

Facile Preparation of Poly(3,4-ethylenedioxythiophene) Nanoparticles via a Miniemulsion Polymerization Process

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ABSTRACT: Poly(3,4-ethylenedioxythiophene) (PEDOT) nanoparticles were prepared via a miniemulsion polymerization process. The chemical oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT) occurred in the presence of β -1,3-glucan with the injection of an aqueous oxidant solution, and the nanodroplets of EDOT were transformed to PEDOT nanoparticles dispersed in the aqueous medium. The aqueous emulsion of PEDOT nanoparticles showed relatively long emulsion stability (> 8 weeks), and the recovered solid nanoparticles were also redispersible in deionized water without deposition. The size and size distribution

of PEDOT nanoparticles could be controlled by adjusting the operating conditions of the ultrasonifier before the polymerization process. The building-up of a shearing force decreases the size of the PEDOT nanoparticles and also causes the occurrence of a multimodal size distribution for the PEDOT nanoparticles. The electrical conductivity of the PEDOT nanoparticles was $0.28\text{--}1.20\text{ S cm}^{-1}$. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1442–1449, 2011

Key words: conducting polymers; particle size distribution; nanoparticle; emulsion polymerization; TEM

INTRODUCTION

Conducting polymers with conjugated double bonds have been increasingly applied in the rapidly developing area of nanotechnology, particularly in optoelectronics¹ and medical diagnostics.² However, the insolubility in most solvents of conjugated polymers restricts their common use and large scale development. Intensive research efforts to overcome this drawback have concentrated on the solubility enhancement of conjugated polymers by introducing side chains to the rigid backbone³ or by preparing hybrid composites with other polymers.⁴ Another strategy for improving the tractability of conjugated polymers is to prepare them in the form of water-based emulsions using chemical oxidative polymerization, which provides environmental and economic advantages for their comprehensive application. The recovery of conjugated polymer nanoparticles from water-based emulsions allows the control of their processability and mechanical and electronic properties.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most attractive conducting polymers because

of its excellent environmental stability, high conductivity, and transparency in thin oxidized films.⁵ The preparation of stable aqueous PEDOT dispersions with the help of polystyrene sulfonic acid (PSSA) is a practically useful route to circumvent the insolubility problem of PEDOT, the so-called Baytron P commercialized by Bayer AG. The structure of Baytron P is known to be that the oligomeric PEDOT chains of about 6–18 repeating units are attached to the PSSA having a much longer chain length.⁵ Different strategies have been developed to prepare well-defined PEDOT nanoparticles, including direct synthesis of the nanoparticles in emulsion,^{6–18} dispersion,^{19–21} and the precipitation^{22–31} polymerization processes. Among them, of special interest is the chemical oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT) in the presence of single-chain schizophyllan.^{22,23} Successful preparation of water-soluble PEDOT nanoparticles as small as 70 nm using a natural β -1,3-glucan polysaccharide with dimethylsulfoxide (DMSO) has been claimed.

Most of research reports on the preparation of PEDOT nanoparticles have not evidently shown separate particles with clear structures and definite morphologies. The electron microscopy images of PEDOT nanoparticles published to date^{8,9,11–14,16,21–25,29} show an inclination toward the aggregation of particles. The formation of irregular aggregated structures is known to be induced by π - π stacking interactions between PEDOT nanoparticles.²⁵ In

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recent years, several reports have claimed that the PEDOT nanoparticles showing unambiguous structures were prepared by applying the distinctive preparation processes such as the emulsion polymerization initiated by an ultrasonic irradiation,⁶ the emulsion polymerization using a bicellar template,⁷ the microemulsion polymerization using a cationic surfactant,¹⁰ and the dispersion polymerization using a reactive stabilizer.¹⁹

Water is not a suitable polymerization medium for the synthesis of PEDOT because EDOT is poorly soluble in it (0.21 g/100 mL at 20°C), and it retards the polymerization.¹⁸ The miniemulsion polymerization process is an appropriate preparation strategy for the preparation of PEDOT nanoparticles because it provides separated nanoreactors comprised of the organic phase that are dispersed in the aqueous medium, and the chemical oxidative polymerization of EDOT solely occurs in the organic droplets.

In this study, we sought to develop a facile preparation process for conducting PEDOT nanoparticles by applying the miniemulsion polymerization process. In addition, a β -1,3-glucan extracted from *Sparassis crispa* was added to the organic phase with EDOT to obtain a stable aqueous emulsion of PEDOT. The emulsion stability of PEDOT was investigated by testing a variety of surfactants and oxidants and choosing an appropriate hydrophobe. In this study, we not only successfully obtained well-defined PEDOT nanoparticles showing clear and separate spherical structures but also determined how to control their sizes and size distributions. The PEDOT nanoparticles prepared in this study show an excellent emulsion stability and redispersibility in water.

