Polyaniline Dispersions. 6.[†] Stabilization by Colloidal Silica Particles

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ABSTRACT: Aniline was polymerized in the presence of ultrafine colloidal silica particles (hydrodynamic diameter 35 nm) in aqueous media and, given a sufficient silica concentration, colloidally stable polyaniline−silica particles were obtained. The particle size of the resulting dispersions was determined by both dynamic light scattering and disk centrifuge photosedimentometry. The typical size of these polyaniline−silica particles is in the range 300−600 nm and is insensitive to the concentration of components in the reaction mixture, temperature, or acidity of the reaction mixture. Particles produced at 0 °C are spherical and their shape becomes less defined when polymerization proceeds at 25 °C. As the silica size is increased, the composite particles become larger and their raspberry morphology more distinct. The electrical conductivity of a typical polyaniline (37.8 wt%)−silica composite is 6.1×10^{-2} S cm^{-1} at 25 °C. It grows with increasing temperature and does not depend on the frequency in the investigated range from 20 Hz to 1 MHz.

Introduction

Polyaniline[1,2] (PANI) is an electrically conducting polymer that can exist in a variety of forms.[3,4] These differ by degree of protonation or extent of oxidation and, consequently, have various optical and electrical properties. The preparation of colloidal PANI dispersions is one way of improving the processibility of this interesting, but intractable, polymer.

During dispersion polymerization,[5] a monomer soluble in the reaction medium is converted into a polymer which is insoluble under those conditions. Aggregation of growing insoluble polymer chains results in macroscopic precipitation of the polymer. If, however, a steric stabilizer is present in the system, the precipitation may be prevented and a dispersion of polymer particles, typically of submicrometer to micrometer size, is produced instead.[5] The steric stabilizer is usually another polymer soluble in the reaction medium. It becomes either physically adsorbed or chemically grafted onto the precipitating polymer. The resulting "hairy" particles are colloidally stable[6,7] and they do not aggregate.

Conventional dispersion polymerization techniques have been successfully applied by various research groups to the preparation of sterically stabilized particles of electrically conducting polymers such as polypyrrole and PANI. The preparation of dispersions solves some problems of their limited processibility. A wide range of steric stabilizers based on various water-soluble polymers, e.g. poly(2-vinylpyridine),[8,9] poly(vinyl alcohol) or poly(vinyl alcohol-*co*-vinyl acetate),[10−17] poly(oxyethylene),[18−20] poly(*N*-vinylpyrrolidone),[12,16,21,22] poly(vinyl methyl ether),[23−25] or proteins[16] have been reported by various research groups.

Armes *et al.* have recently shown tht PANI and polypyrrole colloids can be prepared by using colloidal silica[27−31] (and, in case of polypyrrole, also tin(IV) oxide sols[32]) instead of polymeric stabilizers. It is believed that, in the early stages of polymerization, the precipitating conducting polymer deposits onto the individual silica particles, which act as a high-surface-area substrate. The polymer-coated particles then aggregate.[33] Although the full details of the mechanism of the particle formation have yet to be elucidated, most of the experimental evidence indicates that silica particles are incorporated throughout the composite particles[34] rather than just on their surfaces. Eventually, no more conducting polymer is formed, and provided that there is still a sufficient excess of silica, the growing polymer−silica particles get coated by a final overlayer of silica particles. These provide long-term colloidal stability of produced submicrometer structures by both the well-known charge stabilization mechanism[7] and via steric effects. X-ray photoelectron spectra[35] and the measurements of electrophoretic mobilities[36] have confirmed that the surfaces of both PANI−silica and polypyrrole−silica particles are invariably silica-rich.

Several papers describe the effect of varying synthesis parameters such as silica concentration and morphology on the size, shape, and structure of polypyrrole−silica

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particles.[29−31] On the other hand, only a preliminary communication[26] reported the effect of silica concentration on the composition of PANI−silica particles. As far as we are aware, no other detailed follow-up studies have been published. The present work thus describes the effect of varying synthesis parameters on the size and uniformity of PANI−silica composite particles.

