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Ethylhydroxyethylcellulose stabilized polypyrrole dispersions

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Oxidative dispersion polymerization of pyrrole using ethylhydroxyethylcellulose stabilizer in water or aqueous alcohol medium yields stable dispersions of submicrometre-sized conducting spherical polypyrrole particles. Transmission electron micrograph images of the particles from the original dispersion distinguish two kinds of particles: one very small, ~20 nm in diameter, and the other eight to ten times larger. The former constitutes about 1% of the total mass of particles. Similar results were obtained with a poly(vinyl methyl ether) stabilized polypyrrole dispersion.

(Keywords: dispersion polymerization; polypyrrole; ethylhydroxyethylcellulose)

Introduction

Conducting polymer dispersions have the potential of increased processability. Preparation of dispersions of conducting polypyrrole (PPy) and their characterization have been reported for a number of polymeric stabilizers[1–9]. The dispersions are generally prepared by oxidative polymerization of pyrrole in the presence of a polymeric stabilizer. In this work, we report the use of ethylhydroxyethylcellulose (EHEC) as a stabilizer in the preparation of PPy latices by way of dispersion polymerization of pyrrole. EHEC has a number of attractive properties, for example, good surface active properties, non-ionic character, lack of a gel point and tolerance of cations[10]. Because of the latter property, it should perform well since a large quantity of $FeCl_3$ ($[FeCl_3]/[Py] \approx 2.4$) is used in the oxidative dispersion polymerization of pyrrole.

Experimental

Materials. Pyrrole (E. Merck, Germany) was freshly distilled under reduced pressure. Anhydrous $FeCl_3$ (E. Merck, Germany) and a medium viscosity grade EHEC (Berol Nobel, Sweden) were used as received. Ethyl alcohol was purified as reported earlier[9,11].

Polymer synthesis. Pyrrole was added to a solution of $FeCl_3$ and EHEC in 50% aqueous ethanol. The reaction mixture was stirred magnetically for 6 h at 2°C under N_2 atmosphere. PPy was obtained as a fine dispersion. It was sedimented by centrifugation at 35 000 rev min^{-1} for 2 h. The separated PPy was washed three times with 0.1 mol dm^{-3} HCl followed by ethanol. The polymers to be used for conductivity measurement were dried in vacuum at room temperature for 24 h, while samples for chemical analysis were further dried in vacuum at 70°C for 24 h.

Polymer characterization. Conductivity of the pelletized materials was measured by the standard four-probe method using a constant d.c. source (Keithley, model 224) and a nanovoltmeter (Keithley, model 181). Transmission electron microscopy (TEM) studies were made on dilute (~200 ppm) dispersions dried on carbon-coated copper grids using a Jeol JEM 100CT electron microscope. Estimation of N, Cl and Fe in the samples was performed as described earlier[9].

Results and discussion

Dispersion polymerization was carried out satisfactorily in water but was better in aqueous alcohols. For example, in water a minimum of 0.5% EHEC was required to be used with a pyrrole concentration of 2%, while in 50% ethanol, 0.3% EHEC was sufficient to make a stable dispersion. The greater effectiveness of 50% ethanol as the dispersion medium compared to water may be attributed to the former being a better solvent for the stabilizer than the latter. This relative solvent power of the two solvents towards EHEC was established from intrinsic viscosity studies. For the EHEC sample used in this work, the values of $[\eta]$ in water and in 50% ethanol are, respectively, 0.563 and 0.652 $dm^3\,g^{-1}$ at 25°C. Earlier, Armes *et al.*[3] pointed out that PPy colloids prepared by using polymeric stabilizers are sterically stabilized. One would expect steric stabilization to be better in a medium in which the stabilizer exerts greater excluded volume effect. Also, the better the solvent power of the medium towards the stabilizer, the greater is the excluded volume effect.

The dispersion dialysed against 50% ethanol to remove iron salts and low molecular weight species remained stable for a long time (tested for up to 6 months). *Table 1* gives the polymerization recipe and the characterization data of the PPy produced. The amount of non-conducting EHEC incorporated in the PPy particles increases, and consequently the conductivity of PPy decreases, with increase in EHEC concentration used initially in the reaction mixture. The transmission electron micrograph of the particles from the dialysed dispersion of sample 6 dried on TEM grids is shown in *Figure 1*. The micrograph reveals the presence of two kinds of spherical particles, one very small, ~20 nm in diameter, and the other of much larger size, with average diameter

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of $\sim 160 \pm 40$ nm. The small particles account for only about 1% of the total mass of particles. To our knowledge, the presence of individual particles as small as 20 nm in PPy dispersions has not been reported in the literature. In fact, all the published papers report the TEM image of redispersed particles but not of particles in clean, as-prepared dispersions. *Figure 2* indeed shows that the small particles are absent in the TEM image of a redispersion of sample 6. For the latter preparation, the particles in the original dispersion were sedimented by centrifugation, washed, suspended in the dispersion medium and sonicated. The absence of the small particles in the redispersion is due to the fact that they were not sedimented by the g force attained in the centrifuge (100 000g). This conclusion was reached from the TEM study of the supernatant liquid, which shows the presence of only the small (~ 20 nm) particles. The presence of particles of two different sizes in the original dispersion is not, however, unique to EHEC stabilizer. The same observation was made with the original dispersion of PPy prepared using poly(vinyl methyl ether) (PVME) stabilizer in 50% ethanol[8,9], as shown in *Figure 3*. The very small particles in the original dispersion may represent primary particles, which eventually aggregate to form larger particles. Indeed, Armes *et al.*[12] have shown by scanning tunnelling microscopy that the spherical particles seen in the TEM image of a PPy redispersion are compound particles comprising very small (5–10 nm diameter) spherical primary particles.

