

Dispersion polymerization of pyrrole using poly(vinyl methyl ether) as stabilizer

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Polypyrrole (PPy) dispersions are prepared at room temperature by oxidative polymerization using FeCl_3 oxidant in the presence of poly(vinyl methyl ether) (PVME) as stabilizer, and ethanol or aqueous ethanol as the dispersion medium. With water as dispersion medium, lower temperatures are required when the solvent property of water towards the PVME stabilizer becomes good enough to effect steric stabilization. PPy prepared in 50% ethanol or in water exhibits high specific conductivity, about 10 S cm^{-1} , while PPy prepared in ethanol under similar conditions has a conductivity two to four decades lower, depending on the FeCl_3 concentration and temperature used in the preparation. Transmission electron micrographs of PPy reveal that the particles are spherical but polydisperse.

(Keywords: dispersion polymerization; polypyrrole; stabilizer)

INTRODUCTION

One of the important areas of research on conducting polymers concerns methods for making them processable. Three main approaches have been reported¹: (i) synthesizing a soluble derivative²⁻⁸, e.g. poly(3-octyl pyrrole); (ii) polymerization in the matrix of a soluble polymer leading to a composite^{9,10}; and (iii) making dispersions of the insoluble conducting polymers¹¹⁻³⁰. The last method is of interest to us, because dispersion in a variety of solvents immensely increases processability. For example, apart from ease in coating applications, composites with other polymers that are soluble in the dispersion medium can be easily made.

However, dispersions of only a few conducting polymers have been reported so far. These polymers are polyacetylene (PAC)^{11,12}, polypyrrole (PPy)¹³⁻²¹ and polyaniline (PAN)²²⁻³⁰. The dispersion medium generally used was water, but some non-aqueous solvents have also been used for PPy¹⁹. In a preliminary communication we have reported the synthesis of conducting PPy particles dispersible in both aqueous and non-aqueous media²¹. This was achieved by dispersion polymerization of pyrrole in absolute or aqueous ethanol using FeCl_3 as initiator dopant and poly(vinyl methyl ether) (PVME) as the dispersant. PVME is adsorbed on the conducting polymer particles during synthesis and prevents their agglomeration by steric stabilization^{14,31-34}. The conducting PPy particles can be isolated by centrifugation and redispersed in a variety of solvents, including water, since PVME is soluble in both water and several organic solvents. Here we present details of the synthesis and characterization of the dispersible conducting PPy particles.

EXPERIMENTAL

Purification of reagents and chemicals

Pyrrole (E. Merck, Germany) was distilled at a reduced pressure of 60–70 mmHg. The middle fraction of the distillate was collected, transferred into a number of small tubes, degassed in a vacuum line (1×10^{-5} torr), sealed and stored in the dark at -10°C . PVME (Aldrich) was obtained as a 50% solution in water. It was purified three times by dissolution in water and isolation by warming the solution. It was then dried under vacuum at 70°C for 72 h. The viscosity-average molecular weight of PVME was determined to be 52 000. Anhydrous FeCl_3 (E. Merck, Germany) was used without purification. Ethanol (Bengal Chemical and Pharmaceutical Works, India) was purified following the method of Danner and Hildebrand³⁵. It was fractionally distilled using a fractionating column 1 m long packed with 3 mm porcelain rings. Commercial distilled water was redistilled from alkaline permanganate solution in an all-glass distillation unit, and the middle fraction was used.

Polymer synthesis

Polymerization was carried out in double-walled glass vessels; thermostated water was circulated through the outer jacket of the vessels to maintain constant temperature. Pyrrole was added to the solution of FeCl_3 and PVME dissolved in the solvent (water, ethanol or 50% water/ethanol mixture) and the reaction mixture was stirred magnetically under nitrogen atmosphere. Polymerization time was varied from 5 to 24 h depending upon the solvent and concentration of FeCl_3 used. After polymerization, the PPy particles were separated from the dispersions by centrifugation, washed three times with hot ($\sim 80^\circ\text{C}$) 0.1 mol l^{-1} HCl and twice more with hot water in order to remove impurities (Fe^{2+} and Cl^-) and

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dried in vacuum at 70°C for 24 h for conductivity measurements. For chemical analyses, the polymers were dried further at 70°C in vacuum 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 microscopic studies were made on dilute (~200 ppm) dispersion dried on carbon-coated copper grids using a Jeol JEM 100CT electron microscope.

