bromide (TTAB); nonionic surfactant: poly(ethylene oxide) (10) iso-octylphenyl ether (Triton X-100) etc. Other groups reported that the size of PPy nanoparticles with cationic surfactant could be controlled by emulsion polymerization.[3,14] In this study, PPy nanoparticles were prepared in the presence of mixed surfactants system; anionic surfactant DBSA and nonionic surfactant Triton X-100. The morphology, particle size, conductivity, zeta potential for surface charge, of PPy nanoparticles were examined.

EXPERIMENTAL

Materials

Pyrrole monomer was purchased from Acros and purified by distillation under pressure before use. Dodecylbenzene sulfonic acid (DBSA) and isooctylphenyl ether (Triton X-100) were obtained from Kanto Chemical and Aldrich, respectively. Iron(III) chloride hexahydrate (270.3 g/mol) was purchased from Aldrich and was used as received.

Preparation of the PPy nanopartilces

DBSA and Triton X-100 were dissolve in a 40 mL of distilled water at 3°C with mechanical stirring. About 0.5 g (7.45 mmol) of pyrrole was added dropwise into the stirred micelle solution formed by DBSA and Triton X-100. About 4.7 g (17.39 mmol) of Iron(III) chloride dissolved in 5 mL of distilled water was added to the pyrrole/DBSA and Triton X-100 solution. The reaction was carried out for 3 hrs at 3°C. Reaction was terminated by pouring an excess amount of methanol. The precipitated PPy nanoparticles were washed with distilled water, acetone, and methanol. The resulting PPy powder was dried in a vacuum oven at room temperature.

Measurement

FTIR spectra were obtained by averaging 32 scans at a resolution of 4 cm^{-1} with an AVATAR 360 FTIR spectrometer. Zeta potential was measured by Otsuka ELS-8000. Electrical conductivity was determined by van der Pauw's four probe method at room temperature using a Keithely 2400 source meter. Field-emission scanning electron microscopy (FE-SEM) was taken with a Hitachi S-4200.

RESULTS AND DISCUSSION

It is well known that anionic surfactant can promote polymerization rate in emulsion polymerization.[10,15,16] Although utilization of the anionic surfactant such as DBSA leads good conductivity and yield, excessive charges formed on the surface of nanoparticles due to the formation of micelle could cause the aggregation of these nanoparticles. To obtain well dispersed nanoparticles, it is required to control these surface charges. Because utilization of neutral nonionic cosurfactant to form micelle is a good method to reduce surface charges of resultant nanoparticles, PPy nanoparticles were prepared in the presence of anionic surfactant and nonionic surfactant in this study. Triton X-100 consists with 10 repeating oxyethylene units as a head and isooctylphenyl as a tail without any charge was used as the nonionic surfactant. According to similar research synthesized PANI with SDBS and Triton X-100,[5] Triton X-100 participated into the formed micelle structures and acted as a portion of micelle. Triton X-100 occupied some portion of the micelle forming space and as a result of this replacement, the surface charges of the produced PPy nanoparticles were reduced, and the aggregation of PPy nanoparticles was diminished.

Figure 1 shows the synthetic scheme of this study and the procedure of forming micelle with mixed surfactants system. To evaluate the effect of Triton X-100 as a cosurfactant, concentration of Triton X-100 was varied whereas the concentration of DBSA was fixed. The optimum condition of initiator $FeCl_3 \cdot 6H_2O$ to monomer pyrrole molar ratio was fixed at 2.3, which was reported in the literature[10,17] providing optimum condition for conductivity and yield. Because it was reported that the conductivity of PPy was increased[17] and the size of nanoparticles was decreased[3] when polymerized at low temperature, the polymerization temperature was kept at 3°C.