EXPERIMENTAL

Materials

In the preparation of PEDOT nanoparticles via a miniemulsion polymerization process, various types of surfactants such as dodecylbenzene sulfonic acid (DBSA) (70 wt % solution in 2-propanol, Aldrich), sodium butylnaphthalenesulfonate (NaBNS) (40% in water, Tokyo Chem), and 2-naphthalenesulfonic acid (2-NSA) (70%, Aldrich) as anionic surfactants, decyltrimethylammonium bromide (DETAB) (Tokyo Chem) as a cationic surfactant, and polyoxyethylene-11-decylether (*Lutensol*, BASF AG) as a nonionic surfactant were added to confirm a stable aqueous polymer emulsion. For the chemical oxidative polymerization of EDOT (Aldrich), various oxidants such as ammonium persulfate (APS) (98%, Aldrich), iron(III) *p*-toluenesulfonate hexahydrate [Fe-*p*TS] (Aldrich), iron(III) sulfate hydrate [Fe₂(SO₄)₃·H₂O; Fe-S] (97%, Aldrich), cerium sulfate [Ce(SO₄)₂; Ce-S]

(Aldrich), and ammonium cerium nitrate (ACe-N) (98.5%, Aldrich) were added as an aqueous solution in the reaction mixture, and then a stability of the resulting PEDOT emulsions was checked. Dimethylsulfoxide (DMSO) (99.6%, Aldrich) and β -1,3-glucan (MW = 5.1×10^5 ; *Sparan*, Hanabiotech) were added to the organic phase with EDOT, and either cetyl alcohol (CA) (Tokyo Chem) or hexadecane (HD) (Aldrich) as a hydrophobe was included in the organic phase. The chemicals in this study were used as supplied without further purification.

Synthesis of PEDOT nanoparticles via a miniemulsion polymerization process

The organic phase made up of EDOT (0.189M), β -1,3-glucan (10 g L⁻¹), and a hydrophobe (3.16 mM) in the presence of DMSO was thoroughly mixed with the aqueous phase including deionized (DI) water and surfactant (1.05 mM). If not specified otherwise, the polymerization employed β -1,3-glucan, DMSO, and CA (hydrophobe) along with EDOT. Then, the resulting mixture was transferred to an ultrasonifier (Model 450, Branson) and treated for 10 min (50% duty cycle, power 5) in an ice bath. The chemical oxidative polymerization was initiated with the addition of the aqueous oxidant solution (0.098M) in the reaction mixture, and the reaction was maintained at 35°C for 48 h in a nitrogen atmosphere. After the completion of polymerization, the solid products were recovered from the reaction mixture by filtration and cleaning with a copious amount of DI water. The precipitated particles were separated by thrice-repeated centrifugation and then dried under vacuum at 60°C for 24 h. The reaction yield estimated by a gravimetric analysis showed over 85% for most polymerizations in this study.

Characterization of PEDOT nanoparticles

For the identification of PEDOT nanoparticles, Fourier transform infrared (FT-IR) spectroscopy analysis was carried out on samples dispersed in KBr discs using a Varian Model Scimitar 1000. The X-ray diffraction (XRD) pattern was taken with 40 kV, 30 mA Cu K α radiation using a Philips Model X-Pert APD. The detector was moved step by step ($\Delta 2\theta = 0.05$ – 0.04°) in a scanning range from $2\theta = 2^\circ$ to 40° at a speed of 6° min^{-1} .

The morphologies of PEDOT nanoparticles prepared in this study were analyzed by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). Particles for FE-SEM analysis were coated with Pt/Pd by sputtering for 150 s. The FE-SEM images were obtained on a Hitachi Model S-4300SE operating at 5 kV. Drops of aqueous PEDOT emulsion were dried on a

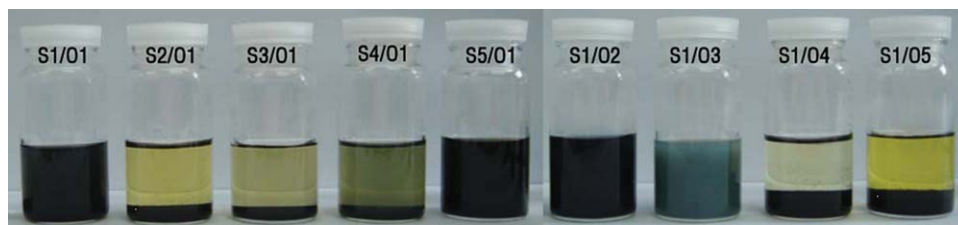


Figure 1 Confirmation of emulsion stability after 8 weeks; surfactants: S1(DBSA), S2(NaBNS), S3(2-NSA), S4(DETAB), S5(*Lutensol*); oxidants: O1(APS), O2(Fe-*p*TS), O3(Fe-S), O4(Ce-S), O5(ACe-N). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

carbon-coated copper grid for TEM analysis, and the TEM images were obtained on a Hitachi Model H-7500 operating at 80 kV. Particle sizes and size distributions were determined using a Beckman Coulter LS Particle Size Analyze (PSA) instrument.

The electrical conductivity was measured using a Mitsubishi Chemical Analytech Model Loresta-EP MCP-T360 four-probe resistivity meter at room temperature. For the preparation of electrical conductivity specimens, the vacuum-dried PEDOT nanoparticles were comingled with a small portion of carboxymethyl cellulose (CMC) (< 5 wt %) in the presence of DI water and then ground with pestle in a mortar. The rectangular-shaped thin specimen with a dimension of 7 mm × 7 mm was prepared by coating the PEDOT nanoparticle slurry with a doctor blade. The specimen was dried under vacuum at 60°C for 24 h and then transferred for the electrical conductivity measurement. The electrical conductivity was calculated by the equation $\sigma = \frac{1}{\rho_s t}$, where σ is the conductivity in S cm⁻¹, ρ_s is the surface resistance in Ω/sq, and t is the thickness of specimen.