The N content of PPy was estimated by semimicro Kjeldahl technique³⁶. The Cl content was estimated by burning the samples in an oxygen flask (Heraeus, Germany) followed by absorption of the gases and titration, according to a standard method³⁷. The accuracy of the method was checked using *p*-chlorobenzoic acid and found to be satisfactory. The amount of PVME adsorbed per unit mass of PPy for the composites was calculated on the basis of reduced nitrogen content of the composites relative to that of pure PPy.

For the determination of Fe in PPy the samples were digested with conc. HNO₃ and the Fe³⁺ in the resulting solution was reduced by hydroxylamine to Fe²⁺ which was estimated spectrophotometrically after reacting with *o*-phenanthroline³⁸.

RESULTS

Dispersion polymerization using PVME stabilizer is not supported in water at room temperature but can be carried out in water at lower temperature ($\approx 0^\circ\text{C}$). In absolute or in aqueous ethanol (minimum 30% ethanol by volume) dispersion polymerization takes place both at ambient and lower temperatures ($\approx 0^\circ\text{C}$). Figure 1 shows the cloud temperature (T_p) of 4% (w/v) solution of PVME in water and in aqueous ethanol with changing ethanol concentration. It is evident from the figure that increasing the ethanol concentration increases the cloud point and hence makes the aqueous ethanol a better solvent for PVME than water. These results also indicate that the solvent power of water as well as of aqueous ethanol towards PVME increases with decreasing temperature. Cloud points of solutions with ethanol content greater than about 40% were not studied. However, the measurement of intrinsic viscosity of PVME in 50% ethanol and in ethanol reported in our earlier work revealed that the former is a better solvent than the latter²¹. These results are used for

discussion of the importance of the solvent character of the dispersion medium towards PVME in sustaining dispersion polymerization.

Figure 2 shows that the rate of polymerization (R_p) is decreased greatly when the medium is changed from 50% ethanol to absolute ethanol and also that increasing FeCl₃ concentration brings about an increase in rate.

Table 1 gives the details of the polymerization using 50% aqueous ethanol as the polymerization medium and the characterization data of the polymers and their particle sizes. The PVME content of the polymers increases with increase in initial PVME concentration. The adsorption isotherms relating mass of PVME (m) adsorbed to that of PPy with the equilibrium PVME concentration in 50% aqueous ethanol medium are

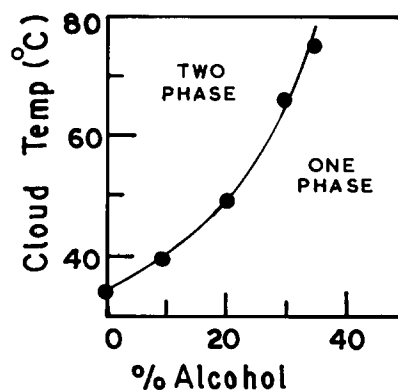


Figure 1 Cloud temperatures of solutions of PVME (4% w/v) in water and aqueous ethanol media

