

Preparation of Aqueous Polyaniline Dispersions by Micellar-Aided Polymerization

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ABSTRACT: Polyaniline (PAn) dispersed in water was prepared with sodium dodecylsulfonate (SDS) as a surfactant with varying concentrations of aniline and HCl and molar ratios of SDS/aniline. The PAn dispersion was homogeneous and stable, and its pH value could be adjusted. The conductivity of PAn powder, precipitated from this dispersion, was as high as 20 S/cm. The transmission electron

microscopy morphology of PAn assembled in the dispersion was particle-like, fiber-like, or coil-like, depending on the initial concentration of SDS and aniline. The polymerization of aniline was accelerated by SDS, which was confirmed by open-circuit potential measurement during the polymerization process. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1550–1555, 2003

INTRODUCTION

Polyaniline (PAn) is one of the most promising candidates for practical application among organic conducting polymers because of its high environmental stability, ease of preparation, and low cost. Many attempts to produce colloidal PAn or aqueous dispersions of PAn have been made because this may be a practical way to alleviate the poor processability characteristic associated with this material. These attempts have included the use of surfactants, such as dodecylbenzenesulfonic acid and sodium dodecylsulfonate (SDS); stabilizers, such as polyvinyl alcohol, polyvinylmethylether, and polyvinyl-*co*-acrylate;^{1–9} reactive stabilizers containing pendant aniline groups as graft sites;^{10–15} and dopants containing water-soluble counterions.^{16,17} In addition, another method, which was first developed by Epstein and coworkers, was the preparation of PAn derivatives containing strong hydrophilic substitutes such as $-\text{SO}_3\text{Na}$.¹⁸

Among these methods, from the authors point of view, the use of SDS as a surfactant has been the most economical method, bridging the gap toward practical application. Kuramoto et al. have reported an acceleration of PAn growth in electropolymerization in the presence of SDS due to the high local concentration of aniline monomer in the reaction domain.⁹ A

PAn dispersion was also prepared by chemical oxidation in the presence of SDS.⁸ Absorption spectra of the PAn dispersion at various pH values showed that the transition from the emeraldine salt to the emeraldine base form occurred at about pH 7–8 in this anionic micellar system.

In this study, water-dispersed PAn was prepared with SDS as a surfactant. Long-term stable and homogeneous PAn dispersions were obtained in a broad range of pH values and aniline and SDS concentrations. The acceleration of polymerization was confirmed further by open-circuit potential (OCP) measurement. Transmission electron microscopy (TEM) images showed that the morphology of the dispersed PAn was different, depending on the concentration of SDS and aniline.

EXPERIMENTAL

Materials

Aniline p.a. was distilled under reduced pressure; freshly distilled aniline was stored in a refrigerator before use. All other chemicals were analytical reagents and were used as received.

The aqueous dispersion of PAn was prepared by the addition of ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS) as an oxidant into a mixed solution of SDS and aniline containing added HCl. A typical experiment follows: 1.9 mL (0.02 mol) of freshly distilled aniline and 11.6 g of SDS (0.04 mol) were each dissolved in 600 mL of 0.1 mol/dm³ HCl solution. The two solutions were stirred for 30 min and then mixed APS [4.6 g (0.02 mol)] was dissolved in 200 mL of 0.1 mol/dm³ HCl solution and added into this mixture under stirring. The reaction mixture was stirred for 5 h.

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TABLE I
Preparation of the PAN Dispersions at Various c_{HCl} 's^a

	c_{HCl}								
	2.0	0.5	0.2	0.16	0.15	0.1	0.05	0.02	0.01
State of product ^b	x	x	⊗	⊗	○	○	○	○	○

^a Aniline (0.19 mL); APS (0.46 g), and SDS (1.16 g) were fixed in 140 mL HCl solution.

^b x = precipitate; ⊗ = precipitate and dispersion; ○ = homogeneous dispersion.

