Novel Colloidal Polyaniline Fibrils Made by Template Guided Chemical Polymerization

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The colloidal fibrils of polyaniline–poly(acrylic acid) complex were first synthesized by template guided chemical polymerization; their morphology and the electronic absorption spectra in aqueous solution are reported.

Although polyaniline is likely to be among the most useful of all conducting polymers,[1] its lack of solubility has severely limited its applications. Recent studies on colloidal suspensions[2] and substituted polyaniline[3] have been designed to address this problem. We report here a new method for preparing colloidal polyaniline fibrils by chemical polymerization. In addition to the advantage of aqueous dispersion, these fibrils were found to be very uniform in shape, and the colloid was solution doped and undoped to obtain substantially the same colour changes as solid polyaniline films on substrate.[4,5]

A key to the synthesis of such colloidal polyaniline fibrils is the chemical polymerization of aniline in the presence of polyacids. For example, commercial poly(acrylic acid) (25 ml) (Aldrich, M_W = 90000, 25 wt.% solution in water) was dissolved in tetrahydrofuran (THF) (200 ml) to provide a homogeneous clear solution. To this solution was added an excess of freshly distilled aniline, and the mixture was vigorously stirred to give a gel composed of a molecular complex of aniline and poly(acrylic acid). The gel complex was washed with THF (2 × 30 ml) to remove the excess of aniline and redissolved in HCl (200 ml; 1 mol dm^{-3}), also to afford a clear solution. Then, hydrogen peroxide (1 ml; 30%) and iron(III) chloride (5 ml; 5%) were added to the reaction mixture. Stirred for 1 h, the reaction mixture turned dark green with slight turbidity. A small amount of particulate matter was removed by filtering with quantitative grade filter paper (Fisher Scientific, Fisherbrand Cat. No. 09-790-2A, particle retention 2–5 μm) to provide an almost clear, dark-green solution.

The solution was found to contain a colloidal suspension of fibrils of two different sizes. Fig. 1 shows a scanning electron micrograph (SEM) of long fibrils with diameter *ca.* 50 nm (excluding sputter coating thickness) and length between 1–5 μm. These fibrils were captured by refiltering with a 5 μm polycarbonate membrane filter (Poretics, Cat. No. 13068). The filtrate is a clear, dark-green colloidal suspension containing smaller fibrils about 50 nm in diameter and 100–200 nm in length as shown in Fig. 2; this transmission electron micrograph (TEM) was obtained by using 1% ammonium molybdate in 2% sodium acetate as staining solution. It is interesting to note that the diameter of the small fibrils is about the same as that for the long fibrils mentioned above, and that the small fibrils are remarkably uniform in shape.

In the above-mentioned method we were able to prepare colloidal suspensions, while in contrast, solid precipitates of aniline were formed in the conventional chemical polymerization methods. Other polyacids can also be used for forming colloidal suspensions. As an example, we made colloidal suspensions of poly(2-chloroaniline) in the presence of poly(styrenesulphonic acid) in a variation of the above method. The colloids were examined under TEM (without staining) and globular particles of *ca.* 100 nm diameter with S to Cl ratio of approximately 1:1 were observed. X-Ray microanalyses during the TEM measurements was used to determine the S:Cl ratio. The colloids contain a mixture of polyaniline and poly(styrenesulphonate). The globular particles, also seen in preparations in which the Cl atom was changed to H, have the same morphology as that of the electrochemically synthesized counterpart reported in ref. 6, except that the electrochemically synthesized solid film appears to be composed of aggregations of the globular particles.

The morphology of the long fibrils shown in Fig. 1 is the same as the polyaniline–poly(acrylic acid) complex made by

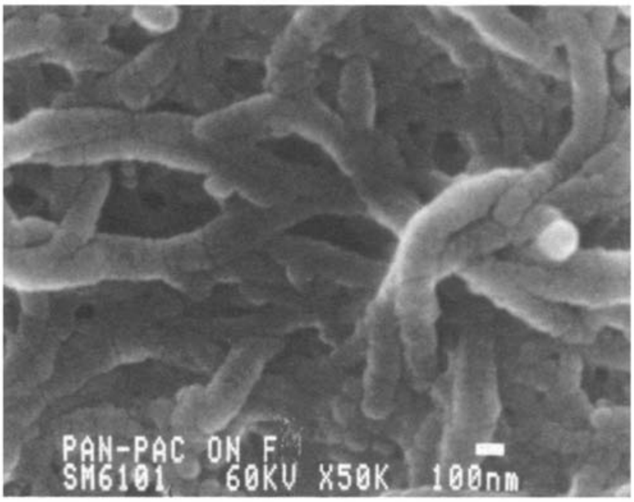

Fig. 1 SEM of long fibrils captured by membrane filter. These fibrils contain polyaniline–poly(acrylic acid) complexes.

