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SHORT COMMUNICATION

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Preparation, characterization, and adhesion of monodispersed polypyrrole particles

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Abstract Uniform colloidal polypyrrole particles ranging from 17 to 59 nm in diameter were prepared by the oxidation of pyrrole with sodium persulfate in the presence of the nonionic Rhodasurf TB970 polymeric stabilizer and 4-ethyl benzenesulfonic acid. The adhesion of these particles on glass beads was studied as a function of the pH using the packed column technique. Polypyrrole was found to deposit on glass only at pH values below its isoelectric point (i.e.p.), forming a monolayer. The entire amount of the adhered polypyrrole could be rapidly removed by rinsing the column with 1×10^{-2} mol dm^{-3} NaOH solution.

Key words Adhesion of polypyrrole – polypyrrole colloidal – polypyrrole interactions with glass

Introduction

The preparation of colloidal polypyrrole particles by oxidation of pyrrole in the presence of polymeric stabilizers was reported in several studies [1–10]. The particle size and the stability of the resulting dispersions depended on the amounts and types of stabilizers and oxidizers used. Different polymers, such as poly(vinylacetate), poly(vinyl methyl ether), poly(styrenesulfonate), and oxidizers, including $FeCl_3$, $Fe(NO_3)_2$ in 0.1 mol dm^{-3} HNO_3, and $(NH_4)_2S_2O_8$, yielded polypyrrole particles of varying degrees of polydispersity, with modal diameters ranging between 50 and 400 nm [1–12].

It was also reported that the use of dopants such as benzenesulfonic [13], toluenesulfonic [14], and styrenesulfonic [15] acids enhanced the conductivity of polypyrrole particles. However, such additives were not required with $FeCl_3$ as oxidizer, since in this case polypyrrole became doped with $FeCl_4^-$ ions formed in the reaction.

In the present work uniform polypyrrole particles of 17–59 nm in modal diameters were prepared by the oxidation of pyrrole with sodium persulfate, $Na_2S_2O_8$, in the presence of the polymeric nonionic surfactant Rhodasurf TB970 (stabilizer) and 4-ethylbenzenesulfonic acid (dopant).

The problems of interactions of polypyrrole with different materials, including the formation of films on metal oxide particles [16] and chemically modified substrates, such as glass [17, 18] and silicon [19], have been addressed in the literature. In the present study the adhesion of uniform polypyrrole particles on glass beads at various pH values was evaluated by the packed column technique [20], in order to establish the conditions under which an insulating material can be coated with a layer of a colloidal conducting polymer.

Experimental

Preparation of polypyrrole particles

To prepare a suspension of monodispersed spherical polypyrrole particles, the Rhodasurf TB970 surfactant

Table 1 The amounts of reagents used in the polypyrrole synthesis and the average size of the resulting particles. Final dispersion volume is 1 dm^3

Batch	Stabilizer (Rhodasurf TB970) [$g\,dm^{-3}$]	Dopant ($C_2H_5C_6H_4SO_3H$)[a] [$g\,dm^{-3}$]	Pyrrole [$g\,dm^{-3}$]	Oxidizer stock solution volume[b] [cm^3]	Particle size/nm
1	10.0	55.0	10.0	88.5	17
2	11.1	61.1	11.1	98.3	28
3	16.0	88.0	16.0	142	42
4	19.2	106	19.2	170	59

[a] 4-ethylbenzene-sulfonic acid.
[b] The stock solution contains 400 $g\,dm^{-3}$ of $Na_2S_2O_8$.

(Rhône-Poulenc Co.) was dissolved in ~500 cm^3 of deionized water, to which the ethylbenzenesulfonic acid was added, resulting in the formation of a greyish emulsion. Pyrrole was then admixed under stirring and, finally, the aqueous stock solution of the oxidizer, containing 400 $g\,dm^{-3}$ of $Na_2S_2O_8$, was slowly introduced, causing the entire content to turn instantaneously black. Before the addition of the oxidizer the reaction mixture was diluted with a sufficient amount of water to yield a total final reaction volume of 1 dm^3. The process required one hour to proceed under stirring.

A summary of the concentrations of the reactants used is given in Table 1.

Characterization of polypyrrole particles and glass beads

Polypyrrole particles were analyzed by the transmission electron microscopy (TEM), and their size distribution was determined from the TEM micrographs with a TGZ-3 particle size analyzer (Carl Zeiss) by counting 2500 particles.

The electrophoretic mobility of the synthesized polypyrrole particles was determined as a function of the pH with the DELSA 440SX instrument (Coulter Electronics).

The electrokinetic potential of glass beads in the presence of the Rhodasurf TB970 surfactant was determined by electroosmosis using the apparatus and method described earlier [21, 22].