Measurements

A PAN dispersion was prepared in 0.01 mol/dm³ HCl solution with initial concentrations of aniline, APS, and SDS of 0.015, 0.015, and 0.03 mol/dm³, respectively. Its pH value was adjusted from 1 to 9 before precipitation. PAN precipitated when excess methanol was added into the dispersion. The precipitate was filtered and then dried in a vacuum oven at 40°C for 48 h. The PAN powder was pressed into tablets, and the electronic conductivity was measured by a standard four-probe method.

PAN precipitate was thoroughly washed with methanol, HCl (1.0 mol/dm³), NH₄OH (1.0 mol/dm³), and water. The washed PAN powder was dried in a vacuum oven at 40°C for 48 h. Fourier transform infrared (FTIR) spectra were measured with KBr tablets.

Platinum wire and SCE were used as the working and reference electrodes, respectively. The distance of the two electrodes was fixed, and they were immersed into the reaction mixture, which acted as an electrolyte solution. OCP was measured during the polymerization process with a high-impedance voltmeter at intervals of 15 s.¹⁹

PAN dispersions were diluted by water to an appropriate concentration and then coated on carbon-film-covered copper grids. Samples were dried in a vacuum oven at 30°C for 24 h. TEM images were taken with a Philips CM 200 TEM microscope.

RESULTS AND DISCUSSIONS

Preparation of the PAN dispersion

PAN dispersions could be made in the range of HCl concentration (c_{HCl}) from 0.15 to 0.01 mol/dm³ (see

TABLE III
Preparation of PAN Dispersions as a Function of the SDS/Aniline Molar Ratio

c_{HCl} (mol/dm ³)	SDS/aniline				
	2	1	0.75	0.5	0.25
0.02	○	○	×	×	×
0.05	○	○	○	×	×
0.1	○	○	○	×	×

○ = homogeneous dispersion; × = precipitate.

Table I). When c_{HCl} was higher than 0.20 mol/dm³, a precipitate was formed. When c_{HCl} was lower than 0.01 mol/dm³, aniline did not polymerize in 1 week because sufficient H⁺ was necessary for the APS to oxidize aniline. When c_{HCl} was in the range from 0.16 to 0.20 mol/dm³, both dispersion and precipitate were generated.

The influence of aniline concentration and the molar ratio of SDS to aniline was also investigated. The PAN dispersion could be prepared when the aniline concentration was equal to or lower than 0.02 mol/dm³. Otherwise, a precipitate was formed (see Table II). As can also be seen from the table, aniline polymerized even when its concentration was as low as 5.0 × 10⁻⁴ mol/dm³. At this concentration, when the same molar concentrations of aniline and APS were mixed and stirred at room temperature, aniline did not polymerize in 1 week. This phenomenon is discussed further later. Results obtained with different molar ratios of SDS to aniline are shown in Table III. PAN precipitate was formed when the molar ratio of SDS to online was lower than 0.75.

Properties of the dispersion and the bulk PAN

PAN dispersions were dark green and homogeneous and did not precipitate in 3 months. They could be diluted with water, HCl, or NH₄OH solutions. Thus, their pH values could be adjusted from 1 to 10. The conductivity of PAN powder as a function of the pH value of the dispersions is shown in Table IV. The conductivity was 20 S/cm at pH 1. It decreased to 1.1 × 10⁻³ S/cm at pH 2. Conductivity decreased gradually with increasing pH value from 2 to 9. Its value arrived at 4.0 × 10⁻⁷ S/cm at pH 9, indicating that the

TABLE II
Preparation of PAN Dispersions at Various Aniline Concentrations^{a,b}

(mol/dm ³)	Aniline concentration (mol/dm ³)						
	1 × 10 ⁻⁴	5 × 10 ⁻⁴	0.002	0.008	0.02	0.025	0.05
State of product ^c	—	○	○	○	○	⊗	⊗

^a c_{HCl} was 0.1 and 0.05 mol/dm³.

^b SDS/aniline/APS = 2/1/1.

