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# Preparation of Polyaniline Nanoparticles in Micellar Solutions as Polymerization Medium

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*Received November 23, 1999. In Final Form: May 1, 2000*

Chemical oxidative polymerization of aniline was studied in a conventional aqueous solution and in micellar solutions of sodium dodecyl sulfate (SDS, anionic surfactant) and nonylphenol ethoxylate(9) (NP-9, nonionic surfactant) to investigate the effect of molecular structure of surfactants on the polymerization kinetics and particle size. The polymerization kinetics in NP-9 micellar solution were very slow, and this result was explained based on the structural characteristics of surfactant. SDS micellar solutions resulted in a highly transparent solution without any precipitates, whereas some precipitates were visually observed in the NP-9 micellar solution after the reaction finished. The electrical conductivities of polyaniline pellets formed with particles prepared in SDS and NP-9 micellar solutions and aqueous solution showed about 20, 4, and 4 S/cm, respectively. The highest electrical conductivity of particles from SDS micellar solution might be due to the smallest size of particles and the highest doping level of polyaniline.

## Introduction

Polyaniline (PANI) is an electrically conducting polymer with many features that could be exploited in various applications. Among other conducting polymers, such as polypyrrole, polythiophene, polyacetylene, and polyphenylenevinylene, polyaniline has been most extensively studied because it exhibits good environmental stability and its electrical properties can be modified by both the oxidation state of the main chain and protonation. However, the poor thermal stability and difficult processability of polyaniline should be overcome for the successful application of this electrically conducting polymer.<sup>1–3</sup>

To improve the thermal stability and processability of PANI, various kinds of dopants instead of HCl such as benzenesulfonic acid (BSA), sulfosalicylic acid (SSA), *p*-toluene sulfonic acid (TSA), camphor sulfonic acid (CSA), and dodecylbenzene sulfonic acid (DBSA) have been examined in our previous study.<sup>4</sup> The preparation of PANI in colloidal form is one of ways to improve the processability of this polymer and obtain electrically conducting composites. PANI dispersion has been prepared by polymerization of aniline in micelle,<sup>5</sup> emulsion,<sup>6,7</sup> reverse microemulsion as polymerization medium,<sup>8</sup> and steric stabilizer.<sup>9</sup>

A microemulsion has been employed as a polymerization medium for the synthesis of polymeric nanoparticles.<sup>10,11</sup>

Pitchumani et al. prepared nanoparticles of polyaniline in the reverse microemulsion composed of water–cyclohexane–sodium bis-2-ethylhexylsulfosuccinate (AOT).<sup>12</sup> The size of PANI particles obtained was 10–50 nm, which was the same order of diameter of water droplets. In this case, each water droplet acts as a nucleus for the polymer chain growth. As the polymerization proceeds in microemulsion droplet, the size of droplet controls the ultimate size of PANI particles.

In the method of using steric stabilizer, the aniline (aniline hydrochloride) monomers were dissolved in reaction medium (water) containing steric stabilizer, the polymerization was started by addition of initiator such as ammonium peroxydisulfate (APS), and then polymer (PANI) dispersion was obtained. The macroscopic precipitation of polymer is prevented by the presence of the steric stabilizer such as poly(vinyl alcohol),<sup>13</sup> poly(*N*-vinylpyrrolidone),<sup>14</sup> poly(vinyl methyl ether),<sup>15</sup> cellulose ethers,<sup>16</sup> or sophisticated tailor-made copolymer architectures.<sup>17,18</sup>

Kuramoto et al. have successfully prepared the nanoparticles of PANI in SDS (sodium dodecyl sulfate) and DBSA (dodecylbenzene sulfonic acid) micellar solution with APS as initiator, and they proposed the polymerization mechanism for the formation of particles in SDS micelles.<sup>5</sup> The acceleration of polyaniline growth in SDS micelles was observed due to the high local concentration of aniline monomer in the reaction medium. They also tried to prepare the nanoparticles in Triton X-100 nonionic micelles. But the preparation of PANI particles was not successful in this nonionic surfactant. In their study, they did not report the size of PANI particles formed in SDS micelles and did not give any explanation why the

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**Table 1. Compositions of Polymerization Mixtures before APS Solutions Were Added and Characteristics of PANI Synthesized Therein**

	aniline monomer (g mol <sup>-1</sup> )	surfactants (g mol <sup>-1</sup> )		total (mL)	N <sup>+</sup> /N	conductivity
		SDS	NP-9			
mixture 1	0.0043	0.034	0.0	100	0.46	20
mixture 2	0.0043	0.0	0.034	100	0.36	4
mixture 3	0.0043	0.0	0.0	100	0.37	4

synthesis of PANI nanoparticles in Triton X-100 nonionic micelles was not successful.

