# Poly(3,4-ethylenedioxythiophene) 나노입자의 제조 및 연구

**최정완, 한문규, 임승순**
*한양대학교 섬유공학과*

# Preparation and Characterization of Poly(3,4-ethylenedioxythiophene) nanoparticles

**Jeong Wan Choi, Moon Gyu Han and Seong Soon Im**
*Department of Textile Engineering, Hanyang University, Seoul, Korea*

## 1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT), one of the most successful conducting polymers in the market place, has been attracting much interest because of its excellent environmental stability, high conductivity and transparency in thin, oxidized state. Since PEDOT was first synthesized in early 1990s by Jonas *et al.*, many studies on PEDOT have been done to solve its insoluble property in any organic solvents and to extend its application fields[1].

To circumvent the insolubility problem of conducting polymers and to supply mass production, fine particles are generally prepared by chemical oxidation, and in most cases, suspension polymerization with various polymeric surfactants has been employed to produce nano-sized particles for pyrrole and thiophene derivatives[2]. Meanwhile, few studies on emulsion polymerization using monomeric surfactants have been reported. Arems *et al*[3], for the first time, reported the preparation of colloidal dispersions of polypyrrole(Ppy) of 200-500 nm diameter using a monomeric surfactant and they also proposed polymerization conditions for colloidal stability. Kudoh *et al* have prepared polypyrrole[4] and PEDOT[5] with high conductivity using various monomeric surfactants with $Fe_2(SO_4)_3$ as oxidant. In our study on PEDOT, it was found that PEDOT nanoparticles could be prepared at high concentration of anionic surfactant in aqueous polymerization solution. This study was focused on the investigation of the preparation condition of dispersible PEDOT nanoparticles in alcoholic solvent and the effects of the polymerization conditions on the electrical properties and the polymer structure.

## 2. Experimental

Synthesis of the PEDOT nanoparticles was carried out as follows: prescribed quantity of Dodecylbenzenesolfonic acid(DBSA) and 3,4-ethyelenedioxythiophene were dissolved in deionized water for 1 h. Then $FeCl_3$ or $(NH_3)_2(SO_4)_2$(APS) in deionized water was syringed quickly and the mixtures were stirred for 20 h at 30 ℃. The resultants were collected by filtration and then washed with water and methanol successively, dried under vacuum at 40 ℃ for 24 h. Before drying the washed sample, very small amounts of the samples were redispersed in ethanol by mechanical stirring to investigate the particle morphologies and colloidal stability.

## 3. Result and Discussion

Typical FE-SEM images of dried, diluted PEDOT dispersions are shown in Fig. 1 and 2. Even though there seem to be some aggregates of primary particles in both images, the isolated particles synthesized in DBSA-APS surfactant-oxidant system appear to be quite spherical and their sizes vary from 35 to 60 nm in diameter as shown in Fig. 1. For DBSA-$FeCl_3$ surfactant-oxidant system in Fig. 2, the sizes of the spherical particles are observed to be 60-120 nm. The dispersibility and colloidal stability of the PEDOT particles appeared to depend on the dispersion media and the dispersion concentration. The dispersed PEDOT colloids in methanol showed long-term colloidal stability for several months at a solid concentration of ca. 0.1 % w/w.

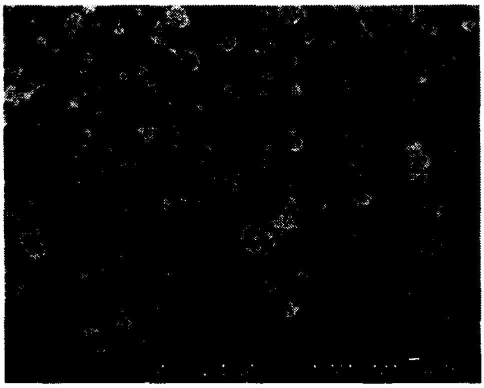

Fig. 1. FE-SEM image of PEDOT particles prepared from APS-DBSA system; DBSA conc. 0.044M

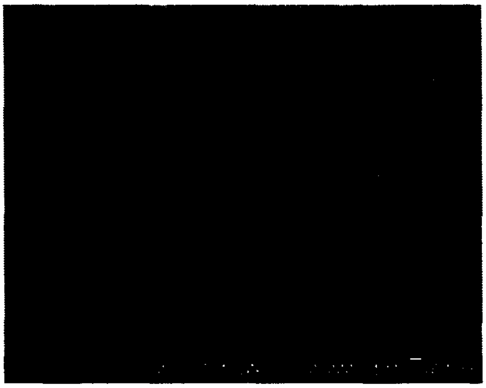

Fig. 2. FE-SEM image of PEDOT particles prepared from $FeCl_3$-DBSA system; DBSA conc. 0.044M

Figure 3 shows the electrical conductivities of pelletized PEDOT particles prepared from DBSA-$FeCl_3$ and DBSA-APS system. In comparison of the two surfactant-oxidant systems, on the whole, DBSA-APS system gave PEDOT samples low conductivities, i.e., less than 1 S/cm whereas DBSA-$FeCl_3$ system gave much higher conductivities up to 50 S/cm. When APS was used as oxidant, the conductivity was increased with increasing DBSA content. When $FeCl_3$ was used as oxidant, on the other hand, the conductivity tended to decrease as DBSA concentration increased. This different effect of the oxidant-anionic surfactant combinations on the conductivity can be explained by the existence of complexation between oxidant and anionic surfactant. DBSA-$FeCl_3$ combination in aqueous media causes insoluble complextion between iron (III) species and dodecylbenzene sulfonate anion. It is possible that the high attractive force between the oxidant and the anionic surfactant resulting from this complexation leads to an increase of the doping efficiency of the anionic surfactant on the PEDOT particles. The conductivity drop with increasing DBSA concentration is most likely to be resulted from excess DBSA. On the other hand, DBSA-APS combination does not form considerable complex, hence there is not likely to be any driving force to increase the doping efficiency of anionic surfactant. In this system, the higher DBSA concentration seems to result in the higher DBSA doping with increasing conductivity.