^c ○ = homogeneous dispersion; ⊗ = precipitate and dispersion.

TABLE IV
Conductivity (σ) of PAN as a Function of pH

	pH				
	1	2	3	4	9
σ (S/cm)	20	1.1×10^{-3}	6.5×10^{-4}	7.7×10^{-5}	4.0×10^{-7}

PAN sample was not completely dedoped at this pH value. It was reported that the conductor-insulator transition of conventional PAN is at about pH 4.²⁰ The higher transition pH value observed here may have been caused by the strong interaction between doped PAN and SDS anions. This result agreed with previously published ultraviolet-visible spectra reported by Kuramoto et al.⁹

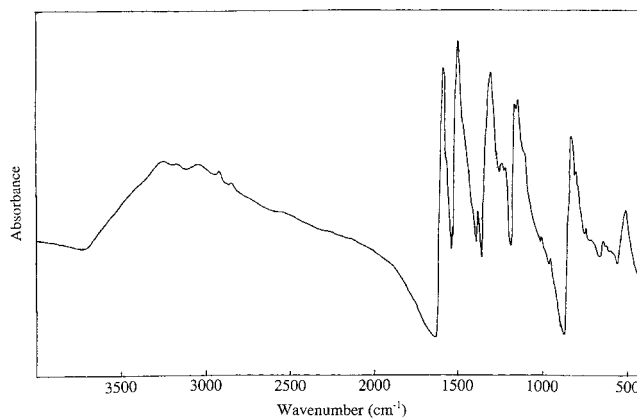


Figure 1 FTIR spectrum of PAN powder precipitated from its dispersion.