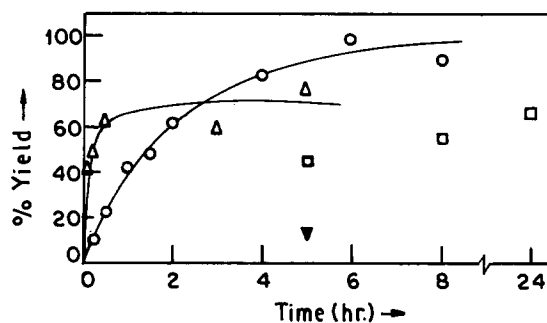


Figure 2 Yield of PPy with time in dispersion polymerization. Medium = 50% ethanol: O, [FeCl₃]=0.35 mol l⁻¹, PVME=0.1% w/v, temperature = 20°C; Δ, [FeCl₃]=0.7 mol l⁻¹, PVME=0.5%, temperature = 2°C. Medium = absolute ethanol: □, [FeCl₃]=0.7 mol l⁻¹, PVME=0.5%, temperature = 20°C; ▼, [FeCl₃]=0.7 mol l⁻¹, PVME=0.5%, temperature = 2°C

Table 1 Preparation of PPy dispersions in 50% aqueous ethanol using 0.7 mol l⁻¹ FeCl₃ at 2°C. [FeCl₃]:[Py]=2.4, polymerization time = 5 h, [pyrrole]=0.288 mol l⁻¹

| Sample | PVME (% w/v) | Yield (%) | PVME/PPy (w/w) | Cl/N | σ (S cm ⁻¹) | Particle size ^a (nm) | Fe content (%) |
|--------|--------------|-----------|----------------|------|--------------------------------|---------------------------------|----------------|
| 1 | 0.0 | 48 | 0.0 | 0.34 | 23.0 | — | 1.74 |
| 2 | 0.4 | 100 | 0.069 | 0.30 | 11.7 | 134 ± 29 | 0.47 |
| 3 | 0.5 | 100 | 0.098 | 0.31 | 10.5 | 107 ± 23 | 0.51 |
| 4 | 0.6 | 100 | 0.120 | 0.30 | 9.8 | 118 ± 29 | 0.60 |
| 5 | 0.7 | — | 0.175 | 0.30 | 9.1 | 118 ± 33 | 0.61 |
| 6 | 0.8 | — | 0.164 | 0.31 | 7.6 | 124 ± 27 | 0.79 |

^a Average of 100 particles

shown in Figure 3 for two different temperatures, namely 2 and 20°C. A higher FeCl₃ concentration was used at the lower temperature. At 0.35 mol l⁻¹ FeCl₃ concentration at 20°C, a plateau appears in the adsorption curve when the equilibrium PVME concentration is 0.15% and the saturation value of *m* is 0.17. At the higher FeCl₃ concentration, namely 0.7 mol l⁻¹, but at lower temperature (2°C) the plateau occurs at higher equilibrium PVME concentration (~0.5%) and the value of *m* at the plateau is also somewhat higher, being 0.2. One further characteristic of the isotherms is that at the lower temperature, adsorption is very low at the lower PVME concentration region.

In our earlier communication²¹ we reported that dispersion polymerization of pyrrole at 20°C in 50% aqueous ethanol medium using 0.35 mol l⁻¹ FeCl₃ yielded PPy particles of specific conductivity ~2 S cm⁻¹. The present results given in Table 1 show that particles of conductivity as high as 11.7 S cm⁻¹ are obtained when FeCl₃ concentration is 0.7 mol l⁻¹ and the temperature is lower (~2°C). Table 1 also shows that as the content of the non-conducting PVME in the particles increases (column 4) conductivity decreases, as is expected. But the surprising feature is that the conductivity decrease in respect of pure PPy on incorporation of the non-conducting PVME is not as great as would be expected if all the particles are covered with the non-conducting PVME on the surface. The Fe content of the particles is negligible and it therefore follows from the high Cl content that the dopant is mostly Cl⁻ ion. The Cl/N ratio indicates that one in approximately every three pyrrole units in PPy is doped (oxidized). The transmission electron micrograph (Figure 4) shows that the particles are spherical but not monodisperse. The average particle diameters of 100 randomly chosen particles are given in Table 1. In view of the polydispersity and the rather small number of particles counted, the values are not free from sampling errors. Hence, the sizes of the particles reported in Table 1 are at best semiquantitative. However, in our previous work²¹ using lower FeCl₃ concentration (0.35 mol l⁻¹) at 20°C, it was found that the particle size decreases with increasing PVME concentration. This trend is less certain at the higher FeCl₃ concentration used to prepare the dispersions shown in Table 1.

