Polyaniline Nanoparticles Prepared in Rodlike Micelles

P. A. Hassan,*,† Shilpa N. Sawant,† Nitin C. Bagkar,† and J. V. Yakhmi‡

Novel Materials and Structural Chemistry Division and Technical Physics & Prototype Engineering Division, Bhabha Atomic Research Center, Mumbai 400 085, India

The effect of aniline hydrochloride (AHC) on the size and shape of sodium dodecyl sulfate (SDS) micelles has been investigated by dynamic light scattering. A monotonic decrease in the diffusion coefficient of the micelles was observed with an increase in AHC at fixed SDS concentration. This was ascribed to prolate ellipsoidal growth of the micelles due to decrease of the effective headgroup area/molecule by adsorption of AHC on SDS micelles. The length of the micelles can be tuned by controlling the ratio of concentrations of AHC to SDS. Polymerization of aniline in micelles of different sizes leads to the formation of colloidal polyaniline with variable sizes. A direct correlation between size of micelles and size of polyaniline particles was observed. Combination of static and dynamic light scattering experiments reveal that the conformations of the polymer do not change significantly with size of the colloid.

Introduction

Among conducting polymers such as polyaniline (PANI), polypyrrole, polythiophene, and polyacetylene, PANI has been extensively studied because of its high environmental stability, tunable electrical properties, and relatively low cost. By a suitable change in pH (protonation reaction), one can alter the electrical conductivity of these polymers to tune them up as an insulator, semiconductor, or conductor.[1] PANI exists in various oxidation states ranging from the reduced leucoemeraldine form to fully oxidized pernigraniline form. However, among various forms of PANI, only the emeraldine salt is conducting.[2] The leucoemraldine form has a band gap of nearly 4 eV, whereas the emeraldine base and fully oxidized pernigraniline forms have a band gap of the order of 2 eV.[3] One of the problems associated with successful application of this polymer is the difficulty in processing of this material due to its very low solubility in different solvents.

The processability of PANI can be readily improved by increasing its solubility in organic solvents. Doping of PANI with protonic acids such as camphorsulfonic acid (CSA) or dodecylbenzenesulfonic acid (DBSA) is known to increases the solubility of emeraldine salt form in solvents such as *m*-cresol, xylene, etc.[4,5] This is because of the negatively charged sulfonate group of the dopant that associates with the positively charged backbone of the emeraldine salt form of the polymer through Coulomb attraction thereby providing a hydrophobic side chain compatible with organic solvents. DBSA is known for its surfactant action but can act simultaneously as a dopant. Another approach to improve processability of this material has been to prepare them as colloidal nanoparticles. Different strategies have been employed for the preparation of PANI dispersions in colloidal form. Typically, they are produced by chemical polymerization of aniline in the presence of various polymeric stabilizers such as poly-(ethylene oxide), poly(vinyl alcohol), poly(*N*-vinylpyrrolidone), poly(vinyl methyl ether), hydroxypropyl cellulose, methyl cellulose, etc.[6–12] Colloidal silica particles have been used as a steric stabilizer for the prepartion of PANI dispersions.[13–16] There are a few reports describing synthesis of stable PANI dispersions by employing amphiphilic block copolymer micelles as the reaction medium.[17,18] The size, stability, and morphology of PANI particles were strongly dependent on the choice of stabilizers, oxidant, and reaction conditions.[19] PANI nanoparticles have also been synthesized on a highly oriented pyrolytic graphite (HOPG) surface by electrochemical polymerization using the pulsed potentiostatic method.[20]

Microemulsions, miniemulsions, inverted emulsions, and other template-free methods have also been used for the successful generation of PANI nanostructures.[21–26]

---

* Corresponding author. Tel: + 91-22 25592327. Fax: + 91-22 25505151. E-mail: hassan@apsara.barc.ernet.in.

† Novel Materials and Structural Chemistry Division.

‡ Technical Physics & Prototype Engineering Division.

(1) Heeger, A. J. *Curr. Appl. Phys.* **2001,** *1,* 247.

(2) Tawde, S.; Mukesh, D.; Yakhmi, J. V. *Synth. Met.* **2002,** *125,* 401.

(3) Gettinger, C. L.; Heeger, A. J.; Pine, D. J.; Cao, Y. *Synth. Met.* **1995,** *74,* 81.

(4) Cao, Y.; Smith, P. Heeger, A. J. *Synth. Met.* **1992,** *48,* 91.

(5) Cao, Y.; Treacy, G.; Smith, P.; Heeger, A. *J. Appl. Phys. lett.* **1992,** *60,* 2711.

(6) Vincent, B.; Waterson, J. *Chem. Commun.* **1990,** 683.

(7) Stejskal, J.; Kratochvil, P.; Helmstedt, M. *Langmuir* **1996,** *12,* 3389.

(8) Armes, S. P.; Aldissi, M.; Agnew, S. F.; Gottesfeld, S. *Langmuir* **1990,** *6,* 1745.

(9) Banerjee, P.; Bhattacharyya, S. N.; Mandal, B. M. *Langmuir* **1995,** *11,* 2414.

(10) Chattopadhyay, D.; Banerjee, S.; Chakravorty, D.; Mandal, B. M. *Langmuir* **1998,** *14,* 1544.

(11) Chattopadhyay, D.; Mandal, B. M. *Langmuir* **1996,** *12,* 1585.

(12) Gospodinova, N.; Mokreva, P.; Terlemezyan, L. *Chem. Commun.* **1992,** 923.

(13) Riede, A.; Helmstedt, M.; Riede, V.; Stejskal, J. *Langmuir* **1998,** *14,* 6767.

(14) Riede, A.; Helmstedt, M.; Riede, V.; Stejskal, J. *Colloid Polym. Sci.* **1997,** *275,* 814.

(15) Stejskal, J.; Kratochvil, P.; Armes, S. P.; Lascelles, S. F.; Riede, A.; Helmstedt, M.; Prokes, J.; Krivka, I. *Macromolecules* **1996,** *29,* 6814.

(16) Gill, M.; Armes, S. P.; Fairhurst, D.; Emmett, S. N.; Idzorek, G.; Pigott, T. *Langmuir* **1992,** *8,* 2178.

