polymer communications

Polyaniline dispersions: preparation of spherical particles and their light-scattering characterization

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Polyaniline dispersions can be prepared by the oxidative polymerization of aniline in the presence of the steric stabilizer, poly(vinyl alcohol). Dispersion particles are spherical and relatively uniform. Dynamic light scattering was used to determine their hydrodynamic radius and static light scattering to estimate mass-average particle mass. From a series of experiments, a typical example of the preparation and characterization of polyaniline dispersion is described.

(Keywords: polyaniline; polyaniline dispersion; light-scattering characterization)

Introduction

The redox process, in which the anilinium cation reacts with an oxidizing agent, e.g. with persulphate, yields a protonized form of polyaniline (PANI)[1]. PANI is a conducting polymer with good thermal and oxidative stability. However, besides concentrated sulphuric acid, no other solvent has been reported to dissolve PANI quantitatively. The preparation of PANI dispersions[2–9] thus offers an interesting route to improve the polymer processibility.

Experimental

Polymerization. The reaction mixture contained[2] aniline (7.0 wt%), poly(vinyl alcohol) [PVAL, 10 wt%, hydrolysed poly(vinyl acetate) with 86 mol% vinyl alcohol units, molar mass $M_w = 230\,000\ \mathrm{g\,mol^{-1}}$] and ammonium persulphate (3.3 wt%) in 1 M HCl. The acidic solution of the aniline containing the steric stabilizer was cooled down to 0°C, and the ammonium persulphate solution was added in a single charge. Within a few minutes, the solution developed a blue colour which became more intense and finally turned emerald green.

Light scattering. The hydrodynamic radius (R_h) of the particles was determined with a Coulter Nano-Sizer. Static light scattering (SLS) was measured using Fica 50 apparatus with a primary beam of wavelength $\lambda_0 = 546$ nm.

Results and discussion

When aniline polymerization is carried out in the presence of steric stabilizer, submicrometre-sized spherical dispersion particles are produced (*Figure 1*). The spherical particles have acceptable uniformity. Aggregation of some particles occurs during the preparation of the sample for SEM; no such aggregates were detected in solution by light scattering methods.

Since aniline hydrochloride is miscible with the aqueous medium, while the resulting polymer is not, and the macroscopic precipitation of polymer is prevented by the presence of the steric stabilizer, the process can be regarded as typical dispersion polymerization[10,11].

Analysis of reaction mixture. Low molar mass components of the reaction mixture were removed by exhaustive dialysis. No green components passed through the semipermeable membrane (molar mass cut-off ~6000–8000 $\mathrm{g\,mol^{-1}}$).

During centrifugation of the diluted dialysed dispersion (2 h, 20 000 $\mathrm{rev\,min^{-1}}$), the particles sediment quantitatively. The amount of free PVAL in the supernatant liquid was determined after precipitation into excess methanol. Only ~5 wt% of steric stabilizer was fixed to the dispersion particles. The concentration of the residual aniline hydrochloride in the supernatant liquid was measured by u.v. spectroscopy (absorption at $\lambda_0 = 254$ nm) after calibration. In this way, conversion of aniline to PANI of ~20 wt% was estimated.

Light scattering characterization. Dynamic light scattering (DLS) and SLS can be used with advantage for characterization of dispersion particles[12]. DLS enabled the R_h of the particles (= 116 nm) to be determined. The value was somewhat higher than the geometric radius obtained by SEM, $R \cong 75$ nm (*Figure 1*), because it included the contribution from a swollen PVAL shell. The non-uniformity of particles, expressed by the mass- to number-average molar mass ratio from DLS, was $M_{wD}/M_{nD} = 2.3$.

SLS was used to determine the mass-average particle molar mass, $M_w = 5.2 \times 10^8\ \mathrm{g\,mol^{-1}}$ (*Figure 2*). Despite its high value, the particle mass can be determined with good accuracy[12], because the particle size is still smaller than the wavelength of light used in the scattering experiments ($\lambda_0 = 546$ nm). The only uncertainty in interpretation of SLS data is due to the experimental