The characteristic FTIR spectra of the various PPy nanoparticles formed with different surfactant were illustrated in Figure 2. The bands at 1541, 1533, and 1544 cm^{-1} are corresponding to C—C stretching vibration of the pyrrole ring. The bands of C—N stretching vibration are attributed at 1468, 1446, and 1478 cm^{-1} in PPy FTIR spectrum. The band of C—C stretching vibration of the pyrrole ring located at 1541 cm^{-1} in the IR spectrum of the PPy-DBSA
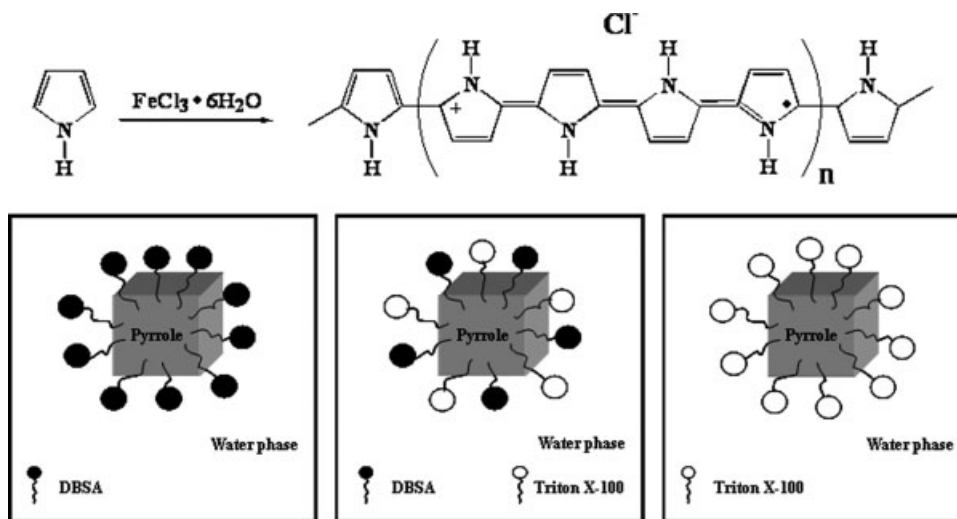
Figure 1 Synthetic scheme and schematic diagram of micelle forming process.

nanoparticles (PPy nanoparticles prepared with DBSA only as a surfactant) red-shifted to 1533 cm^{-1} for the sample PPy-DBSA/Triton X-100 nanoparticles (PPy nanoparticles prepared with DBSA as a surfactant mixed with Triton X-100 as a cosurfactant). The measured conductivity of the PPy-DBSA/ Triton X-100 nanoparticles was higher than that of the PPy-DBSA nanoparticles. On the other hand, in the FTIR spectrum of PPy-Triton X-100 nanoparticles (PPy nanoparticles prepared with Triton X-100 only as a surfactant) peak showed a small blue shift, and the conductivity of this sample was low than that of the PPy-DBSA nanoparticles. This trend is similar with the previous report[10] that the nanoparticles with higher conductivity showed red shift, whereas nanoparticles with lower conductivity showed blue shift.