RESULTS AND DISCUSSION

Confirmation of PEDOT emulsion stability

The aqueous emulsion of PEDOT nanoparticles was left intact for 8 weeks after the completion of the miniemulsion polymerization process to confirm the emulsion stability depending on the variation of the surfactants and oxidants. Figure 1 shows that the emulsion stability is affected by the choice of surfactant and oxidant. It reveals that the desirable choices of surfactant and oxidant for the emulsion stability are DBSA/APS, *Lutensol*/APS, and DBSA/Fe-*p*TS. The ionic surfactant having hydrophilic component and hydrophobic chain segment is in general used in the miniemulsion polymerization process. In comparison with NaBNS, 2-NSA, and DETAB, the aliphatic chain length of hydrophobic segment for DBSA is so long that it could provide a steric stabilization for the organic droplets to maintain the emulsion stability. Also the nonionic surfac-

tant, *Lutensol*, has relatively long chain length and it is an effective surfactant for the emulsion stability. Table 1 shows the molecular structures of surfactants used in this study. The steric effect of surfactant in the stabilization of emulsion system was also claimed by Müller et al.¹⁰

A β-1,3-glucan polysaccharide exists as a single random coil in DMSO, and it is transformed to a triple helix in water. This specific structural transformation is known to make β-1,3-glucan form stable water-soluble complexes with PEDOT.²³ Figure 2 shows that β-1,3-glucan (i.e., *Sparan*) must be included in the organic phase to obtain a stable PEDOT emulsion. In the miniemulsion polymerization process, the organic monomer droplets are dispersed in the aqueous continuous medium, and the polymerization occurs solely in dispersed droplets of less than 500 nm (“nanoreactor”). While the polymerization proceeds, either molecular diffusion degradation (i.e., Ostwald ripening) or coalescence may cause the emulsion instability. To suppress

TABLE I
Surfactants Used in a Miniemulsion Polymerization Process for the Preparation of PEDOT Nanoparticles

Molecular structure	Name
	Dodecylbenzene sulfonic acid (DBSA)
	Sodium butylnaphthalanesulfonate (NaBNS)
	2-Naphthalenesulfonic acid (2-NSA)
$\text{CH}_3-(\text{CH}_2)_9\text{N}(\text{CH}_3)_3\text{Br}$	Decyltrimethylammonium bromide (DETAB)
$\text{CH}_3-(\text{CH}_2)_9\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{10}-(\text{CH}_2)_2\text{OH}$	Polyoxyethylene-11-decylether (<i>Lutensol</i>)

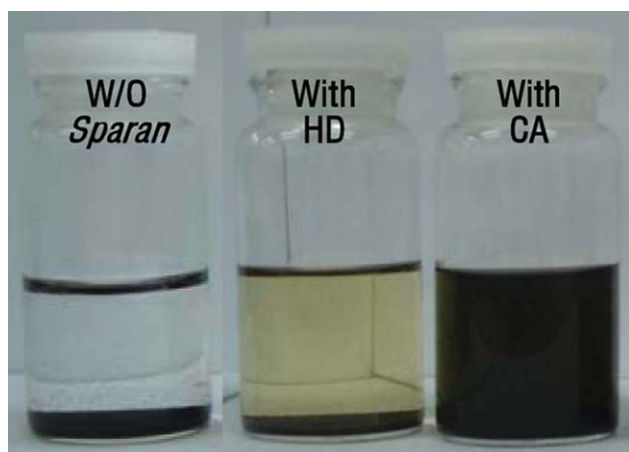


Figure 2 Change of emulsion stability due to the absence of β -1,3-glucan (i.e., *Sparan*) and the variation of hydrophobe type (HD or CA) (surfactant and oxidant: DBSA and APS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the Ostwald ripening, a small amount of highly monomer-soluble and water-insoluble agent called a hydrophobe is added to the organic phase with the monomer. The osmotic pressure, which results from the addition of the hydrophobe, balances the Laplace pressure of the droplet.^{32,33} The organic droplets undergo structural changes to establish a situation of zero effective pressure for realizing the miniemulsion stability. Figure 2 indicates that CA makes the PEDOT emulsion stable, and HD is not an appropriate hydrophobe. It is noted that the organic droplets dispersed in the aqueous phase are comprised of EDOT, β -1,3-glucan and DMSO besides a hydrophobe (CA), and they are finally transformed into the polymer particles after polymerization, in which PEDOT molecules are enclosed by β -1,3-glucan.²² The surfactant molecules organize an unusual bilayer on the outside of the hydrophilic β -1,3-glucan surrounding the PEDOT molecules. A surfactant bilayer structure in the miniemulsion polymerization process not only facilitates the system stabilization in water but also makes EDOT be polymerized in a bimolecular layer. There are also some noteworthy reports for the formation of surfactant bilayer in the emulsion polymerization process.^{34,35} Thus CA effectively provides an osmotic pressure for the pressure equilibration of the organic droplets because of the superior molecular interaction between CA having alcohol group and β -1,3-glucan.

The recovered PEDOT nanoparticles after centrifugation and vacuum-drying were redispersed in DI water, and then the resulting emulsion was sonicated for 10 min. The redispersed PEDOT emulsion showed the continuation of emulsion stability for over 30 days (Fig. 3) due to the presence of β -1,3-glucan enclosing the PEDOT molecules.