(17) Kim, D.; Kim, J. Y.; Kim, E. R.; Sohn, D. *Mol. Cryst. Liq. Cryst.* **2002,** *377,* 345.

(18) Sapurina, I.; Stejskal, J.; Tuzar, Z. *Colloids Surf., A* **2001,** *180,* 193.

(19) Stejskal, J.; Spirkova, M.; Riede, A.; Helmstedt, M.; Mokreva, P.; Prokes, J. *Polymer* **1999,** *40,* 2487.

(20) Zhiyong, T.; Shaoqin, L.; Zhenxin, W.; Shaojun, D.; Erkang, W. *Electrochem. Commun.* **2000,** 32.

(21) Gan, L. M.; Chew, C. H.; Hardy, S. O.; Ma, L. *Polym. Bull.* **1993,** *31,* 347.

(22) Selvan, S. T.; Mani, A.; Athinarayanasamy, K.; Phani, K. L.; Pitchumani, S. *Mater. Res. Bull.* **1995,** *30,* 699.

(23) Marie, E.; Rothe, R.; Antonietti, M.; Landfester, K. *Macromolecules* **2003,** *36,* 3967.

Recently, micellar solutions of sodium dodecyl sulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS) were employed to produce colloidal polymeric particles dispersible in water.[27−32] Previous reports mainly focused on the effect of monomer and surfactant concentration on composition, morphology, crystalline nature, and conductivity of PANI particles. Attempts have also been made to understand conformation of CSA-doped polyaniline in organic solvents such as *m*-cresol or *N*-methylpyrrolidinone (NMP) using dynamic light scattering, and the results suggest that in dilute solutions the polymer exists as a true molecular solution and the behavior is similar to that of polyelectrolytes.[3,33] However, to our knowledge, there are no detailed reports on the study of effect of micelle size or shape on size of colloidal polyaniline nanoparticles and its conformation in aqueous solutions. A systematic study in this direction is particularly important because the presence of positively charged anilinium ions can significantly change the structure of anionic micelles due to adsorption of the aromatic anions on the surface of the micelles.

In this study, we investigate the effect of micelle size and shape on size, morphology, and stability of PANI nanoparticles prepared in anionic SDS micelles. Addition of inorganic or organic salts to ionic micelles can induce structural changes in micelles through screening of electrostatic interactions. Organic salts that contain a hydrophobic part and possess a charge opposite to that of the surfactant molecule are highly efficient in promoting a structural transition in micelles. Sodium salts of organic acids such as salicylates, *p*-toluenesulfonates, chlorobenzoates, alkyl sulfates, and hydroxynaphthalenecarboxylates are well-known examples of additives that changes the structure of cationic micelles from globular to rodlike or even long polymerlike micelles.[34−40] Recently, we observed a sphere to rod transition in anionic SDS micelles with the addition of a cationic hydrotropic salt, *p*-toluidine hydrochloride (PTHC).[41,42] The size and shape of micelles strongly depends on the ratio of salt to surfactant. Considering the similarity of this salt to aniline hydrochloride, it can be envisaged that when polymerization of aniline is carried out in the presence of SDS micelles there could be a significant change in the structure of micelles

depending on the ratio of monomer to surfactant and this in turn could affect the particle size and morphology of the final polymer product.

With a view to investigate the above effect, polymerization of aniline was carried out at different ratios of monomer to surfactant and a correlation between the size of PANI particles and the size of the micelles was obtained. Addition of the monomer aniline in acidic medium to anionic micelles of SDS changes the microstructure of micelles from nearly spherical aggregates to rodlike micelles. The change in microstructure of micelles and effect of micelle structure on size and stability of colloidal polymeric particles were investigated using dynamic light scattering (DLS). A direct correlation was observed between size of the particles and size of the micelles. By proper control of the micelle size and concentration, stable PANI colloidal suspensions with an average hydrodynamic diameter of 15−200 nm could be prepared in SDS micelles.

Experimental Section

1. Chemicals. SDS (electrophoresis grade) was obtained from Sisco Research Laboratories, Mumbai, India. Aniline hydrochloride (AHC) was from Fluka, and ammonium peroxodisulfate (APS) (AR grade) was purchased from Thomas Baker, Mumbai, India. Deionized water from a Millipore-MilliQ system (resistivity ∼ 18MΩ cm) was used in all cases to prepare aqueous solutions.

2. Polymerization. Polymerization of aniline was carried out in the presence of SDS micelles using APS as the oxidant at room temperature. Two sets of experiments were carried out: one at constant SDS concentration and varying the molar ratio of AHC to SDS and the second at constant ratio of AHC to SDS with varying SDS concentration. The molar ratio of AHC to APS is kept constant in all the experiments.

3. Instrumentation. Dynamic light scattering (DLS) measurements were performed using a Malvern 4800 Autosizer employing a 7132 digital correlator. The light source was an Ar-ion laser operated at 514.5 nm with maximum power output of 2 W. The correlation functions were analyzed by the method of cumulants[43] and using a CONTIN algorithm for inverse Laplace transformation.[44,45] Measurements were made at five different angles ranging from 50 to 130°. The samples of micellar solutions were filtered through 0.2 μm filters (Acrodisc) to avoid interference from dust particles. For polymer characterization, the samples (surfactant and monomer mixture) were filtered before polymerization and a small volume of the final polymer was diluted with filtered deionized water.

AFM measurements were carried out in contact mode using a scanning probe microscope (SPM-Solver P47, NT-MDT, Russia). Rectangular cantilevers of silicon nitride having force constant of 3 N/m were employed for measurement. Optical absorption measurements were carried out on a Chemito Spectrascan UV2600 spectrophotometer in the wavelength range of 400−1100 nm.

Results and Discussion

1. Effect of Monomer on Micelle Size. To investigate the effect of dissolved monomer on size and shape of anionic SDS micelles, DLS measurements were carried out on 50 mM SDS solutions at different concentration of AHC. The concentration of surfactant was kept constant (50 mM), and the ratio of concentrations of salt to surfactant (x_{AHC} = [AHC]/[SDS]) was varied from 0 to 1. When the ratio x_{AHC} was greater than 1.1, the solution was found to become turbid due to complexation of cationic anilinium ions with anionic dodecyl sulfate forming an insoluble ion pair. This result is very similar to reports published on other cationic−anionic mixtures where an insoluble catanionic

(24) Zhang, Z. M.; Wei, Z. X.; Wan, M. X. *Macromolecules* **2002**, *35*, 5937.