The charge distribution of these nanoparticles was studied with surface charge potential and bulk conductivity of nanoparticles. To confirm the control of PPy nanoparticles surface charge in the presence of mixed surfactants system, the zeta potential was measured. The zeta potential of PPy nanoparticles prepared in the presence of 0.3M DBSA showed only 36.83 mV, whereas PPy nanoparticles prepared with 0.3M Triton X-100 exhibited only 4.06 mV. Figure 3 shows zeta potential of PPy nanoparticles decreased with the increasing concentration of Triton X-100 in the mixed surfactants system when the concentration of DBSA was fixed at 0.3M. It is clear that Triton X-100 contributes to the decrease of the zeta potential of PPy nanoparticles. This result coincided with the previous report[5] that the surface charge density of micelle was reduced by mixing a
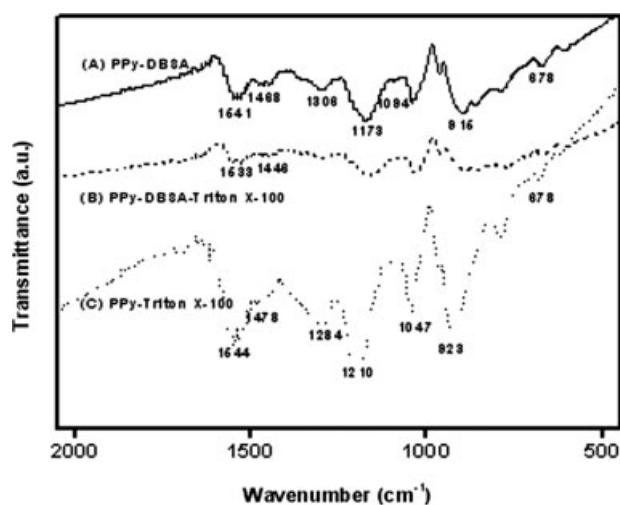
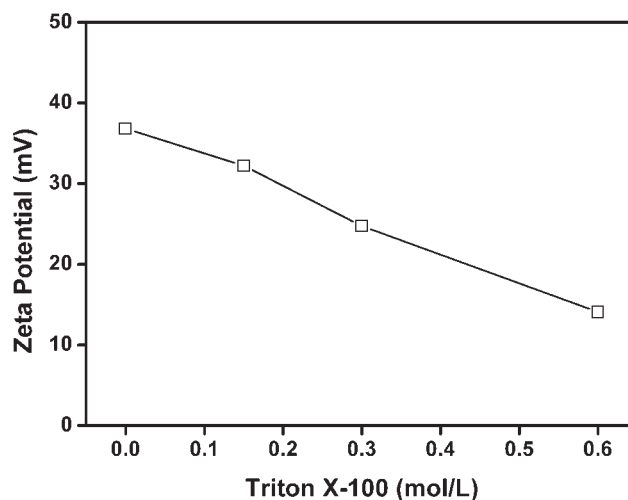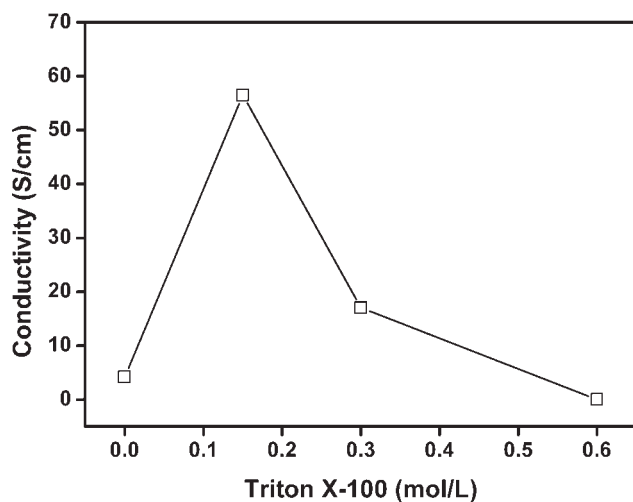

Figure 2 FTIR spectra of PPy nanoparticles.

Figure 3 Effect of nonionic surfactant for the surface charge (zeta potential) of PPy nanoparticles.

Figure 4 Conductivity of PPy nanoparticles as a function of nonionic surfactant.

nonionic surfactant with the ionic surfactant, which resulted in the increment of the amount of un-doped conducting polymer particles. Meanwhile, the bulk conductivity of PPy nanoparticles was 4.18 S/cm with 0.3M DBSA as an only surfactant and 0.05 S/cm with 0.3M Triton X-100 as an only surfactant. In mixed surfactants system, the concentration of DBSA was also fixed at 0.3M to investigate the effect of Triton X-100. When the concentration of Triton X-100 was 0.15M in the mixed surfactants system, the conductivity of nanoparticle was increased to 56.53 S/cm, which was almost 15 times increase when compared with that of PPy prepared with only DBSA as shown in Figure 4. This increase in conductivity when the additional amount (0.15M) of cosurfactant was added into the surfactant system can be explained as follows. Because of the addition of cosurfactant Triton X-100 into the micelle forming system, DBSA used to form micelle can be liberated from the role of micelle shell formation and acted as a dopant. Because the size of the Triton X-100 is bigger than that of DBSA, the micelle aggregation number should be decreased. Therefore, when the amount of Triton X-100 was 0.15M, more dopant molecules were available for doping so that the conductivity was increased when compare with that of 0.3M DBSA alone. However, as the amount of Triton X-100 was increased further, the situation for formation of micelle changed. In other words, when the amount of Triton X-100 was increased to 0.3M (i.e., total concentration of surfactant was 0.60M), the number of micelles formed in the reaction media was increased. Because DBSA not only acts as a surfactant but also as a codopant, as the number of micelles formed in the reaction media was increased, there would be less liberated DBSA molecules which could act as a dopant. It was proven that the surfactant was incorporated into the conducting polymer chain.[18] Increased number of micelles were obvious because the size of nano particles formed were smaller than that of 0.15M Triton X-100 case according to morphological study using SEM.