Table 2 gives the results of the dispersion polymerization and the characterization data for the polymers prepared in ethanol at 20°C. The conductivity does not show any systematic variation either with the Cl/N ratio or with the concentration of PVME used in preparing the

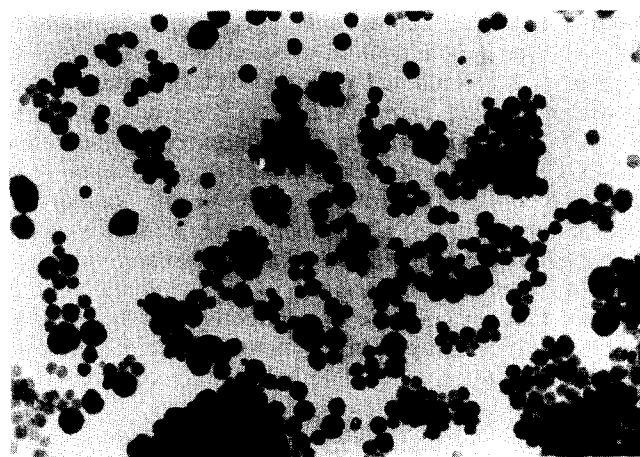


Figure 4 Transmission electron micrograph of sample 4 prepared in 50% ethanol, and redispersed in ethanol after isolation and drying. Magnification 17 500 ×

Table 2 Preparation of PPy dispersions in absolute ethanol at 20°C. [FeCl₃]:[Py] = 2.4, polymerization time = 24 h

| Sample | [FeCl ₃] (mol l ⁻¹) | [Pyrrole] (mol l ⁻¹) | PVME (%, w/v) | Cl/N | σ (S cm ⁻¹) |
|--------|--|-------------------------------------|------------------|------|----------------------------|
| 7 | 0.35 | 0.144 | 0.0 | 0.20 | 1.3 × 10 ⁻⁴ |
| 8 | 0.35 | 0.144 | 0.1 | 0.19 | 3.3 × 10 ⁻⁴ |
| 9 | 0.35 | 0.144 | 0.3 | 0.18 | 1.2 × 10 ⁻² |
| 10 | 0.35 | 0.144 | 0.5 | 0.18 | 6.8 × 10 ⁻³ |
| 11 | 0.70 | 0.288 | 0.1 | 0.17 | 6.2 × 10 ⁻⁴ |
| 12 | 0.70 | 0.288 | 0.3 | 0.25 | 1.3 × 10 ⁻³ |
| 13 | 0.70 | 0.288 | 0.5 | 0.20 | 5.0 × 10 ⁻⁴ |

Table 3 Effect of FeCl₃ concentration on PPy conductivity. Medium = absolute ethanol, [FeCl₃]:[Py] = 2.4, polymerization temperature = 20°C

| Sample | [FeCl ₃] (mol l ⁻¹) | Polymerization time | Yield (%) | σ (S cm ⁻¹) |
|--------|--|---------------------|--------------|----------------------------|
| 14 | 0.35 | 24 h | 65 | 1.3 × 10 ⁻⁴ |
| 15 | 1.00 | 4.5 h | 31 | 5.2 |
| 16 | 2.50 | 20 min | 46 | 74.3 |

Table 4 Preparation of PPy dispersions in absolute ethanol at 5°C. [FeCl₃]:[Py] = 2.4, polymerization time = 5 h, [pyrrole] = 0.288 mol l⁻¹, [FeCl₃] = 0.7 mol l⁻¹

| Sample | PVME (%, w/v) | Cl/N | σ (S cm ⁻¹) |
|--------|------------------|------|----------------------------|
| 17 | 0.1 | 0.29 | 1.2 × 10 ⁻¹ |
| 18 | 0.3 | 0.28 | 6.5 × 10 ⁻² |
| 19 | 0.5 | 0.30 | 3.9 × 10 ⁻² |

dispersions. The conductivity of the samples is also much lower, σ being in the range of 1 × 10⁻² to 1 × 10⁻⁴ S cm⁻¹. The doping level, as given by the Cl/N ratio, is also low in these samples, being around 0.2.