Identification of PEDOT nanoparticles

The identification of vacuum-dried PEDOT nanoparticles was carried out with FT-IR and XRD. Figure 4(a) shows the FT-IR spectrum of PEDOT nanoparticles prepared with DBSA and APS in the presence of β -1,3-glucan. The characteristic peak at 1401 cm^{-1} is attributed to the quinoidal C—C and C=C structures in the thiophene ring of PEDOT and 1102 cm^{-1} to the C—O—C bond stretching, with 923 , 703 , and 600 cm^{-1} attributed to the C—S—C bond vibrations in the thiophene ring. Most of the characteristic peaks for PEDOT appear in the position shifted to a lower frequency compared with the reported frequency for them.^{10,12} The shifts are known to be caused by an enhanced *p*-doping of PEDOT.¹² A noticeable peak at 1639 cm^{-1} shows the existence of a carbonyl group, which is ascribed to the overoxidation caused by the use of APS as an oxidant, as reported by Choi et al.¹³ The broadened and enlarged transmittance covering from 2200 to 3800 cm^{-1} appears in the FT-IR spectrum and it may be due to an overlapping of three peaks. It includes a high background transmittance in the high energy region above 2000 cm^{-1} , which is characteristic of conducting polymers and attributed to the tailing of the electronic bipolaronic absorption from oxidatively doped regions in the polymer.¹⁷ There is an inclusion of peaks ranging from 2800 to 3000 cm^{-1} , which are assigned to the aliphatic C—H stretching mode depending on the long alkyl tail of DBSA.¹³ Moreover, there is an overlapping of peak at 3300 cm^{-1} assigned to OH stretching of β -1,3-glucan.^{36,37} Figure 4(b) shows the XRD pattern of PEDOT nanoparticles prepared with DBSA and APS. A gradual peak at $2\theta \approx 23.6^\circ$ clearly appears in the XRD pattern, and it is assigned to the (0 2 0) reflection. The XRD pattern for PEDOT nanoparticles in general shows three peaks: 6.1 – 6.7° for the (1 0 0) reflection, 12.1 – 12.8° for the (2 0 0) reflections and 25.0 – 25.8°

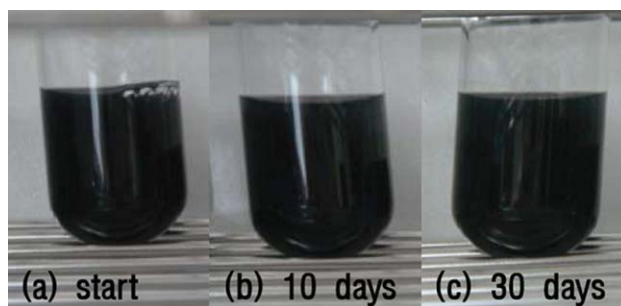


Figure 3 Continuation of emulsion stability after redispersion in DI water of the recovered PEDOT nanoparticles (surfactant and oxidant: DBSA and APS): (a) immediately after redispersion, (b) 10 days later and (c) 30 days later. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

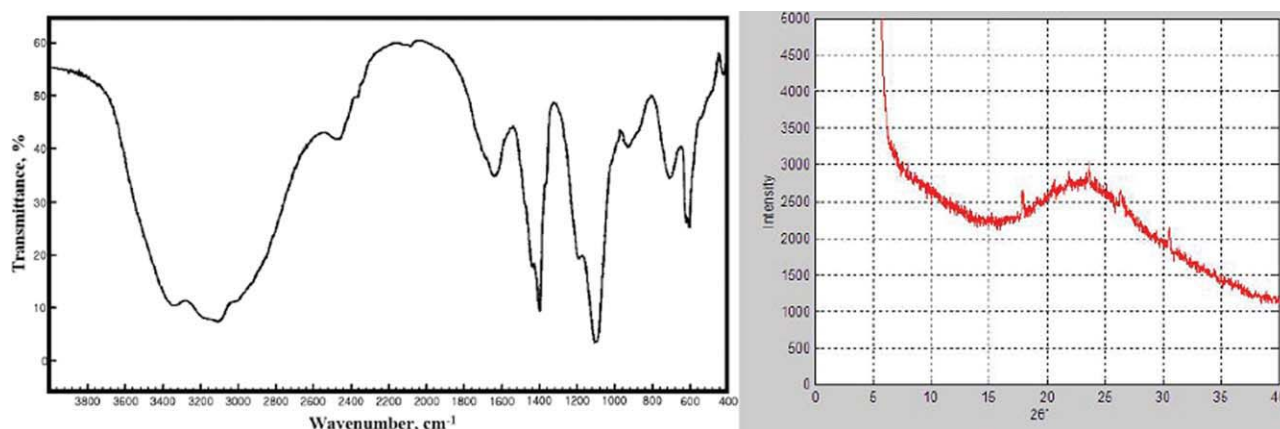


Figure 4 Identification of PEDOT nanoparticles (surfactant and oxidant: DBSA and APS): (a) FT-IR spectrum; (b) XRD pattern. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for the (0 2 0) reflection,^{8,12,13,26} while there is a report that a single major peak assigned to the (0 2 0) reflection solely appears²⁴ and it is in agreement with our observation. The (0 2 0) reflection peak shift to a lower angle (i.e., 25° to 23.6°) shows that the packing of the PEDOT backbone planes is loose due to insufficient *p*-doping, and thus the face-to-face distance between the stacked *p*-doped PEDOT sheets becomes long.

Figure 5 shows that the color change from white to dark blue-black gradually occurs during the course of the miniemulsion polymerization process of EDOT with DBSA and APS. It indicates that the chemical oxidative polymerization of EDOT caused by the redox mechanism between EDOT and sulfate ions²⁸ is initiated early (~ 10 min), but its progress is quite slow.