Therefore, the conductivity was decreased when compared with that of nanoparticles prepared with 0.15M Triton X-100 as a cosurfactant and 0.3M DBSA as a surfactant. Furthermore, the conductivity of PPy nanoparticles prepared in the mixed surfactants system with higher Triton X-100 gradually decreased to 17.05 S/cm (0.3M of Triton-100) and 0.02 S/cm (0.6M of Triton X-100) with the increasing concentration of Triton X-100. It is expected that the amount of free DBSA molecules, which can be acted as a dopant decreased with increasing total number of micelle. Because the conductivity of a mixed surfactants system (0.15M Triton and 0.30M DBSA) showed marked enhanced conductivity, the conductivity of nanoparticles formed with comparable surfactant amount (i.e., 0.45M DBSA only, to form almost same number of micelle in the system) was examined for comparison. When 0.45M DBSA was used to prepared nanoparticles, the conductivity of formed nanoparticles was 18.0 S/cm. Even though this value is higher than that of 0.3M DBSA only system and a mixed surfactants system of 0.3M Triton/0.3M DBSA, it was much lower than that of the mixed surfactants 0.30M DBSA with 0.15M Triton X-100. The reasonable explanation for this phenomenon is that, because of the different size and shape of each surfactant in a mixed surfactants system, micelle forming number for each micelle could be different. In the mixed surfactants system, because of the relative larger size of Triton X-100, more DBSA can be free from their role to form micelle compare with micelle formed with DBSA only, and hence the additionally liberated DBSA act as a dopant and the conductivity of the nanoparticle increased. From these results, it can be concluded that there is a certain optimum condition for a mixed surfactants condition to impose enhanced conductivity. To obtain well separated nanoparticles with high conductivity, the surface charge has to be controlled meanwhile the bulk conductivity is increased with the increasing amount of dopant.

The morphology of PPy nanoparticles was characterized by FE-SEM as shown in Figure 5. PPy prepared without surfactant showed an arbitrary shape as shown in Figure 5(a), whereas the other PPy samples with surfactant showed a spherical shape in most of the cases. It is indicated that the surfactant provide a space to control morphology as template does. The fine spherical shape nanoparticles of $\sim$ 60 nm in diameter were obtained when pyrrole was synthesized using 0.3M DBSA as an only surfactant as shown in Figure 5(b). When nanoparticles
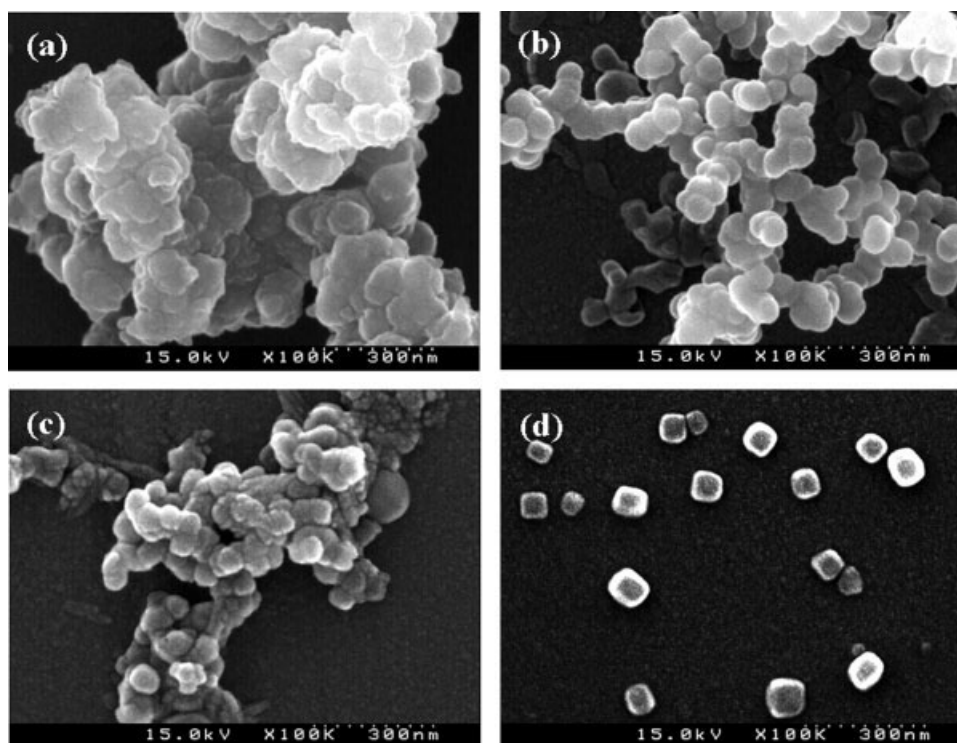
Figure 5 The morphology of PPy nanoparticles: (a) Without surfactant, (b) Using DBSA, (c) Using Triton X-100, (d) Mixed surfactant system with 0.3M DBSA, and 0.15M Triton X-100.

