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SHORT COMMUNICATION

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Polyaniline dispersions 10. Coloured microparticles of variable density prepared using stabilizer mixtures

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Abstract Green polyaniline microparticles of variable density were prepared by the dispersion polymerization of aniline in the presence of a mixture of steric stabilizers. A water-soluble polymer stabilizer, polyacrylamide, and a particulate one, colloidal silica, were jointly used for this purpose. Silica was preferentially incorporated into the dispersion particles. The size of the particles was determined by dynamic light scattering. The colour of the polyaniline colloids was characterized by the absorption spectra. The density of the particles increased with increasing silica content, while the conductivity of the composites prepared from dispersions was reduced at the same time.

Key words Polyaniline · Polyaniline dispersion · Conducting polymer · Mixed stabilization · Particle density

Introduction

There are three major objectives that promote research on microparticles based on electrically conducting and coloured polymers, polyaniline (PANI) and polypyrrole being typical representatives. The preparation of colloidal dispersions can be regarded as a goal aimed at the preparation of processible forms of such polymers, the way to prepare microparticles for specific applications, and a tool to observe the formation of conducting polymers and to investigate their structure by various methods. While in the first case the conductivity, the optical absorption, and other physical properties of the bulk material composed of particles are of primary interest, the physicochemical properties of colloidal microparticles in relation to their size and morphology dominate the second field. The prevention of the macroscopic precipitation of conducting polymers during their preparation is the common denominator of all three cases.

Colloidal dispersions composed of sub-micrometre-sized PANI particles have often been investigated [1]. Such dispersions are prepared by the dispersion polymerization of aniline in an aqueous medium in the presence of a suitable steric stabilizer. Two types of steric stabilizers have been exploited: organic water-soluble polymers and inorganic colloids. Cellulose ethers [2, 3], poly(ethylene oxide) [4, 5], poly(methyl vinyl ether) [6], poly(styrenesulfonic acid) [7, 8], poly(vinyl alcohol) [9, 10], poly(vinyl alcohol-*co*-vinyl acetate) [11, 12], and poly(*N*-vinylpyrrolidone) [13, 14] have been the most frequently used polymers in the stabilization of PANI colloids, although the list is far from complete. The latter group is represented especially by ultrafine colloidal silica, which has been applied for the stabilization of both PANI and polypyrrole dispersions [15–17].

Sub-micrometre-sized PANI and polypyrrole particles have been proposed for potential uses as markers in diagnostics assays [18] and in isoperichoric focusing studies of colloids [19, 20]. The intrinsic colour of the particles is welcome for their easy detection and the control of the particle density is crucial for the separation processes involving these particles. The factors affecting the sedimentation of the particles are important for the processing of dispersions. The properties of dispersions, especially the particle size and shape, depend on the concentrations of the reactants, the reaction temperature, and on the selection of the steric stabilizer and of the medium. Another possibility for influencing the characteristics of the dispersion is the use of a mixture of steric stabilizers in the dispersion polymerization. This approach has not yet been reported in the literature and it is applied in the present work for control of the particle density. While the density of most organic polymers used for the stabilization is in the range 1.0–1.3 g cm^{-3}, that of inorganic microparticles is considerably higher and exceeds 2.1 g cm^{-3} in the case of silica [16]. Consequently, PANI particles stabilized with an inorganic colloid have a higher density [17] compared to dispersions stabilized with organic polymers. The use of the mixture of polymer and particulate stabilizers thus offers a possibility to control the dispersion properties in general and the particle density in particular by the selection of the stabilizer mixture composition. An example of PANI dispersions stabilized with mixtures of polyacrylamide (PAAm) and colloidal silica is demonstrated in the present study.