(25) Rao, P. S.; Sathyanarayana, D. N.; Palaniappan, S. *Macromolecules* **2002**, *35*, 4988.

(26) Kim, D.; Choi, J.; Kim, J. Y.; Han, Y. K.; Sohn, D. *Macromolecules* **2002**, *35*, 5314.

(27) Kuramoto, N.; Genies, E. M. *Synth. Met.* **1995**, *68*, 191.

(28) Kuramoto, N.; Tomita, A. *Polymer* **1997**, *38*, 3055.

(29) Gospodinova, N.; Mokreva, P.; Tsanov, T.; Terlemezyan, L. *Polymer* **1997**, *38*, 743.

(30) Kim, B. J.; Oh, S. G.; Han, M. G.; Im, S. S. *Langmuir* **2000**, *16*, 5841.

(31) Kim, B. J.; Oh, S. G.; Han, M. G.; Im, S. S. *Synth. Met.* **2001**, *122*, 297.

(32) Han, M. G.; Seok, K. C.; Oh, S. G.; Im, S. S. *Synth. Met.* **2002**, *126*, 53.

(33) Sehgal, A.; Seery, T. A. P. *Macromolecules* **1999**, *32*, 7807.

(34) Rehage, H.; Hoffman, H. *Mol. Phys.* **1991**, *74*, 933.

(35) Buwalda, R. T.; Stuart, M. C. A.; Engberts, J. B. F. N. *Langmuir* **2000**, *16*, 6780.

(36) Carver, M.; Smith, T. L.; Gee, J. C.; Delichere, A.; Caponetti, E.; Magid, L. J. *Langmuir* **1996**, *12*, 691.

(37) Hassan, P. A.; Candau, S. J.; Kern, F.; Manohar, C. *Langmuir* **1998**, *14*, 6025.

(38) Hassan, P. A.; Valaulikar, B. S.; Manohar, C.; Kern, F.; Bourdieu, L.; Candau, S. J. *Langmuir* **1996**, *12*, 4350.

(39) Hassan, P. A.; Yakhmi, J. V. *Langmuir* **2000**, *16*, 7187.

(40) Hassan, P. A.; Manohar, C. *J. Phys. Chem. B* **1998**, *102*, 7120.

(41) Hassan, P. A.; Raghavan, S. R.; Kaler, E. W. *Langmuir* **2002**, *18*, 2543.

(42) Hassan, P. A.; Fritz, G.; Kaler, E. W. *J. Colloid Interface Sci.* **2003**, *257*, 154.

(43) Brown, J. C.; Pusey, P. N.; Dietz, R. *J. Chem. Phys.* **1975**, *62*, 1136.

(44) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213.

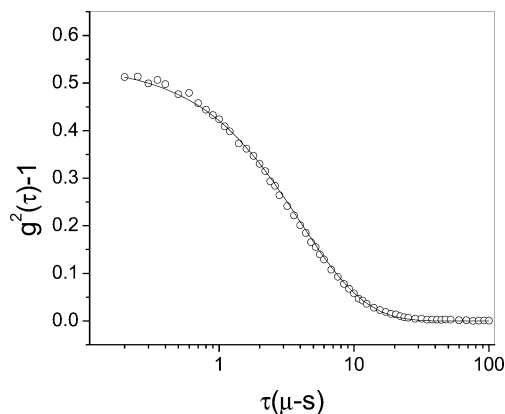(45) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 229.

Figure 1. Representative plot of the intensity correlation function for 50 mM SDS with $x_{AHC} = 0.3$ at a scattering angle of 130°. The solid line is fit to the data using the method of cumulants.

Figure 2. Angular variation of the average decay rates (Γ) of the electric field correlation function as a function of q^2 for 50 mM SDS at different x_{AHC} values.

salt is precipitated near the equimolar ratio of the mixture.[46,47] For a mixture of SDS (50 mM) and PTHC such precipitation occurs when the ratio of salt to surfactant, x_{PTHC}, is >0.7.[41] The precipitation at higher value of x_{AHC} as compared to x_{PTHC} is due to the lesser hydrophobicity of AHC as compared to that of PTHC. The formation of an insoluble catanionic salt with additives is very much sensitive to the hydrophobicity of the additive as well as the asymmetry in chain lengths of the two cationic−anionic pairs.[37,48] For example, in cationic micelles such as CTAB (100 mM), no precipitation occurrs when sodium salicylate is used as the additve but a catanionic precipitate is formed near the equimolar ratio when sodium hydroxy naphthalene carboxylate is used as the additive.[49]

Figure 1 shows a representative plot of the intensity correlation function measured for 50 mM SDS with $x_{AHC} = 0.3$ at a scattering angle of 130°. Measurements of the autocorrelation function were not made for $x_{AHC} < 0.3$ due to very low scattering intensity of ionic SDS micelles. Small-angle neutron scattering (SANS) studies clearly reveal that, in the absence of salt, 50 mM SDS forms nearly globular micelles with a repulsive intermicellar interaction as evident from the existence of a correlation peak in the spectra.[42] The wavelength of light being large compared to the size of micelles, the average light scattering intensity of micelles will be proportional to the osmotic compressibility of the fluid. A repulsive intermicellar interaction would lead to a decrease in the compressibility of the fluid and hence a decrease in the intensity of light scattered. With the addition of salt the intermicellar interaction decreases and hence increases the compressibility and thereby the scattering intensity. This increases the signal-to-noise ratio and enables measurements of the intensity correlation spectra. Thus, DLS measurements were restricted to the range $0.3 < x_{AHC} \leq 1$, where a clear isotropic phase exists.