Experimental Section

Preparation of Polyaniline Dispersions. Aniline hydrochloride (and hydrochloric acid in one series of experiments) was dissolved in water, and colloidal silica (typically Ludox AS-40, E.I. DuPont de Nemours product distributed by Aldrich; 40 wt % SiO_2 aqueous suspension) was added. The mixtures were thermostated to the required temperature, and a calculated volume of a 1 M aqueous solution of ammonium peroxydisulfate was added to start the polymerization of aniline. Equal molar concentrations of aniline hydrochloride and ammonium peroxydisulfate were used in all cases. In a typical experiment the reaction mixture thus contained 259 mg (2 mmol) of aniline hydrochloride, the calculated volume of colloidal silica, 1 mL of 10 M hydrochloric acid (if added), 2 mL of 1 M ammonium peroxydisulfate, and water up to 10 mL. The mixture was not stirred[21] during the polymerization. The reaction was usually completed in less than 1 h.[37,38] The resulting dispersion was then stored at room temperature. The conversion of aniline to PANI was determined spectrophotometrically,[38] ranging between 50 and 80% (the theoretical value is[3,4] 80% for equimolar mixtures of aniline hydrochloride and ammonium peroxydisulfate).

Particle Size and Uniformity by Dynamic Light Scattering. The hydrodynamic diameter of colloidal silica and PANI−silica particles, D_{DLS}, was determined by dynamic light scattering (DLS) with an Auto-Sizer Lo-C (Malvern Instruments) after dilution of dispersions with 1 M hydrochloric acid. The apparatus yields also the nonuniformity parameter, σ^2 (statistical variance of the particle-size distribution according to the manufacturer), ranging from 0 for monodisperse particles to 1 for extremely polydisperse ones. Occasionally, sedimentation of particles during repeated DLS measurements caused an apparent increase in both particle size and nonuniformity. In such cases, dilution of dispersions with a more dense medium (1 M hydrochloric acid in 5 M sodium chloride) substantially improved the reproducibility of these measurements.

Disk Centrifuge. Weight-average particle diameter, D_w, was determined by disk-centrifuge photosedimentometry (Brookhaven Instruments Corp.) as described previously.[27] The PANI−silica dispersions were centrifuged at 10 000 rpm for 20 min and the resulting dark-green sediments were redispersed in 1 M hydrochloric acid in an ultrasonic bath. The centrifugation−redispersion cycle was repeated four times in order to remove the excess silica and low molecular weight components. The sediments were then dried at 70 °C *in vacuo*. The polyaniline content was determined from the elemental analysis (MEDAC Analytical Services, Brunel University) by comparing the carbon content to that of PANI bulk powder prepared in the absence of silica. The particle densities of PANI−silica dispersions were calculated assuming the additivity rule from the densities of PANI, 1.42 g cm^{-3}, and silica, 2.14 g cm^{-3}, determined by helium pycnometry. These particle densities were used in subsequent disk-centrifuge particle-sizing measurements, which were carried out as described previously.[27]

Electrical Measurements. One of the sediments obtained after the centrifugation−redispersion cycles was carefully dried for 1 week over phosphorus pentoxide. The powder was then pressed into pellets (diameter 13 mm) with a manual hydraulic press Graseby Specac, model P/N 15.011 at 7×10^3 kg cm^{-2}, and gold electrodes were deposited *in vacuo*. The DC conductivity was measured using a DMM Solartron 7081, and the frequency characteristics were measured with LCR Hewlett-Packard meters HP 4275 A and HP 4284 A controlled by a computer.