Morphology of PEDOT nanoparticles

The morphology of PEDOT nanoparticles was observed by FE-SEM and TEM. Figure 6 shows that the morphology and size of PEDOT nanoparticles prepared with DBSA and APS are highly influenced by the EDOT and DBSA content in the polymerization recipe. It is necessary to add a certain concentration of EDOT (0.945M) to suppress the aggregation of particles [Fig. 6(a1,a2) versus Fig. 6(b1,b2)]. The size of the PEDOT nanoparticles

increases with the concentration of EDOT [Fig. 6 (a1,a2,b1,b2,c1,c2)]; however, it inversely decreases with the concentration of DBSA [Fig. 6(c1,c2) versus Fig. 6(d1,d2)]. These observations correlate with the reasoning of the basic principles of the miniemulsion polymerization process.

Figure 7 shows that the morphology and size of PEDOT nanoparticles prepared with DBSA and APS are dependent on the operation conditions of the ultrasonifier treatment in the miniemulsion polymerization process. To obtain PEDOT nanoparticles of decreased size, the intensity [Fig. 7(a1,a2,b1,b2,c1,c2)] or the treatment time must be increased [Fig. 7 (a1,a2) versus Fig. 7(d1,d2)] in the ultrasonification operation. The organic phase made up of EDOT, β -1,3-glucan, CA, and DMSO forms monomer droplets dispersed in the aqueous continuous phase, and they are broken into nanodroplets by the high shearing force of the ultrasonifier. The intensity and treatment time of the ultrasonification operation are efficient control variables to obtain a miniemulsion in a steady state given by rate equilibrium of droplet fission and fusion. After the homogenization process using an ultrasonifier, the droplets are transformed to PEDOT nanoparticles through the chemical oxidative polymerization of EDOT that occurs independently in each nanodroplet ("nanoreactor") with maintaining a state of droplets. The SEM and TEM images (Figs. 6 and 7) of PEDOT particles prepared

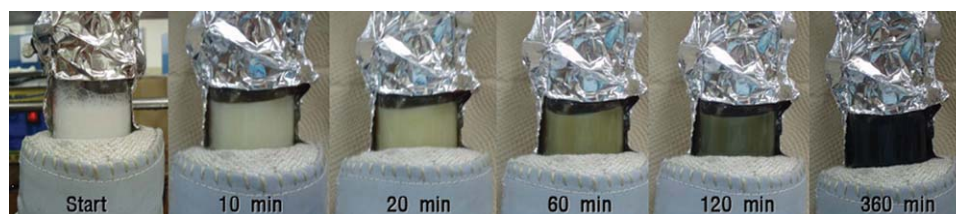


Figure 5 Color change of reaction mixture during the course of the miniemulsion polymerization process (surfactant and oxidant: DBSA and APS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

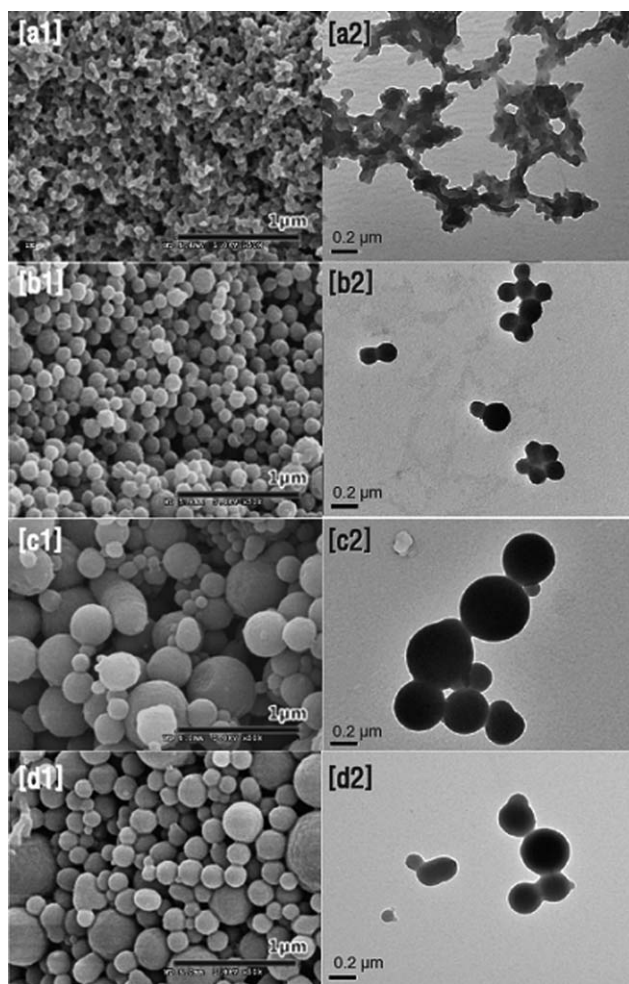


Figure 6 FE-SEM ([a1]-[d1]) and TEM ([a2]-[d2]) images of PEDOT nanoparticles depending on the molar concentration of EDOT and/or DBSA (oxidant: APS): [a1] and [a2]: $[\text{EDOT}]_0 = 0.189\text{M}$, $[\text{DBSA}]_0 = 1.05\text{ mM}$; [b1] and [b2]: $5\times[\text{EDOT}]_0$, $1\times[\text{DBSA}]_0$; [c1] and [c2]: $10\times[\text{EDOT}]_0$, $1\times[\text{DBSA}]_0$; [d1] and [d2]: $10\times[\text{EDOT}]_0$, $2\times[\text{DBSA}]_0$.

in this study show that the particle size is in the range of 140 ± 15 to 500 ± 20 nm depending on the ultrasonifer operating condition or the polymerization recipe. PSA was employed to analyze the PEDOT particle sizes and their size distributions. Figure 8 shows how the PSA results for PEDOT nanoparticles are affected by the molar concentration of EDOT. The increase in the EDOT concentration in the polymerization recipe causes not only the size of PEDOT nanoparticles to increase but also their size distribution to broaden [Fig. 8(a→b→c)]. Also it is noted that there occurs a bimodal size distribution at $[\text{EDOT}] = 0.945\text{M}$ [Fig. 8(b)]. Figure 9 shows how the operation conditions of ultrasonifer affect the PSA results for PEDOT nanoparticles. An increased shearing force in the ultrasonifer treatment of reaction mixture makes the particle size small, and it also causes the bimodal size distribution [Fig. 9(a→b) and Fig. 9(a→d)]. The size distribution profile of PEDOT

nanoparticles is divided up into bimodal distribution [Fig. 9(a→b)] and then multimodal distribution [Fig. 9(b→c)] as an ultrasonifer intensity increases.