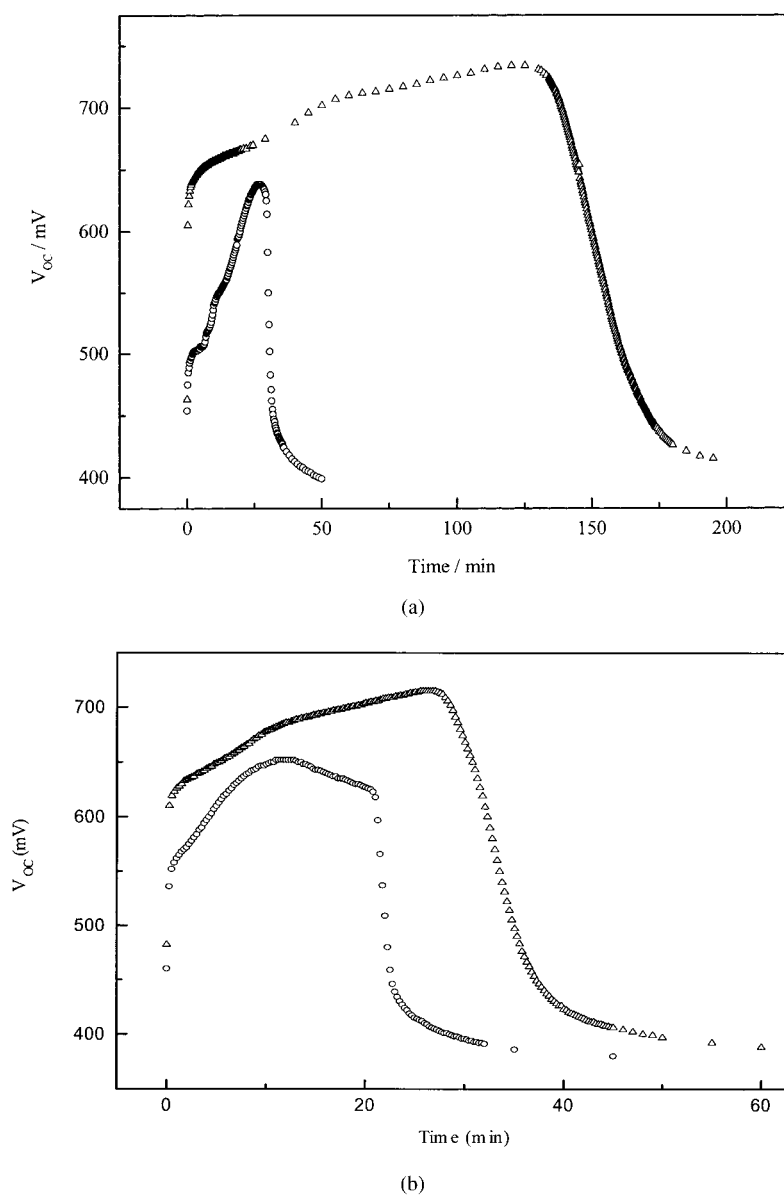


Figure 2 OCP versus reaction time for the polymerization of aniline: (a) 0.004 and (b) 0.015 mol/dm³, circle with and triangle without SDS.

FTIR spectra of PAn powder precipitated from its dispersion, as shown in Figure 1, presented typical peaks of PAn. The peaks at about 1583 and 1494 cm^{-1} were characteristic of benzoid structure and quinoid (Q) structures, respectively. The peak at about 1305 cm^{-1} was caused by the stretching of C-N bonds; the peak at about 1163 cm^{-1} was assigned to the Q=N=Q bending; and the peak at about 828 cm^{-1} was characteristic of para-disubstituted benzoid structures.

Polymerization process

OCP of the platinum electrode in the polymerization solution was measured as described elsewhere.¹⁹ Figure 2 shows the OCP as a function of reaction time

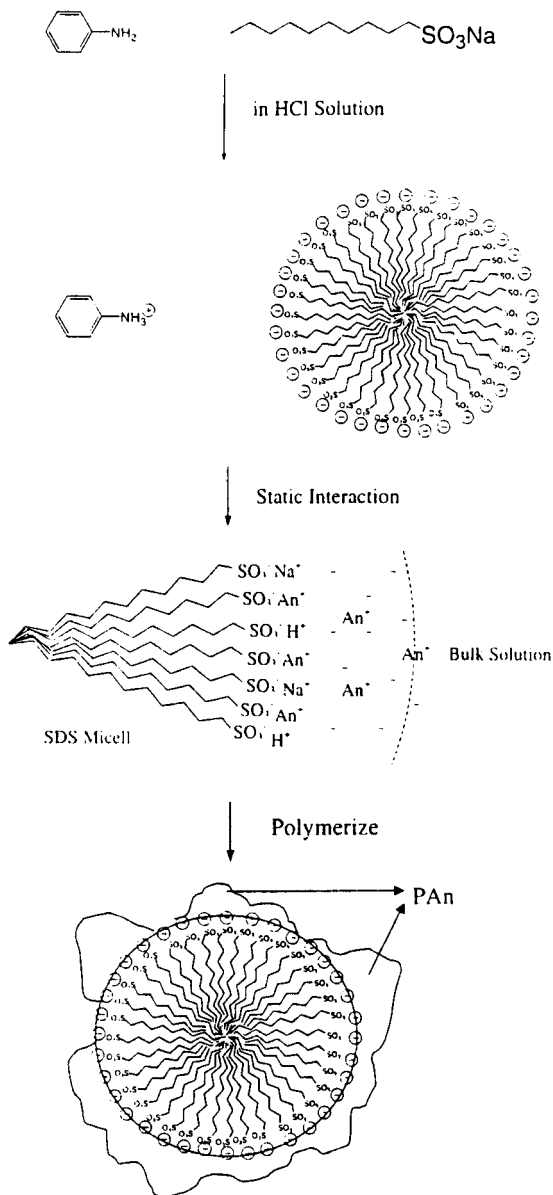
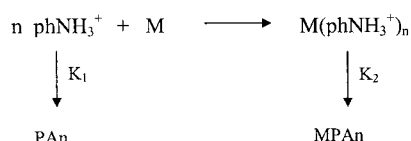


Figure 3 Schematic diagram of micellar-aided polymerization.