In the present study, we prepared the nanoparticles of PANI in anionic SDS and nonionic NP-9 (nonylphenol ethoxylate (9 mol)) with APS as initiator, and correlated the size of micelles with the size of PANI particles formed in micelles. Also the polymerization kinetics was studied in different kinds of micelles. The differences in polymerization kinetics were explained based on the structure of surfactants. The electroconducting behavior of PANI particles was investigated and compared with PANI prepared by an aqueous precipitation method.

### Experimentals

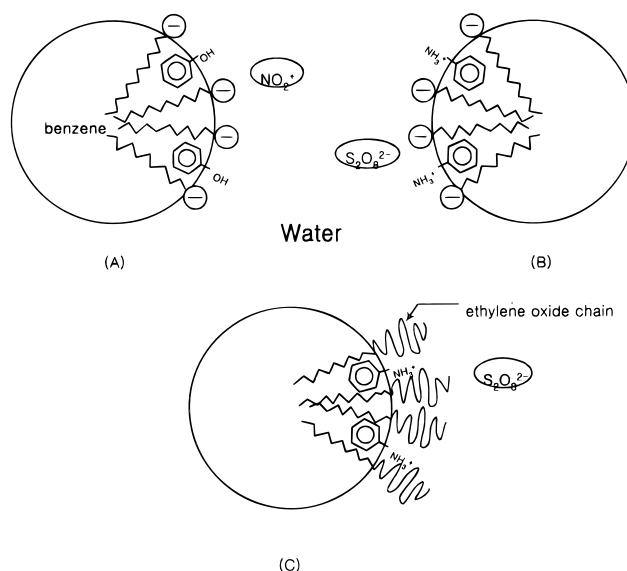
**Materials.** Aniline monomers (99.9%) were purchased from Sigma. SDS (99%, Sigma) and NP-9 (Ilchil Chemical Co., Korea) were used to form micelles in solution. APS (98%, Kanto Chemical Co.) was used to initiate the polymerization. Methanol (Mallinckrodt, 99.9%) and acetone (Kanto Chem., 96%) were used to wash the PANI particles after reaction. HCl (Matsunoen, 35%) was used as doping agent. All reagents were used as received without further purification.

**Synthesis of Particles.** The 0.1 M HCl solution was prepared by adding doubly distilled water into 35% HCl solution and used as an aqueous solution in micellar solution. The 0.49 g (0.0021 mol) of APS was dissolved in 10 mL of 0.1 M HCl solution and added dropwise into 100 mL of mixtures shown in Table 1 at 1.0 mL/min. The molar ratio of aniline to APS was kept as 2.0 through the entire experiment, and the total volume of mixture after the addition of initiator was 110 mL. Since the Krafft point of SDS is around 16 °C, the polymerization was performed at 20 ± 0.1 °C with the mechanical stirring at 500 rpm in a two-neck round-bottomed flask mounted in a thermostat for 12 h.

**Polymerization Kinetics.** Since the rate of addition of initiator (0.0021 mol of APS in 10 mL of 0.1 M HCl solution) was kept at 1.0 mL/min, it took 10 min to complete the addition of initiator into mixtures. A 0.05-g sample was taken from the reaction mixture every 10 min just after the start of addition of initiator to the mixture, and the sample was diluted with 3.0 mL of 0.1 M HCl solution. The optical absorbance of these diluted samples at 800 nm using a UV-vis spectrometer (Spectronic 20<sup>+</sup>, MILTON ROY) was measured to investigate the rate of PANI formation because the leveling off of absorption value at 800 nm, polaron band, could be thought of as the completion of reaction.<sup>19</sup>

**Washing and Drying of PANI Particles.** An excess amount of methanol was added into the HCl-doped PANI dispersion to precipitate PANI powder by breaking the hydrophilic-lyphophilic balance of the system and to stop the reaction. The precipitates were collected in a glass filter and washed two times each with methanol, acetone, and pure water to remove unreacted chemicals, aniline monomers and SDS. Then, the PANI particles were dried in the desiccator under the vacuum for 72 h at room temperature. The absence of moisture and surfactant molecules at the surface of PANI particles, which may act as adsorbents or dopant counterions, was confirmed with FT-IR spectroscopy by checking the sp<sup>3</sup> C-H stretching of the alkyl chain emerging around 2900 cm<sup>-1</sup>.