Experimental

PANI dispersions

Aniline hydrochloride (0.2 M) was oxidized with ammonium peroxydisulfate (0.2 M) in aqueous mixtures of PAAm (poly (acrylamide-*co*-1.5 wt% acrylic acid), $M_w \approx 5 \times 10^6$, Aldrich) and colloidal silica (Ludox AS-40, 40 wt% SiO_2, DuPont product distributed by Aldrich). Aniline hydrochloride (778 mg) was dissolved in 15 ml of an aqueous solution containing PAAm and colloidal silica in various proportions. Water was added to 24 ml, the solution was brought to 0 °C in a thermostat, and ammonium peroxydisulfate solution (6 ml 1 M aqueous solution, equivalent to 1.369 g ammonium peroxydisulfate) kept at the same temperature was added to start the polymerization. The mixture was not stirred during the polymerization. The reaction was complete in about 1 h.

Characterization of the dispersions

The visible absorption spectra of the dispersions after dilution with 1 M HCl were recorded the day after preparation in a 0.1-cm cell with a Lambda 20 (Perkin Elmer, UK) UV/vis spectrometer. The hydrodynamic diameter of the particles and their polydispersity (relative statistical variance of the particle size distribution) were determined on dispersions diluted with 1 M HCl by dynamic light scattering with an Auto-Sizer Lo-C (Malvern Instruments, UK).

Analysis of the particles

The dispersion was centrifuged in a Beckman L8-55 preparative ultracentrifuge at 20,000 rpm for 4 h. The supernatant liquid was removed, the green sediment was redispersed in 1 M HCl, and the centrifugation was repeated. Another redispersion–centrifugation cycle in ethanol followed. The sediment was then dried at 60 °C in vacuo directly in the centrifugation tubes. A part of the composite material obtained after centrifugation was compressed into a pellet of 13-mm diameter and about 1-mm thickness with a manual hydraulic press at 700 MPa in vacuo.

The weight fraction of PANI hydrochloride in the particles was calculated from the chlorine content found by elemental analysis. Polyaniline hydrochloride prepared under the same conditions but in the absence of the steric stabilizer contained 13.0 wt% of chlorine. The weight fraction of the silica was determined as an ash.

Density and conductivity

The sample density was determined by weighing pellets on a Sartorius Research R160P balance in air and in decane. The accuracy of the density determination was better than 0.002 g cm^{-3}.

The conductivity was measured on pellets at room temperature in the four-probe setup [21] comprising a Solartron-Schlumberger 7841 digital multimeter, a Keithley 220 current source, and a Keithley 705 scanner with a Keithley 7052 matrix scanner.

Results and discussion

The concept of mixed steric stabilization was tested for the design of PANI dispersion particles of variable density. If PAAm (density 1.302 g cm^{-3} given by Aldrich for the material containing 10–15 wt% of water) and colloidal silica (density [17] at 20 °C of 2.17 g cm^{-3}) are incorporated in various proportions into PANI particles (density of PANI hydrochloride [22] at 20 °C of 1.33 g cm^{-3}), control of the overall particle density may be anticipated.

Dispersions stabilized with single stabilizers

Unlike the silica-stabilized colloids, which have been investigated in detail [15–17], the use of PAAm in the stabilization of conducting-polymer colloids has only recently been reported [23–25]. Particles prepared by dispersion polymerization of aniline in the presence of PAAm are spherical (Fig. 1a). They are often aggregated into larger objects of particle size exceeding 1 μm (Table 1), which could be reduced by sonication to 500–700 nm. The aggregates are thus decomposed, at least partly, into individual particles, as in the case of the particles stabilized with hydroxypropylcellulose [3, 14]. Commercially available PAAm contains a small number, 1.5 wt%, of acrylic acid units. The electrostatic interaction of carboxylic groups with a PANI polycation is likely to improve the stabilizing efficiency of PAAm. Poly(acrylic acid) itself has been used successfully for the stabilization of PANI colloids [8, 26]. Carboxyl groups are also produced on the PAAm chain by acid hydrolysis and thus are also expected to originate during the dispersion polymerization. The spherical shape of the