were prepared by using 0.3M Triton X-100 as an only surfactant, the size was $\sim$ 50 nm in diameter with the spherical shape as shown in Figure 5(c). According to these results, the size difference between PPy-DBSA and PPy-Triton X-100 comes from hydrocarbon chain lengths of the surfactant. Hydrophobic tail group of DBSA and Triton X-100 consist of C12 and C8 chains, respectively, which is a part of surfactant to restrict the space for organics within micelle. This result coincides with previous research reporting that the average size of nanoparticle produced with short hydrocarbon surfactant is smaller than that of long hydrocarbon surfactant.[9] It is also reported that the particle size could be determined by using a difference of hydrocarbon chain lengths.[17] Therefore nanoparticles formed with Triton X-100 will be smaller than that of DBSA. The PPy prepared in the presence of 0.3M DBSA and 0.15M Triton X-100 showed $\sim$ 60–100 nm in size with cubic shape. According to FE-SEM image, it was clear that the micelle changed its shape from spherical to cubic form. The shapes of microstructure are quite diverse in oil–water-surfactant phase diagram.[19] The complicated shape changes from sphere to cubic hexagonal and lamellar liquid crystalline shape in the presence of the surfactant in conducting polymer nanoparticle preparation.[20] As mentioned earlier, both size and shape of the nanoparticle have a profound influence on the properties of nanoparticles. We believe this change in shape

from sphere to cubic form for a mixed surfactants system of 0.15M Triton/0.3M DBSA caused abrupt increase in conductivity. The nanoparticles prepared with 0.3M of DBSA [Fig. 5(b)] and 0.3M of Triton X-100 [Fig. 5(c)] showed minor aggregation problem, whereas PPy nanoparticles prepared with mixed surfactants were well isolated as shown in Figure 5(d). It is clear from this study that the particle aggregation problem can be solved by controlling surface charge using mixed surfactants system.

CONCLUSIONS

PPy nanoparticles were prepared in the mixed surfactants system. The surface charge of PPy nanoparticles could be controlled by changing the composition ratio of the ionic and nonionic characteristics within mixed surfactants system. In addition, the morphology of PPy nanoparticles which depends on the shape of micelle could be altered by changing concentration of the surfactant. Utilization of nonionic cosurfactant system in preparing conducting nanoparticles, the bulk conductivity of nanoparticles was reduced; however, it also reduced the surface charge of the nanoparticles which measured with zeta potential and diminished coulomb interaction between nanoparticles leading reduction in aggregation of prepared PPy nanoparticles. Consequently, well dispersed PPy nanoparticles of 60–100 nm in diameter with cubic shape were obtained whose conductivity was

56.53 S/cm. It can be concluded that there is a certain optimum surfactant concentration (with appropriate ratio of ionic surfactant and nonionic cosurfactant) to reduce surface charge without diminishing the bulk conductivity to form well isolated conducting nanoparticles. This novel approach for preparing conducting polymer nanoparticles could expand into the electronic and optical applications.

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