The APS oxidant system gave higher yields up to 42% whereas the maximum yield of $FeCl_3$ oxidant system was 32%. The yield tended to increase with increasing DBSA concentration to 0.1M, but at the higher DBSA concentration the yield somewhat decreased. This slight reduction of yield may be due to rather low pH of polymerization solution[6]. As the polymerization temperature increased, the yield increased and the conductivity decreased without considerable changes on colloidal stability and morphology of the produced PEDOT particles.

X-ray diffraction patterns of PEDOT nanoparticles obtained from both DBSA-APS and DBSA-$FeCl_3$ system are shown in Fig. 4. It is believed that this x-ray diffraction patterns prove the increased doping efficiency of DBSA in $FeCl_3$ oxidant system. The diffraction peak observed at scattering angle $2\theta \approx 6.5^\circ$ seems to be (100) reflection of the polymer backbone. The d-spacing of this (100) reflection is about 13.6 Å, which is almost coincide with the result of Aasmundtveit et al.[7]. The peak of DBSA-$FeCl_3$ system shows higher intensity than that of DBSA-APS system (compare Fig. 4(a) and (b)). This prominent peak intensity is indicative of effective doping and consequent high orderness of polymer chains. The second peak at $2\theta \approx 12.8^\circ$ corresponds to (200) reflection because the d-spacing is about half of the (100) reflection. The fourth peak at near $2\theta \approx 25^\circ$ seems to be (020) reflection. This peak shifts to higher angle about $1^\circ$ for the DBSA-FeCl3 system, which is also an evidence of effective doping because attractive effect between polymer chains induced by doping can lead to this decrease of the d-spacing of b-axis[8].

In our system, we found that adding the PEDOT monomer last to the reaction mixture lead to ca. two fold increase in conductivities of the PEDOT particles but did not considerably affect the particle size and colloidal stability. In case of adding the PEDOT monomer last, the intensity of the peak at $2\theta \approx 6.5^\circ$ highly increased and the peak at $2\theta \approx 25^\circ$ is further shifted to higher angle as shown in Fig. 4(c). These results suggest that the preformed complex between oxidant and surfactant seems to play an important role in the increment of the doping efficiency and concomitant rise in orderness of chain structure.

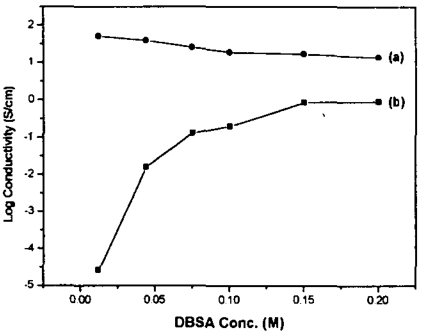

Fig. 3. The conductivity changes as a function of DBSA concentration; (a) PEDOT prepared from APS-DBSA system, (b) PEDOT prepared from FeCl3-DBSA system.

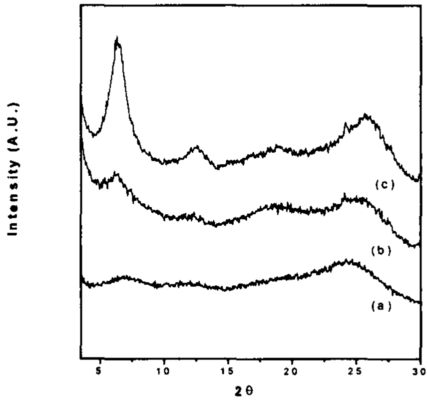

Fig. 4. WAXD patterns of dried PEDOT nanoparticles; (a) PEDOT prepared from APS-DBSA system, (b) PEDOT prepared from FeCl3-DBSA system, (c) PEDOT prepared by adding the monomer last to the polymerization solution.

## 4. References

[1] Groenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. Adv. Mater. 2000, 12, 481-493

[2] Armes, S. P. Current Opinion in Colloid & Interface Science, 1996, 1, 214-220

[3] DeArmitt, C.; Armes, S. P. Langmuir 1993, 9, 652-654

[4] Kudoh, Y. Synth. Met. 1996, 79, 17-22

[5] Kudoh, Y.; Akami, K.; Matsuya, Y. Synth. Met. 1998, 98, 65-70

[6] Seo K. I.; Chung, I. J. Polymer 2000, 41, 4491-4499

[7] Aasmundtveit, K. E.; Samuelsen, E. J.; Pettersson, L. A. A.; Inganäs, O.; Johansson, T.; Feidenhansl, R. Synth. Met. 1999, 101, 561-564

[8] Kawai, T.; Nakazono, M.; Yoshino, K. *J. Mater Chem.* 1992, 2, 903-906