Results of experiments conducted in the absence of PVME given in Table 3 show that the conductivity of PPy increases greatly with increase in FeCl₃ concentration when ethanol is used as the polymerization medium. A 2.5 mol l⁻¹ concentration of FeCl₃ at 20°C yields PPy of conductivity 74.3 S cm⁻¹, which is in sharp contrast to the value of 1.3 × 10⁻⁴ S cm⁻¹ achieved using FeCl₃ at 0.35 mol l⁻¹.

Comparison of the results given in Tables 2 and 4

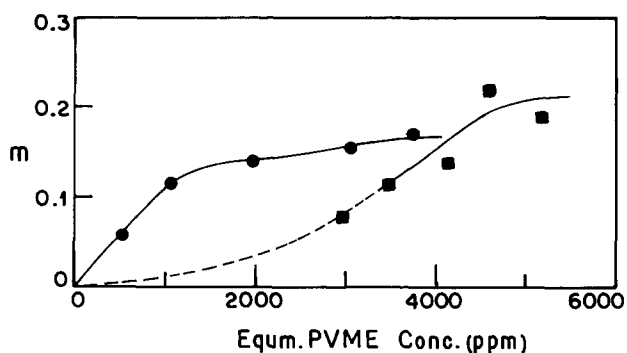


Figure 3 Adsorption isotherm of PVME on PPy latex particles in 50% ethanol. Latex prepared with 0.35 mol l⁻¹ FeCl₃ at 20°C (●) and 0.7 mol l⁻¹ FeCl₃ at 2°C (■)

reveals that with ethanol as the polymerization medium, lowering the polymerization temperature from 20 to 5°C improves the conductivity by two orders of magnitude, reaching a value of $\sigma = 0.12 \text{ S cm}^{-1}$. Earlier, Machida *et al.*³⁹ reported that, for PPy prepared in methanol using FeCl_3 oxidant, the conductivity increases with decrease in polymerization temperature, reaches a maximum at about 0°C and then decreases slowly as the polymerization temperature is further lowered.

From the Cl/N data given in Tables 2 and 4 it is evident that the increase in conductivity with lowering polymerization temperature is associated with a greater level of oxidation as manifested in an increased Cl/N

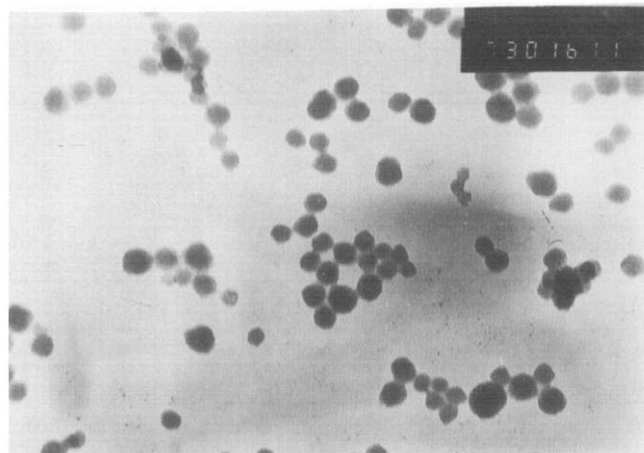


Figure 5 Transmission electron micrograph of sample 17 prepared in ethanol and redispersed in ethanol after isolation and drying. Magnification 73 000 ×