A bimodal or multimodal particle size distribution was frequently observed in the miniemulsion polymerization process.^{38–40} A mathematical model for the bimodal particle size distribution in miniemulsion polymerization was developed and validated against the reported experimental data.^{41,42} At the initial stage of homogenization process using an ultrasonifer, the droplet size distribution is broad with a large fraction of small droplets. In the presence of a hydrophobe, the droplets do not completely lose their monomer and can exist as small droplets. Therefore, the instability of droplets causes a bimodal distribution consisting of these smaller droplets that cannot attain stability and larger droplets that can attain stability.⁴¹ Also there has been known that a bimodal particle size distribution is favored when applying the insuitable content of a

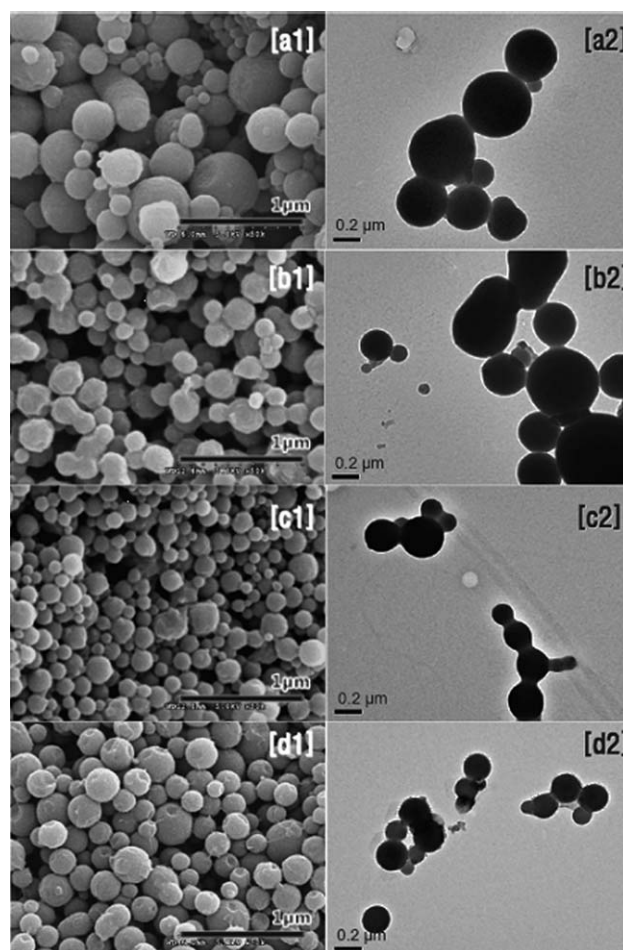


Figure 7 FE-SEM ([a1]-[d1]) and TEM ([a2]-[d2]) images of PEDOT nanoparticles depending on the operation conditions of ultrasonifer (surfactant and oxidant: DBSA and APS): [a1] and [a2]: power 5, 10 min; [b1] and [b2]: power 6, 10 min; [c1] and [c2]: power 7, 10 min; [d1] and [d2]: power 5, 60 min.

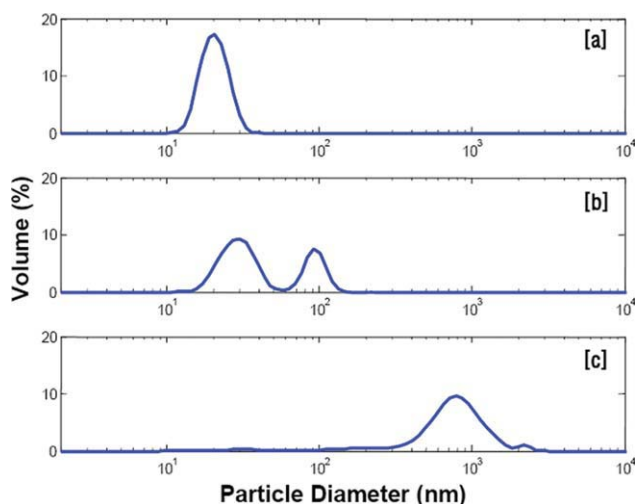


Figure 8 PSA results of PEDOT nanoparticles depending on the molar concentration of EDOT (surfactant and oxidant: DBSA and APS): [a]: $[\text{EDOT}]_0 = 0.189\text{M}$; [b]: $5 \times [\text{EDOT}]_0$; [c]: $10 \times [\text{EDOT}]_0$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrophobe.^{32,33} Note that besides hydrophobe (i.e., cetyl alcohol) and monomer (i.e., EDOT), the organic droplets contain β -1,3-glucan polysaccharide and DMSO. Thus the miniemulsion system prepared in this study could show a multimodal size distribution due to the additional effect of osmotic pressure caused by the presence of β -1,3-glucan in the organic droplets. One of the most noteworthy observations made in this study is that in the preparation of a conjugated polymer (i.e., PEDOT) via a miniemulsion polymerization process, a bimodal and even a multimodal size distribution can be obtained by