The nature of the correlation function shown in Figure 1 reveals a unimodal distribution of relaxation rates, and hence, the data were analyzed by the method of cumulants using a two-parameter fit with the mean and variance of
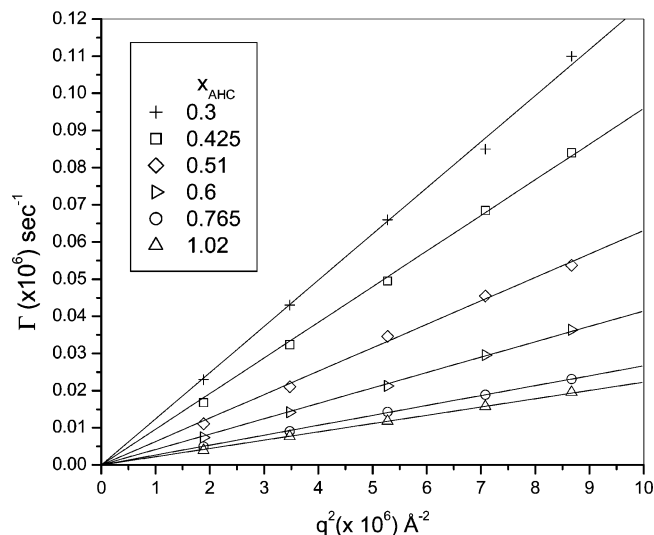
the relaxation rate as the fitted variable. The solid line in Figure 1 is fit to the data with a relaxation rate (Γ) of $0.11 \, \mu s^{-1}$ and a polydispersity index (variance/(mean)^2) of 0.2 and, it reveals a reasonably good fit with this model. Using the CONTIN algorithm that uses a constraint regularization method, an analysis has been made to obtain the inverse Laplace transform of the measured data which shows only one peak in the distribution supporting the validity of the cumulants method. Thus, we restrict our analysis to the method of cumulants for estimating the diffusion coefficient of micelles. The angular variations of the average decay rates (Γ) of the electric field correlation function obtained from the fit are shown in Figure 2 as a function of q^2, where q is the magnitude of the scattering vector given by $q = (4\pi n/\lambda) \sin(\theta/2)$, n being the refractive index of solvent, λ the wavelength of light, and θ the scattering angle. For all the samples the data falls on a linear plot passing through the origin indicating translational diffusion of the scatterers. A progressive decrease in the slope of the Γ vs q^2 plots with an increase in x_{AHC} points to a decrease in the apparent diffusion coefficient of the micelles.

Figure 3 shows the variation of apparent diffusion coefficient, D_a, as obtained from the slope of the plots of Γ vs q^2 at different molar ratios x_{AHC} for 50 mM SDS. It is observed that, for $x_{AHC} = 0.3$, the D_a is in the same range as that expected for small globular micelles with a hydrodynamic diameter of 3.9 nm as calculated using the Stokes−Einstein relationship. With successive addition of AHC, the D_a drops steeply reflecting a sudden increase in the average dimension of the micelle. At $x_{AHC} = 1$, the D_a value is 19.1×10^{-8} cm^2/s, which corresponds to an equivalent sphere diameter of 25.6 nm. However, it is unrealistic to have an isotropic spherical micelle having a diameter of 25.6 nm from SDS molecules as this will leave a vacuum at the center of the micelles, the maximum extended length of a dodecyl chain being only 1.7 nm. The observed drastic decrease in D_a suggests that the micelle has to grow anisotropically either as an oblate ellipsoid or as a prolate ellipsoid. A drastic change in the relative viscosity of the fluid is also observed with addition of AHC to SDS micelles. It is known that the change in the relative viscosity of a suspension of oblate ellipsoids is much smaller than that for prolate ellispoids. Thus, it is reasonable to consider the micellar growth in terms of prolate ellipsoids. The added salt AHC is analogous to

(46) Herrington, K. L.; Kaler, E. W.; Miller, D. D.; Zasadzinski, J. A.; Chiruvolu, S. *J. Phys. Chem.* **1993**, *97*, 13792.

(47) Kaler, E. W.; Herrington, K. L.; Murthy, A. K.; Zasadzinski, J. A. N. *J. Phys. Chem.* **1992**, *96*, 6698.

(48) Shiao, S. Y.; Chhabra, V.; Patist, A.; Free, M. L.; Huibers, P. D. T.; Gregory, A.; Patel, S.; Shah, D. O. *Adv. Colloid Interface. Sci.* **1998**, *74*, 1.

(49) Mishra, B. K.; Samant, S. D.; Pradhan, P.; Mishra, S. B.; Manohar, C. *Langmuir* **1993**, *9*, 894.
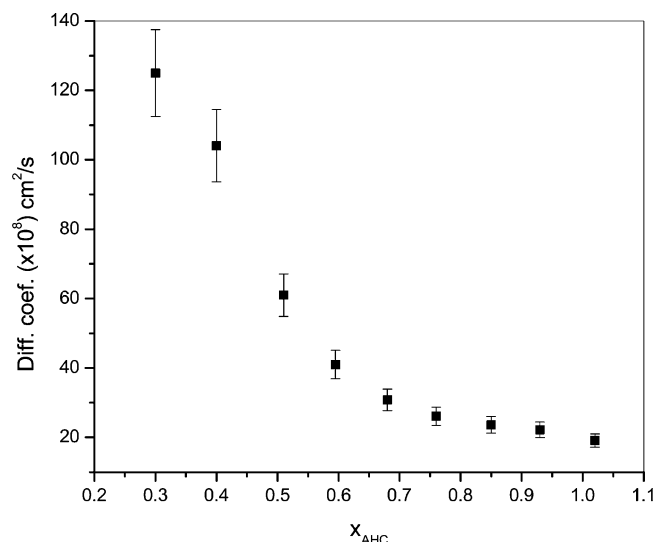
Figure 3. Variation of apparent diffusion coefficient, D_a (obtained from the slope of the plots of Γ vs q^2), at different molar ratios, x_{AHC}, for 50 mM SDS.

Figure 4. Average length (L) of the micelle as a function of x_{AHC} calculated from the diffusion coefficient data assuming a prolate ellipsoidal structure for the micelles.