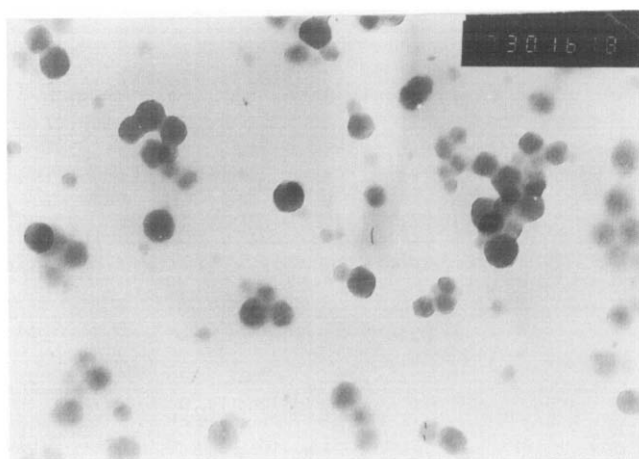


Figure 6 Transmission electron micrograph of sample 21 prepared in water and redispersed in water after isolation and drying. Magnification 73 000 ×

ratio at lower polymerization temperature. However, even though the Cl/N ratio reached the level of 0.3 for PPy prepared in ethanol at 5°C, the conductivity still remains about two decades lower than the value found for PPy samples prepared in 50% ethanol at 2°C (reported in Table 1), when the doping level was about the same. It may be further noted for the polymers prepared in ethanol at lower temperature (5°C) (Table 4) that the conductivity variation with PVME concentration used in the synthesis is no longer erratic, unlike those prepared at 20°C (Table 2). The conductivity decreases as the PVME concentration increases, as is expected. Concentrations of FeCl_3 much higher than 0.7 mol l^{-1} could not be used for dispersion polymerization in ethanol because dispersions are not obtained in these solutions. A transmission electron micrograph of the PPy particles prepared in ethanol (Figure 5) shows that the particles are spherical but polydisperse like the PPy colloids prepared in 50% ethanol. Comparison of the particle diameter ($46 \pm 8 \text{ nm}$ for sample 17) with those given in Table 1 for dispersions prepared in 50% ethanol using the same FeCl_3 concentration but a higher stabilizer concentration reveals that much smaller size particles are obtained in ethanol.

Table 5 shows the results of dispersion polymerization at 2°C using water as the dispersion medium. With 0.5% PVME stabilizer, the dispersion polymerization is effected at low FeCl_3 concentration, namely 0.14 mol l^{-1} , but partial coagulation takes place when the FeCl_3 concentration is increased to 0.35 mol l^{-1} (sample 22). This result indicates that, apart from steric stabilization, there is some contribution of charge on the colloidal PPy particle to colloid stabilization. Increasing the PVME concentration to 1% eliminates the problem of coagulation (sample 23). The Cl/N ratios of the samples are similar to those attained in 50% ethanol (cf. Table 1) and the conductivity is as good. The transmission electron micrograph (Figure 6) of the PPy particles prepared as well as redispersed in aqueous medium shows that spherical but polydisperse particles are obtained in this medium also. The particle diameter ($51 \pm 9 \text{ nm}$) measured for the sample (no. 21) prepared using the lowest FeCl_3 concentration (0.14 mol l^{-1}) turns out to be smaller than those prepared in 50% ethanol.

DISCUSSION

In the dispersion polymerization process, the dispersant is adsorbed on the suspended PPy particles and acts as a steric stabilizer³¹⁻³⁴. It is therefore expected that the stabilizer will act better in a medium where its hydrodynamic volume is greater. Figure 1 indicates that water is a poor solvent for PVME whereas absolute or