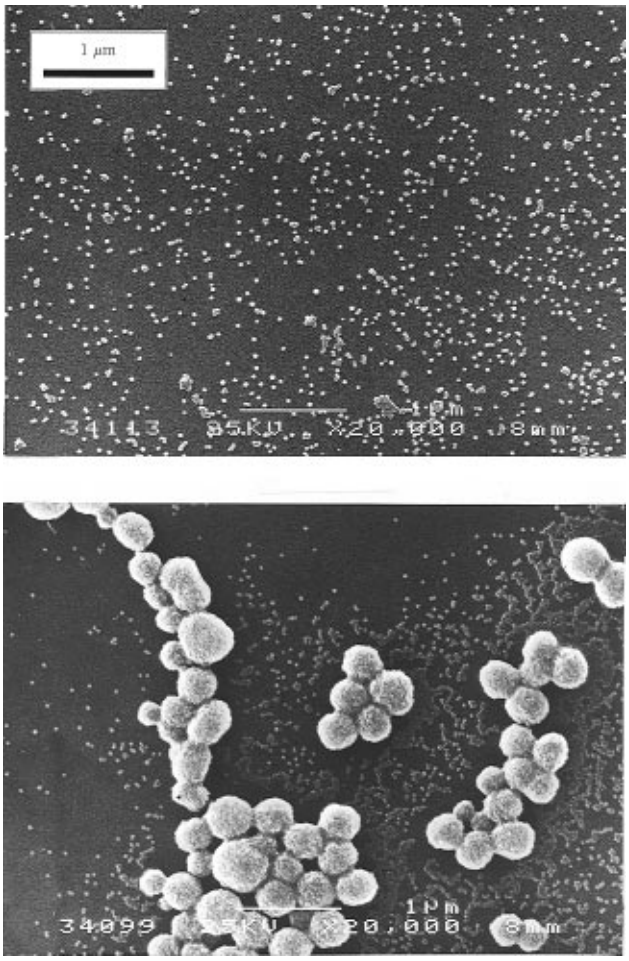

Figure 1. SEM micrographs of (a, top) colloidal silica particles (Ludox AS-40) and (b, bottom) polyaniline−silica particles obtained after dispersion polymerization of aniline.

Scanning Electron Microscopy (SEM). Dispersions were diluted with water and microsprayed on a mica substrate. The samples were sputter-coated with a 10 nm gold layer, and a JSM 6400 JEOL electron microscope was used to take micrographs.

Results and Discussion

When aniline is oxidized in the presence of ultrafine colloidal silica (Figure 1a), colloidal PANI−silica particles of composite nature are produced (Figure 1b). These particles are approximately spherical and they are covered on a surface with silica. Recent results obtained with similar polypyrrole−silica dispersions indicate that such particles have a raspberry morphology;[30,33,34] i.e., the ultrafine silica particles are present not only on the particle surface (as it would be in core−shell structure) but also distributed throughout the interior of the particles. Free colloidal silica accompanies the PANI-silica dispersion particles (Figure 1b), i.e., its incorporation into the composite particles is not complete. The dispersions have a good long-term colloidal stability, and their properties do not change for years. The apparent aggregation of particles seen in Figure 1b occurs only during drying: Dynamic light scattering measurements confirm that no aggregates of particles are present in the original dispersion (cf. Table 1).

The Effect of Silica Concentration and Acidity of the Medium. Initially, we made two series of polymerizations with an approximately constant amount of produced PANI and gradually increasing concentra-

Table 1. Effect of Silica Concentration, c_s, on the Composition, w_{PANI}, Size, D, and Nonuniformity, σ^2, of Polyaniline-Silica Dispersion Particles[a]

	1 M hydrochloric acid				no acid added	
$10^2 c_s$, g cm^{-3}	w_{PANI}, wt %	D_w, nm	D_{DLS}, nm	σ^2	D_{DLS}, nm	σ^2
1.25			1761	0.23	6060	0.26
2.5	41.2	515	1510	0.52	1740	0.18
3.75	37.2	385	508	0.18	1036	0.24
5.0	37.8[b]	385[c]	430	0.12	436	0.12
7.5	36.0	375	399	0.11	369	0.09
10	35.0	275	373	0.20	356	0.17
15	32.8	265	345	0.13	287	0.08
20	14.8	222	331	0.12	274	0.24