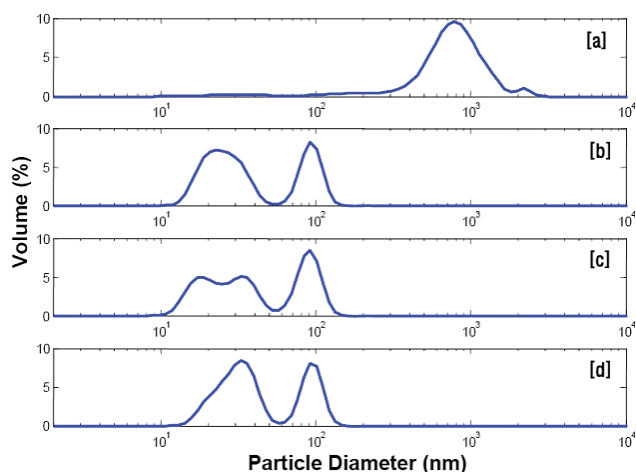


Figure 9 PSA results of PEDOT nanoparticles depending on the operation conditions of ultrasonifier (surfactant and oxidant: DBSA and APS): [a]: power 5, 10 min; [b]: power 6, 10 min; [c]: power 7, 10 min; [d]: power 5, 60 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

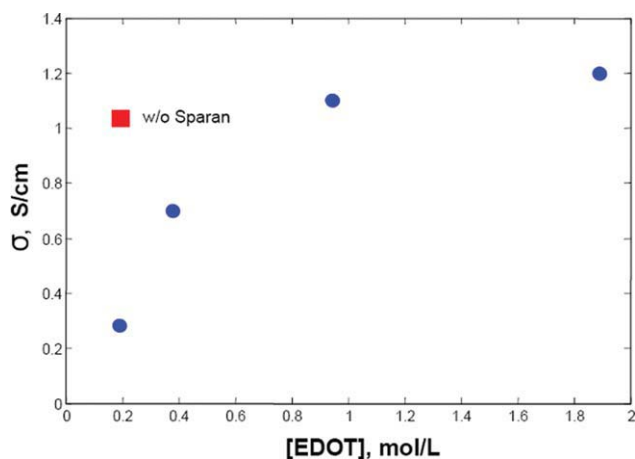


Figure 10 Conductivity of PEDOT nanoparticles depending on the molar concentration of EDOT (surfactant and oxidant: DBSA and APS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

adjusting the polymerization recipe or the homogenization process.

Conductivity of PEDOT nanoparticles

Figure 10 shows that with increasing molar concentration of EDOT, the conductivity of PEDOT nanoparticles increases in the beginning and then reaches a certain constant value (1.20 S cm^{-1}). The measured conductivity values of PEDOT nanoparticles prepared in this study are smaller than the reported values ($10\text{--}50 \text{ S cm}^{-1}$) for the emulsion polymerization of EDOT using APS and DBSA.¹³ Note that a β -1,3-glucan was added to the organic phase with EDOT in this study. It has been shown that a single chain of β -1,3-glucan encloses the PEDOT chain molecule due to the templating effect of β -1,3-glucan polysaccharide during the polymerization of EDOT.^{22,23} The β -1,3-glucan molecules coexisting with PEDOT suppress the electrical conduction of PEDOT. The conductivity value of PEDOT nanoparticles prepared without adding β -1,3-glucan ("Sparan") is 1.05 S cm^{-1} , which is higher compared to the value of 0.28 S cm^{-1} (at $[\text{EDOT}] = 0.189\text{M}$). In comparison, the commercially available Baytron P exhibits a conductivity of $1 \times 10^{-5} \text{--} 1.0 \text{ S cm}^{-1}$ depending on the PEDOT-PSSA ratio.⁵

CONCLUSIONS

An aqueous emulsion of PEDOT nanoparticles prepared via a miniemulsion polymerization process with the addition of β -1,3-glucan in the organic phase remained stable even after 8 weeks. The solid PEDOT nanoparticles recovered from the aqueous emulsion maintained emulsion stability for more

than 30 days after redispersion in DI water. The chemical structure of PEDOT was confirmed by the identification of characteristic peaks (C—C and C=C, C—O—C, C—S—C) in the FT-IR spectrum and a single reflection peak from (0 2 0) in the XRD pattern.

Separate PEDOT nanoparticles with a definite spherical structure were obtained when more than 0.945M of EDOT was added to the organic phase for the miniemulsion polymerization process. To decrease the size of the PEDOT nanoparticles, a building-up of shearing force was applied during the ultrasonification process by increasing the intensity and/or treatment time. Such an increase in the shearing force causes not only a size decrease but also multimodality in the size distribution profile of PEDOT nanoparticles. The electrical conductivity of PEDOT nanoparticles was less than 1.20 S cm^{-1} due to the presence of β -1,3-glucan molecules along with PEDOT; however, it is comparable to that of Baytron P. A recommended strategy for the improvement of electrical conductivity for PEDOT nanoparticles is a quantitative increase of EDOT and/or a quantitative decrease of β -1,3-glucan in the polymerization recipe.