Packed column

The experimental setup for the study of the adhesion of polypyrrole particles on glass beads was essentially the same as in previous studies [20]. A cylindrical Kontes jacketed column with cross-sectional area $S = 0.79\,cm^2$ was filled with the collector glass beads (Ballotini, $49 \pm 7\,\mu m$ in diameter), packed in a bed 1.3 ± 0.1 cm high, having a porosity $\phi = 0.34$. The outer jacket of the column was connected to a circulating water bath kept at $23.0 \pm 0.1\,^{\circ}C$. The flow rate of the suspension passing through the column was controlled by a peristaltic pump at $1.56 \pm 0.07\,cm^3\,min^{-1}$.

Particle adhesion experiments

The bed packed with glass beads was rinsed for 2 h with a $4.8 \times 10^{-3}\,g\,dm^{-3}$ Rhodasurf TB970 solution, having the same pH as the diluted polypyrrole suspension, containing 2×10^{17} particles per m^3 (C_0), which was then pumped through the column. The particle concentration, C, in the collected effluent was assayed from its turbidity, monitored as a function of time. A linear relationship between the turbidity and particle number concentration was established over the concentration range of interest in the present study. The collected effluent was diluted fivefold with a solution having the same pH and the same stabilizer content as the original polypyrrole suspension, in order to be within the range of the calibration line. Obviously, this dilution was taken into consideration when interpreting the adhesion data in terms of the breakthrough curves, based on the plots of the C/C_0 ratio as a function of time.

It was also veified that no detachment took place, when the already loaded column was rinsed with a solution of the same pH and stabilizer concentration as that of a suspension from which the particles were originally deposited.

Results and discussion

Particle preparation and characterization

The described procedure yields uniform particles of polypyrrole as illustrated in Fig. 1, which corresponds to batch 4 in Table 1. The latter contains also the results of particle size analyses on all four batches, showing that the larger polypyrrole particles were formed when higher concentrations of the stabilizer, dopant, pyrrole, and oxidizer were used, while the ratio of all these components was kept the same. No stable colloids could be obtained, if the concen-

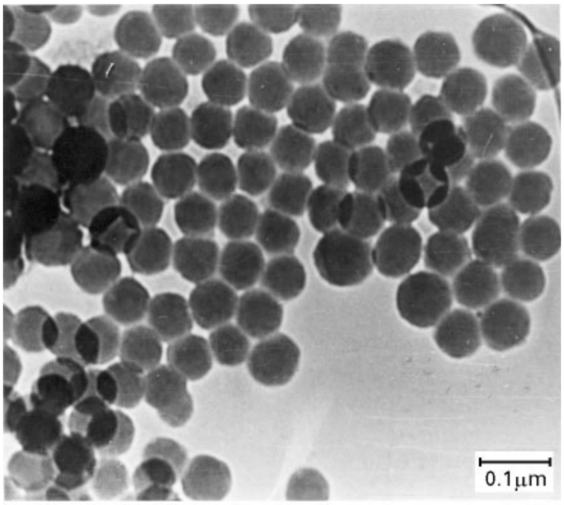

Fig. 1 Transmission electron micrograph of polypyrrole particles obtained by the oxidation of pyrrole with sodium persulfate, using polymeric Rhodasurf TB970 stabilizer and 4-ethylbenzene-sulfonic acid dopant, as described in Table 1 (batch 4)

trations of reagents were below those used in batch 1 or above those in batch 4 (Table 1), at the employed ratios of reactants. The prepared polypyrrole dispersions were stable for 1 month.

Previous studies [9, 23] showed the importance of the order in which chemicals were mixed, emphasizing that monodispersed particles could only be obtained, if pyrrole was added last. This work indicates that it was still possible to prepare uniform polypyrrole particles even when the oxidizer was introduced last.

The electrophoretic mobilities as a function of the pH at two different Rhodasurf TB970 concentrations of the largest (59 nm) polypyrrole particles yielded the isoelectric point (i.e.p.) at pH ~ 9.7 (Fig. 2). Previous studies [6, 24] reported the i.e.p. of such dispersions to be at pH ~ 3–4. The latter was found with polypyrrole samples prepared using $FeCl_3$ as the oxidizer and dopant, which could cause the contamination of particle surface with Cl^- ions, resulting in the shift of the i.e.p. to a lower pH value. The ethylbenzenesulfonic acid and sulfate ions produced in the reaction are probably less effective contaminants than chlorides, and hence "purer" polypyrrole was obtained. Figure 2 also indicates that the concentration of the stabilizer in the system had no significant effect on the electrokinetic properties of these particles.

Due to the poor scattering of light by polypyrrole, it was not possible to measure the electrophoretic mobilities of particles smaller than 59 nm in diameter. It is, however, reasonable to assume that the i.e.p. does not vary for samples of interest in this study.