PTHC addition of which indeed leads to a growth of prolate ellipsoids.[41,42]

Assuming a prolate ellipsoidal growth, the lengths of the micelles were estimated using Perrin's formula[50] that relates the average diffusion coefficient to the axes of the ellipsoid. For anisotropic scatterers such as rods or ellipsoids, the intensity correlation function could be modified by the coupling between translational and rotational diffusion.[51] At low scattering vectors, $qL < 3$, where L is the length of a rod, only translational motion contributes significantly to the dynamic structure factor.[50] As qL becomes larger, the rotational motion of the rod increasingly contributes to the signal. This leads to a nonlinear dependence of Γ vs q^2 plots at higher q values. As can be seen from Figure 2, a linear dependence of Γ vs q^2 plots indicates that there is negligible contribution from rotational motion of anisotropic micelles for all the concentrations studied. A correction for the measured D_a for possible hydrodynamic and thermodynamic contributions were applied during the data analysis as reported earlier.[41] The semiminor axis of the ellipsoid is taken as constant at 1.67 nm, and only the semimajor axis is varied. The average length L of the micelle as obtained from the major axis of the ellipsoid is depicted in Figure 4. A marked increase is observed in the length of the micelles, viz. from 4.8 to 163 nm with addition of AHC.

The main influence of an added salt to an ionic surfactant micelle is to screen the electrostatic repulsion between the charged headgroups of the amphiphiles and thereby decrease the average area/headgroup (a_o) at the hydrocarbon–water interface. In case of hydrophobic salts, the decrease of headgroup repulsion is further facilitated by the formation of a catanionic salt. Geometric packing considerations suggest that a decrease in the value of a_o can lead to a transition in the micellar geometry from spheres to cylinders.[52] Surfactant molecules in the hemispherical ends of a cylindrical micelle possess excess packing free energy, known as the end-cap energy, and the average micelle length increases exponentially with
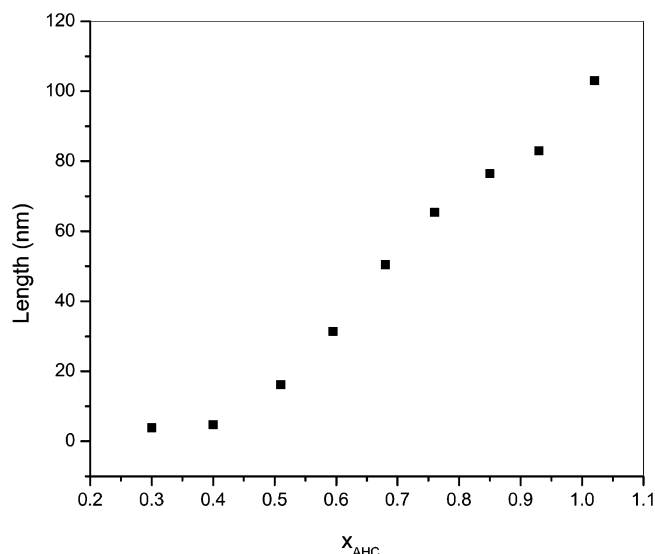
the end-cap energy leading to the formation of long micelles.[53] The above DLS results indicate that the micelles exhibit a linear growth resulting in the formation of rodlike micelles. Thus, by adjusting the ratio of monomer to surfactant, it is possible to tranform the geometry of the micelles from spheres to long rods in a controlled fashion.

2. Preparation of PANI Nanoparticles. Polymerization of aniline adsorbed on the surface of anionic micelles was carried out chemically using APS under different morpholgy of micelles. For polymerization studies, the SDS concentration is fixed at 50 mM and x_{AHC} is varied from 0.2 to 1.0. It is known that the presence of an acid is necessary for polymerization to proceed since a protonated polymer can alone accept a new monomer.[54] In this study, no acid is added to the medium as we used the salt aniline hydrochloride, instead of aniline. Moreover, in the presence of SDS, PANI is already protonated even at pH 7 while in the absence of SDS a pH of 4 is required for protonation.[55] The existence of the PANI in the emeraldine salt form at a higher pH (pH = 7) in the presence of SDS can be explained in terms of the formation of a stable complex between the dodecyl sulfate anion and the cationic emeraldine salt form of the polymer. Preliminary studies indicated that the size of the polymer particles depends also on the molar ratio of APS to aniline, and thus, this ratio is kept constant (equal to 1) in all the samples. Previous reports also show that the amount of oxidizing agent has a great influence on the molecular weight of the polymer.[23] The polymerization of aniline progressed quickly after a small induction period of 10–15 min and a bluish green color developed in the solution. Surfactant-stabilized stable colloidal suspensions of polyaniline nanoparticles were formed in all samples. The slow kinetics of polymerization of aniline in SDS micelles could be because of the complexation of cationic anilinium ions with anionic surfactant. The optical absorption spectra of the as-prepared PANI particles indicate that the polymer exists in the emeraldine salt form. The transition from emeraldine salt to emeraldine base form by the addition

(50) Berne, B. J.; Pecora, R. *Dynamic Light Scattering: With Application to Chemistry Biology And Physics*; J. Wiley and Sons: New York, 1976.

(51) Phalakornkul, J. K.; Gast, A. P.; Pecora, R. *Macromolecules* **1999**, *32*, 3122.

(52) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans.* **1976**, *72*, 1525.

(53) Cates, M. E.; Candau, S. J. *J. Phys.: Condens. Matter* **1990**, *2*, 6869.

(54) Gospodinova, N.; Terlemezyan, L. *Prog. Polym. Sci.* **1998**, *23*, 1443.

(55) Kiriy, A.; Gorodyska, G.; Minko, S.; Jaeger, W.; Stepanek, P.; Stamm, M. *J. Am. Chem. Soc.* **2002**, *124*, 13454.
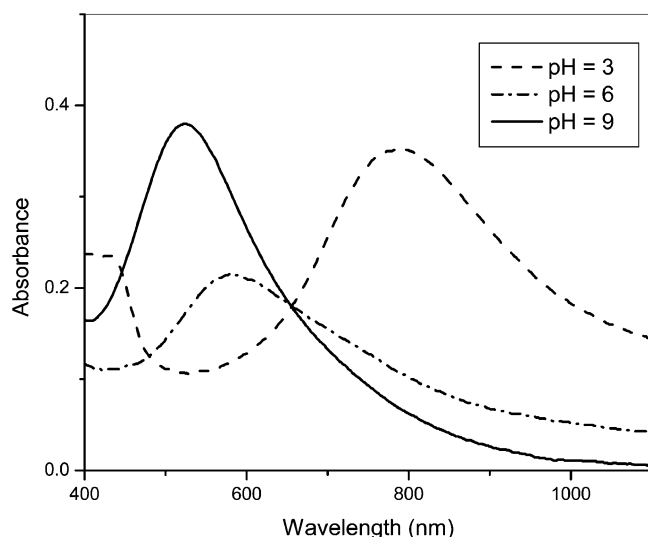
Figure 5. Optical absorption spectra of polyaniline nanoparticles at three different pH values.