Scheme 1

with and without added SDS. The time when the APS solution was added was set as 0. In all cases, after APS was added, the OCP of the system increased quickly to a value higher than $E_{\text{SCE}} = 0.5 \text{ V}$. The OCP maintained a value higher than 0.5 V during the introduction and increasing steps of the polymerization. After that, it suddenly decreased to about $E_{\text{SCE}} = 0.4 \text{ V}$, indicating the end of polymerization.

With SDS in the solution, the polymerization time from the addition of APS until the drop of OCP to about $E_{\text{SCE}} = 0.4 \text{ V}$ decreased from about 170 min to about 30 min when the initial concentration of aniline was equal to 0.004 mol/dm^3 and from 35 to 20 min when the initial concentration of aniline was equal to 0.015 mol/dm^3 . Obviously, the polymerization was accelerated by SDS. This effect was much more notable when the aniline concentration was relatively lower.

Kuramoto explained this phenomenon by invoking the high local concentration of aniline monomer in the reaction medium.⁹ Aniline is protonated (phNH_3^+) and SDS forms micelles, which are negatively charged, after being dissolved in HCl solution. The attractive static interaction between SDS micelles and phNH_3^+ may cause phNH_3^+ to concentrate within a thin layer around the micelles (see Fig. 3). As a result, in our study, the interfacial concentration of phNH_3^+ was much higher than that of the bulk solution. Therefore, the polymerization process was accelerated.²¹ This effect can be called *micellar-aided polymerization* (see Scheme 1). It was probably the reason that aniline could polymerize in very dilute solution (see Table II). When the aniline concentration was equal to $5.0 \times 10^{-4} \text{ mol/dm}^3$, which was too dilute to be polymerized by APS alone without SDS, the local concentration of phNH_3^+ may have been much higher than the value of bulk solution and enough for polymerization. This effect may have also been the reason that PAn precipitate was formed when c_{HCl} was higher than 0.2 mol/dm^3 (see Table I). According to Figure 3, both H^+ and phNH_3^+ had attractive interactions with SDS micelles. The interaction between SDS micelles and phNH_3^+ may have been affected by H^+ in high- H^+ -concentration solution. As a result, the polymerization took place in the bulk solution, and PAn was precipitated. In a control experiment, hexadecyltrimethylamino bromide [$\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$], a cationic surfactant, was used as surfactant instead of SDS. In this case, PAn precipitate, instead of the PAn dispersion,