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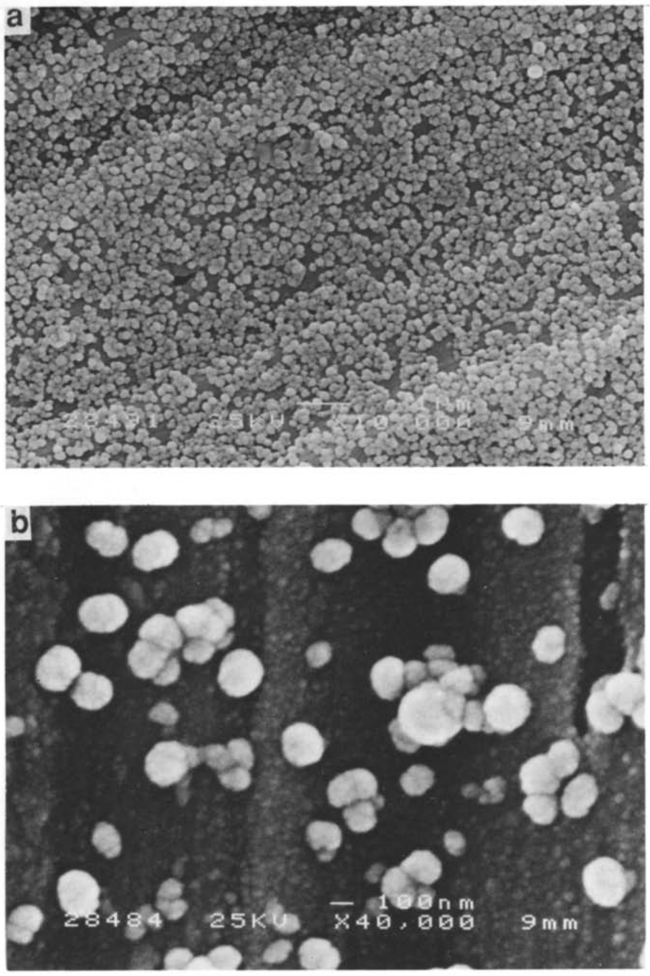

Figure 1 (a) An overview SEM micrograph of PANI dispersion stabilized by PVAL (dispersion concentration $c = 1.6 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$ prior to evaporation); (b) detailed picture of PANI particles (dispersion diluted × 10, magnification increased × 4)

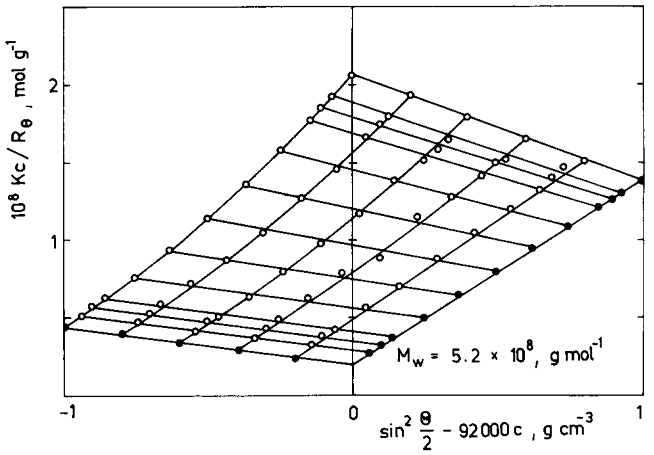

Figure 2 Evaluation of SLS data for a PANI dispersion in 0.1 M HCl by the Zimm method. For explanation of symbols cf. references 12 and 14

inaccessibility of the refractive index increment. This quantity for PANI was estimated as $0.25\,\mathrm{cm^3\,g^{-1}}$ (0.1 M HCl, $\lambda_0 = 546\,\mathrm{nm}$, 25°C); it was assumed that the change of the refractive index and of the density during the conversion of aniline into PANI was the same as that observed during the polymerization of styrene to polystyrene.

The introductory experiments have shown that the size and uniformity of particles can be controlled within certain limits by choice of temperature or by variation of component concentrations or both.

Steric stabilization. The dispersion polymerization of aniline has many common features with that of pyrrole[13], as far as steric stabilizers are concerned. In test experiments (2 wt% aniline, 2 wt% steric stabilizer and 2 wt% ammonium persulphate in 1 M HCl), spherical PANI dispersion particles were obtained with PVAL [both completely and partly hydrolysed poly(vinyl acetate)] and with poly(vinylpyrrolidone). Hydroxypropylcellulose, gelatin and polyoxyethylene provided marginal results, while polyacrylamide, dextran, starch and polyoxyethylene-*block*-polyoxypropylene proved to be ineffective as stabilizers.

The physico-chemical and chemical role of the steric stabilizer in the formation of spherical particles is not completely understood. The use of PVAL seems to provide well-defined spherical particles. More sophisticated functionalized versions of the steric stabilizer, like PVAL with incorporated aniline moieties[3–6], which would promote the grafting of PANI to PVAL, should be more effective. Surprisingly, this is not the case, and only rice-grain morphology of PANI particles has been obtained[3–6]. Also poly(vinylimidazole)[7] and polyoxyethylene[8] with incorporated aniline units proved to be of limited efficiency in the control of particle morphology. Only with a graft copolymer with an acrylic backbone, polyoxyethylene grafts and pendant glycidyl groups, did PANI yield spherical but non-uniform particles[9].

Studies of PANI dispersions combine chemical, physico-chemical and physical approaches with good prospects for potential applications; that is why such studies are of interest and lead to further investigation.

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