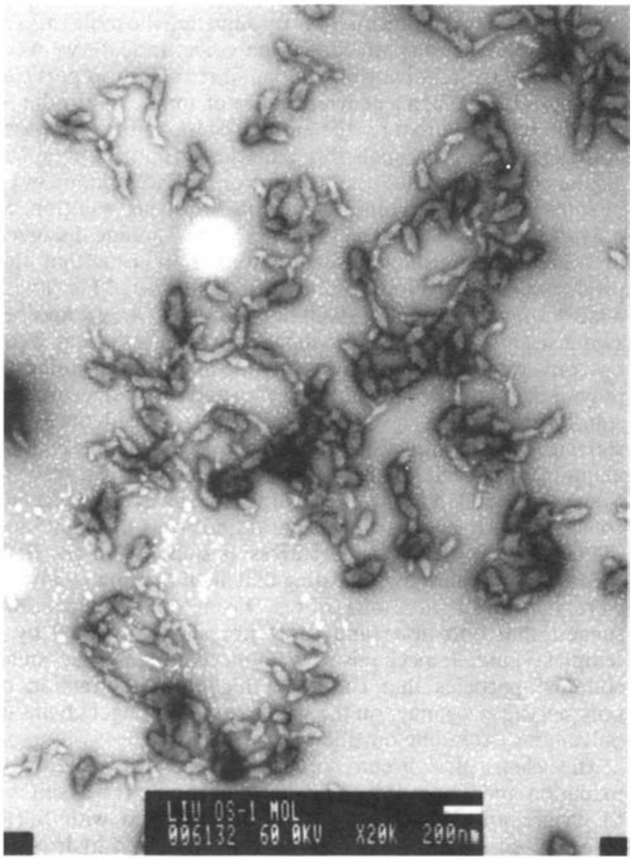

Fig. 2 TEM of small fibrils within the dark-green solution. These fibrils contain polyaniline–poly(acrylic acid) complexes.

electrochemical polymerization reported previously.[6] It was noted in ref. 6 that these fibrils contain molecular complexes of polyaniline and poly(acrylic acid) as supported by elemental analysis[6] and by the fact that the polyacid strongly controls polymer morphology. The electrochemically synthesized polyaniline–poly(acrylic acid) and polyaniline–poly(styrenesulphonic acid) each have morphological signatures that are in striking contrast with those obtained from ordinary electrochemical synthesis. The observed strong morphological control suggests a template guided chemical polymerization process that involves the binding of monomers of aniline onto the polyacid, followed by polymerization of the monomers attached to the polyacid template. When the template molecule is an extended linear chain of poly(acrylic acid), the morphology of the polymer is that of the long fibres. When the template molecule is poly(styrenesulphonic acid), the random coil conformation of the template–monomer complex leads to the observed globular morphology. Since polyaniline and poly(acrylic acid) are, respectively, polycation and polyanion, the product belongs to the general class of polycation–polyanion complexes sometimes used as hydrogel.[7] In the chemical synthesis reported here we find morphological signatures that parallel those found in the electrochemical synthesis. Furthermore, these morphologies are distinct from those of other chemically synthesized polyanilines. Therefore, we propose that the fibres of Fig. 1, like its counterpart in electrochemically synthesized fibres, also consists of the polyaniline–poly(acrylic acid) complex. This approach for colloidal formation is significantly different from the previous work on sterically stabilized colloidal suspensions of polyaniline. In that work the stabilizer, a copolymer, was chemically grafted[2] onto polyaniline micro-particles.

Because of the difference in size between the small particles of Fig. 2 and the long fibres of Fig. 1, one might suspect that there exist two different mechanisms for the formation of particles of disparate sizes. However, a number of observations seem to favour a close relationship between the mechanisms for their formation. By adjusting the mole ratio of the aniline monomers attached to poly(acrylic acid), we were able to vary the relative yield of long fibres and short particles in the product. When a heavier dosage of aniline is introduced into the reaction mixture, the amount of long fibres increases at the expense of the small fibril particles. In another chemical synthesis, we increased the amount of aniline monomers by introducing the monomers into the aqueous solution of polyacid and oxidant *via* an organic phase of aniline dissolved in toluene. Electron microscopy studies indicate that this product contained almost exclusively long fibres of Fig. 1 with a much smaller content of small fibrils of Fig. 2. In yet another synthesis, we showed that the short fibril particles of Fig. 2 can be converted into long fibres by allowing more aniline to polymerize onto the short fibrils. We used the green colloidal solution containing short fibrils of Fig. 2 and oxidants as the starting solution (long fibres were removed by 5 μm filter), an aliquot of organic phase containing aniline dissolved in toluene was added to it while stirring vigorously. The product consists mainly of long fibres that do not pass through 5 μm filters, and the filtrate is colourless as opposed to the dark green starting solution, indicating that all of the small particles were converted into long fibres. From this evidence, we suggest that both long and short fibres were formed by a template guided mechanism. We speculate that the small colloidal particles that contain a higher mole fraction of poly(acrylic acid) may, on the whole, exist as longer chains of polyanions extending outside the particles.