[a] Reaction mixture: 0.2 M aniline hydrochloride, 0.2 M ammonium peroxysulfate, and silica (Ludox AS-40) and hydrochloric acid as given above. The temperature was 0 °C. D_w is the weight-average particle diameter from disk centrifuge photosedimentry, D_{DLS} is the particle size by DLS, and σ^2 is a measure of non-uniformity (statistical variance of the particle-size distribution). [b] 47.7 vol % PANI. The electrical properties of this sample are given in Figure 5. [c] Particles are shown in Figure 1b.

tion of colloidal silica (Table 1). In the first set, aniline hydrochloride was oxidized with ammonium peroxydisulfate in 1 M hydrochloric acid at[37] pH ≈ 0−2. In the second series of experiments, water was used as the polymerization medium; i.e. the polymerization proceeded in a less acidic medium (pH ≈ 2−4).

Formation of PANI, manifested at the end of polymerization by the green coloration of the reaction mixture, takes about 1 h in water at 0 °C, while in 1 M hydrochloric acid it is completed within 20−30 min, in accord with earlier observations.[37] Unlike the rate of PANI formation, the colloidal properties are not significantly affected by the acidity of the medium (Table 1). Water was therefore used as a dispersion medium in most experiments.

The weight-average particle diameter, D_w (Table 1), obtained from disk centrifuge photosedimentometry is lower than the hydrodynamic size, D_{DLS}, obtained from DLS (evaluated from the *z*-average diffusion coefficient using the Stokes−Einstein equation). This indicates that the particles are not uniform in size, and this fact is further confirmed by the nonzero values of the nonuniformity parameter, σ^2.

The diameter of the PANI−silica particles gets smaller with increasing silica concentration in the reaction mixture (Table 1). After the initial silica concentration exceeds about 0.05 g cm^{-3}, the changes in the size and nonuniformity of composite particles are negligible (Table 1). Obviously, as long as the silica is present at a concentration which is effectively able to stabilize particles, stable dispersions are obtained, and excess silica has virtually no effect on particle size. Similar observations were reported for PANI[13,14] or polystyrene dispersions stabilized with polymeric stabilizers.

Variation of PANI Loading. In another set of polymerizations, the concentration of silica particles was kept constant, while the amount of PANI was gradually increased by increasing the concentrations of both the aniline hydrochloride monomer and the ammonium peroxydisulfate oxidant (Table 2). The colloidal properties of PANI-silica particles show similar trends as the results discussed above (Table 1). Typical particle-size distributions obtained using the disk centrifuge are narrow (Figure 2), often with shoulders, similar to those reported for polypyrrole−silica particles.[30] As more PANI is produced at fixed silica concentration, the particle size grows, and for aniline concentrations $C_a >$ 0.3 mol L^{-1}, the dispersions become colloidally unstable. The polydispersity index, σ^2, is then close to unity, indicating the presence of large aggregates and/or macroscopic particles.

Table 2. Effect of Aniline Hydrochloride Concentration, C_a, on the Composition, w_{PANI}, Size, D, and Nonuniformity, σ^2, of Polyaniline−Silica Dispersion Particles[a]

C_a, mol L^{-1}	w_{PANI}, wt %	D_w, nm	D_{DLS}, nm	σ^2
0.1	24.0	180[b]	312	0.13
0.2	18.2	255[b]	446	0.09
0.3	26.5	370[b]	760	0.12
0.4	45.0	915	1439	0.57
0.5	46.0	1030	2973	0.98

[a] For the meaning of the symbols, see Table 1. The concentrations of aniline hydrochloride and peroxydisulfate were equal; the concentration of colloidal silica (Ludox AS-40) was 0.05 g cm^{-3}, in all cases. The temperature was 0 °C. [b] Particle-size distributions are shown in Figure 2.