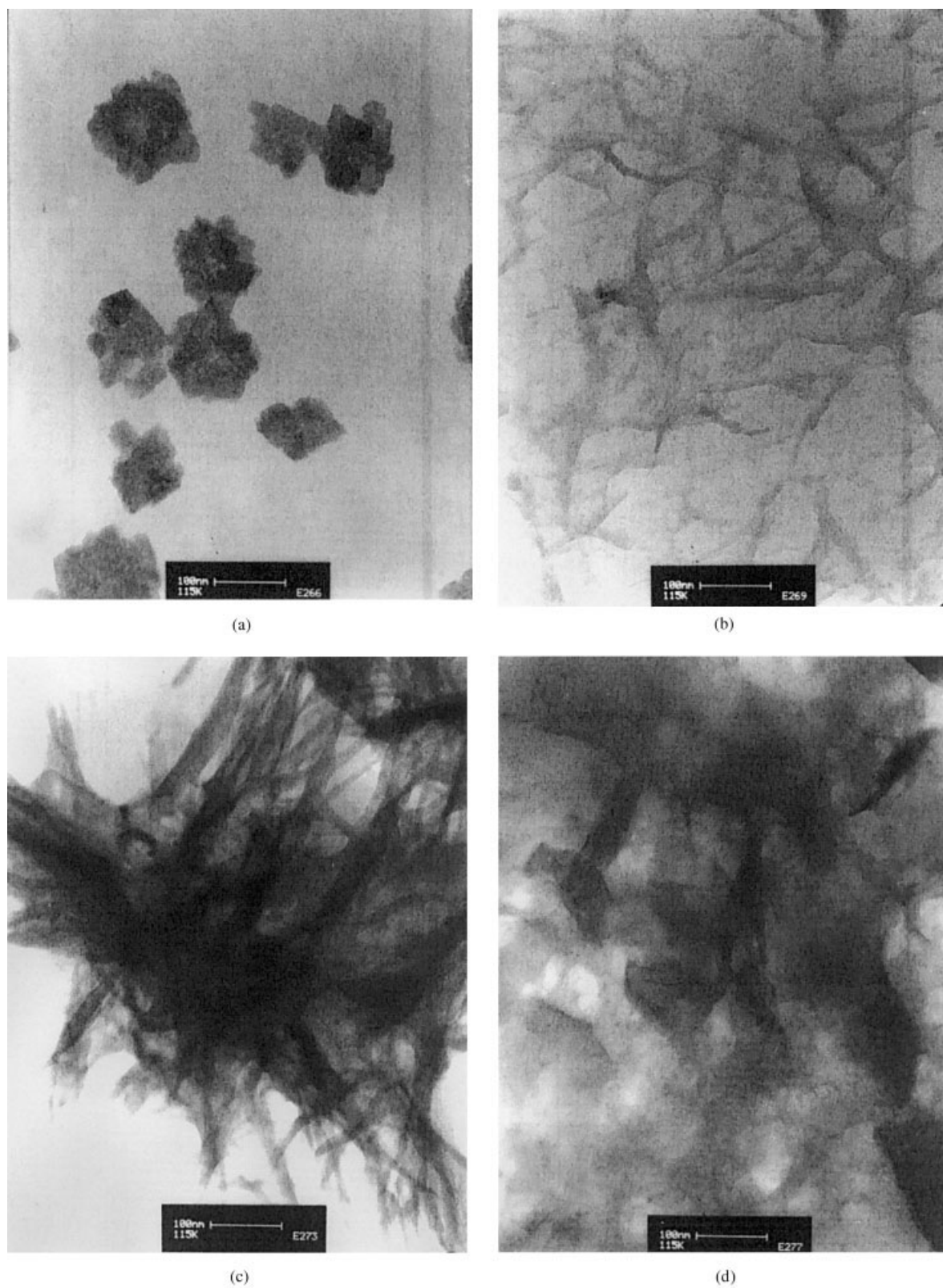


Figure 4 TEM picture of dispersed PAN from initial aniline concentrations of (a) 0.001, (b) 0.004, (c) 0.008, and (d) 0.015 mol/dm³.

was generated. Thus, it is likely that the attractive interaction between micelles and pH_3^+ played a critical role for the formation of the PAN dispersion.

TEM images of dispersed PAN

TEM images of dispersed PAN with various initial concentrations of aniline (the molar ratio of SDS to aniline was fixed at 2) are shown in Figure 4. When the initial aniline concentration was $1 \times 10^{-3} \text{ mol/dm}^3$, the obtained polymer in the dispersion was particle-like [see Fig. 4 (a)]. The diameter of the particles was about 50–100 nm. With increasing concentrations of aniline and SDS, the morphology of the dispersed PAN changed to fiber-like and coil-like, progressively, [see Fig. 4 (b,c)]. When the aniline concentration reached 0.015 mol/dm^3 and the SDS concentration reached 0.03 mol/dm^3 at the same time, the polymer aggregated after it was coated on the copper grid [see Fig. 4 (d)]. As suggested previously, the polymerization of aniline took place on the surface of micelles. The morphological change of the dispersed PAN was probably due to the change of micellar structure with increasing SDS concentration. Micelles were spheroid when SDS concentration was very low. This may change to bar-like, branch-like, laminate, and sponge-like step by step with increasing surfactant concentration.^{22,23}