References

- Kong, F.; Wu, X. L.; Huang, G. S.; Yuan, R. K.; Chu, P. K. *Thin Solid Films* 2008, 516, 6287.
- Englebienne, P.; Hoonacker, A. V. *J Colloid Interface Sci* 2005, 292, 445.
- Zotti, G.; Zecchin, S.; Schiavon, G.; Groenendaal, L. B. *Macromol Chem Phys* 2002, 203, 1958.
- Jung, Y. J.; Lee, S. J.; Choi, S. W.; Kim, J. H. *J Polym Sci A Polym Chem* 2008, 46, 5968.
- Kirchmeyer, S.; Reuter, K. *J Mater Chem* 2005, 15, 2077.
- Zhong, X.; Fei, G.; Xia, H. *J Appl Polym Sci* 2010, 118, 2146.
- Sheng, K.; Shi, G. *Synth Met* 2010, 160, 1354.
- Dai, C. A.; Chang, C. J.; Chi, H. Y.; Chien, H. T.; Su, W. F.; Chiu, W. Y. *J Polym Sci A Polym Chem* 2008, 46, 2536.
- Yoon, H.; Chang, M.; Jang, J. *Adv Funct Mater* 2007, 17, 431.
- Müller, K.; Park, M.; Klapper, M.; Knoll, W.; Müllen, K. *Macromol Chem Phys* 2007, 208, 1394.
- Müller, K.; Klapper, M.; Müllen, K. *Macromol Rapid Commun* 2006, 27, 586.
- Lei, Y.; Oohata, H.; Kuroda, S.; Sasaki, S.; Yamamoto, T. *Synth Met* 2005, 149, 211.
- Choi, J. W.; Han, M. G.; Kim, S. Y.; Oh, S. G.; Im, S. S. *Synth Met* 2004, 141, 293.
- Oh, S. G.; Im, S. S. *Curr Appl Phys* 2002, 2, 273.
- Kudoh, Y.; Akami, K.; Kusayanagi, H.; Matsuya, Y. *Synth Met* 2001, 123, 541.
- Henderson, A. M. J.; Saunders, J. M.; Mrkic, J.; Kent, P.; Gore, J.; Saunders, B. R. *J Mater Chem* 2001, 11, 3037.
- Seo, K. I.; Chung, I. *J Polym* 2000, 41, 4491.
- Kudoh, Y.; Akami, K.; Matsuya, Y. *Synth Met* 1998, 98, 65.
- Cloutet, E.; Mumtaz, M.; Cramail, H. *Mater Sci Eng C* 2009, 29, 377.
- Pozo-Gonzalo, C.; Marcilla, R.; Salsamendi, M.; Mecerreyes, D.; Pomposo, J. A.; Rodriguez, J.; Bolink, H. J. *J Polym Sci A Polym Chem* 2008, 46, 3150.
- Mumtaz, M.; Cuendias, A.; Putaux, J. L.; Cloutet, E.; Cramail, H. *Macromol Rapid Commun* 2006, 27, 1446.
- Sada, K.; Takeuchi, M.; Fujita, N.; Numata, M.; Shinkai, S. *Chem Soc Rev* 2007, 36, 415.
- Li, C.; Numata, M.; Hasegawa, T.; Fujisawa, T.; Haraguchi, S.; Sakurai, K.; Shinkai, S. *Chem Lett* 2005, 34, 1532.
- Wu, J.; Li, Y.; Feng, W. *Synth Met* 2007, 157, 1013.
- Sun, X.; Hagner, M. *Macromolecules* 2007, 40, 8537.
- Park, C. M.; Kim, T. Y.; Kim, W. J.; Kim, Y. S.; Suh, K. S. *Polymer (Korea)* 2005, 29, 363.
- Fornés, V.; Garcia, H.; Gómez-García, C. J.; Peris, E. *Chem Phys Lett* 2005, 415, 271.
- Chiu, W. W.; Travaš-Sejdić, J.; Cooney, R. P.; Bowmaker, G. A. *Synth Met* 2005, 155, 80.
- Ha, Y. H.; Nikolov, N.; Pollack, S. K.; Mastrangelo, J.; Martin, B. D.; Shashidhar, R. *Adv Funct Mater* 2004, 14, 615.
- Yamamoto, T.; Abla, M. *Synth Met* 1999, 100, 237.
- Corradi, R.; Armes, S. P. *Synth Met* 1997, 84, 453.
- Landfester, K. *Macromol Rapid Commun* 2001, 22, 896.
- Schorck, F. J.; Luo, Y.; Smulders, W.; Russum, J. P.; Butté, A.; Fontenot, K. *Adv Polym Sci* 2005, 175, 129.
- Jiang, J. *Eur Polym J* 2007, 43, 1724.
- Wijaya, A.; Hamad-Schifferli, K. *Langmuir* 2007, 23, 9546.
- Lee, S. J.; Ahn, K. H.; Park, C. S.; Yoon, B. D.; Kim, M. S. *Kor J Microbiol* 2009, 45, 63.
- Shin, J.; Lee, S.; Bae, I. Y.; Yoo, S.; Lee, H. G. *J Agric Food Chem* 2007, 55, 3368.
- Huang, X.; Sudol, E. D.; Dimonie, V. L.; Anderson, C. D.; El-Aasser, M. S. *Macromolecules* 2006, 39, 6944.
- Musyanovych, A.; Rossmanith, R.; Tontsch, C.; Landfester, K. *Langmuir* 2007, 23, 5367.
- Mori, Y.; Kawaguchi, H. *Colloids Surf B Biointerf* 2007, 56, 246.
- Sood, A.; Awasthi, S. K. *J Appl Polym Sci* 2003, 88, 3058.
- Sood, A. *J Appl Polym Sci* 2009, 114, 49.