Figure 6. Variation of the average hydrodynamic diameter of polyaniline particles prepared in 50 mM SDS micelles with different x_{AHC} values at different reaction times.

of aqueous NaOH to the colloidal PANI is evident from the absorption spectra. Figure 5 shows the optical absorption spectra of PANI colloids at three different pH values, e.g., pH 3.0, 6.0, and 9.0. The absorption spectra of SDS-stabilized PANI particles and its pH dependence were similar to that reported earlier.[27] It is worth mentioning that formation of PANI nanoparticles could certainly alter the strucutre of micelles due to consumption of AHC monomers.

Dynamic light scattering (DLS) measurements were carried out on surfactant-stabilized PANI particles during the course of the polymerization process to assess the average hydrodynamic diameter of the particles. For DLS mesurements, an aliquot of the sample is diluted enough so as to reach a surfactant concentration of 1 mM. As the concentration of surfactant is much less than the cmc, there is little possibility of contribution from the scattering of micelles. Also, dilution of the polymer particles will ensure the absence of interparticle interactions. Due to the strong absorption of PANI particles in solution, thermal lensing and consequent coning of the laser beam could introduce additional errors in the measurement.[33] This error can also be minimized by dilution so that the absorbance is small at the wavelength of measurement. All samples were characterized as-prepared after diluting with filtered deionized water so that polyaniline exists in the emeraldine salt form for which the absorbance show a minimum at the wavelength of measurement.

The effective hydrodynamic diameter of polymer particles increases successively with time and finally reaches a constant value. Thus, the particles were analyzed at different times of polymerization process. Figure 6 shows a plot of variation of the average hydrodynamic diameter of particles with x_{AHC} at diferent reaction times. The intensity correlation function was analyzed by CONTIN algorithm to get an estimate of the size distribution. CONTIN was preferred to cumulants as it was observed that in certain cases, unlike micelles, the particles were bimodal in nature probably because of some agglomeration of the particles. However, the contributions from larger size particles are significantly smaller indicating a very small population of larger particles and the distribution became unimodal with increase in time. Considering the fact that DLS measures the z-average diffusion coefficient of the particles and the distribution will be heavily weighted toward larger size particles, a small population of larger particles in the intensity weighted results can
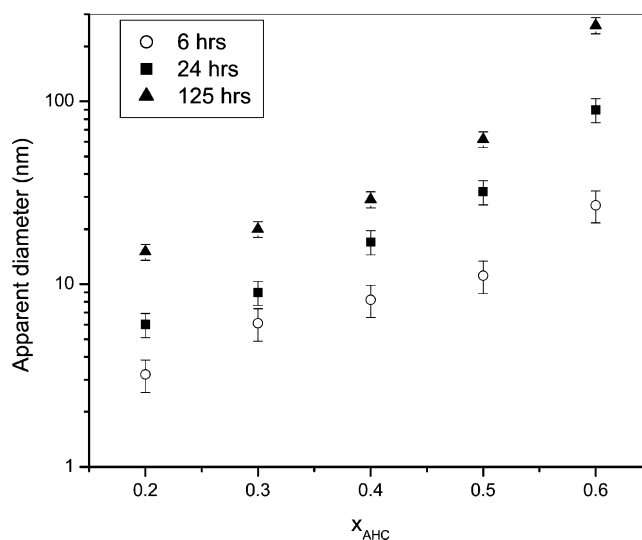
be neglected. The angular variation of the relaxation rate is consistent with the center-of-mass diffusion of the polymers indicating little contribution from the internal chain dynamics.

As x_{AHC} increases, an increase in the average diameter (size) of the particles was observed. When $x_{AHC} > 0.6$, the average size of the polymer particles grows leading to sedimentation of the particles after keeping for several days. Thus, no DLS is carried out on samples above $x_{AHC} = 0.6$. All polymer particles prepared at $x_{AHC} < 0.6$ remained as a colloidal suspension without sedimentation even after keeping for more than 3 months. The sedimentation of the particles for $x_{AHC} > 0.6$ is also an indication of an increase in size of the particles with increase in x_{AHC}. Our experiments demonstrate that PANI particles of controlled size from a few nanometers to 200 nm could be prepared as a water-dispersible colloid using SDS micelles of controlled size.

Addition of AHC induces growth of the micelles from spheres to long rods due to the screening of electrostatic interactions and consequent changes in the surfactant packing parameter. At a given volume fraction, an increase in micelle size corresponds to a decrease in the number density of the micelles. Both decrease in number density of the micelles and increase in aniline concentration leads to an increase in the average number of monomers/micelle. Thus, the observed increase in the hydrodynamic diameter of PANI colloids with an increase in x_{AHC} can be thought of as a consequence of increase in number of monomers/micelle. However, the concentration of the monomer also increases with increase in x_{AHC} and it is necessary to check its effect by keeping the micelle size constant. This has been achieved by restricting the ratio x_{AHC} constant and varying SDS concentration so that the number density of micelles is varied. Polymerization of the sample under these conditions revealed that the particle size increases with an increase in micelle concentration. The resulting average sizes of the particles after 125 h with an increase in SDS concentration are plotted in Figure 7. It is observed that the size of the particles increased from 20 to 70 nm by doubling the concentration of monomer, keeping the micelle size the same as opposed to a large increase in size from 20 to 250 nm when the micelle size is increased. Thus, it is clear that both the size of micelles and the monomer concentration play a role in dictating the size of polymer particles. But the effect is more pronounced
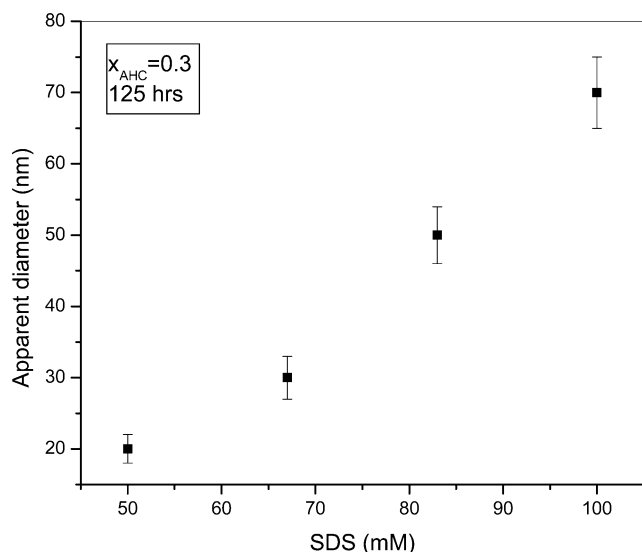
Figure 7. Variation of the average hydrodynamic diameter of the polyaniline particles with an increase in SDS concentration after 125 h of the reaction at $x_{AHC} = 0.3$.