**Morphology of Particles.** The morphologies of PANI particles formed in micelles and in bulk aqueous solution were studied with field emission scanning electron microscopy (FE-



**Figure 1.** Orientation of phenol at the oil-water interface (from ref 21) (A) and our proposed orientation of anilinium cations in SDS micelles (B) and steric hindrance by ethylene oxide chain for disulfate ion from contacting anilinium ions (C).

SEM, JEOL model JSM-6340F). Particles for SEM pictures were coated with gold by sputtering for 10 s. Photographs were obtained at 5 or 15 kV and at a working distance 8 or 10 nm as shown in the pictures.

**Doping Level Measurement.** To investigate doping levels, N1s core level spectra for each three pelletized samples were obtained with a Mg Kα X-ray source (1253.6 eV). The X-ray power supply was operated at 200 W (20 mA × 10 kV). The pressure in the analysis chamber during scans was kept below 3 × 10<sup>-9</sup> Torr. To compensate for the surface charging effect, all binding energies were referenced to a C1s neutral carbon peak at 285.0 eV. N1s spectra, after background subtractions, were decomposed into suitable components consisting of a Gaussian line shape with a Lorentzian broadening function. Peaks were analyzed with a least-squares fitting routine assuming the constant full width at half-maximum of the peak components of N1s spectra.

**Electrical Conductivity Measurement.** A 0.02-g sample of PANI particles was loaded into pelletizer of 1.2 cm diameter, and 170 atm of pressure was applied for 3 min. Then, the electrical conductivities of pellets were measured by a four-point probe connected to a Keithley voltmeter-constant current source system.

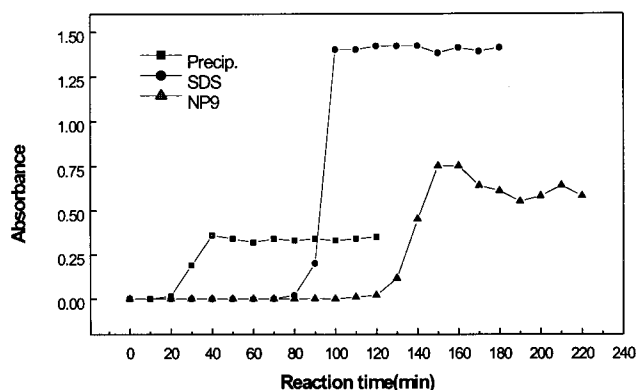
### Results and Discussion

**Solubilization of cationic anilinium ions in micelles.** The presence of the hydrophobic (micellar core) and hydrophilic interface in normal micellar solution may induce orientation of reactants in micelles, which in turn affect the regioselectivity of reaction and reaction kinetics.<sup>20</sup> It has been reported that conventional nitration of phenol in bulk aqueous media results in an approximate 2:1 ratio of para to ortho isomer. When the reaction is performed in an AOT (bis-2-ethylhexyl sulfosuccinate)-based microemulsion, a selectivity for ortho-nitration in the order of 80% can be obtained.<sup>21</sup> The preference for nitration in the ortho position when the reaction is performed in microemulsion is likely to be due to accumulation of phenol at the oil-water interface, with the phenolic hydroxyl group oriented into the water phase, as is illustrated in Figure 1A. Since the reacting nitronium ion species resides entirely in the aqueous domain, an

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**Figure 2.** Polymerization kinetics for the formation of polaron as measured by the variation of UV absorption at 800 nm wavelength.

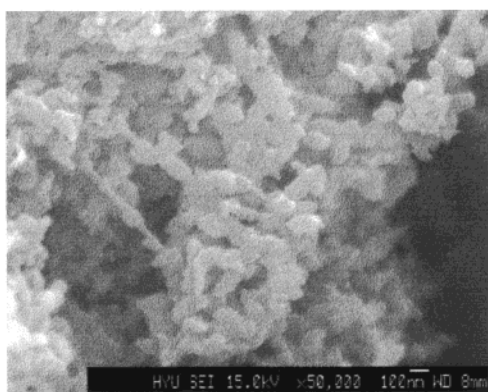
attack at the para position is less likely than at the ortho position. It is interesting that also a relatively nonsurface active molecule, such as phenol, exhibits such a marked orientation effect.

