

Conducting Polypyrrole Particles Dispersible in both Aqueous and Non-aqueous Media

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Dispersion polymerization of pyrrole in absolute alcohol or water–alcohol mixtures using poly(vinyl methyl ether) (PVME) dispersant and FeCl_3 initiator–dopant yields conducting polypyrrole (PPy) particles which after isolation and purification can be redispersed in water as well as in many common organic solvents to give submicronic stable dispersions.

Conducting polymer dispersions provide an effective method of processing such polymers which are in general intractable. Dispersions of several conducting polymers in aqueous media have been reported.^{1–9} Of these, PPy dispersions have been studied in some detail.^{3–8} The dispersion is generally prepared

by polymerizing pyrrole in aqueous media containing a water soluble polymeric dispersant and using FeCl_3 as initiator–dopant. The PPy isolated from this dispersion for purification purposes could be redispersed in water. Not all water soluble polymeric dispersants are, however, effective for preparing

PPy dispersions.³⁻⁸ Recently, Armes and Aldissi reported the preparation of PPy dispersions in non-aqueous media as well using FeCl_3 as initiator-dopant and poly(vinyl acetate) as dispersant.¹⁰ The stability of these dispersions is due to the steric hindrance to agglomeration of the particles effected by the dispersants adsorbed on them.⁴⁻¹⁰ It occurred to us that the use of a dispersant polymer such as poly(vinyl methyl ether) (PVME) which is soluble both in water and in many non-aqueous solvents may give rise to PPy particles dispersible in a number of solvents, both aqueous and non-aqueous. This would add variety to the dispersions and increase their range of applicability as far as processing is concerned. For example, apart from coating applications others such as making blends or composites of PPy with other polymers soluble in the dispersion media could be easily made. In an earlier communication we reported that polymerization in aqueous media using PVME dispersant and FeCl_3 initiator-dopant did not result in a dispersion polymerization.¹¹ We now report that dispersion polymerization easily occurs if absolute or aqueous alcohols are used as polymerization media instead of water. The successful dispersion polymerization in alcohol or aqueous alcohol is presumably due to the larger hydrodynamic volume of PVME in these solvents than in water. For example, the intrinsic viscosities of the PVME (used in this work) at 30 °C in water, 50% alcohol and pure alcohol are 0.0325, 0.0460 and 0.0415 $\text{dm}^3 \text{g}^{-1}$, respectively. Furthermore, viscosities of water-alcohol mixtures are greater than the viscosity of water and have a maximum value at 1:1 (v/v) composition.¹² These higher viscosities of the dispersion media containing alcohol also help in deterring the settling of the suspended particles.

We present here some of our results of polymerization conducted in a 1:1 (v/v) mixture of ethyl alcohol and water. In our experiments pyrrole was added to the solution of anhydrous FeCl_3 and PVME in alcohol-water mixture and the reaction mixture was stirred magnetically for 24 h at 20 ± 2 °C under N_2 atmosphere. It was found that the conductivity of the polymers was very sensitive to the purity of the reagents used. In our work pyrrole (Merck) was freshly distilled under reduced pressure. PVME (Aldrich) was purified thrice by dissolution in water and precipitation by warming the solution. Anhydrous FeCl_3 (Merck) was used as such. Ethyl alcohol (Bengal Chemical & Pharmaceutical Works) was purified following the method of Danner and Hildebrand,¹³ dried over lime and then fractionated using a 1 m long column packed with 3 mm porcelain rings. Commercial distilled water was redistilled over alkaline permanganate. The PPy was obtained as a fine dispersion from which it was separated by centrifugation at 30 000 rpm for ca. 1 to 2 h. The separated PPy was then washed three times with hot (≈ 80 °C) 0.1 mol dm^{-3} HCl and two more times with hot distilled water

(in which PVME is insoluble). The polymers were then dried in vacuum at room temperature for 24 h for conductivity measurements. For chemical analysis the polymers were further dried in vacuum at 70 °C for 24 h. The PPy so purified and dried could be redispersed by sonication in many solvents e.g. water, alcohol, chloroform, acetone and dimethylformamide. The electron micrograph of a representative dispersion of redispersed PPy in ethyl alcohol is shown in Fig. 1. It is evident from the micrograph that the particles are not monodisperse. The particle diameter decreases with increase in dispersant concentration (Table 1) as one would expect. PVME turns out to be a very efficient dispersant for PPy since although its molecular weight was low ($M_v = 52\ 000$) it yielded small size particles when used at rather low concentrations. The dispersions do not yield free standing films presumably because the molecular weight of PVME used as dispersant was rather low. The conductivity was therefore measured using pellets of the polymers prepared at a pressure of 7.5×10^8 Pa. A visible-near IR absorption spectrum of the colloidal dispersion is similar to that reported by previous workers for electrochemically synthesized PPy films.¹⁴