with increase in size of micelles. The dynamic equilibrium of micelles could permit collisions and subsequent exchange of monomers among micelles. Such redistributions of components among droplets of water-in-oil microemulsions are well documented.

Anionic surfactants can influence the formation of PANI colloids in different ways. They can act as a dopant thereby stabilizing the emeraldine salt form of the polymer. Doping with surfactants are known to improve the solubility of the polymer in organic solvents. Owing to the hydrophobic nature of aniline, these monomers can preferentially get partitioned into the micellar phase thereby increasing its local concentration in the reaction medium. The positively charged nature of anilinium ion in AHC further facilitates the adsorption of this molecule on the surface of anionic micelles through electrostatic interactions. The orientation of the monomers on micellar surface is specific in nature, and such specific orientations can induce regioselectivity to the reaction and change the reaction kinetics. The locus of solubilization and orientation of solubilized molecules in micelles can be inferred from NMR spectroscopy. NMR studies on an analogous salt PTHC (a substituted aniline) in SDS micelles showed that the molecule resides on the surface of the micelles with the NH₂ group and the *ortho* protons experience a hydrophilic environment while the *meta* and *para* protons experience a hydrophobic environment.[41] We expect a similar orientation for AHC due to similarity in chemical structure. We believe that both the orientation of the monomers and the changes in local concentration could play a role in controlling the size and morphology of the particles.

To compare the results from DLS, AFM observations were made on PANI dispersions prepared at a surfactant concentration of 100 mM and $x_{AHC} = 0.3$. A drop of the dilute colloidal solution of PANI was dried on a polished silicon wafer, and the wafer was successively rinsed with methanol many times to remove any excess surfactant and again dried in air. The air-dried specimens were left under an IR lamp for 1 h before AFM observation, and the corresponding image is shown in Figure 8. The image shows nanosized colloidal particles of PANI with lateral dimensions (*x* and *y*) of the order of 100 nm (see inset of Figure 8), and in the vertical direction (*z*) an average height of 30 nm is observed. The asymmetry of the particle size in the lateral and vertical directions of the image could
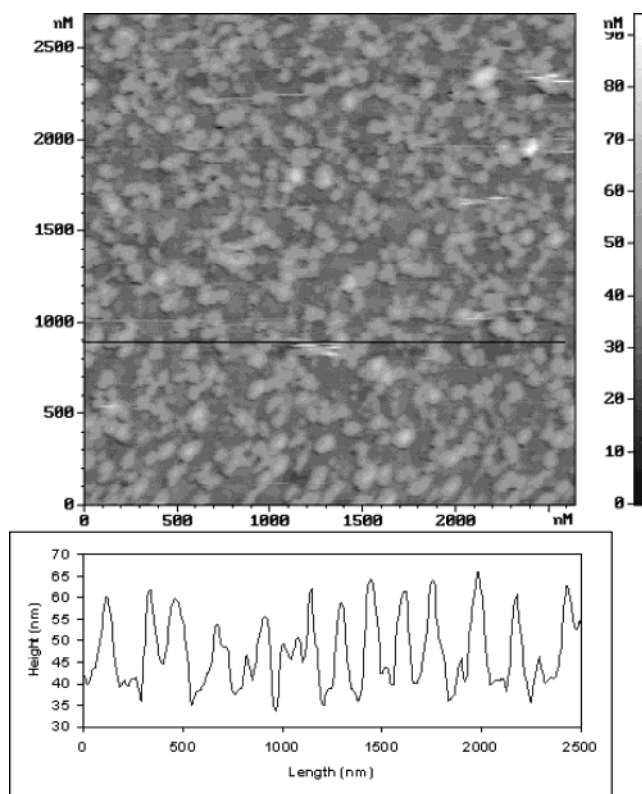

Figure 8. (a) Representative contact mode AFM micrograph of PANI particles at 100 mM SDS and $x_{AHC} = 0.3$. (b) Height profile along the horizontal plane marked on the image.

be due to the collapse of the polymer particles during the drying process leading to a decreased dimension in the vertical direction and spreading of the polymer chains in the lateral direction. DLS studies on theses particles showed an effective diameter of 70 nm that is intermediate between the two dimensions observed by AFM, suggesting conformational change of the polymer particles during drying. Recent studies on single-molecule imaging of a kinetically frozen hydrophobic flexible polyelectrolyte, poly(2-vinylpyridine), on a mica surface suggest that the polymer undergoes a collapse in the *z*-direction during solvent evaporation.[55] Because of the charged nature of the backbone of PANI, the behavior of these polymers in solution can be compared to that of polyelectrolytes. Polyelectrolytes undergo diverse conformational changes with changes in ionic strength, pH, temperature, concentration, etc., driven by interplay between short-range attractive van der Waals forces and long-range repulsive Coulomb interactions. Thus, it is expected that the polymer morphology could be altered during evaporation of the solvent.