Table 5 Preparation of PPy dispersions in aqueous medium at 2°C

| Sample | $[\text{FeCl}_3]$ (mol l^{-1}) | $[\text{Pyrrole}]$ (mol l^{-1}) | PVME (%, w/v) | $[\text{FeCl}_3]:[\text{Py}]$ | Cl/N | σ (S cm^{-1}) |
|-----------------|--|---|------------------|-------------------------------|------|------------------------------------|
| 20 ^a | 0.35 | 0.144 | 0.0 | 2.4 | 0.27 | 8.3 |
| 21 | 0.14 | 0.144 | 0.5 | 1.0 | 0.31 | 4.4 |
| 22 ^b | 0.35 | 0.144 | 0.5 | 2.4 | 0.32 | 10.2 |
| 23 | 0.35 | 0.144 | 1.0 | 2.4 | 0.32 | 4.2 |

^a Polymerization temperature 30°C

^b Partial coagulation occurred

aqueous ethanols are good solvents, hence dispersion polymerization is supported in these latter solvents but not in water at room temperature. The cloud temperatures indicate that the solvent property would be better the lower the temperature. Hence, the dispersion polymerization has been possible in water at the low temperature ($\sim 2^\circ\text{C}$). A further consequence of solvent power is that it will be less easy to adsorb from solution in a solvent whose solvent power is better. This explains the adsorption isotherms, which show that at lower temperature higher equilibrium PVME concentration is required to achieve the same degree of adsorption as attained at higher temperature.

The stabilizer adsorption in the present case may be assisted by the formation of H bonds involving the $-\text{O}-$ group of PVME with the $>\text{N}-\text{H}$ proton of PPy. There is some evidence in the literature about specific interaction of pyrrole with compounds having ether linkages, such as tetrahydrofuran (THF) and dioxane. Thus, Hawranek and Sobczyk determined weak H-bonding interactions of pyrrole with dioxane and THF from dipole moment measurements⁴⁰. Furthermore, Raveillo and Gomel reported that the excess volumes of pyrrole/dioxane and pyrrole/THF mixtures are all negative⁴¹. These results indicate specific interactions between pyrrole and these ethers.

As has been pointed out earlier in this paper, the conductivity of the PPy particles is rather insensitive to the presence of a non-conducting PVME layer on their surface. This was noted earlier by Armes *et al.*¹⁷. Assuming that all the PVME was on the surface, an adsorption layer about 2.2 nm thick was estimated for sample 4 in Table 1 from the particle size, the amount of PVME adsorbed and its density. Armes *et al.* pointed out that the layer is too thick for an electron tunnelling mechanism of conduction to operate¹⁷. Subsequently, using scanning tunnelling microscopy on both PPy and PAN latex particles, Armes *et al.*⁴² showed that the stabilizer coating is non-uniform in dried particles. Thus, physical contact of particles through the bare surfaces is possible and the conductivity is not greatly affected by the stabilizer. The non-uniformity in stabilizer coating is believed to occur during drying of the particles⁴².

As regards the size of the particles obtained in the different media, it may be noted that the coalescence of the particles will continue until the attractive force between the particles becomes equal to the steric repulsive force. In a better solvent for the stabilizer, this repulsive force will be greater for a given size of the particle with the same degree of stabilizer coverage, because of greater hydrodynamic volume of the stabilizer in such a medium. On the other hand, the rate of adsorption of the stabilizer on the particle surface will be lower the better the solvent environment. Also, to stabilize a dispersion of a given particle concentration, a greater amount of stabilizer adsorption would be needed in a poorer solvent in view of the lower hydrodynamic volume of the stabilizer in such solvents. This can be achieved only when the particle surface area is larger, i.e. when particles are smaller in size. Thus, particles of smaller size are obtained in the two media, water and ethanol, which are inferior to 50% ethanol in terms of solvent power towards PVME, where larger size particles are obtained.

The slower polymerization in ethanol-rich solvents is attributable to FeCl_3 being complexed by ethanol⁴³ and the complex oxidizing pyrrole at a slower rate.