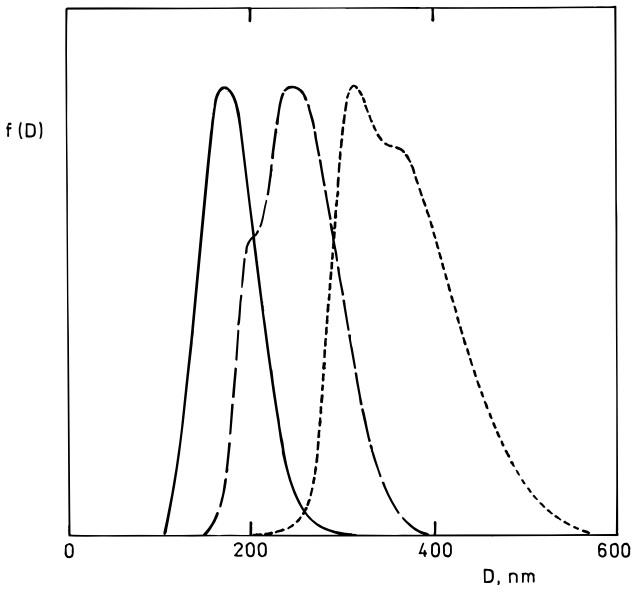

Figure 2. Differential volume distribution, *f(D)*, of particle diameter, *D*, obtained from disk centrifuge photosedimentometry for several PANI−silica samples (cf. Table 2).

Polymerization Temperature. Large polydisperse aggregates are produced when the polymerization of aniline proceeds above 30 °C. Under these conditions, the formation of PANI is rapid (a few minutes) and we assume that the diffusion of the ultrafine silica that controls the formation of composite particles is too slow to accommodate PANI into well-defined near-spherical aggregates. In the range from −10 to 30 °C, the size of PANI-silica dispersion particles is little affected by the polymerization temperature (Table 3), and only a slight decrease in particle size, as reflected by DLS, was observed with decreasing temperature. The PANI−silica particles formed at room temperature have an irregular shape (Figure 3a) while the particles prepared at 0 °C are smaller and more spherical (Figure 3b). The polymerization temperature thus affects the morphology of composite particles and not merely the particle size.

The reaction mixture used in this series of experiments freezes below −15 °C. The polymerization of aniline proceeds well even in the frozen state, although the reaction rate reduces with decreasing temperature. At −40 °C, several days were needed for the polymerization of aniline to take place. No dispersions were formed when polymerization progressed in the solid

Table 3. Dependence of the Particle Size, D_{DLS}, and Nonuniformity Parameter, σ^2, of Polyaniline−Silica Dispersion Particles on Polymerization Temperature, t[a]

t, °C	D_{DLS}, nm	σ^2	t, °C	D_{DLS}, nm	σ^2
50	2760	0.44	5	463	0.16
40	1090	0.78	0[b]	443	0.11
30	592	0.25	−5	438	0.07
25	567[b]	0.19	−10	489	0.12
20	586	0.21	−15	749	0.42
15	536	0.09	<−15	no dispersions result	
10	500	0.11			

[a] Reaction mixture: 0.2 M aniline hydrochloride, 0.2 M ammonium peroxydisulfate, and 0.05 g cm^{-3} colloidal silica (Ludox AS-40). [b] Particles are shown in Figure 3.