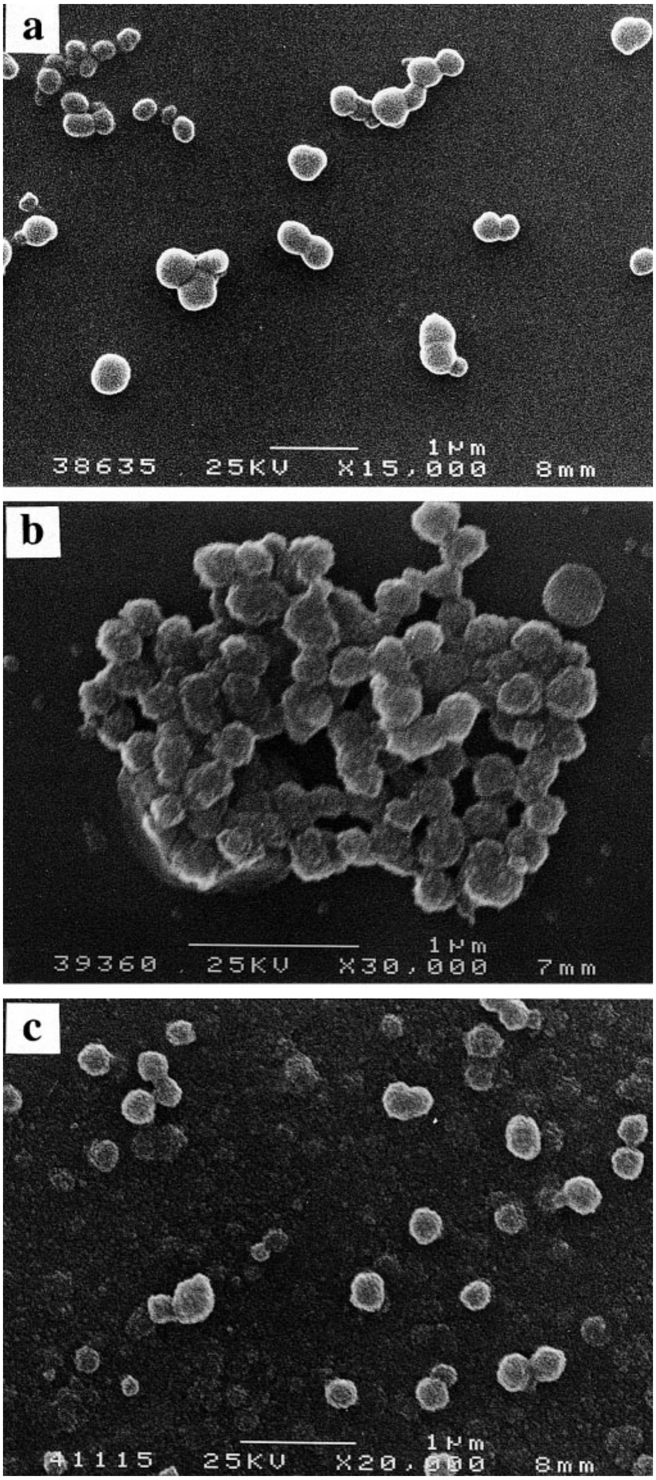

Fig. 1 Micrograph of polyaniline particles stabilized with **a** polyacrylamide **b** a mixture of steric stabilizers (80 wt% PAAm and 20 wt% colloidal silica), and **c** with colloidal silica

silica-stabilized PANI particles (Fig. 1c) and their properties have been documented earlier [17].