CONCLUSIONS

Stable and homogeneous PAN water dispersions were prepared with SDS as a surfactant. The suitable H^+ and aniline concentrations were lower than 0.15 and 0.02 mol/dm^3 , respectively. The molar ratio of SDS to aniline should have been higher than 0.75. The dispersion could be diluted by water, HCl, and NH_4OH solutions. Its pH value was adjustable from 1 to 10. SDS accelerated the polymerization of PAN, which was confirmed by OCP measurement, probably because of a micellar-aided effect. TEM images provided

evidence for micellar-aided polymerization. The morphology of the dispersed PAN was particle-like when the initial aniline concentration was very low and changed to fiber-like or coil-like with increasing initial aniline concentration.

References

1. Lin, J. M.; Yang, S. C. *J Chem Soc Chem Commun* 1991, 1529.
2. Gospodinova, N.; Mokreva, P.; Terlemezyan, L. *J Chem Soc Chem Commun*, 1992, 923.
3. Banerjee, P.; Digar, M. L.; Bhattacharyya, S. N.; Mandal, B. M. *Eur Polym J*, 1994, 30, 499.
4. Banerjee, P.; Bhattacharyya, S. N.; Mandal, B. M. *Langmuir* 1995, 11, 2414.
5. Gospodinova, N.; Terlemezyan, L.; Mokreva, P.; Stejskal, J.; Kratochvil, P. *Eur Polym J*, 1993, 29, 1305.
6. Kuramoto, N.; Tomita, A. *Polymer* 1997, 30, 3055.
7. Österholm, J. E.; Cao, Y.; Klavetter, F.; Smith, P. *Synth Met* 1993, 55–57, 1034.
8. Kuramoto, N.; Genies, E. M. *Synth Met* 1995, 68, 191.
9. Kuramoto, N.; Michaelson, J. C.; McEvoy, A. J.; Grätzel, M. *J Chem Soc Chem Commun* 1990, 1478.
10. Armes, S. P.; Aldissi, M. *J Chem Soc Chem Commun* 1989, 88.
11. Armes, S. P.; Aldissi, M. *Mater Res Soc Symp Proc* 1989, 173, 311.
12. Armes, S. P.; Aldissi, M.; Agnew, S. F.; Gottesfeld, S. *Langmuir* 1990, 6, 1745.
13. Armes, S. P.; Aldissi, M.; Agnew, S. F.; Gottesfeld, S. *Mol Cryst Liq Cryst* 1990, 190, 63.
14. Bay, R. F. C.; Armes, S. P.; Pickett, C. J.; Ryder, K. S. *Polymer* 1991, 32, 2456.
15. Tadros, P.; Armes, S. P.; Luk, S. Y. *J Mater Chem* 1992, 2, 125.
16. Sun, Z. C.; Wang, X. H.; Li, J.; Zhang, J. Y.; Yu, L.; Jing, X. B.; Wang, F. S.; Lee, C. J.; Rhee, S. S. *Synth Met* 1999, 102, 1224.
17. Geng, Y. H.; Sun, Z. C.; Li, J.; Jing, X. B.; Wang, X. H.; Wang, F. S. *Polymer* 1999, 40, 5723.
18. Yue, J.; Epstein, A. J. *J Am Chem Soc* 1990, 112, 2800.
19. Wei, Y.; Hsueh, K. F.; Jang, G. W. *Polymer* 1994, 35, 3572.
20. Genies, E. M.; Boyle, A.; Lipkowski, M.; Tsintavis, C. *Synth Met* 1990, 36, 139.
21. Tzou, K.; Gregory, R. V. *Synth Met* 1992, 47, 267.
22. Junginger, H. E. In *Surfactant in Cosmetics*; Rieger, M. M.; Rhein, L. D., Eds.; Marcel Dekker: New York, 1997; Chapter 7.
23. Lange, K. R. In *Surfactants*; Lange, K. R., Ed.; Hanser-Verlag: Munich, Germany 1999; Chapter 1.