In solubilization, aniline is analogous to phenol molecules to the point that both of them are benzene derivatives substituted by polar moieties,  $-\text{NH}_2$  and  $-\text{OH}$ , respectively. Thus we assumed that anilinium cation would be oriented the same way as phenol molecules as shown in Figure 1B for SDS micelles and Figure 1C for NP-9 micelles. Phenol molecules solubilized in NP-9 micelles mainly reside in the ethylene oxide mantle forming a hydrogen bond with the oxygen molecules. But

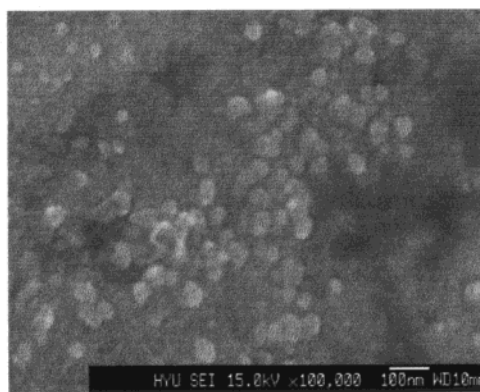
in our system (pH of initial reaction mixture, 1.8), formation of hydronium ions in ethylene oxide units at low pH would affect solubilization locus of anilinium ions and reaction rate in some way.

**Reaction Kinetics.** For the lipase-catalyzed hydrolysis of triglyceride in microemulsion, the reaction rate was rapid in microemulsion based on the ionic surfactants such as AOT. But it was extremely sluggish when normal nonionic surfactants are used. The difference in reaction rate depending upon the kinds of surfactant was attributed to the differences in accessibility of triglyceride to the enzyme. In the AOT system the lipase was anticipated to have a good access to the interface between the oil and water domain. On the other hand, in the systems based on nonionic surfactants the poly(ethylene glycol) (PEG) chains stretching out from the interface would effectively prevent the enzyme from entering into the interfacial region.<sup>23</sup>

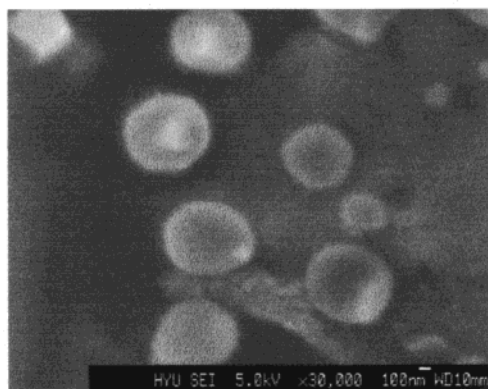
The reaction rate in SDS micelles for the formation of PANI particles was quite fast as shown in Figure 2 even though it was slower than that in conventional aqueous solution. The slow reaction in SDS micellar solution compared with that in bulk aqueous solution might be due to the electrical repulsion between anionic micellar surface and anionic disulfate ions. The degree of ionization of SDS micelles in ordinary water at 20 °C is 20%.<sup>24</sup> This means that 80% of the anionic dodecyl sulfate ions in micelles are bound with cationic sodium ions. Thus, the net electric charge of SDS micelles is generated due to the remaining 20% of unbound anionic dodecyl sulfate ions. In strong acidic solution, SDS micelles would have even



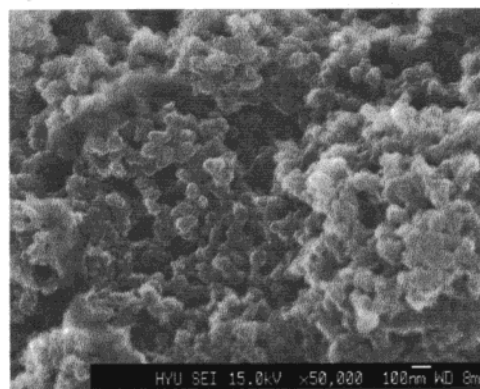
(A)