Table 1 Colloidal properties of polyaniline dispersions stabilized by mixtures of organic and inorganic stabilizers, polyacrylamide and colloidal silica. The total concentration of the stabilizers was 2.0 g cm^{-3}, w_{silica} is the weight fraction of silica in a mixture of stabilizers, D is the particle size, P is the polydispersity factor, and A is the optical absorption of the dispersion at the maximum, $\lambda_{\max}$, after 60-fold dilution with 1 M HCl (0.1-cm cell thickness)

No.	w_{silica} (wt%)	D (nm)	P	A	$\lambda_{\max}$
1	0	1040[a]	0.59	0.669	439
2	12	1080[a]	0.33	0.742	434
3	24	1190[a]	0.36	0.688	431
4	35	1160[a]	0.47	0.679	428
5	45	695	0.36	0.673	427
6	55	690	0.44	0.593	423
7	65	630	0.37	0.583	419
8	74	530	0.35	0.801	417
9	83	515	0.38	0.759	418
10	92	535	0.31	0.687	416
11	100	360	0.05	0.917	405

[a] The particle size was reduced after sonication to 500–700 nm

Mixed stabilization

When solutions of organic water-soluble polymers were mixed with colloidal silica, phase separation usually took place. Poly(*N*-vinylpyrrolidone) solution and colloidal silica were observed to precipitate on mixing by Gill et al. [15]. Hydroxypropylcellulose solution precipitated when mixed with colloidal silicas Ludox TMA and Ludox CL (Aldrich). It was compatible with Ludox AS-30 and Ludox AS-40 silica but precipitation occurred in acidic conditions needed for the polymerization of aniline. PAAm solution was, however, found to be miscible with Ludox AS-40 in all proportions, even in acidic media, while systems comprising other tested silicas became phase-separated immediately or after several days. A marked decrease in the viscosity of PAAm solution after the introduction of silica Ludox AS-40 indicates an interaction between the components. The polymerization of aniline hydrochloride in the presence of PAAm, colloidal silica Ludox AS-40, or their mixtures, produced stable PANI dispersions in all cases (Table 1).

The size of the particles stabilized completely or predominantly with PAAm (Table 1) decreased after sonication. This means that the size observed by dynamic light scattering is also affected by the presence of particle aggregates. A large cluster of dispersion particles is shown in Fig. 1b. As the fraction of silica in a mixture of stabilizers increased, the size of the scatterers became smaller because of the reduced aggregation (Table 1).

Optical properties

Optical absorption in the 400 and 800 nm regions (Fig. 2) is responsible for the emerald-green colour of

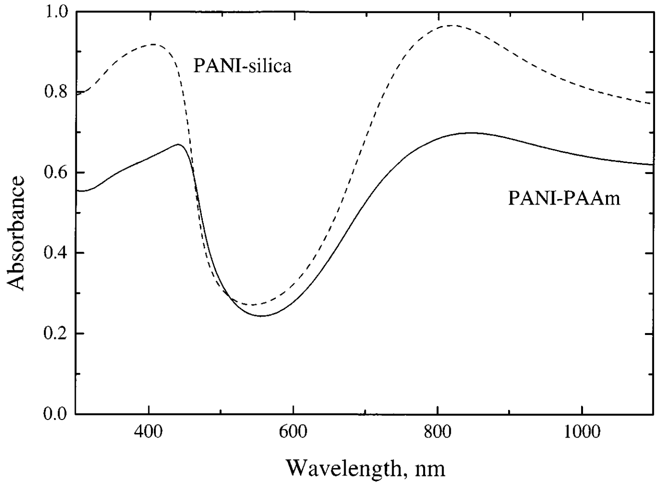

Fig. 2 Visible spectra of a PANI dispersion stabilized with PAAm (*solid line*) and with colloidal silica (*dashed line*). Diluted 60 times with 1 M HCl, cell thickness 0.1 cm

Table 2 Composition and properties of dispersion particles. Characterization of the particles obtained as a sediment after centrifugation. W_{PANI} is the weight fraction of polyaniline hydrochloride in the dispersion particles (from the chlorine content), W_{silica} is the weight fraction of silica (determined as an ash), W_{PAAm} is the weight fraction of polyacrylamide (calculated as $W_{\mathrm{PAAm}} = 1 - W_{\mathrm{PANI}} - W_{\mathrm{silica}}$), ρ is the density, and σ is the conductivity