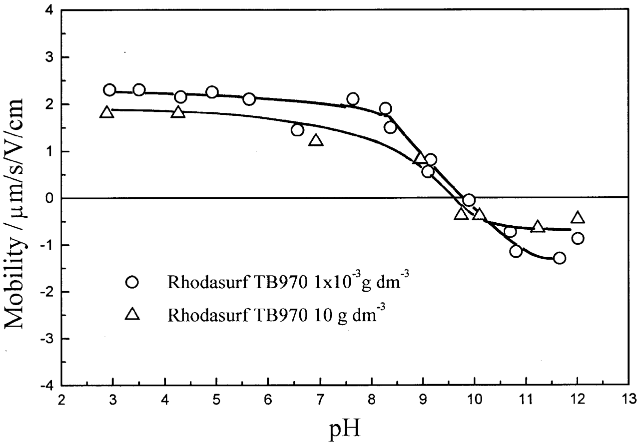

Fig. 2 Electrophoretic mobilities of polypyrrole particles (batch 4) as a function of the pH in the presence of 1×10^{-3} (○) and $10\,\mathrm{g\,dm^{-3}}$ (△) Rhodasurf TB970

Characterization of glass beads by electro-osmosis

The electrokinetic (ζ) potential of glass beads was determined by electro-osmosis in the presence of Rhodasurf TB970 stabilizer at pH = 3. In the absence of this additive ζ equalled to -67 mV, while in the presence of 4.8×10^{-3} and $10\,\mathrm{g\,dm^{-3}}$ of TB970 it was -28 and -25 mV, respectively. This decrease of the potential was probably caused by the outward shift of the slipping plane due to the adsorbed polymeric surfactant [25]. It was not necessary to carry out measurements at other pH values, since it was known from previous work [26], that the electrokinetic potential of glass beads is not significantly affected by the change in the solution pH.

Adhesion of polypyrrole particles on the glass beads

The break-through curves for the deposition of 17 nm polypyrrole particles on glass beads as a function of the solution pH are shown in Fig. 3. These curves are in very good agreement with the electrokinetic data of polypyrrole particles (Fig. 3). Below pH = 8.5, where the latter are positively charged and their mobilities are constant, monolayer deposition occurs; the characteristic S-shaped break-through curves are typical when the particles and collectors are oppositely charged [26–28]. At pH = 3, 4, and 6.5 the attraction between polypyrrole and glass is very strong; no particles could be detected in the effluent during the first 40–60 min of the experiments. The rapid increase in the C/C_0 values is consistent with the visual observation that the column was saturated with polypyrrole.

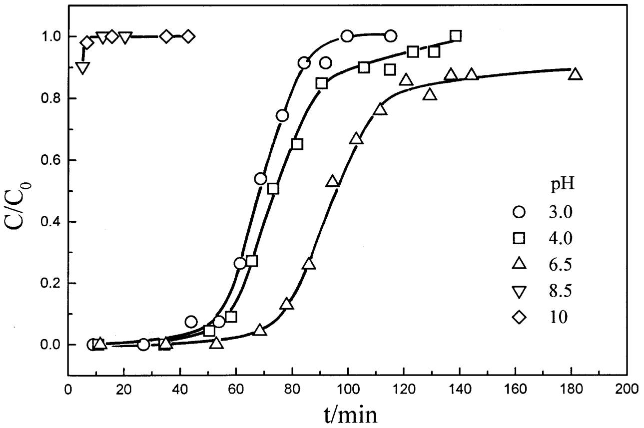

Fig. 3 Break-through curves for the deposition of polypyrrole particles (batch 1) on glass beads at pH 3 (○), 4 (□), 6.5 (△), 8.5 (▽), and 10 (◇) at 23.0 ± 0.1 °C and the flow rate of 1.56 ± 0.07 $cm^3 min^{-1}$. All suspensions contained 4.8×10^{-3} $g dm^{-3}$ of Rhodasurf TB970 stabilizer and had particle number concentration $C_0 = 2 \times 10^{17}$ particles per m^3

There was little or no uptake from suspensions at pH $\geq$ 8.5, which also agrees with the electrokinetic data (Fig. 2), showing that the particles are either only slightly charged, or neutral under these conditions.

Earlier studies [27–29] showed that multilayer deposition of particles took place at pH close to their i.e.p., which was not the case with the present system. The finding that no material was deposited at pH = 10 can be explained by the fact that the essentially neutral polypyrrole particles were sterically stabilized by the Rhodasurf TB970 surfactant.

When the packed column, saturated with polypyrrole particles at pH $\leq$ 6.5, was rinsed with 1×10^{-2} $mol dm^{-3}$ NaOH solution, a rapid removal of the entire adsorbed amount of polypyrrole was observed. The ease with which the detachment took place suggests that the polymer particles were only physically adsorbed on the glass. Under similar conditions colloidal hematite (α-Fe_2O_3), deposited in a monolayer in the presence of an anionic surfactant (sodium 4-octylbenzenesulfonate), required considerably longer times to be separated from glass [30], and no complete removal was achieved. The weaker binding of polypyrrole on glass may be caused by the polymeric nature of the adsorbed Rhodasurf TB970 molecules, which caused particles to deposit at larger distances from the collector surface. A surfactant with a much shorter hydrocarbon chain used in the study with hematite [30] probably allowed for closer approach of the adhered positively charged hematite to negatively charged glass, resulting in stronger particle-collector attraction, and hence in a more difficult detachment upon rinsing with NaOH.

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