Further insight into the conformation of the polymer in aqueous solutions can be obtained from a comparison of the static and dynamic light scattering data. In static light scattering (SLS), the excess scattering intensity of the polymer over the solvent as a function of the angle of scattering is measured. SLS permits one to estimate the radius of gyration (R_g) of the polymer colloids. For low-scattering vectors, i.e. $qR_g < 1$, the scattering intensity follows the well-known Guinier law,

$$I(q) = I(0) \exp(-q^2 R_g^2/3)$$

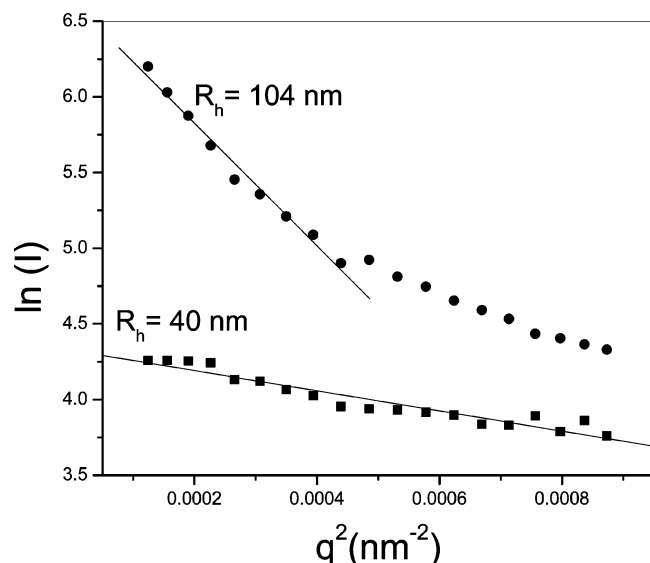from which the *z*-averaged mean square radius of gyration of the polymer can be estimated. DLS provides the average

Figure 9. Static light scattering data in the form of Guinier plots for two different size polyaniline dispersions (R_h = 40 and 104 nm).

hydrodynamic radius (R_h) that characterizes the center of mass diffusion of the polymer chains in the solvent at the specified condition. SLS measurements were carried out on two different size PANI particles having average hydrodynamic radii of 40 and 104 nm, respectively, and the corresponding Guinier plots are shown in Figure 9. For a polymer with R_h = 40 nm, the Guinier plot is linear in the entire q-range and gives an R_g of 45 nm. However, for a polymer with R_h = 104 nm, the curve shows a nonlinear variation and extrapolation of the data at small q values gives an R_g of 115 nm. The nonlinearity of the plot at higher q values arises from the fact that as $qR_g > 1$, SLS probes the interior of the polymer colloids. The R_g values were estimated at two different dilutions of the samples, and no significant change in the R_g was observed thereby discarding the possibility of any contribution from interparticle interactions. The value of R_g/R_h is found to be ~1.1 for both the samples suggesting that the conformation of the polymer is same irrespective of its molecular weight. For a Gaussian coil in Θ solvents, the value of R_g/R_h is expected to be 1.56, and for hard sphere colloids it is 0.78.[56] The observed value of 1.1 for the present system suggests that the conformation of the polymer is intermediate between a fully swollen state (Gaussian coils) and a collapsed state. The conformations of polyelectrolytes are found to be sensitive to its persistence length as well. Reports on the emeraldine salt form of PANI in m-cresol show that based on scaling theories the power law exponents fall intermediate between intrinsically rigid and flexible polymers.[8] A coillike conformation with a persistence length much larger than the effective conjugation length is observed in similar linear conjugated polymers.[57,58] SDS can act as a dopant for the emeraldine salt thereby making the polymer hydrophobic, and subsequent adsorption of excess SDS leads to stabilization of this colloid.

The X-ray diffraction patterns of the PANI powders polymerized at different micelle sizes were obtained after precipitating the polymer by adding methanol. The precipitated polymer is filtered out, washed successively with water to remove excess surfactant, and then dried in a vacuum. The XRD patterns were similar to those reported earlier and had very broad peaks at around 2θ = 20 and 25°.[31] No changes in the diffractograms were observed with changes in particle size of the polymer. All the polymer particles exhibited poor crystallinity as judged from the widths of the XRD peaks possibly due to the very low particle sizes or amorphous nature of the polymer. A high degree of crystallinity of the polymer is a signature of good conductivity. The observed diffractograms of the nanoparticles reveal poor crystallinity to the material. The decrease in molecular weight of the polymer and the changes in the kinetics of nucleation and growth of the particles in micelles could significantly affect the crystallinity of the material. Reports show that introduction of surfactant molecules can alter the crystallinity of the material.[25] We believe that by properly controlling the kinetics of the reaction one can improve upon the crstallinity and obtain highly ordered PANI particles with fewer structural defects. More work is required in this direction to optimize the conditions for obtaining materials with improved crystallinity. A low reaction temperature (<5 °C) and high acidity (pH < 2) of the reaction medium are favorable for the production of PANI with high crystallinity.[31] Due to precipitation of surfactants below its Kraft point polymerization could not be carried out in SDS micellar media at temperatures as low as 5 °C. In addition to crystallinity, other factors such as doping level, polaron mobility and concentration, grain boundries, etc., can also modify the conductivity of the material. Thus, the conductivity of the PANI nanoparticles could be improved by controlling these parameters.

Conclusions

Polyaniline nanoparticles have been synthesized in anionic micelles of varying size to control the particle size of the polymer. The effects of monomer concentration on the size and shape of SDS micelles were investigated by DLS. Solubilization of aniline hydrochloride in SDS micelles leads to uniaxial growth of the micelles from nearly spherical to rodlike micelles. The micelle size can be tuned from small 3 nm spheres to rods of length around 100 nm by controlling the ratio of AHC to SDS. Polymerization of aniline in micelles of different sizes leads to colloidal PANI particles of varying sizes. The polymerization is rather slow, and the particle size increases with reaction time until it reaches a constant value. A direct correlation between the sizes of the polymer particles and sizes of the micelles was observed. Both the micelle size and the monomer concentration influence the size of the polymer particles. AFM studies indicate a change in the conformations of the polymer during drying. Combined static and dynamic light scattering data suggest that in water the polymer exists in a partially swollen state, a conformation intermediate between Gaussian coil and globule. XRD data suggest poor crystallinity of PANI when prepared as colloidal nanoparticles.

(56) Skouri, M.; Munch, J. P.; Candau, S. J.; Neyret, S.; Candau, F. *Macromolecules* **1994**, *27*, 69.
(57) Cotts, P. M.; Swager, T. M.; Zhou, Q. *Macromolecules* **1996**, *29*, 7323.
(58) Yue, S.; Berry, G. C.; McCullough, R. D. *Macromolecules* **1996**, *29*, 933.