No.	W_{PANI} (wt%)	W_{silica} (wt%)	W_{PAAm} (wt%)	ρ (g cm^{-3})	σ (S cm^{-1})
1	69.6	0	30.4	1.345	8.3
2	56.9	26.9	16.2	1.471	6.5
3	46.3	36.3	17.4	1.572	5.5
4	35.8	46.6	17.6	1.617	5.3
5	34.3	53.0	12.7	1.662	3.9
6	28.0	57.8	14.2	1.682	3.6
7	36.0	62.4	1.6	1.663	2.5
8	30.8	63.7	5.5	1.697	1.1
9	29.8	68.3	1.9	1.711	1.0
10	25.0	69.1	5.9	1.748	0.75
11	24.8	74.3	(0.9)	1.858	0.47

the dispersions [27], typical for the protonated emeraldine form of PANI. The absorption at 400 nm was comparable for all dispersions (Table 1), indicating that the conversion of aniline to PANI was nearly complete [27] and that it was independent of the presence of steric stabilizer. The increased absorption of the silica-stabilized colloid can be explained by the small size of the particles. The shift of the absorption maximum from 439 nm for PAAm stabilization to 405 nm for silica-stabilized particles is most likely caused by the different microenvironment provided by the individual stabilizers. Acidity within the particles may vary for the individual stabilizers due to the difference in the preferential sorption of protons and the optical spectra, which depend on the acidity [27], also differ. The particles acquire the blue colour of emeraldine base in an alkaline medium.

Particle density

The dispersion particles were separated by centrifugation and dried. From the composition of the sediment (Table 2) we can conclude that silica is preferentially incorporated into the dispersion particles and that its participation in the particles was always greater compared with that in the reaction mixture (Fig. 3). The density of the particles sharply increased accordingly as even small amounts of silica had been introduced into the reaction mixture (Table 2) and changed only moderately at a high silica content. The density of the particles varied from 1.345 g cm^{-3} for stabilization with PAAm to 1.858 g cm^{-3} for the silica-stabilized PANI colloid (Table 2). It has to be mentioned that the density of the particles can be modified, even in the case when silica alone is used for stabilization, by changing the content of silica in the polymerization mixture. Flitton et al. [28] reported that as the silica content in the polypyrrole–silica colloids was increased from 41 to 71 wt%, the particle density could be varied from 1.80 to 2.00 g cm^{-3}. At the same time the particle size decreased from 200 to 80 nm. The mixed stabilization offers, however, the control over a broader range of densities.

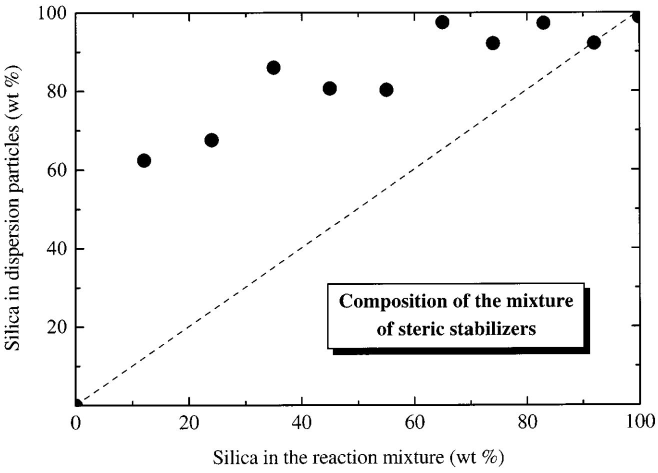

Fig. 3 The dependence of the composition of the steric stabilizers in the dispersion particles on the composition of the stabilizer mixture in the reaction medium

Electrical conductivity

The conductivity decreases as the weight fraction of PANI in the composite material, produced after separation of the dispersion particles, becomes lower (Table 2). The content of PANI is well above the percolation limit in all cases and good conduction in the composites is feasible. The conductivity is only a little reduced compared with pure PANI hydrochloride [22], 11.8 S cm^{-1}, prepared under the same reaction conditions.