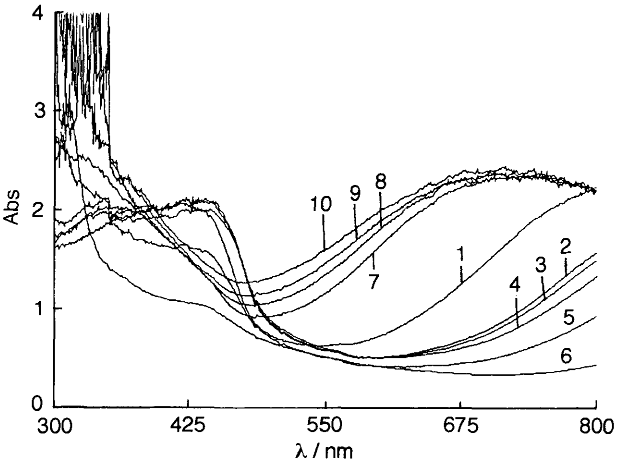

Fig. 3 Electron absorption spectra obtained during titration of the colloidal polyaniline with reductant and oxidant, spectra 2–4 (0.1 mol dm^{-3} $SnCl_2$), spectra 5–6 (2 mol dm^{-3} $SnCl_2$), spectra 7–10 [0.1 mol dm^{-3} $Ce(NH_4)_2(SO_4)_3$]. Conditions are given in Table 1.

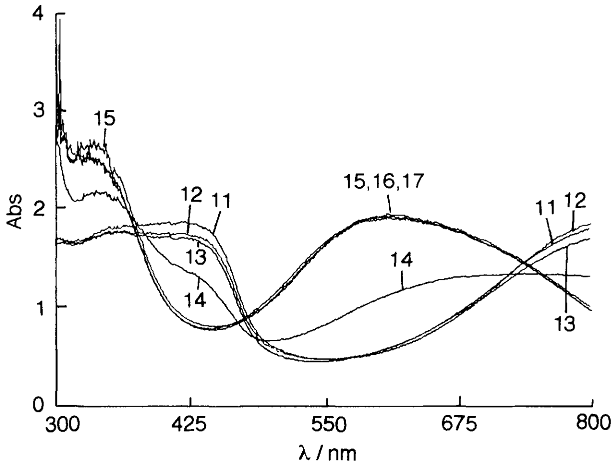

Fig. 4 Electronic absorption spectra obtained during titration of the colloidal polyaniline with 0.1 mol dm^{-3} NaOH. Conditions are given in Table 1.

Table 1 Rest potential (RP) *vs.* SCE and pH for spectra in Figs. 3 and 4

Spectrum	RP/*V*	pH
1	0.445	2.169
2	0.259	1.606
3	0.244	1.240
4	0.152	0.955
5	0.014	−0.011
6	0.041	−0.844
7	0.463	1.989
8	0.472	1.964
9	0.481	1.950
10	0.481	1.933
11	0.392	2.257
12	0.372	2.743
13	0.332	3.484
14	0.209	6.627
15	−0.039	10.911
16	−0.060	11.370
17	−0.070	11.507

The clear, dark-green solution can change colour by oxidation–reduction or by acid–base reactions. It was diluted to ensure an absorbance <3.00, then titrated with tin(II) chloride, ceric ammonium sulphate and sodium hydroxide. Some representative *in situ* spectra are shown in Fig. 3 and 4, the rest potential (RP) and pH value for each spectrum are listed in Table 1. The spectra shown in Fig. 3 are not significantly different from those for electrochemically synthesized polyaniline films[4,5] at the corresponding pH and electrochemical potential. The initial diluted reaction mixture was measured RP = +0.445 and pH = 2.169, and spectrum 1 recorded. As more reductant was added to the initial diluted reaction mixture, the absorbance at 320 nm increased and the 800 nm band levelled off (spectrum 6), which indicated that the complex fibrils were close to the fully reduced leuco form. When ceric ammonium sulphate was added dropwise to the initial reaction mixture, the 800 nm band is blue shifted towards 610 nm in the sequence of spectra 7 to 10, and there is a concurrent increase of absorbance at 330 nm. This indicates that the colloidal green conductor can be chemically oxidized to yield colloidal blue insulator in the aqueous solution.

Fig. 4 shows the spectra that result from base titration. The absorbance changed very little during the initial stage of titration when free HCl or the excess carboxylic group in solution are being neutralized. As more base was added to reach pH 10.9, the RP changed to −0.039 (spectrum 15), and the colour turned blue, consistent with the previously reported pH–potential phase diagram.[8] It should be noted that the short fibrils can undergo transformation to all accessible forms of polyaniline and that they remain as a colloidal suspension in aqueous solution over a wide range of pH and oxidation states. However, the colloidal suspension is precipitated by addition of strong oxidant. When ceric ammonium sulphate (1 ml) was added to the base-treated reaction mixture (spectrum 17) the short complex fibrils begin to precipitate. This indicates that the complex fibrils are less stable in the fully oxidized form than in the fully reduced leuco form. The stability of the polyaniline–polyacid complex seems to be established by the attractive force between the secondary amine of polyaniline and the carboxylic group of poly(acrylic acid) within the fibrils.

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