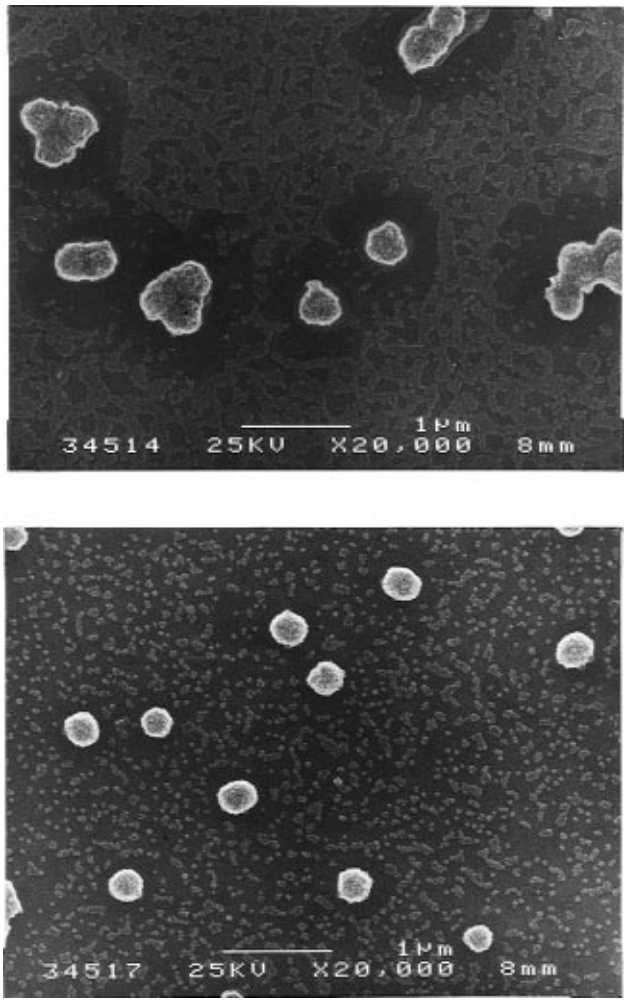

Figure 3. SEM micrographs of polyaniline−silica particles (stabilized with Ludox AS-40) prepared at (a, top) 25 °C and (b, bottom) 0 °C.

state, and only coarse precipitates were obtained after the reaction mixture had been melted.

The Influence of Silica Particle Size. The dimensions of silica particles obtained from DLS in 1 M hydrochloric acid were always higher than those provided by the manufacturers (Table 4). This is because the silica particles are rather polydisperse and different sizing methods provide various averages of particle size. There is also the possibility of the silica sols "aging" to form larger aggregates. There seems to exist a general tendency for the formation of larger PANI−silica particles when colloidal silica of larger size (as indicated by DLS) was used in the experiments (Table 4). It would be premature to draw any quantitative conclusions because commercial silicas also differ in terms of stabilizing counterions, specific surface area, etc.

Table 4. Dependence of the Particle Size, D, and Nonuniformity Parameter, σ^2, of Polyaniline−Silica Dispersion Particles on the Size of Colloidal Silica[a]

	silica			PANI−silica particles	
silica type	D_{manf}, nm	D_{DLS}, nm	σ^2	D_{DLS}, nm	σ^2
Negative Particle Charge					
Ludox SM-30	7	25	0.46	365	0.12
Ludox AS-40	22	35[b]	0.22	436[b]	0.12
Nyacol 215	10	50	0.45	549	0.13
Nyacol 5050	50	75	0.19	668	0.20
Ludox TMA	22	115	0.48	756	0.24
Non-commercial	−	195[b]	0.10	1860[b]	0.22
Positive Particle Charge					
Ludox CL[c]	12	38	0.46	856	0.24

[a] Reaction mixture: 0.2 M aniline hydrochloride, 0.2 M ammonium peroxydisulfate, 1 M hydrochloric acid, and 0.05 g cm^{-3} silica. The temperature was 0 °C. D_{manf} is the silica diameter according to the manufacturer, D_{DLS} is the size determined experimentally by DLS. Ludox is produced by E.I. DuPont de Nemours; Nyacol is distributed by Nyacol Products. [b] Particles shown in Figures 1 and 4. [c] Colloidal silica coated with a layer of alumina.