Conclusions

PAAm is able to stabilize PANI dispersions, although such dispersions contain aggregated particles. The aggregates could be partly decomposed by sonication. Silica-stabilized PANI colloids are composed of nearly uniform spherical particles. The density of the particles prepared in the presence of a mixture of steric stabilizers, PAAm and colloidal silica, depended on the silica content in the particles. The particle density could be varied between 1.345 and 1.858 g cm^{-3}. Silica was always preferentially incorporated into the dispersion particles.

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References

1. Armes SP (1998) In: Skotheim TA, Elsenbaumer RL, Reynolds JR (eds), Handbook of conducting polymers, 2nd edn. Dekker, New York, pp 423–435
2. Chattopadhyay D, Banerjee S, Chakravorty D, Mandal BM (1998) Langmuir 14:1544–1547
3. Stejskal J, Špírková M, Riede A, Helmstedt M, Mokreva P, Prokeš J (1999) Polymer 40:2487–2492
4. Cooper EC, Vincent B (1989) J Phys D Appl Phys 22:1580–1585
5. Innis PC, Norris ID, Kane-Maguire LAP, Wallace GG (1998) Macromolecules 31:6521–6528
6. Banerjee P, Bhattacharyya SN, Mandal BM (1995) Langmuir 11:2414–2418
7. Nakao H, Nagaoka T, Ogura K (1997) Anal Sci 13:327–331
8. Yang SM, Chen WM, You KS (1997) Synth Met 84:77–78
9. Armes SP, Aldissi M, Hawley M, Beery JG, Gottesfeld S (1991) Langmuir 7:1447–1452
10. Eisazadeh H, Spinks G, Wallace GG (1995) Polym Int 37:87–91
11. Gospodinova N, Terlemezyan L, Mokreva P, Stejskal J, Kratochvíl P (1993) Eur Polym J 29:1305–1309
12. Gospodinova N, Janča J (1998) Int J Polym Anal Charact 4:323–332
13. Stejskal J, Kratochvíl P, Helmstedt M (1996) Langmuir 12:3389–3392
14. Riede A, Helmstedt M, Riede V, Stejskal J (1998) Langmuir 14:6767–6771
15. Gill M, Baines FL, Armes SP (1993) Synth Met 55–57:1029–1033
16. Maeda S, Armes SP (1994) J Mater Chem 4:935–942
17. Stejskal J, Kratochvíl P, Armes SP, Lascelles SF, Riede A, Helmstedt M, Prokeš J, Křivka I (1996) Macromolecules 29:6814–6819
18. Miksa B, Slomkowski S (1995) Colloid Polym Sci 273:47–52
19. Janča J, Špírková M (1996) Collect Czech Chem Commun 61:819–824
20. Janča J, Gospodinova N (1998) Collect Czech Chem Commun 63:155–163
21. van der Pauw LJ (1958) Philips Res Rep 13:1–9
22. Stejskal J, Sapurina I, Prokeš J (1999) Synth Met 105:195–202
23. Ghosh P, Chakrabarti A, Siddhanta SK (1999) Eur Polym J 35:803–813
24. Ghosh P, Siddhanta SK (1999) J Polym Sci Polym Chem 37:3243–3256
25. Saunders BR, Saunders JM, Mrkic J, Dunlop EH (1999) Phys Chem Chem Phys 1:1563–1568
26. Liu JM, Yang SC (1991) J Chem Soc Chem Commun 1529–1531
27. Stejskal J, Kratochvíl P, Radhakrishnan N (1993) Synth Met 61:225–231
28. Flitton R, Johal J, Maeda S, Armes SP (1995) J Colloid Interface Sci 173:135–142