Regarding polydispersity of the particles it may be noted that Armes and Aldissi also obtained polydisperse PPy particles when they polymerized pyrrole in some ester solvents using FeCl_3 oxidant and poly(vinyl acetate) stabilizer¹⁹. However, when poly(vinyl alcohol-co-acetate) was used as stabilizer in water as the dispersion medium, the polydispersity was small. Armes and Aldissi attributed greater polydispersity in the former case to very rapid oxidative polymerization taking place in the ester media with which FeCl_3 interacts poorly. However, this explanation does not seem to be tenable in our case since we have shown (Figure 2) that polymerization rate is drastically changed with the solvent composition in the present case, yet polydisperse particles are obtained in every case. The problem will be looked into in our future work.

The electron micrographs show some aggregates of particles. It may be recalled that these micrographs were taken after the particles were isolated, dried and redispersed by sonication. Redispersion of the dried particles yielded dispersions of only low solid content. An explanation for this observation may be obtained from the scanning tunnelling microscopic work of Armes *et al.*⁴², discussed earlier in this paper, who concluded that the stabilizer coating in the dried particles becomes non-uniform. Presumably, the uniform stabilizer coverage is not restored during redispersion, which gives rise to dispersions of low solid content. The non-uniform coverage also helps the particles to adhere together so that aggregates are seen in the electron micrograph. It may be noted that unlike the dried particles, redispersion occurs easily when the isolated particles are not dried.

The low level of conductivity of PPy prepared in absolute ethanol at 20°C at FeCl_3 concentration $\leq 0.7 \text{ mol l}^{-1}$ (Table 2) may be attributed to the poor oxidative environment provided under these conditions. This is reflected in low values of Cl/N ratios in these PPy samples. Evidently, complexing of FeCl_3 with ethanol⁴³ lowers the oxidation power of FeCl_3 . Increase in FeCl_3 concentration increases the oxidation power and indeed it has been shown by Machida *et al.* that the oxidation potential of the Fe(III)/Fe(II) system in methanol increases with increase in FeCl_3 concentration³⁹. It thus follows that the oxidation power of solution containing high FeCl_3 concentrations ($\geq 1 \text{ mol l}^{-1}$) is great enough to effect a large increase in conductivity compared to the case when FeCl_3 concentration is lower, e.g. 0.35 mol l^{-1} (Table 3). However, the conductivity does not depend solely on the overall level of oxidation determined from the Cl/N ratio. For example, although the Cl/N ratio (0.3) of sample 19 prepared in absolute ethanol is similar to that of sample 3 prepared in 50% ethanol (Table 1) under almost similar conditions, the conductivity of the former is more than two decades lower than that of the latter. This discrepancy may be explained by referring to the work of Kang *et al.*, who elucidated the chemical states of N and Cl in PPy samples prepared by FeCl_3 oxidation method in different media with the help of X-ray photoelectron spectroscopy⁴⁴. Their results establish that it is not the Cl/N ratio alone but also the nature of the chemical binding of Cl with PPy that influences the conductivity greatly. According to their finding, the dopant (Cl) is present in three distinct chemical states, ionic, covalent and intermediate. The intermediate Cl was attributed to originate from the 'charge transfer interactions between Cl and the metal

like conducting state of the polymer chain'. High conductivity ($\sigma = 16\text{--}40 \text{ S cm}^{-1}$) in their samples was found to be associated with the presence of this intermediate Cl. The Cl/N ratios of those samples ranged between 0.28 and 0.48. However, in one case, where the intermediate Cl was absent even though the Cl/N ratio was 0.32, the conductivity was indeed low ($\sigma \approx 10^{-2} \text{ S cm}^{-1}$). Furthermore, they concluded that the intermediate Cl was found to be absent in samples prepared under less oxidative environments.

In conclusion, it turns out that PPy particles covering a wide range of conductivity can be prepared in dispersion form using PVME stabilizer, varying the composition of the dispersion medium from water to mixtures of alcohol and water to pure alcohol, and also varying the temperature and concentration of FeCl_3 oxidant.

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