(B)



(C)



(D)

**Figure 3.** SEM pictures of PANI particles prepared in aqueous solution (A), in SDS micellar solution (B), and in NP-9 micellar solution (C) and (D).



lower micellar surface charge since the ionization degree of ionic surfactants is smaller than that in neutral solution.<sup>25</sup> Furthermore, the cationic anilinium ions would decrease the anionic net charge of SDS micelles by solubilizing in micellar surface. Thus, the surface of SDS micelles in the experimental conditions would have a low net negative charge. This low net negative charge of micellar surface retards the approach of disulfate ions into anilinium ions, resulting in a slower reaction rate in SDS micellar solution compared with that in bulk aqueous solution.

The reaction rate was the slowest in NP-9 micelles. This result might be explained based on the same phenomena occurring in the hydrolysis of triglyceride. The long ethylene oxide chain in NP-9 would effectively hinder the sulfate ions (oxidant) from attacking the anilinium cation in micelles (Figure 1C). Thus the formation of PANI particles in NP-9 micelles would be very slow because the disulfate ions should diffuse through the films formed by the ethylene oxide chain to initiate polymerization.

The rate of polymerization was the most rapid in bulk aqueous solution, followed by SDS and NP-9 micellar solutions. The reaction was completed after 40 min in bulk aqueous solution, 90 min in SDS, and 150 min in NP-9 micellar solution at 20 °C.

**Morphology of PANI Particles.** The shapes of PANI particles prepared in aqueous solution, SDS micelles, and NP-9 micelles after 12 h of reaction are shown in Figure 3. The PANI particles prepared in bulk solution have a relatively large and irregular shape. The particles synthesized in SDS micellar solution appeared to be rather spherical, and their sizes varied from 25 to 60 nm in diameter. The size of particles formed in micelles would be closely correlated with that of micelles. The size of SDS micelles in normal aqueous solution is about 6 nm. The diameter of SDS micelles was grown to about 20 nm by adding inorganic salt.<sup>26</sup> In our studies, it would be expected that the size of SDS micelles be much larger than 6 nm since the pH of the initial solution was around 1.8. At this acidic condition, ionization of SDS molecules would be depressed resulting in a decrease of electric repulsion between surfactant headgroups. This reduced electric repulsion and relatively high SDS concentration, 0.34 M, might result in the larger aggregation number and large micellar size.<sup>25</sup> At this reaction condition, the deviation of micellar shape from spherical could not be excluded. Birefringence was not observed, which indicated that initial solutions were optically isotropic.

In NP-9 micellar solution, some precipitates, which had spherical shape and ranged from 0.3 to 0.8  $\mu\text{m}$  in diameter, were observed with the naked eye in the middle of the reaction. Also PANI nanoparticles 60–80 nm in diameter were obtained as shown in panels C and D of Figure 3. The large particles would be formed outside micelles and the small particles inside micelles. It is interesting to see that the shapes of these large particles are quite spherical rather than dendritic, irregular even though they were formed outside micelles in solution. Contrary to the bulk aqueous solution, the growth of PANI particles outside micelles in NP-9 solution cannot proceed freely due to the presence of excess surfactant molecules of empty micelles.

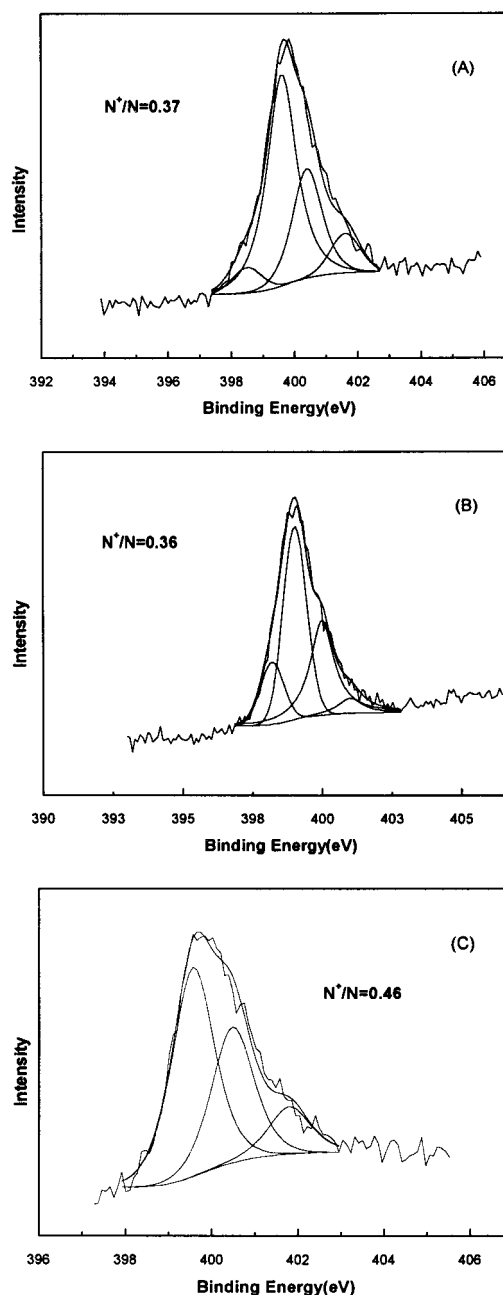
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**Figure 4.** N1s core level spectra of PANI pellets polymerized in aqueous (A), NP-9 (B), and SDS solutions (C).