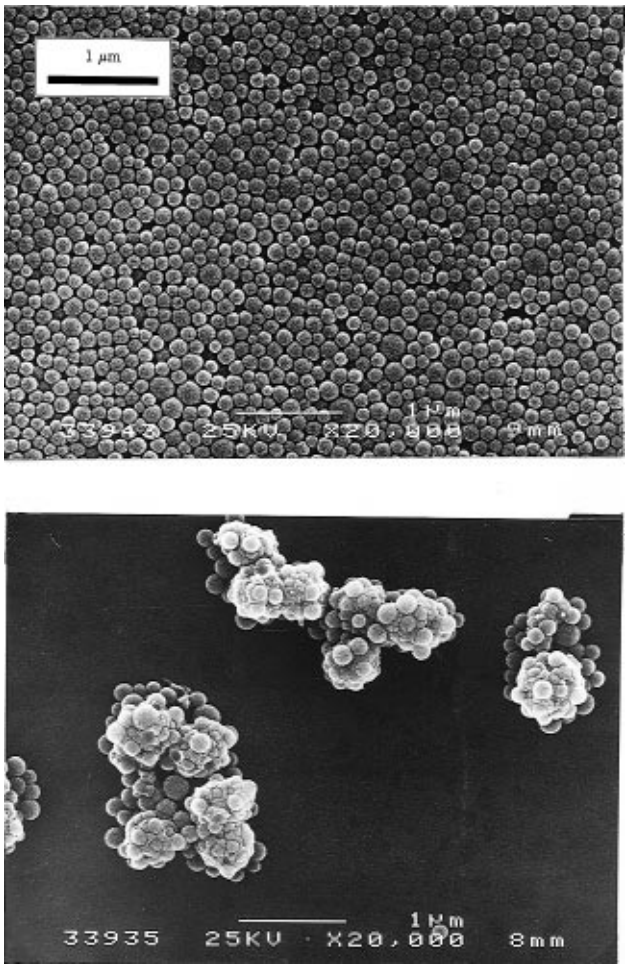

Figure 4. SEM micrographs of (a, top) noncommercial sample of colloidal silica particles (average diameter 195 nm) and (b, bottom) polyaniline−silica dispersion particles obtained after polymerization of aniline.

When aniline hydrochloride is polymerized in the presence of large silica particles (Figure 4a), a raspberry morphology, in which silica particles are glued together by the PANI, is clearly evident (Figure 4b). The size of

the aggregates is in the micrometer range (Table 4), but also in this case, the dispersions are colloidally stable.

Most of the colloidal silicas have a negative surface charge. Since the PANI chains are polycations,[1−4] the attractive electrostatic interactions may play a certain role in the formation of PANI−silica particles. However, this effect does not seem to be dominant: An alumina-coated colloidal silica with positive surface charge can be used for the preparation of PANI-silica particles with a comparable results (Ludox CL in Table 4).

Comparison of Particle- and Polymer-Stabilized Dispersions. There are some common features and some differences between PANI dispersions stabilized with colloidal silica and those stabilized with water-soluble polymers,[14,21] viz., poly(vinyl alcohol) and poly(*N*-vinylpyrrolidone). For example, the particle size and the uniformity of particles prepared under comparable conditions are very similar in all these cases.

For the particle-stabilized dispersions, a raspberry morphology is produced as silica particles become glued together by PANI[33,35] and the surface layer of silica particles prevents further aggregation of composite particles. It should be noted that the inability of aniline to swell PANI favors the formation of this type of morphology.[40] The structure of dispersion particles stabilized with polymers could be, in principle, similar. The polymer steric stabilizer could become entrapped and subsequently incorporated into the forming PANI particle and not be located just on its surface. Penetration of the steric stabilizer throughout the entire core of the dispersion particle was proposed by Pekcan and Winnik[41] (microdomain model) to explain a fast diffusion of anthracene into poly(methyl methacrylate) particles in fluorescence measurements. Whether this model is generally appropriate for polymer-stabilized PANI particles or the core−shell morphology predominates still remains to be decided.

The sedimentation of particles in free-standing samples is a typical feature of silica-stabilized dispersions. This is due to their higher density (typically 1.6−1.8 g cm^{-3}) compared with the PANI particles stabilized by water-soluble polymers. The sedimentation does not cause aggregation of particles, and gentle agitation leads to complete redispersion of the sediment.