Table 1 Preparation of PPy dispersion in 50% aqueous ethanol (using 0.7 mol dm^{-3} $FeCl_3$ initiator at 2 C, $[FeCl_3]$:[Py] = 2.4, polymerization time = 6 h, [pyrrole] = 0.288 mol dm^{-3}) and the characterization data of PPy

Sample no.	EHEC (%, w/v)	Polymer characterization			
		EHEC/PPy[a]	Cl/N[b]	σ (S cm^{-1})	Fe content (%)
1	0	0	0.34	12.43	1.20
2	0.3	0.104	0.32	7.34	0.57
3	0.4	0.138	0.32	4.45	0.31
4	0.5	0.156	0.31	3.60	0.57
5	0.6	0.190	0.32	1.68	0.50
6	0.7	0.203	0.33	1.61	0.54

[a] Weight ratio, calculated on the basis of reduced nitrogen content of the particles relative to pure PPy (sample 1)
[b] Atomic ratio

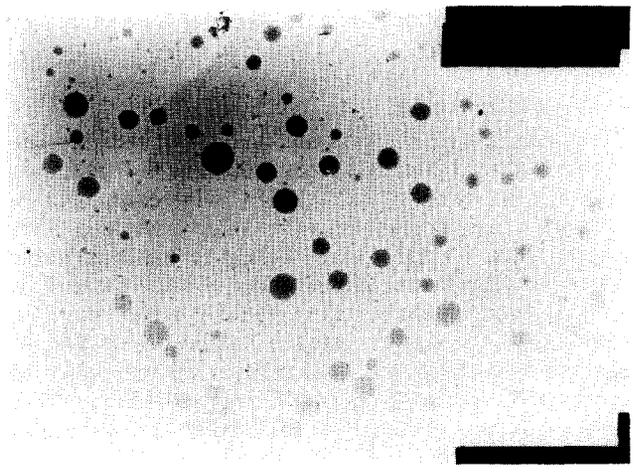

Figure 1 Transmission electron micrograph of the dialysed original dispersion of sample 6; scale: 2 cm = 1.33 μm

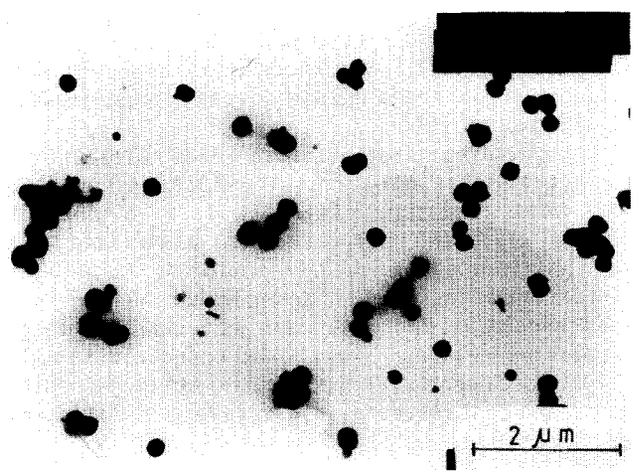

Figure 2 Transmission electron micrograph of sample 6 redispersed in 50% ethanol

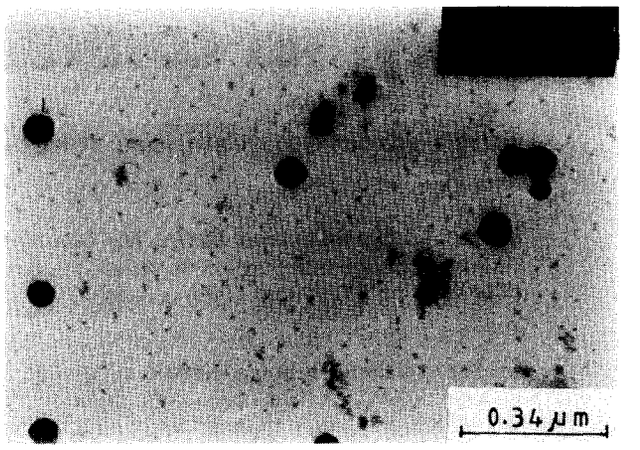

Figure 3 Transmission electron micrograph of the dialysed original dispersion of PPy prepared using PVME stabilizer in 50% ethanol

The chemical analysis of the PPy particles given in *Table 1* reveals that they contained only a very small amount of iron, indicating that the dopant is most likely the Cl^- ion. The Cl/N ratio indicates that one in approximately every three pyrrole units in PPy is doped (oxidized). The conductivity of the particles measured in pressed pellet form increased from 1.6 to 7.3 S cm^{-1} as the EHEC loading in the particles decreased from 20 to 10%.

This work thus shows that EHEC is an effective stabilizer for the dispersion polymerization of pyrrole using $FeCl_3$ initiator (oxidant). The TEM image of the particles from the original dispersion reveals the presence of very small, nanometre-sized (~ 20 nm) particles in addition to particles of 100–200 nm diameter. This result is of course not unique to EHEC stabilizer because PVME stabilized dispersions also showed similar results.

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