The samples were found to contain a very low amount of iron (0.6 to 1 wt%) indicating that the dopant is most likely the Cl^- ion. The conductivities of the PPy-PVME composites given in Table 1 are close to that of pure PPy prepared under

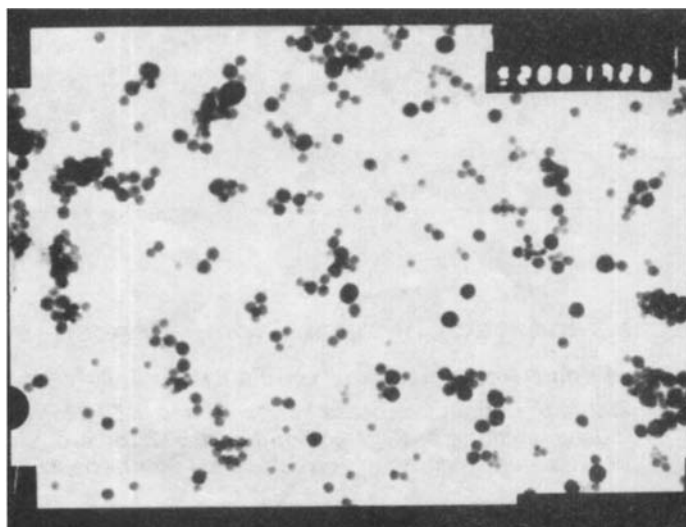


Fig. 1 Transmission electron micrograph of sample 4 redispersed in absolute alcohol; magnification: 20 000

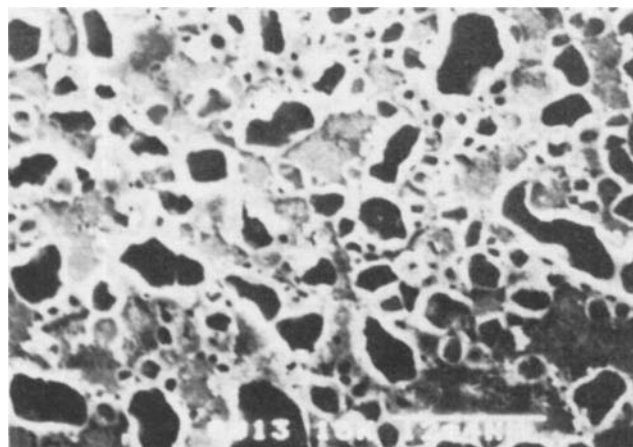


Fig. 2 Scanning electron micrograph of a 2:1 blend film of PPy (sample 2) and polystyrene

Table 1 Preparation of the PPy dispersion in 50% aqueous ethyl alcohol and the characterization of the PPy-PVME composites

Sample no.	Polymerization recipe ^a		Molar ratio		Cond. / S cm^{-1}	Particle size ^c /nm
	PVME /g	Pyrrole Conc./ mol dm^{-3}	$\text{C}_4\text{H}_3\text{N}^b$	$\text{C}_3\text{H}_6\text{O}^b$ Cl/N		
1	0	0.144	—	0.28	2.0	—
2	0.050	0.144	16.1	0.27	2.4	118 ± 19
3	0.150	0.144	7.1	0.29	1.6	88 ± 17
4	0.248	0.144	5.9	0.28	1.4	80 ± 15

^a Total reaction volume = 50 cm^3 ; $[\text{FeCl}_3]/[\text{pyrrole}] = 2.4$. ^b $\text{C}_3\text{H}_6\text{O}$ = repeating unit of PVME; $\text{C}_4\text{H}_3\text{N}$ = repeating unit of PPy. Calculated on the basis of reduced nitrogen content of the composites relative to pure PPy (sample 1). ^c Average of 50 particles measured from the micrographs with the help of a travelling microscope.

similar conditions in the absence of PVME. There is however a small decreasing trend in the conductivity values with increased incorporation of nonconducting PVME in the composites. This result may be indicative of some conductivity lowering effect by the nonconducting PVME in the composites. On the other hand, the conductivity of sample 2 prepared using 0.1% PVME turned out to be a bit higher than that of pure PPy (sample 1). However, the difference is within reproducibility limits. On the whole, it may be concluded that the presence of the nonconducting PVME in the composites does not affect the conductivity significantly. This phenomenon has been reported for some PPy colloids by Armes *et al.*^{5,6}

Since the PPy particles have PVME adsorbed on them, it is possible to prepare blends of PPy well dispersed in other polymers with which PVME is miscible as would be evident from the scanning electron micrograph of a blend of the PPy-PVME composites with polystyrene (PS) shown in Fig. 2. PS is known to be miscible with PVME which provides good adhesion between the dispersed PPy phase and the PS dispersion medium.¹⁵ Similar dispersions were obtained using some poly(acrylate)s and poly(vinyl ester)s as the dispersion media with which PVME is miscible.^{16,17}

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