Dispersions stabilized with silica have low viscosity, in contrast to the dispersions stabilized by polymers. After drying, composite powders are obtained from silica-stabilized dispersions, while polymer-stabilized dispersions yield films with good mechanical properties. On pelletization with a manual hydraulic press, PANI−silica composites yield brittle pellets with poor mechanical properties. On the other hand, these latter composites are likely to find use as tailor-made particulate fillers for the preparation of PANI−silica-based materials[42,43] with controlled dispersion of an electrically conducting component.

Electrical Properties. After drying, the dispersions yield microstructured composites comprising the submicrometer PANI particles dispersed in a matrix of insulating silica particles. The electrical conductivity of pure PANI (protonated emeraldine form) is usually of the order of 10^{-1} S cm^{-1}, depending somewhat on the polymerization and protonation conditions. The electrical properties of PANI−silica composites are illustrated on a sample containing 37.8 wt % (=47.7 vol %) of PANI (Figure 5). Its conductivity at 25 °C is 6.1×10^{-2} S cm^{-1}. As expected with semiconductors, the conductivity increases with increasing temperature (Figure 5). The difference between the conductivity determined at frequencies 20 Hz and 1 MHz was less than 1%; i.e., the conductivity is independent of the frequency. Alternating and direct current conductivities can be thus regarded as being identical. The electrical behavior of the PANI−silica composite is virtually the same as that of PANI−poly(vinyl alcohol) (PVAL) or PANI-poly(*N*-vinylpyrrolidone) (PVP) composites[44,45] of comparable PANI content (Figure 5). Consequently, the electrical properties are independent of the nature and type of the stabilizer, particulate or polymeric, used for the preparation of PANI.

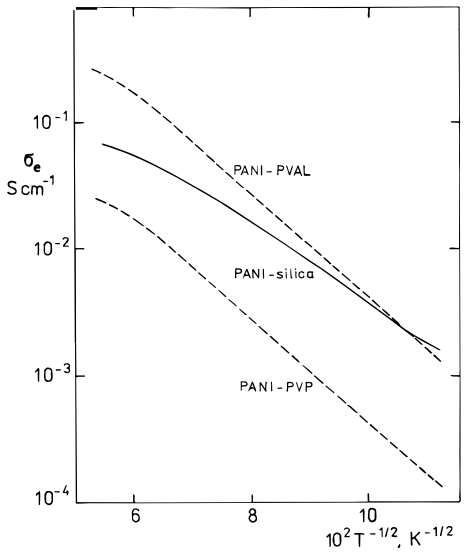

Figure 5. Temperature dependence of the electrical conductivity, σ_e, for a PANI (37.8 wt %)−silica composite (full line) and its comparison with PANI (48.3 wt %)−PVAL and PANI (39.4 wt %)−PVP composites (broken lines).

The mechanism of conduction in polyaniline has been discussed by Li *et al.*[46] in terms of the experimentally observed temperature dependence of the charge-carrier density. The macroscopic conductivity has been interpreted as a result of anisotropic three-dimensional variable-range hopping in a network of rods with metallic behavior. The temperature dependence of the conductivity observed with the PANI−silica sample is in good agreement with this model, which predicts that $\log \sigma_e \propto T^{-1/2}$ (Figure 5). The presence of the insulating silica therefore does not affect the nature of conduction.

Conclusions

The polymerization of aniline in the presence of colloidal silica represents a novel route for the preparation of polyaniline dispersions. Typical polyaniline−silica composite particles are approximately spherical. Close inspection confirms that they have a raspberry morphology. When the concentration of ultrafine silica is sufficiently high, dispersion particles in the 300−600 nm range are obtained. These dispersions have good long-term colloidal stability. Given a sufficient amount of silica, the size of the polyaniline−silica particles and their uniformity are only weakly dependent on the silica concentration, acidity of the medium, temperature of preparation, etc. Small and negatively charged silicas produce the most effective stabilization. The electrical properties of polyaniline−silica composites obtained after drying of dispersions are similar to those composed of polyaniline particles dispersed in a matrix of water-soluble polymers.

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