After the formation of PANI nuclei from anilinium ions in bulk aqueous solution, NP-9 molecules will adsorb onto the surface of nuclei. The presence of surfactant film at the surface of PANI nuclei would prohibit the free growth of particles and forming spherical particles.

**Electrical Conductivity of PANI Particles.** Since the polymerization reaction in SDS micellar solution occurred in the confined space of micelles, the density of PANI particles would be higher than that of particles formed in bulk aqueous solution. Similar results were observed in the preparation of Y–Ba–Cu–O (123) superconductors in microemulsion. The pellet manufactured with superconducting particles formed in microemulsion has very low porosity and had a density corresponding to 97% of the theoretical values.<sup>27</sup> The high-density PANI particles formed in a confined space might induce the

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better thermal stability of PANI, which is one of major barriers in the practical application of PANI.

Among many factors which affect the electrical properties of PANI, such as doping level, crystalline structure, polaron mobility and concentration, grain boundaries, and the presence of ionic species, doping level could be considered as the primary controlling factor of electrical conductivity. Thus, the doping level of PANI particles was determined by X-ray photoelectron spectra (XPS) of the N1s core level which were composed of four subpeaks centered at about 398.2 eV ( $-\text{N}=\text{}$ ), 399.4 eV ( $-\text{NH}-$ ), and  $>400$  eV ( $-\text{N}^+-$ ) in a properly curve-fitted spectra (Figure 4).<sup>28</sup>

$[\text{N}^+]/[\text{N}]$  ratios, which could be correlated with the doping level, were determined by the area ratios of the peaks (N: sum of  $-\text{N}=\text{}$ ,  $-\text{NH}-$ , and  $-\text{N}^+-$ ). The calculated values are shown in Table 1. Since XPS is a highly surface specific tool, sometimes it is not inadequate for obtaining information in the bulk state. But in the case of PANI powders doped with HCl, many research groups have used the XPS technique to investigate the doping level.<sup>28,29</sup> The doping level of PANI particles prepared in SDS micelles was highest compared with those of particles formed in aqueous and NP-9 micellar solution. The

electrical conductivities of pellets formed with particles prepared both in bulk and in NP-9 micellar solution was about 4.0 S/cm. The pellet formed with particles prepared in SDS micellar solution had about 20.0 S/cm.

In conclusion, the rate of polymerization for the formation of PANI was in the following order: in bulk solution  $>$  in SDS micelles  $>$  in NP-9 micelles. The most sluggish polymerization in NP-9 might be a result of the fact that the ethylene oxide chain would effectively hinder the persulfate ions from attacking anilinium ions located on the micellar surface. No precipitates were observed in SDS micellar solution, giving a transparent green solution when the reaction mixture was diluted with excess water, whereas the NP-9 micelles produced two different sizes of particles. The large particles, which precipitated in the middle of the reaction, were initiated from anilinium ions located outside the NP-9 micelles, and the small particles were from anilinium ions solubilized in micelles. PANI synthesized in SDS micellar solution showed the highest conductivity, which could be explained partially by the high doping level.

**Acknowledgment.** This work was supported by the Research Fund of Hanyang University (Project No. HYU-99-015).

LA9915320

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